QUARTERLY REVIEWS

BORON TRIFLUORIDE CO-ORDINATION COMPOUNDS

By N. N. GREENWOOD, M.Sc., Ph.D.*
(Senior Research Fellow, A.E.R.E. Harwell,
nr. Didcot, Berks.)

and R. L. Martin, M.Sc., Ph.D.
(Fellow of Sidney Sussex College, Cambridge, and
Royal Commission for the Exhibition of 1851 Senior Student)

Boron trifluoride forms a great many molecular addition complexes which have excited interest for over a century because of the unusual valency problems they pose. More recently, the remarkable catalytic activity of these complexes in organic reactions has resulted in an extensive study of acid–base catalysis in such systems. Indeed, the greater part of the literature on boron trifluoride deals with the problems of catalysis. The results achieved have been reviewed by D. Kästner,[1] and by H. S. Booth and D. R. Martin.[2] Less is known of the physicochemical and inorganic aspects of boron trifluoride co-ordination chemistry. Of the 300 complexes mentioned in the literature, less than half have had even one physical property determined.

This Review stresses the importance of physicochemical properties in the understanding of the chemistry of boron trifluoride. In the first part, the general factors affecting the stability of the complexes are discussed. Structure and constitution are reviewed in the next section, which is followed by a discussion of each of the physical properties in turn. All the data have been recalculated, a consistent set of constants being used. The quantitative aspects of thermal dissociation and thermochemistry are discussed in the concluding section of the Review.

1. General Factors affecting Stability

Co-ordination compounds of boron trifluoride are known with all degrees of stability. Boron trifluoride–pyridine, BF_3,C_5H_5N, may be distilled without decomposition at 300°,[3] whereas boron trifluoride–carbonyl chloride, $BF_3,COCl_2$, is only stable as a solid, m.p. $-134{\cdot}3°$, and is completely dissociated into its components in the gas phase even at these low

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[1] "Newer Methods of Preparative Organic Chemistry", Interscience Publ. Inc., New York, 1948, p. 249.

[2] "Boron Trifluoride and its Derivatives", John Wiley and Sons, Inc., New York, 1949.

[3] P. A. van der Meulen and H. A. Heller, *J. Amer. Chem. Soc.*, 1932, **54**, 4404.

* Present address, Department of Chemistry, The University, Nottingham.

temperatures.[4] The stability of a complex may be expected to depend on the chemical nature of the ligand, the presence of polar substituents in the donor molecule, steric effects, the state of aggregation, and finally, the stoicheiometric ratio of donor to acceptor molecules in the complex.

(i) **Chemical Nature of the Ligand.**—Only seven elements have been shown with certainty to be capable of co-ordinating to boron trifluoride and all lie in the upper right-hand corner of the Periodic Table :

N	O	F	H
P	S	Cl	

Hydrogen, as the hydride ion, is the donor in boron trifluoride–sodium hydride.[59] Nitrogen, oxygen, and fluorine form more stable bonds to boron than do their congeners, and in the majority of known complexes one of these three elements is the ligand. Intercomparison of stabilities within the first period itself is not so straightforward, as other factors such as state of aggregation intervene. The heat of complex formation is not necessarily a reliable guide to bond strength, as the original bonds in the donor and acceptor molecules are considerably modified in the resulting complex (§2). Acid–base displacement reactions can also be misleading unless solvation energies and crystal lattice energies are known.

The functional group containing the ligand also influences the stability. Amines form more stable linkages to boron trifluoride than do alkyl-substituted acid amides, and these in turn are more stable than complexes with nitriles. Stabilities of complexes with oxygen as donor decrease in the order ethers $>$ alcohols $>$ carbonyl compounds.

Other elements have been claimed to form complexes with boron trifluoride. A carbon–boron bond has frequently been invoked in catalytic mechanisms,[2] but no compound has been isolated and there is little physical evidence to support the assumption. The report [5] that argon forms six different compounds with boron trifluoride, each melting within 1° of pure boron trifluoride, has been discounted by the results of E. Wiberg and K. Karbe.[6]

(ii) **Polar Substituents.**—As the strength of a donor–acceptor bond depends, in part, on the availability of electrons at the donor atom, electronegative substituents will tend to decrease the stability of complexes. H. Meerwein and W. Pannwitz [7] demonstrated the decrease in stability of the acetic acid complex on progressive substitution with chlorine, and also pointed out that the boron trifluoride complexes with crotonic acid, $BF_3,Me{\cdot}CH{:}CH{\cdot}CO_2H$ and $BF_3,2Me{\cdot}CH{:}CH{\cdot}CO_2H$, as well as with oxalic acid, $BF_3,(CO_2H)_2$, were much less stable than the acetic acid complexes $BF_3,Me{\cdot}CO_2H$ and $BF_3,2Me{\cdot}CO_2H$. The same authors have measured the apparent molecular weights of dialcohol complexes in nitrobenzene and find that, whereas boron trifluoride–diethanol, $BF_3,2EtOH$, is not dissociated, yet boron trifluoride–di(chlorohydrin), $BF_3,2ClCH_2{\cdot}CH_2{\cdot}OH$, is $\sim 36\%$ dis-

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[4] D. R. Martin and J. P. Faust, *J. Phys. Colloid Chem.*, 1949, **53,** 1255.

[5] H. S. Booth and K. S. Willson, *J. Amer. Chem. Soc.*, 1935, **57,** 2273.

[6] *Z. anorg. Chem.*, 1948, **256,** 307.

[7] *J. pr. Chem.*, 1934, **141,** 123.

sociated. The corresponding trichloroethanol complex, $BF_3,2CCl_3{\cdot}CH_2{\cdot}OH$, is $\sim 76\%$ dissociated into its components. Boron trifluoride–diphenol, $BF_3,2PhOH$, evolves boron trifluoride quantitatively on warming.[7]

A similar decrease in stability is known for the complexes of boron trifluoride with ether, phenetole, and diphenyl oxide :

$$BF_3,Et_2O > BF_3,Ph{\cdot}OEt > BF_3,Ph_2O$$

The relatively great stability of boron trifluoride–ethyl ether is well known ; phenetole absorbs one mole of boron trifluoride at room temperature but this is evolved quantitatively on warming ; [8, 9] diphenyl oxide does not form a complex at all.[8, 9, 10] Reference to molecular models shows that this is not a steric effect.

An interesting comparison has recently been given of the weak donor properties of trisilylamine $(SiH_3)_3N$ towards boron trifluoride as compared with those of trimethylamine.[11] Other examples of the effect of polar or easily polarisable groups on the stability of co-ordination complexes will be found in §3.

(iii) **Steric Effects.**—The strength of a donor–acceptor bond depends not only on the electron availability or ionisation potential of the donor atom but also on the approachability of the two ligands in the donor and acceptor components. The work of H. C. Brown and his colleagues has recently focused attention on steric strain as a factor in the relative stability of the co-ordination compounds of boron. For example, whereas αα′-lutidine is a stronger base than pyridine in aqueous solution, yet the reverse is true with boron trifluoride as a reference acid, and the complex boron trifluoride–pyridine, BF_3,C_5H_5N, is more stable than boron trifluoride–αα′-lutidine, $BF_3,\alpha\alpha'\text{-}Me_2C_5H_3N$.[12] Steric effects also predominate in determining the decrease in stability of the etherates from boron trifluoride–tetrahydrofuran to boron trifluoride–*iso*propyl ether : [13]

$$BF_3,C_4H_8O > BF_3,Me_2O > BF_3,Et_2O > BF_3,Pr^i{}_2O$$

With nitriles, on the other hand, because the $B{-}N{\equiv}C$ group is linear, steric effects are not important in determining the relative stabilities of the 1 : 1 complexes of boron trifluoride with benzonitrile, *o*-tolunitrile, and mesitonitrile.[14]

Steric effects have also been considered by D. R. Martin and R. E. Dial [15] to explain the fact that ammonia and phosphine both co-ordinate to boron trifluoride but arsine does not, even though complexes of arsine with boron trichloride and boron tribromide are known. The argument here, however, is less compelling than in H. C. Brown's investigations.

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[8] H. Bowlus and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835.

[9] H. Meerwein and H. Maier-Hüser, *J. pr. Chem.*, 1932, **134**, 51.

[10] R. W. Dornte, U.S.P. 2,559,062, July 3rd, 1951. (This reference discusses several chloro- and phenyl-substituted ethers.)

[11] A. B. Burg and E. S. Kuljian, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.

[12] H. C. Brown, H. I. Schlesinger, and S. Z. Cardon, *ibid.*, 1942, **64**, 325.

[13] H. C. Brown and R. M. Adams, *ibid.*, p. 2557.

[14] H. C. Brown and R. B. Johannesen, *ibid.*, 1950, **72**, 2934.

[15] *Ibid.*, p. 852.

(iv) **State of Aggregation and Stoicheiometry.**—Complexes frequently derive much of their stability from either crystal-lattice energy or solvation effects in the liquid state. Stability in the gaseous state is usually considerably lower, and very few co-ordination compounds of boron trifluoride can be distilled without change [see §3(ii)].

The alkali fluoroborates, BF_3,MF (or MBF_4), are stable crystalline solids which may be melted with only slight decomposition, but at higher temperatures the dissociation pressure of boron trifluoride rises rapidly [16, 17, 18, 19] (Table 15). The gas may be evolved quantitatively, leaving the alkali fluoride.[20, 21] Inorganic complexes containing sulphur or phosphorus are also completely dissociated in the vapour phase (see Table 4 for refs.). The dissociation pressure of boron trifluoride monohydrate reaches one atmosphere at room temperature,[22] and the dihydrate is also known to dissociate and decompose in the vapour phase although it is stable indefinitely as a liquid or a solid.[23] The crystalline compound boron trifluoride–ammonia cannot be fused or vaporised unchanged.[24] It disproportionates above 125° to give boron nitride BN and ammonium fluoroborate NH_4BF_4.[25]

Attempts have been made to estimate the lattice energies of metal fluoroborates,[16] but results derived from these estimates [16, 53] cannot now be considered useful in view of the large changes in the accepted value of the dissociation energy of fluorine and the approximations necessitated by the lack of thermodynamic data.

The stability of boron trifluoride complexes with organic compounds also depends considerably on the state of aggregation. Even compounds which distil unchanged (*e.g.*, BF_3,Me_2O) may be considerably dissociated in the vapour phase,[13] and some solids, although stable below the melting point, dissociate partially on fusion.

The stoicheiometric ratio of donor to acceptor has a marked influence on stability. Alcohols and organic acids, like water itself, each form two series of complexes BF_3,ROH and $BF_3,2ROH$, and $BF_3,R{\cdot}CO_2H$ and $BF_3,2R{\cdot}CO_2H$. The 1 : 2 complexes are invariably the more stable; [7, 26] however, Meerwein's claim that 1 : 2 complexes can be distilled in a vacuum without change has not been substantiated by later work.[22, 23, 27] The structure of 1 : 1 and 1 : 2 complexes and the effect of the changing ratio on the physical properties of the complexes are discussed more fully in §2(iv) and §3.

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[16] J. H. de Boer and J. A. M. van Liempt, *Rec. Trav. chim.*, 1927, **46**, 124.
[17] L. J. Klinkenberg, *ibid.*, 1937, **56**, 36. [18] *Idem*, Doctoral Thesis, Leiden, 1937.
[19] G. H. Curtis, *Iron Age*, 1945, **155**, 54.
[20] F. Stolba, *Chem. Zentr.*, 1872, **3**, 395.
[21] I. G. Ryss and E. M. Polyakova, *Zhur. Obshchey Khim.*, 1948, **18**, 286.
[22] N. N. Greenwood and R. L. Martin, *J.*, 1951, 1915.
[23] J. S. McGrath, G. G. Stack, and P. A. McCusker, *J. Amer. Chem. Soc.*, 1944, **66**, 1263. [24] C. A. Kraus and E. H. Brown, *ibid.*, 1929, **51**, 2690.
[25] A. W. Laubengayer and G. F. Condike, *ibid.*, 1948, **70**, 2274.
[26] H. Meerwein, *Ber.*, 1933, **66**, 411.
[27] N. N. Greenwood and R. L. Martin, *J.*, 1953, 757.

(v) **Compounds forming no Complexes with Boron Trifluoride.**—As a result of the operation of one or more of the preceding effects, the tendency to complex formation may be reduced to such an extent that even weak interaction of the components fails to occur. Such examples are important not only for the general theory of donor–acceptor bonding but also in the problems of handling and storing the gas. The formation of a co-ordinate link may, of course, also be precluded by direct chemical interaction.

Alkali and alkaline-earth metals reduce boron trifluoride with incandescence to boron.[28, 29] Aluminium chloride and bromide react to give boron trichloride and tribromide, respectively.[30] Boron trifluoride reacts with various nitrates, carbonates, and oxides of Groups I—IV to form boron oxyfluoride $(BOF)_3$ and the corresponding metal fluoride or fluoroborate.[31, 32] Organic compounds may also react with boron trifluoride without complex formation. With β-diketones,[33] hydrogen fluoride is eliminated from the enol form to give difluorides of the type,

$$BF_2\cdot O\cdot CR{:}CH\cdot CR'{:}O$$

Grignard reagents and other organo-metallic compounds yield trialkyl boron compounds.[34–37] Certain alcohols eliminate water to give an olefin which then polymerises under the catalytic activity of the boron trifluoride hydrate formed.[7, 8] In most other instances organic and inorganic compounds do not react chemically with boron trifluoride.

Elements which have been shown to be unreactive towards boron trifluoride include :

Group O : A, Kr, Xe [6]
I : Cu, Ag, Au [38]
II : Mg, Zn, Cd, Hg [38, 39]
III : Al [38]
IV : C (graphite and amorphous), Sn, Pb [38]

Group V : N_2*
VI : O_2*, Cr, W, U [38, 39]
VII : F_2*, Cl_2*, Br_2*, I [40]
VIII : Fe, Ni, Pt [28, 38, 41, 42]

* Passim.

Without doubt other elements could be added to this list.

Stainless steel is not attacked below 450°.[42] Other materials of constructional importance which are uncorroded below 200° include brass, mild

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[28] H. Davy, *Phil. Trans.*, 1808, I, 1 ; 1808, II, 333 ; 1809, I, 39.

[29] S. G. Rawson, *Chem. News*, 1888, **58,** 283.

[30] E. L. Gamble, P. Gilmont, and J. F. Stiff, *J. Amer. Chem. Soc.*, 1940, **62,** 1257.

[31] P. Baumgarten and W. Bruns, *Ber.*, 1939, **72,** 1753.

[32] *Idem, Ber.*, 1941, **74,** 1232.

[33] G. T. Morgan and R. B. Tunstall, *J.*, 1924, **125,** 1963.

[34] E. Krause and R. Nitsche, *Ber.*, 1921, **54,** 2784 ; 1922, **55,** 1261.

[35] E. Krause and P. Nobbe, *Ber.*, 1930, **63,** 934 ; 1934, **64,** 2112.

[36] J. R. Johnson, H. R. Snyder, and M. G. van Campen, *J. Amer. Chem. Soc.*, 1938, **60,** 115.

[37] A. B. Burg, *ibid.*, 1940, **62,** 2228.

[38] F. Hudswell, J. S. Nairn, and K. L. Wilkinson, *J. Appl. Chem.*, 1951, **1,** 333.

[39] H. S. Booth and J. M. Carter, *J. Phys. Chem.*, 1932, **36,** 1359.

[40] P. Baumgarten and W. Bruns, *Ber.*, 1947, **80,** 517.

[41] H. Moissan, *Compt. rend.*, 1904, **139,** 711.

