157. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part VI.* The System Boron Trifluoride–Methanol.*

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

Specific electrical conductivity–composition isotherms in the system boron trifluoride–methanol indicate the existence of a 1 : 1 and a 1 : 2 complex. These compounds, $BF_3,CH_3{\cdot}OH$, $BF_3,2CH_3{\cdot}OH$, have been obtained as colourless crystalline solids melting at $-18{\cdot}6°$ and $-58{\cdot}1°$, respectively. The electrical conductivity, viscosity, and density of the pure molten compounds have been investigated over a range of temperatures, and from these measurements, the activation energies of ionic migration and viscous flow have been calculated. The compounds show well-defined decomposition potentials above which electrolysis liberates hydrogen at the cathode. Boron trifluoride–monomethanol is shown to be methoxytrifluoroboric acid, $H^+[BF_3{\cdot}OCH_3]^-$, and boron trifluoride–dimethanol to be methoxonium methoxytrifluoroborate, $[CH_3{\cdot}OH_2]^+[BF_3{\cdot}OCH_3]^-$.

This paper presents the results of a systematic investigation on the electrical conductivity, viscosity, and density of the system boron trifluoride–methanol. Two compounds have been isolated, a mono- and a di-methanol complex, *viz.*, $BF_3,CH_3{\cdot}OH$ and $BF_3,2CH_3{\cdot}OH$; both have been reported in the literature, but very few precise physicochemical data are on record.

Gay-Lussac and Thénard ("Recherches physicochimiques," 1811, **2**, 38) first demonstrated the action of boron trifluoride gas on alcohol and suggested that the product on distillation was an ether. Similar results were indicated by the work of Desfosses (*Ann. Chim. Phys.*, 1821, **16**, 72), Liebig and Wöhler (*ibid.*, 1832, **49**, 25), and Kuhlmann (*Annalen*, 1840, **33**, 97, 192) but the stoicheiometry of the reaction was not established. Gasselin (*Ann. Chim. Phys.*, 1894, **3**, 5) showed that boron trifluoride was absorbed by alcohols in equimolar proportions. He believed that the liquid formed by direct absorption at 0° was a mixture, and attempted a separation by distillation. The products isolated were methoxyboron difluoride, $BF_2{\cdot}OCH_3$ (15%), and boron trifluoride–methyl ether, BF_3,OCH_3 (50%). Both these compounds were well characterized by analyses (C, H, and B), density, melting point, boiling point, and chemical reactions, and there seems little doubt of their formation *on distillation.* Nieuwland, Vogt, and Foohey (*J. Amer. Chem. Soc.*, 1930, **52**, 1018) noted that the electrical conductivity of the boron trifluoride–methanol system showed a minimum at 47 wt.% of boron trifluoride and was of the order of 2×10^{-2} ohm^{-1} cm.$^{-1}$ (no temperature was specified). Both the catalytic activity and the conductivity were ascribed to fluoroboric acid, supposedly formed by the reaction $4BF_3 + 3CH_3{\cdot}OH \longrightarrow B(OCH_3)_3 + 3HBF_4$. Further work by Bowlus and Nieuwland (*ibid.*, 1931, **53**, 3835) was interpreted in terms of the formation of boron trifluoride–monomethanol which was postulated to ionize as methoxytrifluoroboric acid, $H^+[BF_3{\cdot}OCH_3]^-$, but no direct proof was forthcoming. O'Leary and Wenzke (*ibid.*, 1933, **55**, 2177) demonstrated the existence of a 1 : 1 compound by tensimetric methods and prepared its mercury salt, $Hg(BF_3{\cdot}OCH_3)_2$. However, it was left for Meerwein (*Ber.*, 1933, **66**, 411) to isolate definitely both the 1 : 1 and the 1 : 2 complex and to determine the boiling point, density, and refractive index of the latter (see also Meerwein and Pannwitz *J. pr. Chem.*, 1934, **141**, 123).