[42] W. W. Watson, J. O. Buchanan, and F. K. Elder, *Phys. Review*, 1947, **71,** 887.

steel, soft solder, silver solder, Pyrex glass, Polythene, polytetrafluoroethylene, and pure polyvinyl chloride.[38] Ready attack was noted at, or somewhat above, room temperature on Perspex, rubber, Paxolin, Nylon, cellulose acetate, commercial polyvinyl chloride, and Apiezon greases L and N.[38]

Many simple inorganic compounds containing potential donor atoms show no tendency to co-ordinate to boron trifluoride owing to the interplay of the various factors outlined above, *e.g.*, CO,[43] N_2O,[44, 45] P_2O_5,[40] I_2O_5,[40] Fe_2O_3,[32] NO_2Cl,[46] $POCl_3$,[47] $SOCl_2$,[47] SO_2Cl_2,[47] PF_3,[48] PSF_3,[48] AsH_3,[15] BCl_3,[49] HCl,[15] HBr,[15] and NiF_2.[50] A more detailed discussion of the individual examples is frequently given in the papers cited. The list is intended to be illustrative rather than exhaustive. Lithium sulphate, in contradistinction to the other alkali sulphates, shows little tendency to form an addition compound with boron trifluoride, and silver sulphate and the alkaline-earth sulphates are also unreactive.[51]

Of organic compounds, the paraffin, olefin, and aromatic hydrocarbons, and their halogen derivatives do not form co-ordination complexes with boron trifluoride.[43, 45, 48] (Triphenylmethyl fluoride is an exception.) Certain ethers such as diphenyl oxide [§1(ii)], dimethylacetal $Me{\cdot}CH(OMe)_2$, and glycol acetal $Me{\cdot}CH(O{\cdot}CH_2)_2$, also appear to be inactive as donors.[8] The position of acid anhydrides other than simple fatty acid anhydrides is still uncertain, although it seems fairly definite that weak donor properties are displayed. Succinic, benzoic, and phthalic anhydrides were reported by H. Bowlus and J. A. Nieuwland to be unreactive; [8] however, H. Meerwein and H. Maier-Hüser [9] claim to have isolated a compound of boron trifluoride and succinic anhydride at − 70°, and P. Given and D. Ll. Hammick report that benzoic and phthalic anhydrides, when dissolved in nitrobenzene, each absorb approximately two moles of boron trifluoride to give crystalline complexes.[52] The reactivity of acyl halides except acetyl fluoride [53] is also small: acetyl chloride forms a weak co-ordination compound at − 70°,[9, 53] but no complex formation was detected with benzoyl chloride or toluene-*p*-sulphonyl chloride at the same temperature.[9]

2. Structure and Constitution

Numerous methods are available for establishing the structure of addition compounds and for demonstrating that such compounds are not merely dipole associations of their components. These methods will be discussed

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[43] V. Gasselin, *Ann. Chim. Phys.*, 1894, **3**, 5.
[44] F. Kuhlmann, *Annalen*, 1841, **39**, 319.
[45] H. S. Booth and D. R. Martin, *J. Amer. Chem. Soc.*, 1942, **64**, 2198.
[46] H. H. Batey and H. H. Sisler, *ibid.*, 1952, **74**, 3408.
[47] A. B. Burg and M. K. Ross, *ibid.*, 1943, **65**, 1637.
[48] H. S. Booth and J. H. Walkup, *ibid.*, p. 2334.
[49] H. S. Booth and S. G. Frary, *ibid.*, p. 1836.
[50] G. Balz and W. Zinser, *Z. anorg. Chem.*, 1935, **221**, 225.
[51] P. Baumgarten and H. Hennig, *Ber.*, 1939, **72**, 1743.
[52] P. H. Given and D. Ll. Hammick, *J.*, 1947, 1237.
[53] F. Seel, *Z. anorg. Chem.*, 1943, **250**, 331.

in detail in this section. It has been found that the structures of the donor and acceptor moieties are modified during complex formation ; bond lengths and bond angles may be changed and the redistribution of electrons results in a large dipole moment.[54] In addition, the charge distribution in the donor may be so altered that ionisation of a radical or atom occurs. Thus boron trifluoride–methanol, BF_3,MeOH conducts electricity ionically as methoxyfluoroboric acid $H^+BF_3.OMe^-$.[27, 81]

Because the formation of a donor–acceptor bond results in a new molecular species with properties quite distinct from those of the parent compounds, it is usually incorrect to suppose that the structure of the new species is given by the conventional formulæ D:A or $D \rightarrow A$. These are merely convenient ways of writing the formula of a molecule whose structure is undetermined, in such a way as to indicate the method of its formation. For example, the addition complex of hydrogen chloride and ammonia HCl,NH_3 or $H_3N \rightarrow HCl$ is more properly considered as ammonium chloride NH_4Cl. In the same way, the formula BF_3,H_2O should not imply that the complex partakes in any way of the properties of its components ; it is more correctly considered as hydroxyfluoroboric acid $H^+BF_3{\cdot}OH^-$. In some instances, however, insufficient chemical or structural information is available to assign a formula with any certainty, and it becomes necessary to employ a dualistic formula. The use of dots or arrows to denote the donor–acceptor bond is not recommended, as this frequently requires assumptions as to which atom in the donor is the ligand, *e.g.*, in boron trifluoride–hydroxylamine $BF_3,NH_2{\cdot}OH$. Nor are such notations readily adaptable to 1 : 2 compounds, *e.g.*, $BF_3,2H_2O$, without implying that both oxygen atoms donate electrons to the boron. In the present Review, uniformity of the tables has been achieved by writing non-committal dualistic formulæ even when the true structure is known. The text, however, frequently refers to the compounds by their " structural " name as well, in the hope that these will in time become more familiar in the literature and render the older formulæ obsolete. This has already occurred with the tetrafluoroborates BF_3,MF, *i.e.*, MBF_4.

(i) **Solid Co-ordination Compounds.**—The structure of boron trifluoride co-ordination compounds in the solid state has been investigated by microscopy, infra-red spectroscopy, and *X*-ray diffraction analysis.

Microscopy.—The alkali fluoroborates, as well as those of thallium and ammonium, form doubly-refracting crystals of orthorhombic symmetry.[55, 56] On being heated they undergo a $\beta \rightarrow \alpha$ transition to an isotropic cubic modification. The transition temperatures, as determined on a microscope stage, are :[56]

Compound :	BF_3,LiF	BF_3,NaF	BF_3,KF	BF_3,TlF	BF_3,NH_4F
Transition temp. :	Melts before dimorphism appears	239—241°	273—280°	203—206°	~ 236°

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[54] A. W. Laubengayer and G. R. Finlay, *J. Amer. Chem. Soc.*, 1943, **65,** 884.

[55] E. Wilke-Dörfurt and G. Balz, *Z. anorg. Chem.*, 1927, **159,** 197.

[56] D. Vorländer, J. Hollatz, and J. Fischer, *Ber.*, 1932, **65,** 535.

The transition has been confirmed by high-temperature *X*-ray diffraction [57] and by thermal analysis.[58] D. R. Martin and J. K. Rieke [58] pointed out that the transition temperature of ammonium fluoroborate is near the sublimation temperature, so that rapid heating on a microscope stage would tend to give inaccurate results. They find a transition temperature of 205° ± 3° by thermal analysis under pressure. Other complexes examined microscopically also form doubly-refracting orthorhombic crystals: nitrosyl fluoroborate BF_3,NOF; [55] boron trifluoride–sodium hydride BF_3,NaH; [59] boron trifluoride–acetonitrile; [60] and boron trifluoride–ammonia.[25] This last compound has interfacial angles of $57° 31' \pm 15'$ and $121° 30' \pm 15'$ with $2V = 90° \pm 3°$ and $2E = 146° \pm 2°$.[25]

Infra-red Spectroscopy.—The spectra of sodium, potassium, and ammonium fluoroborates have been examined in the region 2—25 μ by G. L. Coté and H. W. Thompson.[61] At frequencies below 1400 cm.$^{-1}$ there is a definite parallelism between the three substances with strong groups of bands near 520 and 1050 cm.$^{-1}$ and weaker bands near 770 and 1300 cm.$^{-1}$. These may all be assigned to the fluoroborate ion BF_4^-, and indicate that hydrogen bonding in ammonium fluoroborate does not appreciably affect the B–F bonds. Bands at 1430 and 3330 cm.$^{-1}$ were found only with ammonium fluoroborate and are associated with the NH_4^+ ion. These latter bands show a temperature dependence which may be interpreted in terms of increased hydrogen bonding at lower temperatures.[61]

X-*Ray Diffraction Analysis.*—The early work of B. Pesce [62] in 1930 on the *X*-ray powder analysis of potassium fluoroborate has been followed by more than a dozen papers, notably by J. L. Hoard and his co-workers and by L. J. Klinkenberg and J. A. A. Ketelaar. The results are assembled in Table 1, which lists the space groups, the number of molecules per unit cell, *n*, the lattice parameters, *a*, *b*, and *c*, and axial ratios of the 14 compounds investigated. Except for the last three compounds the symmetry is orthorhombic.

Sodium fluoroborate and boron trifluoride–sodium hydroxide have the same symmetry ($CaSO_4$-type) and remarkably similar parameters.[17] This has been taken to indicate that the latter compound should be formulated as sodium hydroxyfluoroborate $Na^+BF_3{\cdot}OH^-$. However, it is necessary to view these results with caution, as the recent work of I. G. Ryss and M. M. Slutskaya [71] suggests that Klinkenberg's method of preparing the boron trifluoride–sodium hydroxide complex yields predominantly sodium fluoroborate.

The other fluoroborates have a slightly higher symmetry ($BaSO_4$-type). Rubidium and ammonium fluoroborates have practically identical parameters [63] and it would seem that hydrogen bonding plays very little part in

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[57] C. Finbak and O. Hassel, *Z. physikal. Chem.*, 1936, *B*, **32**, 433.

[58] D. R. Martin and J. K. Riecke, *J. Amer. Chem. Soc.*, 1951, **73**, 5895.

[59] J. Goubeau and R. Bergmann, *Z. anorg. Chem.*, 1950, **263**, 69.

[60] A. W. Laubengayer and D. S. Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.

[61] *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

[62] *Gazzetta*, 1930, **60**, 936.

[63] J. L. Hoard and V. Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985.

TABLE 1. X-*Ray diffraction data*

Compound	Space-group	n	a	b	c	$a:b:c$	Ref.
BF_3,NaF .	D_{2h}^{17}-$Bbmm$	4	6·25 ± 0·02	6·77 ± 0·02	6·82 ± 0·01	0·922 : 1 : 1·007	17
BF_3,KF .	D_{2h}^{16}-$Pnma$	,,	7·85	5·68	7·37	1·382 : 1 : 1·297	62
BF_3,RbF .	,,	,,	9·07 ± 0·04	5·60 ± 0·03	7·23 ± 0·04	1·620 : 1 : 1·291	63
BF_3,CsF .	,,	,,	9·43 ± 0·10	5·83 ± 0·07	7·65 ± 0·02	1·617 : 1 : 1·310	17
BF_3,TlF .	,,	,,	9·47 ± 0·03	5·81 ± 0·04	7·40 ± 0·02	1·624 : 1 : 1·274	17
BF_3,NH_4F	,,	,,	9·06 ± 0·04	5·64 ± 0·03	7·23 ± 0·04	1·606 : 1 : 1·282	63
			8·89 ± 0·05	5·68 ± 0·05	7·21 ± 0·03	1·564 : 1 : 1·270	64
BF_3,NOF	,,	,,	8·79 ± 0·03	5·66 ± 0·03	7·10 ± 0·10	1·553 : 1 : 1·254	65
BF_3,NaOH	D_{2h}^{17}-$Bbmm$	,,	6·24 ± 0·02	6·82 ± 0·01	6·85 ± 0·01	0·915 : 1 : 1·004	17
BF_3,$2H_2O$	D_{2h}^{16}-$Pnma$ (?)	,,	8·74 ± 0·06	5·64 ± 0·03	7·30 ± 0·10	1·550 : 1 : 1·294	64
BF_3,NH_3 .	D_{2h}^{15}-$Pbca$	8	8·22 ± 0·03	8·11 ± 0·03	9·31 ± 0·03	1·014 : 1 : 1·148	66
BF_3,MeCN	D_{2h}^{16}-$Pnma$	4	7·76 ± 0·02	7·20 ± 0·02	8·34 ± 0·02	1·077 : 1 : 1·158	67
BF_3,$MeNH_2$	C_{2h}^{2}-$P2_1/m$	2	5·06 ± 0·01	7·28 ± 0·01	5·81 ± 0·01	0·695 : 1 : 0·798*	68
BF_3,Me_2NH	C_{2h}^{5}-$P2_1/c$	4	7·50 ± 0·02	6·06 ± 0·02	12·25 ± 0·02	1·238 : 1 : 2·021†	69
BF_3,Me_3N	C_{3v}^{5}-$R3m$	1	5·76 ± 0·02	—	—	— ‡	70
		3	9·34 ± 0·02	—	6·10 ± 0·02	$c/a = 0{\cdot}653$ §	70

* Symmetry monoclinic, $\beta = 101° \; 31' \pm 10'$. † Symmetry monoclinic, $\beta = 102°$.
‡ Symmetry rhombohedral, $\alpha = 108° \; 16'$, or, alternatively, § hexagonal.

modifying the structure, in agreement with the results of the infra-red work [61] discussed above. The parameters of cæsium and thallium fluoroborates are also identical within the experimental precision.[17] The powder analysis of boron trifluoride–nitrosyl fluoride BF_3,NOF is important in establishing that fluorine, rather than nitrogen or oxygen, is the donor atom ; the complex should be considered as nitrosyl fluoroborate $NO^+BF_4^-$.

The close similarity between the parameters of ammonium fluoroborate and boron trifluoride dihydrate, in conjunction with the known similarity in size between fluorine and the hydroxyl group, has been taken as evidence that the dihydrate is hydroxonium hydroxytrifluoroborate $H_3O^+BF_3{\cdot}OH^-$.[64] However, the data would also be consistent with formulation as hydrofluoronium dihydroxydifluoroborate $H_2F^+BF_2(OH)_2^-$ [73] and it is necessary to invoke the results of electrolysis experiments to decide in favour of $H_3O^+BF_3{\cdot}OH^-$.[22]

High-temperature single-crystal work on potassium and ammonium fluoroborates [57] has confirmed the $\beta \longrightarrow \alpha$ transition discussed in the section

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[64] L. J. Klinkenberg and J. A. A. Ketelaar, *Rec. Trav. chim.*, 1935, **54,** 959.

[65] L. J. Klinkenberg, *ibid.*, 1937, **56,** 749.

[66] J. L. Hoard, S. Geller, and W. M. Cashin, *Acta Cryst.*, 1951, **4,** 396.

[67] J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, *ibid.*, 1950, **3,** 130.

[68] S. Geller and J. L. Hoard, *ibid.*, p. 121.

[69] S. Geller and M. E. Milberg, *ibid.*, 1951, **4,** 381.

[70] S. Geller and J. L. Hoard, *ibid.*, p. 399.

[71] *J. Gen. Chem. U.S.S.R.* (U.S. Transl.), 1952, **22,** 41.

[72] R. W. G. Wyckoff, "Crystal Structures", Interscience Publ. Inc., New York, 1951.

[73] F. J. Sowa, J. W. Kroeger, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57,** 454.

on microscopy. The orthorhombic form changes to the cubic high-temperature-$NaClO_4$ structure :[72]

α-BF_3,KF	a_0 = 7·26 Å	(photograph taken at 300°)
α-BF_3,NH_4F	a_0 = 7·55 Å	(photograph taken at 260°)

The Debye–Scherrer pattern of boron trifluoride–sodium hydride has been published ; the lines could not be indexed as hexagonal or tetragonal, and it seems possible that the crystals are orthorhombic.[59] Chemical evidence suggests the formula $Na^+BF_3H^-$.

An elegant series of complete structure determinations has recently been published by S. Geller, J. L. Hoard, and their collaborators.[66, 67, 68, 70, 74] The series comprises the complexes of boron trifluoride with ammonia, methylamine, trimethylamine, and acetonitrile. The detailed structure of boron trifluoride–dimethylamine could not be determined.[69] The symmetries, space-groups, and parameters are given in Table 1. Boron trifluoride–ammonia and boron trifluoride–acetonitrile crystallise in the orthorhombic system and so are similar to the fluoroborates. The mono- and di-methylamine complexes are monoclinic, and boron trifluoride–trimethylamine is hexagonal. The principal bond distances (± 0·02 Å) and bond angles (± 2°) in these crystals are summarised in Table 2.

TABLE 2. *Bond distances (Å) and angles*

Compound	BF_3,NH_3	BF_3,$MeNH_2$	BF_3,Me_3N*	BF_3,MeCN
Reference	66, 74	68, 74	70, 74	67, 74
B–N	1·60	1·57	1·59	1·64
B–F	1·38	1·38	1·39	1·32
N–C	—	1·50	1·50	(N≡C) 1·13 (C—C) 1·46
∠F–B–F	111°	110·5°	107°	114°
∠F–B–N	107°	108·5°	112°	103°
∠B–N–C	—	114°	105°	108°
∠C–N–C	—	—	114°	—

* Bond distances accurate to ± 0·03 Å instead of ± 0·02 Å as elsewhere.

These molecular constants may be compared with those of the free components. The boron trifluoride molecule forms a plane equilateral triangle with B–F = 1·30 ± 0·01 Å[75, 76, 77] and ∠F–B–F = 120° ± 3°.[75] In its complexes with ammonia, methylamine, and trimethylamine, boron trifluoride becomes tetrahedral, with B–F = 1·38—1·39 Å and ∠F–B–F = 109·5° ± 2°. The complexes are very stable, and the N–B donor–acceptor bond length of 1·58 ± 0·02 Å is significantly shorter than in the unstable complex with acetonitrile for which N–B = 1·64 Å. In boron trifluoride–acetonitrile too, the modification of the boron trifluoride moiety is very

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[74] J. L. Hoard, S. Geller, and T. B. Owen, *Acta Cryst.*, 1951, **4**, 405.
[75] H. A. Levy and L. O. Brockway, *J. Amer. Chem. Soc*, 1937, **59**, 2085.
[76] H. Braune and P. Pinnow, *Z. physikal. Chem.*, 1937, *B*, **35**, 239.
[77] D. M. Gage and E. F. Barker, *J. Chem. Phys.*, 1939, **7**, 455.

much less : the B–F bond distance increases by only 0·02 Å to 1·32 Å, and the deviation from coplanarity is less marked, ∠F–B–F being 114°, *i.e.*, intermediate between equilateral and tetrahedral.

The donor molecule in these complexes undergoes less drastic variation than the acceptor, but it is clear that the nitrogen atom in co-ordinated trimethylamine is no longer tetrahedral: ∠C–N–C = 114° and ∠B–N–C = 105°. There is also a tendency for the methyl groups to move away from the nitrogen, and N–C increases from 1·47 ± 0·02 Å to 1·50 ± 0·02 Å.

There is no evidence for hydrogen bonding in any of the complexes. For a more detailed discussion of these results and further structural information the reader is referred to the original papers.

(ii) **Liquid Co-ordination Complexes.**—Exothermic absorption of boron trifluoride up to a 1 : 1 molecular ratio has been noted from early times. That this absorption results in the formation of stoicheiometric *compounds* at 1 : 1 and 1 : 2 ratios in the liquid state has been demonstrated by singularities in property–composition curves showing the melting point, vapour pressure, or specific electrical conductivity. Results of ultra-violet, infra-red, and Raman spectroscopy indicate that the complexes have spectra which are quite distinct from those of the parent molecules. In favourable instances direct electrolysis of the pure liquids leads to a detailed assignment of the constitution of the co-ordination complexes.

Property–Composition Curves.—Use of the classical phase diagram, in which the melting point of a binary system is plotted against its molar composition, has indicated that one mole of boron trifluoride forms definite compounds with $2H_2O$,[23] H_2S,[78] SO_2,[45] SOF_2,[48] $COCl_2$,[4] $2COCl_2$,[4] $\frac{1}{2}HNO_3$,[79] Me_2O,[80] and EtOH.[8] There is also some evidence for the compounds BF_3,PH_3 and $(BF_3)_2,PH_3$.[15] The melting points of these various compounds are listed in Table 4.

The vapour pressure–composition isotherm for the system boron trifluoride–methanol shows a minimum corresponding to BF_3,2MeOH ($p \sim 9$ mm. at 25°) ; at the 1 : 1 ratio the pressure rises rapidly, indicating that further absorption of boron trifluoride does not occur.[81] In numerous other systems it has been observed that the mixing of equimolar amounts of gaseous boron trifluoride and a donor species results in a large decrease in pressure. This method has recently been employed with notable success in a study of the relative stabilities of 1 : 1 : 1 complexes of boron trifluoride with hydrogen fluoride and the methylbenzenes.[82, 83] The structures of these interesting complexes, which may be considered as fluoroborates $ArH^+BF_4^-$, are discussed more fully in §2(iv).

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[78] A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, 1926, **30**, 369.

[79] H. Gerding, P. M. Heertjes, L. J. Revallier, and J. W. M. Steeman, *Rec. Trav. chim.*, 1952, **71**, 501.

[80] A. F. O. Germann and M. Cleaveland, *Science*, 1921, **53**, 582.

[81] L. A. O'Leary and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1933, **55**, 2117.

[82] D. A. McCaulay, B. H. Schoemaker, and A. P. Lien, *Ind. Eng. Chem.*, 1950, **42**, 2103.

[83] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013.

Electrical conductivity–composition isotherms have established stoicheiometric compounds of one mole of boron trifluoride with H_2O,[22, 84] $2H_2O$,[22] $C_4H_8O_2$ (dioxan),[85] $2C_4H_8O_2$,[85] MeOH,[27, 86] 2MeOH,[27, 86] 2PhOH,[87] $Me{\cdot}CO_2H$,[88] $Me{\cdot}CO_2Me$,[89] and $Me{\cdot}CO_2Et$.[89] The specific conductivity of liquid boron trifluoride itself is negligibly small ($<5 \times 10^{-10}$ ohm^{-1} cm.$^{-1}$)[90] and the conductivity of the free donor liquids is of the order of 10^{-6} ohm^{-1} cm.$^{-1}$ or less. The complexes, however, have very appreciable conductivities (see Table 10) and this, in conjunction with the minima at stoicheiometric ratios, is cogent evidence against the view that the electrical conductivities of these liquids are ascribable to electrolytic impurities.[91]

Ultra-violet, Infra-red, and Raman Spectra.—Very little detailed work has been done in this field. F. V. Dunderman and S. H. Bauer [92] have recorded the ultra-violet spectrum of liquid boron trifluoride–methyl ether between 5000 and 2100 Å. The complex shows faint absorption at longer wavelengths than does methyl ether itself, but at 2300 Å, where the ether absorbs intensely, the extinction coefficient for the complex is still very small. The Raman spectrum of boron trifluoride–methyl ether was studied by the same authors who found that none of the principal lines of the free donor or acceptor molecules appeared in the spectrum of the complex. This is further important evidence that true compound formation rather than dipole–dipole attraction occurs during donor–acceptor interaction.

The infra-red spectrum of boron trifluoride–tri-*n*-butylamine has recently been measured between 2 and 16 μ in chloroform solution.[93] There are eight principal bands characteristic of the compound. Boron trifluoride–*NN*-dimethylacetamide has also been investigated,[94] but the statement that the C=O absorption band at 5·9 μ is not shifted in the complex cannot be taken as evidence that nitrogen is the ligand until more details are available. It is not mentioned whether the measurements were in solution or on the gaseous complex; in either case thermal dissociation of the complex could explain the result. However, other considerations do suggest that nitrogen is the ligand.

The Raman spectrum of aqueous sodium fluoroborate has been analysed by J. Goubeau and W. Bues.[95] In passing from planar BF_3 to tetrahedral BF_4^- the force constant decreases from $6{\cdot}86 \times 10^{-5}$ to $5{\cdot}28 \times 10^{-5}$ dyne cm.$^{-1}$ (*i.e.*, in the ratio 4 : 3) and the B–F bond distance increases from 1·30 to 1·43 Å.

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[84] C. A. Wamser, *J. Amer. Chem. Soc.*, 1951, **73**, 409.

[85] N. N. Greenwood, unpublished observations.

[86] J. A. Nieuwland, R. R. Vogt, and W. L. Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018.

[87] F. J. Sowa, H. D. Hinton, and J. A. Nieuwland, *ibid.*, 1933, **55**, 3402.

[88] N. N. Greenwood, R. L. Martin, and H. J. Emeléus, *J.*, 1951, 1328.

[89] N. N. Greenwood and R. L. Martin, *J.*, 1953, 751.

[90] A. A. Woolf and N. N. Greenwood, *J.*, 1950, 2200.

[91] N. N. Greenwood and R. L. Martin, *J.*, 1953, 1427.

[92] *J. Phys. Chem.*, 1946, **50**, 32.

[93] R. C. Osthoff and F. H. Clark, *J. Amer. Chem. Soc.*, 1952, **74**, 1361.

[94] E. L. Muetterties and E. G. Rochow, *ibid.*, 1953, **75**, 490.

[95] *Z. anorg. Chem.*, 1952, **268**, 221.

The Raman spectrum of molten boron trifluoride–nitric acid BF_3,HNO_3 indicates that the compound is predominantly in the ionic form $NO_2^+BF_3{\cdot}OH^-$.[79] With the liquid complex $(BF_3)_2,HNO_3$, on the other hand, there is virtually no NO_2^+ or $BF_3{\cdot}OH^-$ nor any evidence for free HNO_3 or BF_3 ; the complex exists as an undissociated co-ordination compound.

Electrolysis of Molten Complexes.—Electrolysis has recently been used to investigate the constitution of molten boron trifluoride co-ordination compounds.[96] The ionisation schemes and estimated degrees of ionic dissociation in the melts at room temperature are summarised in Table 3. The symbol H^+ is used for the hydrogen ion although the proton in the melt is undoubtedly solvated.

TABLE 3. *Ionic dissociation of molten complexes*

Compound	Mode of ionisation		Degree of ionic dissociation, %	Ref.
BF_3,H_2O . .	H^+	$BF_3{\cdot}OH^-$	10	22, 91
$BF_3,2H_2O$ . .	H_3O^+	$BF_3{\cdot}OH^-$	20	22, 91
BF_3,Et_2O . .	Et^+	$BF_3{\cdot}OEt^-$	0·07	96, 91
	and possibly also some			
	H^+	$[BF_3,EtO{\cdot}C_2H_4]^-$		
$BF_3,MeOH$ . .	H^+	$BF_3{\cdot}OMe^-$	2	27, 91
$BF_3,2MeOH$.	$MeOH_2^+$	$BF_3{\cdot}OMe^-$	7	27, 91
$BF_3,2Pr^nOH$.	$Pr^nOH_2^+$	$BF_3{\cdot}OPr^{n-}$	3	85, 91
$BF_3,Me{\cdot}CO_2H$.	H^+	$[BF_3,Me{\cdot}CO_2]^-$	5	88, 91
$BF_3,Me{\cdot}CO_2Me$	H^+	$[BF_3,Me{\cdot}CO_2{\cdot}CH_2]^-$	0·2*	100, 91
	and			
	$MeCO^+$	$BF_3{\cdot}OMe^-$		
$BF_3,Me{\cdot}CO_2Et$.	H^+	$[BF_3,Me{\cdot}CO_2{\cdot}C_2H_4]^-$	0·09	101, 91
	and			
	$MeCO^+$	$BF_3{\cdot}OEt^-$		

* At a temperature of 65°.

The hydrates ionise as hydroxyfluoroboric acid and hydroxonium hydroxyfluoroborate, a result consistent with the *X*-ray diffraction data on the solid [§2(i)]. The ionisation of boron trifluoride–ethyl ether as ethyl ethoxyfluoroborate indicates that the electron rearrangement caused by donor–acceptor bond formation results in a weakening of the C–O link and may explain, in part, the reactivity of the compound as a catalyst even under conditions where actual ionic dissociation does not occur. Boron trifluoride–methanol ionises as methoxyfluoroboric acid and not, as is frequently assumed,[102] as methyl hydroxyfluoroborate $Me^+BF_3{\cdot}OH^-$; this is consistent

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[96] N. N. Greenwood, R. L. Martin, and H. J. Emeléus, *J.*, 1950, 3030.
[97] R. L. Burwell and L. M. Elkin, *J. Amer. Chem. Soc.*, 1951, **73**, 502.
[98] R. L. Burwell, L. M. Elkin, and A. D. Shields, *ibid.*, 1952, **74**, 4567.
[99] H. Burton and P. F. G. Praill, *Quart. Reviews*, 1952, **6**, 302.
[100] N. N. Greenwood and R. L. Martin, unpublished observations.
[101] R. L. Martin, unpublished observations.
[102] Ref. (2), p. 167.

with the inability of methanol to alkylate under the influence of boron trifluoride.[103]

Boron trifluoride–acetic acid, when molten, ionises exclusively as acetoxyfluoroboric acid and it is therefore necessary to view with caution reaction mechanisms which require ionisation as acetyl hydroxyfluoroborate $Me{\cdot}CO^+BF_3{\cdot}OH^-$.[104] Preliminary results suggest that the boron trifluoride complexes with methyl and ethyl acetate ionise both as acids (by elimination of an α-hydrogen) and as acetyl alkoxyfluoroborates. Although it is sometimes assumed that the complexes ionise as alkyl acetoxyfluoroborate $R^+BF_3,{\cdot}MeCO_2^-$,[105] this mode of ionisation seems to be excluded by the electrolysis results when the compounds are in the molten state.

It should be stressed that ionic dissociation schemes postulated for pure liquids do not *necessarily* represent the behaviour of complexes in the reaction media of organic chemistry where dielectric constant and ionic environment are quite different.[97, 98, 99]

(iii) **Gaseous Co-ordination Compounds.**—The investigation of the molecular structure of boron trifluoride complexes in the vapour phase is hampered by the very high degree of thermal dissociation of most complexes into their constituent molecules. The quantitative aspects of this thermal instability are dealt with in §4.

One of the more favourable complexes is boron trifluoride–methyl ether, the structure of which has been elucidated by electron-diffraction techniques.[106, 107] Even in this instance the degree of dissociation is greater than 50% and this has necessitated a re-evaluation of the results.[108] The structure is compatible with a tetrahedral arrangement of bonds about both the boron and the oxygen atom and the revised bond distances are:[107] B–F = 1·43 ± 0·03; B–O = 1·50 ± 0·06; C–O = 1·45 ± 0·03 Å. The B–F distance is the same as that given by J. L. Hoard and V. Blair[63] from an *X*-ray analysis of solid ammonium and rubidium fluoroborates, and by J. Goubeau and W. Bues[95] from the Raman spectrum of aqueous sodium fluoroborate, but appears to be significantly longer than the value of 1·38 ± 0·02 Å found for compounds in which nitrogen is the ligand (Table 2). The apparent increase of the C–O bond length from 1·42 Å in methyl ether to 1·45 ± 0·03 Å in the complex may also be real and would be consistent with the known tendency of etherates to ionise in the molten state as alkyl alkoxyfluoroborates [§2(ii)].

(iv) **Structure of 1 : 2-Co-ordination Complexes.**—In the majority of its co-ordination compounds, boron trifluoride combines in 1 : 1 molecular proportions; nearly 200 such monocomplexes have been reported, whereas only about 20 compounds are known in which it combines with two moles

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[103] J. F. McKenna and F. J. Sowa, *J. Amer. Chem. Soc.*, 1937, **59,** 470; N. F. Toussaint and G. F. Hennion, *ibid.*, 1940, **62,** 1145; C. E. Welsh and G. F. Hennion, *ibid.*, 1941, **63,** 2603.

[104] Ref. (2), p. 186.

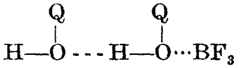
[105] Ref. (2), p. 200.

[106] S. H. Bauer, G. R. Finlay, and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 1943, **65,** 889.

[107] *Idem*, *ibid.*, 1945, **67,** 339.

[108] H. C. Brown and R. M. Adams, *ibid.*, 1943, **65,** 2253.

of the donor. H. Meerwein and W. Pannwitz [7] pointed out that the dicomplexes all have addends which are associated liquids (H_2O, ROH, $R{\cdot}CO_2H$), whereas the 1 : 1 complexes are usually formed from non-associated compounds (R_2O, $R{\cdot}CO_2R'$, R_3N, etc. *). They suggested that the structure of 1 : 2 complexes could be understood in terms of hydrogen bonding :



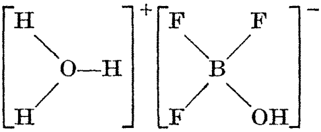
$$\mathrm{H{-}\overset{\overset{\large Q}{|}}{O}\cdots H{-}\overset{\overset{\large Q}{|}}{O}\cdots BF_3}$$

where Q = H, R, or R·CO.

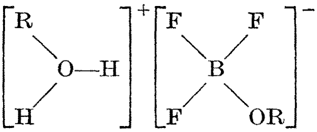
Another classification, rejected by these authors [7] but subsequently used by Ya. M. Paushkin,[109] is related to A. Hantzsch's observation that strong acids form stable addition complexes with weaker acids.[110] This concept is now developed in terms of oxonium compounds to give the present description of the structure of these compounds.

The 1 : 2 complexes are invariably more stable than the corresponding 1 : 1 compounds,[7] which may in some instances be too unstable to be isolated (*e.g.*, the 1 : 1 complexes with Pr^nOH, Pr^iOH, Bu^nOH, $ClCH_2{\cdot}CH_2{\cdot}OH$, $Ph{\cdot}CH_2{\cdot}OH$, $Cl_2CH{\cdot}CO_2H$). This instability is characteristic of many proton acids in the pure state ; *e.g.*, pure HBF_4, H_2CO_3, etc., cannot be isolated, but if a further molecule of the donor were available to " solvate " the proton by donor–acceptor interaction, stabilisation would result.

The hydrates of boron trifluoride may be considered as an example. The monohydrate is hydroxyfluoroboric acid $H^+BF_3{\cdot}OH^-$. The dihydrate is formed by additional donor–acceptor action of the second molecule of water, not with boron trifluoride, but with the hydrogen ion to give hydroxonium hydroxyfluoroborate (I). The dialcoholates should similarly be considered as alkoxonium alkoxyfluoroborates (II). Replacement of the alkoxy-groups R in formula (II) by the acyl group R·CO gives the structure of the boron trifluoride–di(carboxylic acid) complexes. Such formulations are consistent with the known structural and physical properties of the complexes.



(I)



(II)

The hypothetical fluoroboric acid $H^+BF_4^-$, which, unlike its hydroxy-analogue $H^+BF_3{\cdot}OH^-$, cannot be isolated in the pure state, can also be stabilised to some extent by addition of a further molecule of HF to give $BF_3,2HF$, *i.e.*, $H_2F^+BF_4^-$. This compound, though unstable, can be isolated as a solid melting at 56—58°.[110]

If the preceding views are correct there seems no reason why the second

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[109] *Zhur. Priklad. Khim.*, 1948, **21**, 1199.

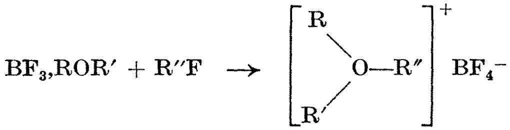
[110] *Ber.*, 1930, **63**, 1789.

* In ref. 7, the compounds written as $BF_3,2R_2O$ and $BF_3,2Et_3N$ in the table of refractivities clearly refer to the 1 : 1 complexes.

addend need be the same as the first. This would lead one to predict the existence of 1 : 1 : 1 compounds and, in fact, about 20 such compounds can be discovered in the literature. Excellent stabilisation of fluoroboric acid is achieved by adding ammonia gas, which results in the exothermic formation of BF_3,HF,NH_3 *i.e.*, $NH_4^+BF_4^-$, an "onium" salt as expected.[111] Addition of one mole of water to the BF_3–HF system also results in a stable complex BF_3, HF,H_2O [112] which is clearly $H_3O^+BF_4^-$. The 1 : 1 : 1 complex of boron trifluoride with hydrogen fluoride and hydrazine is also known $BF_3,HF,H_2N{\cdot}NH_2$,[113] *i.e.*, hydrazinium fluoroborate $[H_2H{\cdot}NH_3]^+BF_4^-$.

Recent investigations on the basicity of methylbenzenes towards mixtures of BF_3 and HF afford another example of the same phenomenon.[82, 83, 114] For instance, liquid hydrogen fluoride is immiscible with hexamethylbenzene, and gaseous boron trifluoride may be admitted at pressure above the liquid without appreciable reaction. However, immediately the system is stirred, the pressure drops and the system becomes homogeneous owing to formation of BF_3,HF,C_6Me_6, *i.e.*, $Me_6C_6H^+BF_4^-$. When the ratio of boron trifluoride to hydrocarbon is varied, a minimum is obtained at the 1 : 1 ratio.[83] (During the writing of this Review a paper has appeared confirming the ionic structures proposed for the $ArH^+BF_4^-$ complexes.[114a]) Similar results are known for systems such as $AlCl_3$–HCl–hydrocarbon,[115] $AlBr_3$–HBr–hydrocarbon,[116] and $SnCl_4$–HCl–hydrocarbon.[117] Much further information on these compounds may be obtained by consulting the original papers. The closely related problem of the catalytic activity of the BF_3–HF couple has been extensively studied but cannot be reviewed here.

The tertiary oxonium compounds studied by H. Meerwein and his collaborators [118–120] may also be considered as 1 : 1 : 1 complexes. Thus boron trifluoride etherates can add one mole of alkyl fluoride to give tertiary oxonium fluoroborates :



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[111] J. L. Gay-Lussac and L. J. Thénard, *Ann. Physique*, 1809, **32,** 1.

[112] Ya. M. Paushkin and A. V. Topchiev, *J. Gen. Chem. U.S.S.R.* (U.S. Transl.), 1949, **19,** a657.

[113] H. Funk and F. Binder, *Z. anorg. Chem.*, 1926, **159,** 121.

[114] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, 1952, **74,** 6246.

[114a] M. Kilpatrick and F. E. Luborsky, *ibid.*, 1953, **75,** 577.

[115] H. C. Brown and H. Pearsall, *ibid.*, 1951, **73,** 4681 ; 1952, **74,** 191 : A. Schneider, *ibid.*, p. 2553 ; A. P. Lien, E. L. d'Ouville, B. L. Evering, and H. M. Grubb, *Ind. Eng. Chem.*, 1952, **44,** 351.

[116] B. Ya. Rabinowich, *J. Gen. Chem. U.S.S.R.* (U.S. Transl.), 1951, **21,** 71 ; G. Baddeley, G. Holt, and D. Voss, *J.*, 1952, 100 ; D. D. Eley and P. J. King, *J.*, 1952, 2517, 4972.

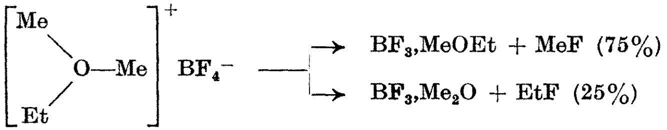
[117] G. Williams and H. Bardsley, *J.*, 1952, 1707.

[118] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. pr. Chem.*, 1937, **147,** 257.

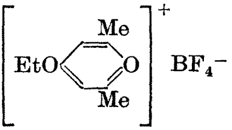
[119] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *ibid.*, 1939, **154,** 83.

[120] H. Meerwein, *Angew. Chem.*, 1951, **63,** 480.

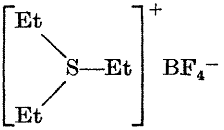
For example, reaction either of ethyl fluoride with boron trifluoride–methyl ether or of methyl fluoride with boron trifluoride–ethyl methyl ether gives ethyldimethyloxonium fluoroborate, which can be dissociated, on careful heating, according to the scheme [118]



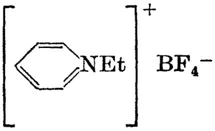
The tertiary oxygen atom can be located in a ring system [53, 118] as in 4-ethoxy-2 : 6-dimethylpyryllium fluoroborate (III), or it may be replaced by sulphur [118] as in triethylsulphonium fluoroborate (IV). Such compounds are extraordinarily reactive and are ionically dissociated in liquid sulphur dioxide solution.[119]



(III)



(IV)



(V)

The analogous quaternary nitrogen compounds have already been mentioned in connection with substituted ammonium fluoroborate. The nitrogen may also be in a heterocyclic system, and the 1 : 1 : 1 compound between boron trifluoride, ethyl fluoride, and pyridine, *i.e.*, ethylpyridinium fluoroborate, may be cited as an illustration (V).[118] The melting points of these various complexes are assembled in Table 4.

It is clear that the examples selected above to illustrate the proposed structure of 1 : 2 and 1 : 1 : 1 complexes by no means exhaust the possibilities, and a large field is open for physico-chemical investigation. The possibility of new types of compound is at once apparent, and novel syntheses of known complexes are also suggested. For example, the conductimetric titration of boron trifluoride–ethyl ether with water establishes a well-defined 1 : 1 : 1 compound having properties remarkably similar to those of boron trifluoride–diethanol, for which the same structural formula may be written : [85]

$$BF_3,Et_2O + H_2O \rightleftharpoons [EtOH_2]^+BF_3{\cdot}OEt^- \rightleftharpoons BF_3,2EtOH$$

However, insufficient data are available yet to claim identity of the two compounds.

3. Physical Properties

The first two sections of this Review have dealt with the general stability and structure of boron trifluoride complexes. In the present section the best available data on the physical properties of these compounds are tabulated and briefly discussed. It is apparent at the outset that there are large gaps in our knowledge. Of about 140 compounds for which any numerical data are known, about 90% have a known melting point, only one-third have

TABLE 4. *Melting points*

Compound	M p *	Ref.
Inorganic		
BF_3,KF	530° d.	16
BF_3,RbF	590 d.	16
BF_3,CsF	550 d.	16
BF_3,NH_4F	487 ± 3	58
BF_3,H_2O	5·9—6·0	22
$BF_3,2H_2O$	6·2	22
BF_3,Na_2SO_4	~ 310	51
BF_3,K_2SO_4	~ 240	51
$(BF_3)_2,Cs_2SO_4$	~ 250	51
BF_3,H_2S	− 137	78
BF_3,SO_2	− 96·0 ± 0·3	45
BF_3,SOF_2	− 140·8 ± 0·5	48
BF_3,HPO_3	~ − 53	121
BF_3,H_3PO_4	~ − 105	121
$(BF_3)_2,H_4P_2O_7$	~ − 82	121
$(BF_3)_3,Na_3PO_4$	~ 350	51
$(BF_3)_3,K_3PO_4$	~ 330	51
$(BF_3)_4,Na_4P_2O_7$	~ 360	51
$(BF_3)_4,K_4P_2O_7$	~ 360	51
$BF_3,COCl_2$	− 134·3 ± 0·5	4
$BF_3,2COCl_2$	− 137·0 ± 0·5	4
BF_3,PCl_3	− 6 d.	40
BF_3,PH_3	(~ − 48)	15
$(BF_3)_2,PH_3$	(~ − 83)	15
BF_3,NH_3	163 ± 1 d.	25
BF_3,HCN	40	123
BF_3,NO	~ − 130	124
$(BF_3)_2,HNO_3$	53	79
$BF_3,2HF$	~ 56—58	110
Ethers		
BF_3,Me_2O	− 14	54
$BF_3,MeOEt$	− 98	54
BF_3,Et_2O	− 57·8 to − 57·7	96
$BF_3,Pr^i{}_2O$	68 d.	13
$BF_3,MeOAm^n$	− 41	9
$BF_3,PhOMe$	− 12 to − 13	9
$BF_3,C_4H_8O^{(a)}$	8—10	13
$BF_3,C_4H_8O_2{}^{(b)}$	~ 50	85
$BF_3,2C_4H_8O_2{}^{(b)}$	~ 20	85
Alcohols		
$BF_3,MeOH$	− 18·6	27
$BF_3,2MeOH$	− 58·1	27
$BF_3,EtOH$	− 19	8
$BF_3,2CCl_3\cdot CH_2\cdot OH$	40—42	7
$BF_3,(CH_2\cdot OH)_2$	42—44	7
Acids		
$BF_3,H\cdot CO_2H$	− 20 to − 21	7
$BF_3,Me\cdot CO_2H$	37·5	88
$BF_3,Et\cdot CO_2H$	28—29	7
$BF_3,Pr^n\cdot CO_2H$	29—30	7
$BF_3,Me\cdot CH{:}CH\cdot CO_2H$	35—36	7
$BF_3,Ph\cdot CO_2H$	~ 98	8
$BF_3,Ph\cdot CH_2\cdot CO_2H$	56—59 d.	7
$BF_3,(CO_2H)_2$	57—58 d.	7
$BF_3,(\cdot CH\cdot CO_2H)_2$	75—82 d.	7
$BF_3,(CH_2\cdot CO_2H)_2$	82—84 d.	7
Esters		
$BF_3,H\cdot CO_2Me$	23·5	125
$BF_3,H\cdot CO_2Et$	3	125
$BF_3,Me\cdot CO_2Me$	65·5	89
$BF_3,Me\cdot CO_2Et$	32·5	89
$BF_3,Me\cdot CO_2Pr^n$	14·7	89
$BF_3,Me\cdot CO_2Bu^n$	17·9	89
$BF_3,Me\cdot CO_2\cdot C_6H_4Me\text{-}p$	146—150	126
$BF_3,Et\cdot CO_2Et$	33	8
$BF_3,Ph\cdot CO_2Me$	40—55 d.	127
Nitrogen donors		
BF_3,Me_2NH	~ 50	128
BF_3,Me_3N	146—146·5	129
$BF_3,EtNH_2$	89	24
BF_3,Et_2NH	(150—165)	24
BF_3,Et_3N	29·7—29·8	85
$BF_3,Bu^n{}_3N$	59—61	93
$BF_3,PhNMe_2$	90—92	130
BF_3,C_5H_5N	48—49	101
$BF_3,\alpha\text{-}MeC_5H_4N^{(c)}$	60—70 d.	101
$BF_3,\alpha\alpha'\text{-}Me_2C_5H_3N^{(d)}$	100—130	12
$BF_3,MeCN$	135·5 ± 0·5	60
$BF_3,PhCN$	105—121 d.	14
$BF_3,o\text{-}C_6H_4Me\cdot CN$	77—86 d.	14
$BF_3,m\text{-}C_6H_4Me\cdot CN$	65—76 d.	14
$BF_3,p\text{-}C_6H_4Me\cdot CN$	111—113 d.	14
$BF_3,Me\cdot CO\cdot NHPh$	133	131
$BF_3,Me\cdot CO\cdot NMePh^{(e)}$	114	131
$BF_3.Ph\cdot CH{:}NPh^{(f)}$	135—145	132
$BF_3,Ph\cdot CMe{:}NOH^{(g)}$	107—113	126
$BF_3,p\text{-}Me\cdot C_6H_4\cdot NH\cdot CH{:}N\cdot C_6H_4\cdot Me\text{-}p^{(h)}$	172—174	133
$(BF_3)_4,(CH_2)_6N_4{}^{(i)}$	155—160	134
Oxonium types		
BF_3,MeF,Me_2O	148 d.	119
BF_3,MeF,Et_2O	99—100 d.	119
BF_3,EtF,Me_2O	120—121 d.	118
BF_3,EtF,Et_2O	92 d.	118
$BF_3,Pr^nF,Pr^n{}_2O$	73—74 d.	119
$BF_3,EtF,Me_2\text{-pyrone}$	90—91	118
$BF_3,EtF,\text{coumarin}$	106 d.	118
$BF_3,EtF,\text{camphor}$	104·5—105·5 d.	118
$BF_3,EtF,(CH_2)_5O^{(j)}$	45	119
$BF_3,Me\cdot COF,Me_2\text{-pyrone}$	139 d.	53
$BF_3,H_2O,2\text{cineole}$	71—73 d.	7
$BF_3,2H_2O,2\text{cineole}$	59·5—61 d.	7
$BF_3,H_2O,C_4H_8O_2{}^{(b)}$	128—130 d.	7
$BF_3,2H_2O,C_4H_8O_2{}^{(b)}$	142 d.	7
BF_3,EtF,Et_2S	105·5	118
BF_3,EtF,C_5H_5N	58·5—59·5	118
$BF_3,Bu^nF,Bu^n{}_3N$	161·8	135
Miscellaneous		
BF_3,Ph_3CF	~ 215 d.	53
$BF_3,Me\cdot COCl$	~ − 70	9
BF_3,Me_2CO	35—40	43
BF_3,Me_3NO	89	136
BF_3,Me_3PO	148—150	137
$BF_3,(Me\cdot CO)_2O$	(194)	8
$(BF_3)_3,[(Me\cdot CO)_2CH\cdot CO]_2O^{(k)}$	195—196	138
$(BF_3)_3,(Me_2CH\cdot CO\cdot CMe_2\cdot CO)_2O^{(l)}$	117—119 d.	138

* d. = With decomposition.

(*a*) Tetrahydrofuran.
(*b*) Dioxan.
(*c*) α-Picoline.
(*d*) αα′-Lutidine.
(*e*) *N*-Methylacetanilide.
(*f*) Benzylideneaniline.
(*g*) Acetophenone oxime.
(*h*) *NN*′-Di-*p*-tolylformamidine.
(*i*) Hexamethylenetetramine.
(*j*) Tetrahydropyran.
(*k*) Diacetic anhydride.
(*l*) Dibutyric anhydride.

known densities, and the boiling points have been measured for only one-quarter. The electrical conductivity of about one-fifth of the compounds has been studied, and a similar proportion holds for vapour pressures. However, interesting correlations emerge even for the lesser studied properties such as viscosity, surface tension, refractive index, and dipole moment, and each of these will be discussed in turn.

(i) **Melting Point.**—Very little of importance can be said from a study of melting point alone, but the known values have been collected together in Table 4 for ease of reference. Other values may frequently be found in the literature, but the present table aims at presenting only the most reliable values. One reference has been given for each compound although in some instances corroborative values are known.

The melting points of the inorganic complexes are distributed fairly evenly over a 730°-range from − 140° to 590°. Complexes involving ethers or alcohols tend to melt below room temperature and the complexes with esters have melting points between 0° and 65° except for boron trifluoride–*p*-tolyl acetate (m.p. ~ 150°). The compounds listed under nitrogen donors and oxonium types have rather higher melting points, ranging from 45° to 175°. The aliphatic acids combine with boron trifluoride to give complexes melting at about room temperature, but substitution by a phenyl group or by a second carboxylic acid group raises the melting point.

There is no simple correlation between melting point and chain length in a given series, nor, apparently, between the melting points of two complexes formed from the same addend in different stoicheiometric ratios. In the inorganic complexes, molecular weight of the alkali radical has no systematic effect on the melting point.

Certain of the values call for brief comment. The alkali fluoroborates have slight dissociation pressures of boron trifluoride at their melting point. From the data of J. H. de Boer and J. A. M. van Liempt [16] these may be

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[121] A. V. Topchiev and Ya. M. Paushkin, *Neftyanoe Khozgaistro* (Oil Economy), 1947, **25,** No. 6, 54.

[122] *Idem, Usp. Chim.*, 1947, **16,** 664.

[123] E. Pohland and W. Harlos, *Z. anorg. Chem.*, 1932, **207,** 242.

[124] G. R. Finlay, *J. Chem. Educ.*, 1947, **24,** 149.

[125] G. T. Morgan and R. Taylor, *J. Soc. Chem. Ind.*, 1931, **50,** 869.

[126] O. J. Grummit, M.A. Thesis, Western Reserve Univ., Cleveland, Ohio, 1934 [cited by ref. (2), pp. 48, 74].

[127] G. T. Morgan and R. Taylor, *J.*, 1932, 1497.

[128] E. Wiberg and P. Buchheit (unpubl.) ; P. Buchheit, Ph.D. Dissertation Munich, 1942 [cited by J. Goubeau, F.I.A.T. Reviews of German Science : Inorganic Chemistry, Vol. I, p. 218].

[129] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J.*, 1945, 146.

[130] J. R. Bright and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1943, **65,** 735.

[131] S. Sugden and M. Waloff, *J.*, 1932, 1492.

[132] H. R. Snyder, H. A. Kornberg, and J. R. Romig, *J. Amer. Chem. Soc.*, 1939, **61,** 3556.

[133] F. Klages and K. Mönkemeyer, *Ber.*, 1952, **85,** 126.

[134] A. B. Burg and LaV. L. Martin, *J. Amer. Chem. Soc.*, 1943, **65,** 1635.

[135] C. R. Witschonke and C. A. Kraus, *ibid.*, 1947, **69,** 2472.

[136] A. B. Burg and J. H. Bickerton, *ibid.*, 1945, **67,** 2261.

[137] A. B. Burg and W. E. McKee, *ibid.*, 1951, **73,** 4590.

[138] H. Meerwein and D. Vossen, *J. pr. Chem.*, 1934, **141,** 149.

calculated as 2, 4, and 1·5 mm. of mercury for the potassium, rubidium, and cæsium salts, respectively. Ammonium fluoroborate, on the other hand, has a much larger vapour pressure; it sublimes at 230—250° [19, 139] and an extrapolation of A. W. Laubengayer and G. F. Condike's data [25] to the melting point leads to a triple-point pressure of 4·9 atm.

Some confusion has arisen about the melting points of the complexes with meta-, ortho-, and pyro-phosphoric acid, as the original paper of A. V. Topchiev and Ya. M. Paushkin [121] omitted the minus signs. This slip was corrected in a subsequent paper by these authors [122] but the error has unfortunately been carried through into *Chemical Abstracts* and H. S. Booth and D. R. Martin's book.[2] The three complexes are viscous liquids at room temperature, not solids.

Towards the end of the table, the melting point of the compound boron trifluoride–acetic anhydride is given in parentheses as 194°. This was corroborated by the work of G. T. Morgan and R. Taylor [125] but subsequent investigations by H. Meerwein and D. Vossen [138] established that the compound formed during the interaction is boron trifluoride–diacetic anhydride, $(BF_3)_3,[(Me{\cdot}CO)_2CH{\cdot}CO]_2O$, m.p. 195—196°. Both values, therefore, apply to the latter compound.

TABLE 5. *Boiling points*

Compound	B p.	Ref.	Compound	B.p.	Ref.
Ethers			*Acids*		
BF_3,Me_2O	126—127°*	43	$BF_3,2H{\cdot}CO_2H$	43—44°/11 mm.*	7
$BF_3,MeOEt$	127 d.*	54	$BF_3,Me{\cdot}CO_2H$	62/11 mm.*	138
BF_3,Et_2O	125—126*	140	$BF_3,2Me{\cdot}CO_2H$	140/746 mm.*	8
BF_3,Am^i_2O	78—79/22 mm.	141	$BF_3,Et{\cdot}CO_2H$	62—63/17 mm. d.*	8
$BF_3,MeOAm^n$	54·8—55/10 mm.	9	$BF_3,2Et{\cdot}CO_2H$	60—60·5/12 mm.*	7
BF_3,C_4H_8O	69/4 mm.*	142	$BF_3,2Pr^n{\cdot}CO_2H$	64/11 mm.	7
			$BF_3,2Pr^i{\cdot}CO_2H$	68—70/15 mm.	138
Hydroxyl compounds			$BF_3,2Me{\cdot}CH{:}CH{\cdot}CO_2H$	81—82/12·5 mm. d.	7
$BF_3,2H_2O$	(58·5—60/1·2 mm.†)	7			
$BF_3,2MeOH$	(58—59/4 mm.)	7			
$BF_3,2EtOH$	(60/4 mm.)	7	*Esters*		
$BF_3,2Pr^nOH$	(56/2 mm.)	7	$BF_3,H{\cdot}CO_2Me$	94/772 mm.	125
$BF_3,2Bu^nOH$	69—70/3 mm.	7	$BF_3,H{\cdot}CO_2Et$	103/772 mm.*	125
$BF_3,2ClCH_2CH_2{\cdot}OH$	59/2·5 mm.	7	$BF_3,Me{\cdot}CO_2Me$	112/772 mm.*	125
			$BF_3,Me{\cdot}CO_2Et$	123/772 mm.*	125
Nitrogen donors			$BF_3,Me{\cdot}CO_2Pr^n$	127 d.*	89
BF_3,Me_3N	238	143	$BF_3,Me{\cdot}CO_2Bu^n$	135 d.*	89
BF_3,Et_3N	80/3 mm.	24	$BF_3,Et{\cdot}CO_2Et$	116/747 mm.*	8
BF_3,C_5H_5N	300 ± 5	3	$BF_3,CH_2(OH){\cdot}CO_2Me$	60/3 mm. d.*	127
$BF_3,MeCN$	101/752 mm.*	8			

* Vapour known to be completely or highly dissociated at b.p.—see §4. Other compounds in the same homologous series are also likely to be dissociated but no measurements have been published.

† The four compounds whose b.p.s are given in parentheses are now known to decompose appreciably on vacuum-distillation.

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[139] W. E. White, U.S.P. 2,403,148, July 2nd, 1946 [cited by ref. (58)].

[140] G. F. Hennion, H. D. Hinton, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55,** 2857.

[141] H. G. Cook, J. D. Ilett, B. C. Saunders, and G. J. Stacey, *J.*, 1950, 3125.

[142] R. C. Osthoff, C. A. Brown, and J. A. Hawkins, *J. Amer. Chem. Soc.*, 1951, **73,** 5480.

[143] J. F. Brown, *ibid.*, 1952, **74,** 1219.

(ii) **Boiling Point.**—Most addition complexes of boron trifluoride either decompose or thermally dissociate in the vapour phase, so the "boiling point" is generally an unsatisfactory means of characterising the compounds. The values given in Table 5 should rather be taken as indicating the temperature at which the pressure above the liquid reaches a specified value; the composition of the two phases may differ appreciably. Even complexes which distil unchanged may be highly dissociated in the vapour phase and, indeed, of all the compounds listed in Table 5, only boron trifluoride–methylamine[144] is known to be monomeric and undissociated at the boiling point.

TABLE 6. *Densities and molar volumes (liquids)*

Compound	Temp.	d	V_M	Ref.	Further refs.
BF_3,H_2O	20°	1·7850	48·1	22	7, 148
$BF_3,2H_2O$	20	1·6320	63·6	22	7, 23, 26, 64, 148
BF_3,HPO_3	20	1·992	74·2	122	121, 149
BF_3,H_3PO_4	20	1·932	85·8	122	121, 149
$(BF_3)_2,H_4P_2O_7$	20	1·950	160·9	122	109, 121
BF_3,Me_2O	20	1·241	91·8	131	43, 54, 145
$BF_3,MeOEt$	25	1·176	108·8	54	—
BF_3,Et_2O	20	1·128	125·8	131	54, 150
$BF_3,MeOH$	20	1·4081	70·9	27	109, 122
$BF_3,2MeOH$	20	1·2120	108·8	27	7, 26
$BF_3,EtOH$	20 (?)	1·353	84·2	122	109
$BF_3,2EtOH$	20	1·1638	137·4	7	26
$BF_3,2Pr^nOH$	20	1·0561	178·0	85	7, 26
$BF_3,2Bu^nOH$	20	1·0442	206·9	26	7
$BF_3,2ClCH_2\cdot CH_2\cdot OH$	20	1·4009	163·4	26	7
$BF_3,PhOH$	20 (?)	1·244	130·2	122	109
$BF_3,2H\cdot CO_2H$	20	1·5145	105·6	7	—
$BF_3,Me\cdot CO_2H$	20*	1·4958	85·5	151	—
$BF_3,2Me\cdot CO_2H$	20	1·3421	140·0	7	8
$BF_3,2Et\cdot CO_2H$	20	1·2283	175·8	7	8
$BF_3,2Pr^n\cdot CO_2H$	20	1·1506	212·1	7	—
$BF_3,H\cdot CO_2Me$	20*	1·424	89·8	131	—
$BF_3,H\cdot CO_2Et$	20	1·322	107·4	131	8
$BF_3,Me\cdot CO_2Me$	65	1·246	113·9	131	—
$BF_3,Me\cdot CO_2Et$	20*	1·251	124·6	131	—
$BF_3,Me\cdot CO_2Pr^n$	20	1·1999	141·6	89	8, 152
$BF_3,Me\cdot CO_2Bu^n$	20	1·1554	159·2	89	152
$BF_3,Me\cdot CO\cdot NMePh$	115	1·192	182·1	131	—
$BF_3,(Me\cdot C_6H_4\cdot O)_3PO$	20	1·264	345·0	109	—

* Compound is supercooled at 20°.

The results of H. C. Brown and R. M. Adams[13] suggest that, at the boiling point, boron trifluoride–methyl ether is more than 60% dissociated into its components. Published values of the boiling point range between 126° and 128°.[13, 43, 54, 131, 145] The boiling points of the homologous

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[144] A. B. Burg and A. A. Green, *J. Amer. Chem. Soc.*, 1943, **65**, 1838.

[145] A. J. Kolka and R. R. Vogt, *ibid.*, 1939, **61**, 1463.

complexes with ethyl methyl ether and diethyl ether are remarkably similar to that of boron trifluoride–methyl ether. Values reported for boron trifluoride–ethyl ether fall in the range 121—127°.[13, 43, 46, 54, 86, 131, 140, 146, 147]

The complexes of boron trifluoride with inorganic compounds all decompose or dissociate completely before boiling. Values quoted for the boiling point of boron trifluoride dihydrate show some variation [7, 26, 64] but this is not surprising since J. S. McGrath, G. G. Stack, and P. A. McCusker [23] have shown that appreciable decomposition occurs to give a mixture of fluoroboric acids on attempted distillation.

Alternative values for some of the complexes with acids and esters may be found in ref. 2, but it must be emphasised strongly that boron trifluoride is frequently lost from the complexes during distillation, even under reduced pressure.

TABLE 7. *Variation of density with temperature* : $d_4^t = d_4^0 - \alpha t$

Compound	d_4^0	$10^3\,\alpha$	Range	Ref.
BF_3,H_2O	1·8078	1·14	0—20°	22*
$BF_3,2H_2O$	1·6590	1·32	5—45	22*†
BF_3,Me_2O	1·264	1·16	20—50	131
BF_3,Et_2O	1·150	1·08	10—50	131
	1·155	1·15	20—60	131
	1·150	$1{\cdot}10_5$	−55—0	150
$BF_3,MeOH$	1·4328	$1{\cdot}23_3$	−20—20	27
$BF_3,2MeOH$	1·2344	1·12	−20—20	27
$BF_3,2Pr^nOH$	1·0748	0·934	−15—25	85
$BF_3,Me{\cdot}CO_2H$	1·5216	1·29	35—45	151*
$BF_3,H{\cdot}CO_2Me$	1·450	1·28	30—55	131
$BF_3,H{\cdot}CO_2Et$	1·346	1·22	20—55	131
$BF_3,Me{\cdot}CO_2Me$	1·324	1·17	60—90	131
$BF_3,Me{\cdot}CO_2Et$	1·276	1·23	40—70	131
$BF_3,Me{\cdot}CO_2Pr^n$	1·2234	$1{\cdot}17_4$	0—25	89, 152
$BF_3,Me{\cdot}CO_2Bu^n$	1·1781	$1{\cdot}13_4$	0—30	89, 152
$BF_3,Me{\cdot}CO{\cdot}NMePh$	1·205‡	0·83‡	115—150	131

* The present equation is a slight modification of the original one owing to a recalibration of the pyknometer.

† The data may be fitted with slightly greater precision by the equation

$$d_4^t = 1{\cdot}6255 - 1{\cdot}31 \times 10^{-3}(t - 25) + 2 \times 10^{-6}(t - 25)^2.$$

‡ For the equation $d_4^t = d_4^{100} - \alpha(t - 100)$.

(iii) **Density and Molar Volume.**—The densities and molar volumes of liquid boron trifluoride co-ordination compounds are collected together in

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[146] J. W. Kroeger, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1937, **59**, 965.

[147] R. Paris and D. Georgen, *Bull. Soc. chim.*, 1952, 1078.

[148] Ref. (18); cited by ref. (2), p. 160.

[149] A. V. Topchiev and Ya. M. Paushkin, *Zhur. Obshchey Khim.*, 1948, **18**, 1537.

[150] E. Wiberg and W. Mathing, *Ber.*, 1937, **70**, 690.

[151] N. N. Greenwood and R. L. Martin, *J.*, 1951, 1795.

[152] *Idem*, *Proc. Roy, Soc.*, 1952, *A*, **215**, 46.

Table 6, and the variations of density with temperature are summarised in Table 7. It is not practicable to compare densities at the boiling point for the reasons indicated in the preceding section. However, considerable regularity is observed even at the arbitrarily chosen temperature of 20° and the density is quite well approximated to by the formula[153]

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

where M is the molecular weight and V_M the molar volume. This relation arises from the additivity of molar volumes, so that

$$\Delta V_M = V_M(\text{complex}) - V_M(\text{donor}) = \text{const.} = 28.$$

The molar volume of co-ordinated boron trifluoride (28 cm.^{3}) is therefore appreciably less than that of the free compound, either as a liquid ($\sim$ 39) or as a solid ($\sim$ 35).[2]

The relations are useful for estimating the densities and molar volumes of complexes when experimental values have not been determined, and also to check existing data. A notable exception to the rule is boron trifluoride–ethyl ether, for which $\Delta V_M = 21{\cdot}95$.

The temperature coefficient of the density (Table 7) is approximately

TABLE 8. *Densities and molar volumes (solids)*

Compound	d	V_M	Remarks*	Ref.
BF_3,NaF	2·53	43·5	XRD	17
BF_3,NaOH . . .	2·46	43·9	XRD	17
BF_3,KF	2·498	50·4	Petrol	20
	2·524	49·9	H_2O	20
	2·554—2·559	49·3—49·2	CCl_4	62
	2·545	49·5	XRD	62
BF_3,RbF	2·820	61·1	—	154
	3·12	55·3	XRD	63
BF_3,CsF	3·47	63·3	XRD	17
BF_3,TlF	4·75	61·3	XRD	17
BF_3,NH_4F	1·851	56·7	—	155
	1·854	56·6	—	50
	1·91	54·8	XRD	64
	1·89	55·6	XRD	63
BF_3,NOF	2·185	53·5	$PhNO_2$	156
	2·20	53·2	XRD	65
BF_3,NaH	2·46	37·3	PhMe	59
BF_3,$2H_2O$	1·92	54·2	XRD	64
BF_3,Me·CO_2H . . .	1·56	81·9	—	151
BF_3,NH_3	1·831	46·3	—	50
	1·864	45·7	PhH	25
	1·82	46·7	XRD	66
BF_3.$MeNH_2$ . . .	1·56	63·2	XRD	68
BF_3,Me_2NH . . .	1·38	82·0	XRD	69
BF_3,Me_3N	1·16	109·3	XRD	70
BF_3,MeCN	1·59	68·4	PhH or PhMe	60
	1·55	70·2	XRD	67

* Compounds mentioned served as confining fluid : XRD = *X*-ray diffraction.

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[153] N. N. Greenwood and R. L. Martin, *J.*, 1953, 4132.

[154] F. Zambonini, *Z. Krist.*, 1906, **41,** 53.

[155] F. Stolba, *Centr. ges. chem. Grossind.*, 1890, **7,** 459 [cited by ref. (2), p. 110].

[156] G. Balz and E. Mailänder, *Z. anorg. Chem.*, 1934, **217,** 161.

the same for most of the complexes, although the value of $0{\cdot}83 \times 10^{-3}$ for boron trifluoride–methylacetanilide, in which nitrogen is the probable ligand, is rather lower.

Less regularity is observed in the densities and molar volumes of solid boron trifluoride complexes (see Table 8). This may be due partly to the effect of varying crystal structure, and partly to the difficulty of obtaining reasonably accurate densities for solids. All the values from *X*-ray diffraction data have been evaluated on the basis of Avogadro's number ($N = 6{\cdot}024 \times 10^{23}$), and many of the densities are presented for the first time.

Values for $\Delta V_M = V_M$(complex) − V_M(donor) show considerable scatter, but the mean value of ~25 [153] appears to be significantly smaller than the value of 28 computed from the densities of the molten complexes. The value calculated from the densities of the dihydrate and ice is anomalously low ($\Delta V_M = 14{\cdot}9$); this is related to the fact that water expands rather than contracts on freezing.

TABLE 9. *Refractive index and molar refraction*

Compound	Temp.	*n*	[*R*]	Ref.
$BF_3,2H_2O$	20°	1·3150	12·51	7
BF_3,NH_3(s)	—	α = 1·335* β = 1·34—1·35 γ = 1·36	α 9·44 β 9·6—9·8 γ 10·1	25
BF_3,Et_3N	—	—	36·34	7
BF_3,Me_2O	20	1·308	17·60	7
BF_3,MeOEt	20	1·327	22·04	54
BF_3,Et_2O	20	1·344	26·63	7
BF_3,C_4H_8O	—	—	28·50	142
BF_3,Pr^n_2O	—	—	36·16	7
BF_3,2MeOH	18	1·3070	19·22	7
BF_3,2EtOH	19·7	1·3344	28·39(a)	7
$BF_3,2Pr^nOH$	20	1·3615	37·65	7
$BF_3,2Bu^nOH$	20·2	1·3732	47·11	7
$BF_3,2Cl{\cdot}[CH_2]_2{\cdot}OH$	17	1·4084	40·33(b)	7
$BF_3,2H{\cdot}CO_2H$	21·1	1·3572	23·15	7
$BF_3,2Me{\cdot}CO_2H$	21·1	1·3692	31·62(c)	7
$BF_3,2Et{\cdot}CO_2H$	21·6	1·3807	40·83	7
$BF_3,2Pr^n{\cdot}CO_2H$	21·8	1·3884	50·14	7

(*a*) Given as 28·17 in ref. (7). (*b*) Given as 38·87 in ref. (7). (*c*) Ref. (146) gives $n_D^{25} = 1{\cdot}3735$, whence [*R*] = 31·94.

* These figures for the solid complex refer to refractive indices parallel to the three crystallographic axes.

(iv) **Refractive Index and Molar Refraction.**—Most of the information on refractive indices of boron trifluoride complexes is due to H. Meerwein and W. Pannwitz.[7] The data are summarised in Table 9. The molar refraction of boron trifluoride itself has been given as 6·00 [157] and 6·09,[158] so that, if this function were additive during complex formation, the difference between

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[157] W. Klemm and P. Henkel, *Z. anorg. Chem.*, 1933, **213**, 115.

[158] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.

the molar refractions of the complex and the donor should be 6·0. This is not observed, and the function $\Delta[R] = [R]_{\text{complex}} - [R]_{\text{donor}}$ varies between 2·4 and 8·5.[100] It is probable that some of this scatter results from partial decomposition of the complex during distillation, and it seems likely that many of the figures in Table 9 will need revising when measurements are available for highly purified, undistilled specimens. Nevertheless, some regularity is observed ; the dialcoholates give $\Delta[R] = 2{\cdot}6 \pm 0{\cdot}2$, and the fatty acid series and dihydrate, $\Delta[R] = 5{\cdot}5 \pm 0{\cdot}5$.

There are insufficient reliable data to decide whether the apparent molar refractivity of co-ordinated boron trifluoride is significantly smaller than that of the free compound, and whether this quantity varies with the nature of the addend.

(v) **Electrical Conductivity.**—Many complexes of boron trifluoride dissociate ionically in the molten state and conduct electricity electrolytically.[91] Table 10, which collects the data available on the electrical properties of the molten complexes, demonstrates that the specific electrical conductivity, κ, is frequently very large and may even approach values characteristic of molten salts or of concentrated solutions of strong electrolytes. For example, the specific conductivity of a saturated aqueous solution of sodium chloride ($\sim$ 320 g./l.) at 25° is $\kappa_{25} = 2{\cdot}5 \times 10^{-1}$ ohm^{-1} cm.$^{-1}$. In many instances the conductivity is known over a range of temperatures. The results are summarised graphically in Fig. 1.

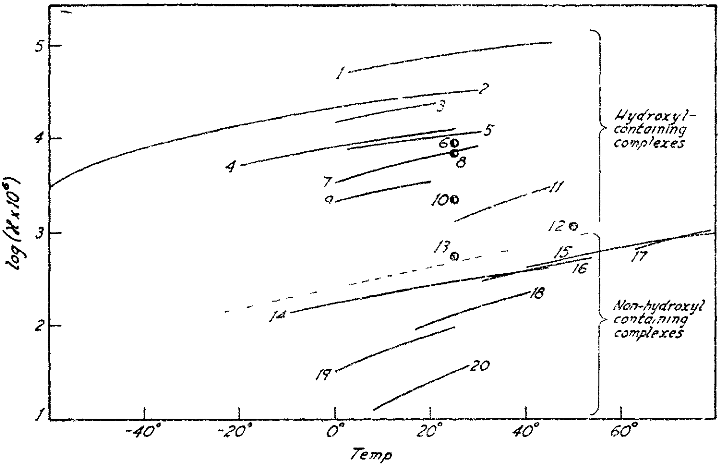

FIG. 1

No.	Compound	(Ref)	No	Compound	(Ref.)	No.	Compound	(Ref)
1.	$BF_3,2H_2O$	(22)	8.	$(BF_3)_2,H_4P_2O_7$	(159)	15.	BF_3,C_5H_5N	(101)
2.	$BF_3,2MeOH$	(27)	9.	$BF_3,2Pr^n{\cdot}OH$	(85)	16.	BF_3,Et_3N	(85)
3.	BF_3,H_2O	(22)	10.	$BF_3,2Me{\cdot}CO_2H$	(88)	17.	$BF_3,Me{\cdot}CO_2Me$	(89)
4.	$BF_3,MeOH$	(27)	11.	$BF_3,Me{\cdot}CO_2H$	(151)	18.	$BF_3,Me{\cdot}CO_2Et$	(89)
5.	$BF_3,2EtOH$	(85)	12.	$BF_3,2PhOH$	(87)	19.	$BF_3,Me{\cdot}CO_2Pr^n$	(89)
6.	$BF_3,EtOH$	(159)	13.	$BF_3,PhOH$	(159)	20.	$BF_3,Me{\cdot}CO_2Bu^n$	(89)
7.	BF_3,H_3PO_4	(160)	14.	BF_3,Et_2O	(96)			

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[159] A. V. Topchiev, Ya. M. Paushkin, T. P. Vishnyakova, and M. V. Kurashov, *Doklady Acad. Nauk S.S.S.R.*, 1951, **80**, 381.

[160] *Idem, ibid.*, p. 611.

TABLE 10. *Electrical properties of molten complexes*

Compound	Temp.	κ, ohm^{-1} cm.$^{-1}$	λ_M, ohm^{-1} cm.^{2}	$\mathfrak{k}$, ohm^{-1} cm.^{2} cp.	E_κ, kcal. mole^{-1}	D, volt	Ref.
BF_3,H_2O	10°	1.82×10^{-2}	8.71×10^{-1}	10·4	3·6	3·25	22
$BF_3,2H_2O$	10	5.82×10^{-2}	3·67	18·7	3·1	2·82	22
BF_3,H_3PO_4	25	7.23×10^{-3}	6.15×10^{-1}	~ 23	4·6	—	159[(a)]
$(BF_3)_2,H_4P_2O_7$	25	6.7×10^{-3}	1·08	~ 105	—	—	159
$BF_3,MeOH$	25	1.24×10^{-2}	8.83×10^{-1}	2·22	3·0	2·8	27
$BF_3,2MeOH$	25	2.95×10^{-2}	3·22	7·34	2·5	1·3	27
$BF_3,EtOH$	25	8.54×10^{-3}	7.18×10^{-1}	—	—	—	159
$BF_3,2EtOH$	25	1.06×10^{-2}	1·46	4·13	2·6	2·62	85
$BF_3,2Pr^nOH$	25	3.8×10^{-3}	6.8×10^{-1}	3·10	4·0	1·78	85
$BF_3,PhOH$	25	5.28×10^{-4}	—	—	—	—	159
$BF_3,2PhOH$	50	1.10×10^{-3}	—	—	—	—	87
BF_3,Et_2O	25	2.96×10^{-4}	3.74×10^{-2}	7.11×10^{-2}	3·3	1·25	96
$BF_3,C_4H_8O_2$	50	2.37×10^{-5}*	—	—	—	—	85
$BF_3,2C_4H_8O_2$	30	3.95×10^{-6}*	—	—	—	—	85
$BF_3,Me{\cdot}CO_2H$	40	2.41×10^{-3}	2.10×10^{-1}	4·67	7·4	2·50	151[(b)]
$BF_3,2Me{\cdot}CO_2H$	25	2.13×10^{-3}	3.01×10^{-1}	—	—	—	88
$BF_3,Me{\cdot}CO_2Me$	70	7.70×10^{-4}	8.80×10^{-2}	1.80×10^{-1}	6·2	1·8	89[(c)]
$BF_3,Me{\cdot}CO_2Et$	35	1.82×10^{-4}	2.30×10^{-2}	9.58×10^{-2}	6·4	2·16	89[(c)]
$BF_3,Me{\cdot}CO_2Pr^n$	25	9.38×10^{-5}	1.33×10^{-2}	9.38×10^{-2}	6·3	1·2	89[(c)]
$BF_3,Me{\cdot}CO_2Bu^n$	25	3.19×10^{-5}	5.12×10^{-3}	3.92×10^{-2}	8·9	1·3	89[(c)]
BF_3,Et_3N	30	2.84×10^{-4}	—	3.23×10^{-1}	5·0	—	85
BF_3,C_5H_5N	50	5.09×10^{-4}	—	—	4·4	—	101

* Preliminary value only. (*a*) See also refs. (121), (160). (*b*) Also ref. (88). (*c*) Also ref. (101).

A more significant comparison uses the molar conductivity $\lambda_M = M\kappa d^{-1}$, where M is the molecular weight and d the density. Values of this quantity are given in Table 10, from which it is seen that λ_M for the inorganic complexes and alcoholates is of the order of unity. The molar conductivities of the acetic acid complexes are somewhat less than this, and for the ether and ester complexes, λ_M is of the order of 10^{-2} ohm^{-1} cm.^{2}.

To eliminate the arbitrary effect of temperature in these comparisons it is necessary to introduce the dynamic viscosity η, which is inversely proportional to conductivity in these systems.[91] The reduced conductivity, which refers to the conductivity of one mole of complex reduced to a standard of unit viscosity (1 centipoise), is defined by $\mathfrak{k} \equiv \lambda_M\eta = M\kappa\eta d^{-1} = M\kappa\nu$; in this last expression ν is the kinematic viscosity (centistokes). Values of the reduced conductivity are numerically equal to the degree of ionic dissosiation providing the complex is a uni-univalent electrolyte,[91] so that col. 5 of Table 10 indicates that many of the complexes are highly dissociated in the molten state. The ions furnished by dissociation of several of the co-ordination compounds were presented in Table 3.

At a given temperature, the conductivity of a 1 : 1 complex is less than that of the corresponding 1 : 2 complex. The specific conductivity also decreases in a homologous series of compounds, and although this is partly due to the concomitant increase in viscosity, even the reduced conductivity shows some tendency to decrease with increase in chain length.

No such systematic variation is observed for the activation energy of ionic migration E_κ, which is obtained from the slope of the log κ–$1/T$ graphs ; nor does the decomposition potential D appear to show any regularity either with chain length in a given series or with change in the functional group containing the ligand.

A considerable amount of further information, and a discussion of other published values of the electrical properties of molten co-ordination compounds, will be found in the papers cited in Table 10.

The electrical conductivity of complexes in the solid state has been much less studied and only isolated values have been published. The specific conductivity of ammonium fluoroborate increases suddenly on fusion,[58] and similar observations have been made for boron trifluoride dihydrate ($\kappa_{2\cdot5} = 7\cdot4 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$) [22] and boron trifluoride–mono(acetic acid) ($\kappa_{27\cdot4} = 1\cdot9 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$).[151]

The electrical conductivity of complexes in solution is less amenable to discussion, as there is frequently the possibility of co-ordination with the solvent itself. For example, it is difficult to interpret the electrical conductivity of boron trifluoride–ethyl acetate dissolved in methanol.[81]

The alkali fluoroborates, as expected, are strong electrolytes in aqueous solution, and ammonium fluoroborate is also an electrolyte in ethanol.[58] The dialcoholates from boron trifluoride–dimethanol to boron trifluoride–di-*n*-butanol conduct electricity when dissolved in nitrobenzene [26] and so also does triphenylmethyl fluoroborate BF_3,Ph_3CF.[135] Of more interest, perhaps, is the conductivity of boron trifluoride–ammonia in liquid ammonia, which has been interpreted in terms of the weak electrolyte aminotrifluoroboric acid $H^+BF_3{\cdot}NH_2^-$.[161]

Quantitative studies have been reported in which liquid sulphur dioxide is the solvent. The equivalent conductivities of trimethyloxonium, triethyloxonium, and triethylsulphonium fluoroborates have been investigated at various dilutions, and at 0°. The equivalent conductivities at infinite dilution fall in the range 120—150.[119] Clearly, the complexes are strong electrolytes in this solvent. The conductivity of boron trifluoride–acetyl fluoride has also been studied in liquid sulphur dioxide and the results have led to a formulation of the complex as acetyl fluoroborate $Me{\cdot}CO^+BF_4^-$.[53] Both the specific and the equivalent conductivities decrease twenty-fold as the temperature is raised from − 70° to 0°. This may be related to the thermal instability of the complex: at − 120° it is completely involatile and at − 50° its vapour pressure is still very low, but at room temperature it dissociates completely into its component gases. However, in all interpretations of conductivity measurements in liquid sulphur dioxide it should be remembered that the solvent itself is a potential addend which is known to form the complex BF_3,SO_2 melting at − 96°.[45] In all instances transport studies would add greatly to our knowledge of the constitution of such solutions.

(vi) **Viscosity.**—The data available on the viscosity of liquid boron trifluoride co-ordination compounds are summarised in Table 11 and Fig. 2. The temperature variation may be expressed either by an exponential relation $\eta = \eta_0 e^{E\eta/RT}$ or by Batschinski's equation $v = b + B\phi$. In these equations η_0 is a constant, E_η the activation energy of viscous flow, v the specific volume, ϕ the fluidity (*i.e.*, η^{-1}), and b and B are constants. The kinematic viscosity ($\nu = \eta d^{-1}$) is also tabulated.

TABLE 11. *Viscosity of molten complexes*

Compound	Temp	η, cp.	ν, cs.	E_η, kcal mole^{-1}	B, cm.^{3} g.$^{-1}$ cp.	b, cm^3 g.$^{-1}$	Ref.
BF_3,H_2O	10°	12·10	6·73	3·8	0·160	0·543	22
$BF_3,2H_2O$	10	8·25	5·02	4·1	0·118	0·594	22
BF_3,H_3PO_4	20	46·7	—	—	—	—	121
$(BF_3)_2,H_4P_2O_7$	20	23	—	—	—	—	121
$BF_3,MeOH$	20	2·77	1·97	3·2	0·109	0·671	27
$BF_3,2MeOH$	20	2·50	2·06	2·9	0·117	0·778	27
$BF_3,2EtOH$	20	3·06	2·63	3·0	—	—	85
$BF_3,2Pr^nOH$	20	5·21	4·93	4·0	0·199	0·909	85
$BF_3,Me{\cdot}CO_2H$	40	22·33	15·18	8·5	0·312	0·666	151
$BF_3,Me{\cdot}CO_2Me$	70	2·05	1·65	5·0	0·0754	0·768	89
$BF_3,Me{\cdot}CO_2Et$	35	3·90	3·38	5·7	0·102	0·787	89
$BF_3,Me{\cdot}CO_2Pr^n$	20	8·64	7·19	7·2	0·182	0·812	89
$BF_3,Me{\cdot}CO_2Bu^n$	20	9·38	8·11	6·9	0·167	0·848	89
BF_3,Et_2O	25	1·93	1·71	3·1	0·0963	0·839	96
BF_3,Et_3N	30	—	6·73	(4·8)	—	—	85

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[161] J. Goubeau and H. Schmenken (unpublished observations); H. Schmenken, Ph.D. Dissertation, Göttingen, 1946 [cited by J. Goubeau, ref. (128), p. 217].

The viscosity of an addend is increased considerably by co-ordination to boron trifluoride, and the activation energy of viscous flow of the complex is also greater than that of the free donor. (An exception to this rule is boron trifluoride monohydrate : the activation energy of 3·8 is slightly lower than that of water itself, where the high value of 4·0 is due to hydrogen bonding.)

The dynamic viscosity of a 1 : 1 complex is larger than that of the corresponding 1 : 2 complex, and, in a homologous series, the viscosity increases steadily with chain length.

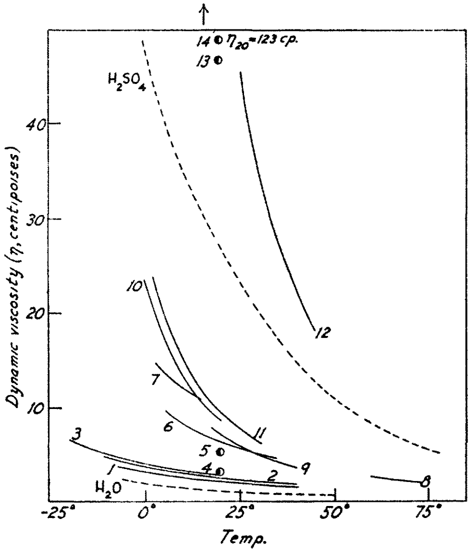

FIG. 2

No.	Compound	(Ref.)	No.	Compound	(Ref.)	No.	Compound	(Ref.)
1.	BF_3,Et_2O	(96)	6.	$BF_3,2H_2O$	(22)	11.	$BF_3,Me{\cdot}CO_2Bu^n$	(89)
2.	$BF_3,2MeOH$	(27)	7.	BF_3,H_2O	(22)	12.	$BF_3,Me{\cdot}CO_2H$	(151)
3.	$BF_3,MeOH$	(27)	8.	$BF_3,Me{\cdot}CO_2Me$	(89)	13.	BF_3,H_3PO_4	(121)
4.	$BF_3,2EtOH$	(85)	9.	$BF_3,Me{\cdot}CO_2Et$	(89)	14.	$(BF_3)_2,H_4P_2O_7$	(121)
5.	$BF_3,2Pr^nOH$	(85)	10.	$BF_3,Me{\cdot}CO_2Pr^n$	(89)			

The activation energy of viscous flow for a given compound is very similar to the corresponding activation energy of ionic migration (Table 10). This suggests that mobility effects rather than changes in the degree of ionic dissociation are the main factors influencing the temperature dependence of the electrical conductivity.[91]

When a molten compound becomes supercooled, there is a discontinuous increase both in the activation energies and also in the Batschinski constant *B*. This effect, which is not confined to boron trifluoride complexes, has recently been discussed by the Reviewers.[152, 162, 163]

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[162] N. N. Greenwood and R. L. Martin, *Nature*, 1951, **168**, 344.

[163] *Idem*, " Changements de Phases ", Compt. rend. 2e Réunion Annuelle, Société de Chimie Physique, Paris, 2—7th June, 1952, p. 421.

TABLE 12. *Surface tension and related properties*

$\gamma = \gamma_0 - \beta t$; $\omega = \gamma V_M{}^{2/3} = \omega_0 - kt$; $[P] = V_M\gamma^{1/4}$

Compound	Temp range	γ_0, dyne cm.^{-1}	β, dyne cm^{-1} deg^{-1}	ω_0, erg $\text{mole}^{-2/3}$	k, erg $\text{mole}^{-2/3}$ deg^{-1}	$[P]$	Ref.
BF_3	−115 to −90°	20·92*	0·22*	249*	2·35*	87·3	150
BF_3,Me_2O	20—60	35·2	0·106	708	1·76	220·6 ± 0·4	131
$BF_3,MeOEt$	—	30·8†	—	—	—	256·2	54
BF_3,Et_2O	15—60	31·7	0·091	787	1·84	294·6 ± 1·5	131
	−25—0	32·6	0·12	807	2·39	294·6 ± 0·4	150
$BF_3,H{\cdot}CO_2Me$	30—60	42·3	0·095	840	1·45	228·4 ± 1·0	131
$BF_3,H{\cdot}CO_2Et$	15—60	37·8‡	0·119	843	2·22	262·7 ± 1·3	131
$BF_3,Me{\cdot}CO_2Me$	65—90	39·8	0·123	904	2·44	269·8 ± 0·5	131
$BF_3,Me{\cdot}CO_2Et$	40—65	34·7	0·079	857	1·52	303·1 ± 0·9	131
$BF_3,Me{\cdot}CO{\cdot}NMePh$	115—150	39·9§	0·100§	1274§	2·7§	453·2 ± 0·4	131

* Constants refer to the equations $\gamma = \gamma_{-117} - \beta(t + 117)$; $\omega = \omega_{-117} - k(t + 117)$.

† Isolated value at 25°.

‡ A second specimen had $\gamma_0 = 38{\cdot}6$ dyne cm.^{-1}.

§ Constants refer to the equation $\gamma = \gamma_{100} - \beta(t - 100)$; $\omega = \omega_{100} - k(t - 100)$.

(vii) **Surface Tension and Parachor.**—Parachor determinations have not proved useful in solving structural problems in boron trifluoride co-ordination chemistry, but the work of S. Sugden and M. Waloff has established that the sharing of an extra pair of electrons by boron in a donor–acceptor bond does not decrease the parachor significantly.[131] Values of the parachor listed in Table 12 agree well with the calculated values. Further discussion is given in ref. (164).

The surface-tension data of several authors have been fitted to linear equations, and the results are tabulated in Table 12 which also gives the equation for liquid boron trifluoride itself. Co-ordination involves a large increase in the numerical magnitude of the surface tension of both donor and acceptor, but the temperature coefficient β appears to decrease at the same time. There is no simple correlation between surface tension and chain length in a homologous series.

The molar surface free energies ω have also been calculated from data in the literature and the results expressed as linear equations in Table 12. The temperature coefficient k is known as the Eötvös constant. When $\omega_0 = kt$ the surface free energy becomes zero and the meniscus vanishes. Eötvös's equation may therefore be used to calculate the critical temperature provided that linear extrapolation beyond the experimental range is valid and that the same molecular species is present in the liquid and in the vapour phase. This obtains for pure boron trifluoride, and the calculated critical temperature (— 11°)[150] agrees well with the experimentally determined value (— 12·25° ± 0·03°).[39]

With the complexes, however, computed values of the critical temperature are so high that decomposition would be complete, and the calculations are therefore invalid. This is emphasised by the two sets of data on boron trifluoride–ethyl ether ; extrapolation gives critical temperatures differing by almost 100°.

TABLE 13. *Dipole moments in benzene at 25°*

Compound	μ, D	ν, megacycle sec.$^{-1}$	Ref	Compound	μ, D	ν, megacycle sec.$^{-1}$	Ref.
BF_3,Me_2O	4·35±0·12	1·57	54	BF_3,C_4H_8O	5·68±0·17	0·100	142
$BF_3,MeOEt$	5·07±0·08	1·57	54	BF_3,Me_3N	5·76±0·02	—	129
BF_3,Et_2O	4·92±0·38	1·57	54	$BF_3,MeCN$	5·8±0·2	1·54	60
	4·96±0·14	0·100	142				
	5·29±0·03*	—	129				

* This value is preferred to the other two listed here.

(viii) **Dipole Moment.**—The dipole moments of several complexes have been measured and the results are summarised in Table 13. In such complicated molecules, any attempt to calculate bond moments is rendered uncertain by the numerous assumptions which must be made. Boron

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[164] A. W. Laubengayer, R. P. Ferguson, and A. E. Newkirk, *J. Amer. Chem. Soc.*, 1941, **63**, 559.

trifluoride, originally planar and with zero dipole moment,[165, 166] becomes tetrahedral, so that some value must be assigned to its contribution to the total moment. It is customary to suppose that this contribution will be about the same as the dipole moment of fluoroform, *i.e.*, $\sim 1{\cdot}5$ D.

A second uncertainty in the calculation of donor–acceptor bond moments from dipole measurements lies in the assumption that the dipole moment of the donor remains unchanged during interaction. It is also generally considered that the sum of the bond moments in a molecule must equal the total dipole moment, but this neglects, quite unjustifiably, the contribution of the lone pairs to the total moment.[167]

With these approximations, values of the O–B and N–B bond moments have been estimated to lie between 2 and 4 D.[54, 129, 142] This has been taken to indicate that only very incomplete sharing of the lone pair of electrons occurs in donor–acceptor bonding, as the product of twice the electronic charge and half the interatomic distance gives a computed value of $\sim 7{\cdot}4$ D. However, even this calculation is of doubtful validity, since it assumes that the lone-pair electrons were originally situated on the atomic nucleus of the ligand. A rough estimation indicates that the most probable position of the lone pair is about 0·3 Å from the nucleus when oxygen or nitrogen is the ligand, and if this is so, equal sharing would result in a bond moment of $\sim 4{\cdot}5$ D. This figure suggests that the bonding electrons are more equally shared than has hitherto been supposed. In view of the inherent difficulties, a more detailed interpretation of the data does not seem profitable at present.

(ix) **Vapour Pressure and Related Properties.**—The possibility of measuring saturation vapour pressures of boron trifluoride complexes is frequently restricted by the simultaneous thermal dissociation which occurs in the vapour phase. This dissociation, which has been discussed qualitatively in §3(ii), will be treated more fully in §4. In a few instances, however, it has been possible to measure reproducible vapour pressures in temperature ranges where the gas phase dissociation is not complete. The results of such determinations are presented in Table 14.

Where possible, the vapour-pressure data from the papers cited have been replotted and represented by the linear equation $\log p_{\text{mm.}} = -AT^{-1} + C$. The constants A and C and the temperature range investigated are listed in the columns 2—4 of Table 14. An approximate idea of the magnitude of the vapour pressure may be obtained from the next two columns, which give the temperatures at which the vapour pressure reaches 1 mm. and 760 mm., respectively. The heat of vaporisation $\Delta H_{\text{vap.}}$, calculated from the relation $\Delta H_{\text{vap.}} = 2{\cdot}303\boldsymbol{R}A = 4{\cdot}576A$, and Trouton's constant $\Delta S_B = \Delta H_{\text{vap.}}/T(\text{b.p.})$ have also been calculated.

The vapour pressures of the etherates are considerably lower than those of the parent ethers, and this is a general effect for co-ordination com-

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[165] H. E. Watson, G. P. Kane, and K. L. Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 130.

[166] R. Linke and W. Rohrmann, *Z. physikal Chem.*, 1937, *B*, **35**, 256.

[167] J. A. Pople, *Proc. Roy. Soc.*, 1950, *A*, **202**, 323.

pounds. The vapour pressure of solid boron trifluoride–*iso*propyl ether has been measured between 23° (6·4 mm.) and 61° (97·8 mm.)[13] but the logarithmic plot is not linear. The data listed in Table 14 for boron trifluoride–tetrahydrofuran[13] are consistent with the more recent results of R. C. Osthoff, C. A. Brown, and J. A. Hawkins.[142]

Figures are available for both solid and liquid boron trifluoride–trimethylamine (Table 14) and the recalculated heats of sublimation and vaporisation may be used to estimate the heat of fusion as 2·9 kcal. mole^{-1}. This appears to be the only latent heat of fusion of a boron trifluoride co-ordination compound in the literature.

TABLE 14. *Vapour-pressure equations :* $\log p_{\text{mm.}} = -AT^{-1} + C$

Compound	A	C	Range	Temp at which p =		$\Delta H_{\text{vap.}}$, kcal mole^{-1}	ΔS_B, cal. deg^{-1} mole^{-1}	Ref
				1 mm.	760 mm			
Liquids								
BF_3,Me_2O .	2650	9·58	?	4°	123°	12·1	30·3	54
	2430	8·80	0—100°	3	137*	11·1	27·8	13
$BF_3,MeOEt$	2860	10·05	?	11	126	13·1	32·7	54
BF_3,Et_2O .	2845	10·02	?	11	126	13·0	32·6	54
	2780	9·79	0—100	11	129†	12·7	32·1	13
BF_3,C_4H_8O .	2930	9·21	40—100	45	(190)	13·4	(29·0)	13
BF_3,C_5H_5N	(4400)	(10·56)	200—300	(145)	(300)	(20·1)	(35)	(*a*)
BF_3,Me_3N .	2963	8·74	145—165	—	233	13·6	26·8	144
Solids								
BF_3,Me_3N .	3600	10·24	100—140	78	—	16·5	—	144
BF_3,NH_4F .	2469	6·82	?	89	354	11·3	—	25

* Ref. (13) states that extrapolation of the data gives " b.p. " 127°.
† Ref. (13) states that extrapolation of the data gives " b.p. " 124°.
(*a*) From vapour-pressure measurements at two temperatures only.[3, 119]

The sublimation pressure of ammonium fluoroborate (Table 14) is of interest as it also represents the pressure above the complex boron trifluoride–ammonia.[25, 50] This arises from a disproportionation reaction : $4BF_3,NH_3 \longrightarrow 3BF_3,NH_4F + BN$. Boron nitride, which is formed in the reaction, is involatile. Disproportionation has also been used to explain the (irreversible) vapour pressure of boron trifluoride–methylamine above 260°.[168]

The vapour pressure of boron trifluoride–pyridine has been measured at two temperatures only, but if one assumes a linear relation between log p and $1/T$ the data listed in Table 14 are obtained. This suggests that the latent heat of vaporisation of this complex is nearly twice as large as the values for the other complexes considered. The related compound boron trifluoride–αα′-lutidine has been investigated between 100° (v.p. of solid = 3·1 mm.) and 194° (v.p. of liquid = 66·0 mm.).[12] However, the logarithmic plot is not linear and appreciable dissociation occurs above 150°.[12]

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[168] G. M. Nichols, Thesis, Cornell Univ., Ithaca, N.Y., 1947 [cited by ref. (74)].

TABLE 15. *Dissociation pressures :* $\log p_{\text{mm}} = -AT^{-1} + C$

Compound	A	C	Range	Temp. at which p =		Reacting states*	$\Delta H_{\text{diss c.}}$, kcal. mole^{-1}	Ref.
				1 mm.	760 mm			
BF_3,LiF	833	4·28	210—320°	– 78°	322°	s ⟶ s + g	3·8	18
BF_3,NaF	3650	6·63	400—700	278	700	l ⟶ l + g	16·7	17
BF_3,NaOH	4024	6·99	400—700	303	706	l ⟶ l + g	18·4	17
BF_3,KF	6317	8·15	510—930	502	925	l ⟶ l + g	28·9	16
BF_3,RbF	5900	7·45	600—1000	520	1018	l ⟶ l + g	27·0	16
BF_3,CsF	5880	7·35	610—1040	527	1042	l ⟶ l + g	26·9	16
BF_3,HCN†	(2440)	(10·97)	0—19	(–50)	(29)	s ⟶ g + g	(22·4)	123
BF_3,MeCN	2896	10·58	20—110	1	103	s ⟶ g + g	26·5	60
BF_3,PhCN	4094	13·90	30—70	22	99	s ⟶ l + g	18·7	14
BF_3,*o*-C_6H_4Me·CN	4246	14·90	30—60	12	(80)	s ⟶ l + g	19·4	14
BF_3,*m*-C_6H_4Me·CN	4554	16·01	30—55	12	(74)	s ⟶ l + g	20·8	14
BF_3,*p*-C_6H_4Me·CN	4252	13·76	55—80	36	(118)	s ⟶ l + g	19·4	14
BF_3,2:4:6-$Me_3C_6H_2$·CN	4380	13·81	60—90	44	(128)	s ⟶ l + g	20·0	14
BF_3,Me·COCl	2877	15·76	–85 to –60	–91	(–50)	l ⟶ l + g	13·2	169
BF_3,CCl_3·CHO	2812	15·00	–80 to –55	–86	(–41)	s ⟶ s + g	12·9	169

* The symbols s (solid), l (liquid), and g (gas) refer to the reaction : complex ⟶ donor + BF_3. Liquid components will in general be saturated with solid and gaseous components.

† Data for two points only.

The precise interpretation of the latent heat of vaporisation when evaporation is accompanied by partial thermal dissociation is not quite clear. The fact that linear plots are obtained suggests that the degree of dissociation α at the pressure of the saturated vapour remains approximately constant with temperature. Thus, the effect of an increase in K_p with temperature, which tends to increase α, is counterbalanced by the greater pressure which tends to repress dissociation. In many instances, the heat of dissociation of the complex is known but it does not seem profitable to correct the experimental heats of vaporisation to the hypothetical state of undissociated vapour.

The vapour-phase dissociation is reflected in the values for the Trouton constant (Table 14). This constant, which represents the entropy increase on vaporisation at the boiling point, is ~ 21 for normal liquids. Higher values result from either association in the liquid phase or dissociation in the vapour phase. With boron trifluoride complexes it is likely that both causes contribute to the increased entropy effect.

The variation of vapour pressure with composition has been discussed in §2(ii).

4. Thermal Dissociation and Thermochemistry

Throughout the Review the effects of thermal dissociation have been stressed and many examples of complete and incomplete dissociation under varying conditions have been discussed. This section summarises briefly the results of some quantitative determinations of dissociation pressures over a range of temperatures, and also presents thermodynamic data which have been obtained from the dissociation equilibria of several complexes.

(i) **Dissociation Pressures of Solid and Liquid Complexes.**—Table 15 lists data on the dissociation pressure above several solid and liquid complexes. The data have been fitted to the equation $\log p_{\text{mm.}} = -AT^{-1} + C$ and the range investigated is also indicated. As in Table 14, the temperatures at which the dissociation pressure reaches 1 mm. and 760 mm., respectively, have been tabulated to give an idea of the magnitudes involved.

Lithium fluoroborate is the least stable of the alkali fluoroborates and even at room temperature the pressure of boron trifluoride above the solid is 30 mm.[18] A temperature of 300° must be attained before dissociation of sodium fluoroborate and boron trifluoride–sodium hydroxide becomes significant,[17] and dissociation of the remaining fluoroborates is not appreciable below 500°.[16, 19, 20, 21] Experiments on barium fluoroborate $(BF_3)_2,BaF_2$ [21] suggest that it is intermediate in stability between lithium and sodium fluoroborate.

The thermal decomposition of the addition complexes of alkali sulphates, phosphates, and pyrophosphates with boron trifluoride has been investigated at high temperatures and related to the stability of the corresponding complexes with sulphur trioxide as acceptor.[51, 170]

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[169] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[170] P. Baumgarten and E. Müller, *Ber.*, 1936, **69**, 2688.

The second group of compounds in Table 15 comprises the complexes with cyanides or nitriles. Here the thermal stabilities are lower than those of the alkali fluoroborates. The dissociation pressure above boron trifluoride–hydrogen cyanide reaches one atmosphere just above room temperature, but the complexes with organic nitriles must be heated to rather higher temperatures. The similarity between the properties of the various methyl-substituted benzonitriles, which was referred to in §1(iii), has been discussed in detail by H. C. Brown and R. B. Johannesen.[14]

The heats of dissociation listed in the final column of Table 15 cannot be directly related to heats of formation in standard states because the terms involving lattice energies and heats of solution are unknown. Nevertheless, they do indicate that large heat effects are involved in rupturing a donor–acceptor bond.

(ii) **Degrees of Dissociation of Gaseous Complexes.**—Tensimetric studies in the vapour phase have enabled the determination of dissociation constants, degrees of dissociation, and free energies, heats, and entropies of dissociation. For the equilibrium,

$$\text{complex (g)} \rightleftharpoons \text{donor (g)} + BF_3\text{ (g)}$$

the dissociation constant may be written $K_p = \alpha^2P/(1 - \alpha^2)$, where α is the degree of dissociation and P the pressure in atmospheres. The free-energy change in the reaction is then $-\Delta G = 2{\cdot}303RT \log K_p = 4{\cdot}576T \log K_p$, and the heat of reaction $-\Delta H = 4{\cdot}576\mathrm{d}(\log K_p)/\mathrm{d}(1/T)$. Finally, the entropy change may be calculated from the equation $\Delta S = (\Delta H - \Delta G)/T$.

TABLE 16. *Thermodynamic functions for vapour-phase equilibria*

Compound	Range	ΔH, kcal. mole^{-1}	ΔS, cal. deg.$^{-1}$ mole^{-1}	ΔG_{50},* kcal. mole^{-1}	$(K_p)_{50}$,* atm.	α_{50}†	Ref.
BF_3,Me_2O	65—100°	13·3	32·3	2·90	0·011	0·57	13
	50—130	~14·0	~35	~3·0	~0·01	~0·5	54
BF_3,Et_2O	70—100	10·9	27·5	2·02	0·043	0·83	13
BF_3,Pr^i_2O	40—50	~14·2	~39·7	1·34	0·115	0·82	13
BF_3,C_4H_8O	95—125	13·4	27·1	4·66	0·0007	0·17	13
BF_3,C_5H_5N	310—360	50·6	79·7	4·98‡	0·0126‡	0·11‡	3

* These figures refer to 50° C. At any other temperature (T° K) ΔG and K_p may be obtained from the relations $\Delta G = \Delta H - T\Delta S$; $\log K_p = (\Delta S - \Delta H/T)/4{\cdot}576$.

† These figures refer to the degree of dissociation at 50° C under the saturation vapour pressure (in atm.). For other temperatures and pressures $\alpha = \sqrt{K_p/(K_p + P)}$.

‡ These figures refer to the b.p., *i.e.*, 300° and 1 atm. At 50° the vapour pressure is of the order of 10^{-3} mm. and the degree of dissociation of the order of 10^{-5}.

Some typical results are given in Table 16. In this table, the heats of dissociation are numerically equal to the heats of formation in the gas phase and it will be noted that, whereas the heats of formation of the various ether complexes are similar, that of boron trifluoride–pyridine is about four times larger. The degree of dissociation of the pyridine complex is also very small at temperatures where the etherates dissociate appreciably.

The stabilities of the complexes with ethers decrease with increasing chain length owing to the influence of steric effects ;[13] when such effects are absent, as in the cyclic-ether complex boron trifluoride–tetrahydrofuran, the stability is very much greater.

Similar measurements on boron trifluoride–trimethylamine have shown that the complex is *associated* in the vapour phase below the boiling point.[144] At 170° the observed molecular weight is 50% greater than the formula weight but this association decreases to 1% at 230°. The equilibrium seems to involve a variable degree of polymerisation.

(iii) **Miscellaneous Thermodynamic and Thermochemical Data.**—In addition to the results summarised in Table 16, it is possible to derive further thermodynamic constants from Table 15 in special cases. For reactions of the type $s \longrightarrow s + g$, if the complex and donor are involatile, then the total pressure is due to boron trifluoride and, as the solid compounds are in their standard states, the equilibrium constant is simply $K_p = P$ (atm.). Hence, $\log K_p = -AT^{-1} + (C - 2{\cdot}88)$ and $\Delta G = 4{\cdot}576A - 4{\cdot}576(C - 2{\cdot}88)T$. The values of $\Delta H = 4{\cdot}576A$ are already listed in Table 15. The coefficient $4{\cdot}576(C - 2{\cdot}88)$ is the entropy change ΔS. Thus, the entropy of dissociation of lithium fluoroborate is 6·4 cal. deg.$^{-1}$ mole^{-1}, and that of boron trifluoride–chloral, 55·4 cal. deg.$^{-1}$ mole^{-1}. As the standard entropies of boron trifluoride (gas) and lithium fluoride (solid) are 60·71[171] and 8·57,[172] respectively, this suggests that the entropy of solid lithium fluoroborate is 62·9 cal. deg.$^{-1}$ mole^{-1}. The value is surprisingly high and may indicate the need to revise the vapour-pressure results. The entropy of solid chloral is not known, but the above figures show that it is only 5·3 units less than that of the complex.

Dissociations of the type $s \longrightarrow l + g$ can be treated similarly on the assumption that the vapour pressure of the saturated liquid solution may be neglected in comparison with the boron trifluoride pressure. If the solid complex and liquid donor are taken to be in their standard states, then again the equilibrium constant is simply $K_p = P$ (atm.). The calculation may be applied to the aromatic nitriles (Table 15) for which the heats of dissociation have already been found to be approximately 20 kcal. mole^{-1}. From the relation $\Delta S = 4{\cdot}576(C - 2{\cdot}88)$ the entropy changes during the dissociation of the complexes with benzonitrile, *o*-, *m*-, and *p*-tolunitrile, and mesitonitrile are 50·4, 55·0, 60·1, 49·8, and 50·0 cal. deg.$^{-1}$ mole^{-1}, respectively.

The other two nitriles in Table 15 dissociate according to the scheme $s \longrightarrow g + g$ so that $K_p = \frac{1}{4}P^2$ atm.^{2}. In terms of the constants given in Table 15,

$$\log K_p = 2 \log P - \log 4 = -2AT^{-1} + 2(C - 2{\cdot}88) - 0{\cdot}602$$

$$\Delta G = 2 \times 4{\cdot}576A - 4{\cdot}576(2C - 6{\cdot}36)T$$

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[171] R. M. Potocki and D. E. Mann, National Bureau of Standards, Report No. 1561, May 15th, 1952 (U.S. Dept. of Commerce).

[172] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Circular of the National Bureau of Standards, 500 : " Selected Values of Chemical and Thermodynamic Properties ", February 1st, 1952.

The values of $\Delta H = 2 \times 4{\cdot}576A$ are already included in Table 15. The value of $\Delta S = 4{\cdot}576(2C - 6{\cdot}36)$ for boron trifluoride–hydrogen cyanide is 71·3, and for the complex with acetonitrile, 67·7 cal. deg.$^{-1}$ mole^{-1}. These values, in conjunction with the standard entropies of hydrogen cyanide gas (48·23)[172] and acetonitrile gas (58·18),[172] lead to standard entropies of the solid complexes as 37·6 and 51·2 cal. deg.$^{-1}$ mole^{-1}, respectively. A similar calculation for boron trifluoride–methyl ether (Table 16) gives the hypothetical entropy of the undissociated gas at 1 atm. as 92·1 cal. deg.$^{-1}$ mole^{-1}.

The direct calorimetric determination of thermochemical quantities has not been used extensively. From A. W. Laubengayer and G. R. Finlay's determinations[54] of the heat of solution of boron trifluoride in ethyl ether (17·3 ± 0·4 kcal. mole^{-1}) and the heat of dilution of the complex in ether (2·7 ± 0·5 kcal. mole^{-1}), together with the heat of vaporisation of ethyl ether (6·21 kcal. mole^{-1}), the following heats of formation may be calculated :

$$\mathrm{Et_2O(l) + BF_3(g) \longrightarrow BF_3,Et_2O(l)} : \quad -\Delta H = 14{\cdot}6 \pm 0{\cdot}9 \text{ kcal. mole}^{-1}$$
$$\mathrm{Et_2O(g) + BF_3(g) \longrightarrow BF_3,Et_2O(l)} : \quad -\Delta H = 20{\cdot}8 \pm 0{\cdot}9 \text{ kcal. mole}^{-1}$$

Similarly, from the heat of displacement of ether from an ethereal solution of boron trifluoride–ethyl ether by gaseous ammonia (24·0 kcal. mole^{-1}), the heat of formation of solid boron trifluoride–ammonia from its gaseous components was calculated as 41·3 kcal. mole^{-1}.[25] It is noteworthy that the heat of solution of boron trifluoride in ethyl ether (17·3 kcal. mole^{-1}) is only about three-quarters of the further heat evolved when ammonia is added to the resulting solution (24·0 kcal. mole^{-1}).

5. Conclusion

This Review of the physicochemical properties of boron trifluoride co-ordination compounds has classified the available information by considering each *property* in turn. A more extensive account would also discuss each group of compounds and tabulate the properties known for each individual complex. Limitations of space have also prevented a discussion of the ingenious experiments of D. Garvin and G. B. Kistiakowski on the kinetics of co-ordinate bond formation in the vapour phase.[173] Their results on the reaction between boron trifluoride and ammonia or simple amines show that the rate constants are comparable to those of free-radical combination.

The chemistry of displacement reactions and relative donor strengths has only been briefly alluded to, although a large amount of work has been concentrated on this field. The kinetics of hydrolysis reactions involving boron trifluoride complexes has also been studied in detail.[71, 84, 174, 175]

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[173] *J. Chem. Phys.*, 1952, **20**, 105.

[174] C. A. Wamser, *J. Amer. Chem. Soc.*, 1948, **70**, 1209.

[175] I. G. Ryss, *Doklady Akad. Nauk S.S.S.R.*, 1946, **52**, 417 ; *J. Gen. Chem. U.S.S.R.* (U.S. Transl.), 1949, **19**, a291 ; I. G. Ryss and M. M. Slutskaya, *Doklady Akad. Nauk S.S.S.R.*, 1947, **57**, 689 ; *Zhur. Fiz. Khim.*, 1947, **21**, 549 ; *J. Gen. Chem U.S.S.R.* (U.S. Transl.), 1949, **19**, a281.

A comparison of the properties of boron trifluoride complexes with those of other Lewis acids and a review of the catalytic activity of such systems falls outside the scope of the present article. It is hoped, however, that this introduction to the precise physical chemistry of the co-ordination compounds of boron trifluoride has emphasised the potentialities of these complexes in the fields of structural chemistry, thermochemistry, and reaction kinetics.

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