---

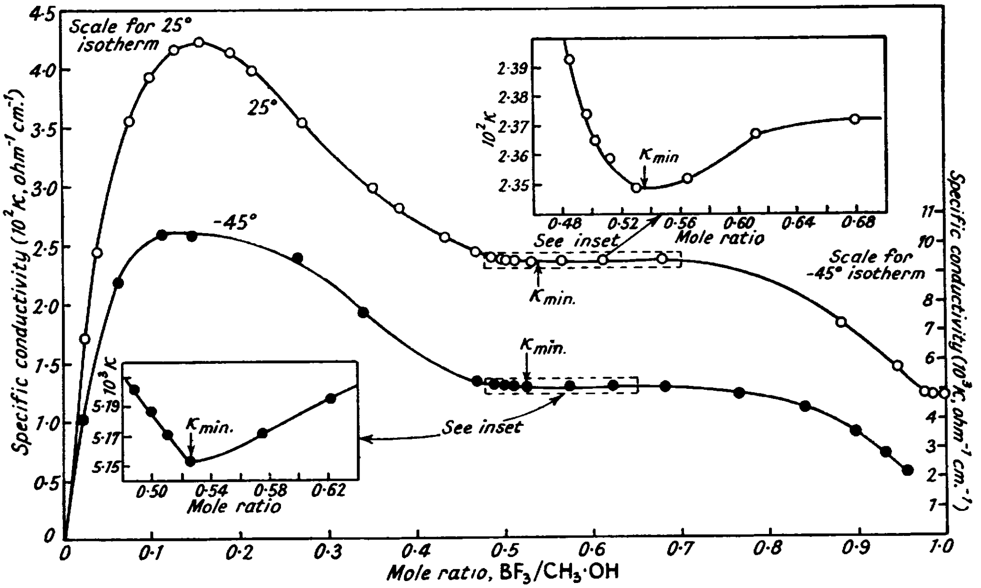
* Part V, preceding paper.

In the present work the compounds were prepared by absorbing the appropriate amount of pure boron trifluoride gas in a weighed amount of cooled methanol, after which they were subjected to fractional freezing. Both compounds were colourless liquids which could be frozen to colourless transparent crystals.

Melting points were determined both by the cooling-curve procedure and by direct observation on individual crystals. The m. p. of boron trifluoride–monomethanol was —18·6°, which is 0·8° higher than the value found by O'Leary and Wenzke (*loc. cit.*); that of boron trifluoride–dimethanol was —58·1°. No comparison of this value with the literature is possible since this compound has not previously been reported as a solid. Both compounds supercooled readily, and the 1 : 2 complex vitrified when cooled to —195°.

The variation of specific conductivity with composition in the system boron trifluoride–methanol is shown in Fig. 1. At 25·0°, addition of only 1 mole % of boron trifluoride results in a 1000-fold increase in electrical conductivity of methanol from *ca.* 10^{-5} to 10^{-2} ohm^{-1} cm.$^{-1}$. Continued addition of boron trifluoride increases the conductivity of the system up to a maximum of $4·25 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ at a mole ratio of $BF_3/CH_3·OH = 0·15$. Thereafter the conductivity decreases and passes through a shallow minimum in the region of the mole ratio 0·5 corresponding to the compound boron trifluoride–dimethanol. In this region the specific electrical conductivity is but slightly dependent on composition; at 25·0°, the conductivity varies by only 2%, from $2·40 \times 10^{-2}$ to $2·35 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$, between the mole ratios 0·48 and 0·70. It will be noted that by lowering the temperature from 25° to —45° (melting chlorobenzene bath) the position of the minimum is displaced from a mole ratio 0·535 to 0·527. The fact that the minimum does not occur precisely at the mole ratio 0·500 does not indicate inaccurate experimentation. Because of the complex interactions occurring in a system of varying composition, density, and viscosity, the minimum in specific conductivity need not occur precisely at the stoicheiometric ratio and indeed may even be masked altogether (Greenwood, Martin, and Emeléus, *J.*, 1951, 1328). This has recently been emphasized by Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 804).

FIG. 1. *Conductivity–composition isotherms for the system boron trifluoride–methanol.*



Further addition of boron trifluoride to the system results in a continued decrease in conductivity until the mole ratio 0·98 is reached, after which further absorption is extremely slow. In no instance could the mole ratio 1·000 be exceeded at atmospheric pressure. The curve at —45° terminates at the mole ratio 0·96 owing to precipitation of the crystalline

1 : 1 complex from the melt at this composition. Further measurements were carried out at 0° and are not shown on the graph. In this way, the conductivity–composition isotherms show the existence of a 1 : 2 complex and indicate that boron trifluoride cannot be absorbed by methanol beyond the mole ratio corresponding to the 1 : 1 complex. These results, in conjunction with melting-point maxima, establish the existence of two compounds in the system, *viz.*, $BF_3,CH_3{\cdot}OH$ and $BF_3,2CH_3{\cdot}OH$.

As unblacked platinum electrodes of diameter only 0·8 cm. were being used in the conductivity measurements, it was important to ascertain the frequency at which polarization effects became disturbing. Fig. 2 shows the dependence of the specific electrical conductivity of boron trifluoride-monomethanol on frequency at 25°. An extended scale has been used for the conductivity along the ordinate to accentuate the effects. At 1000 cycles sec.$^{-1}$ a 1% variation in frequency causes only a 0·03% variation in conductivity, and between the limits of 970 and 1030 cycles sec.$^{-1}$ the conductivity is within one part in 1000 of its value at 1000 cycles sec.$^{-1}$. Instability of the oscillator or slight error in frequency adjustment or calibration, therefore, does not affect the conductivity results significantly.

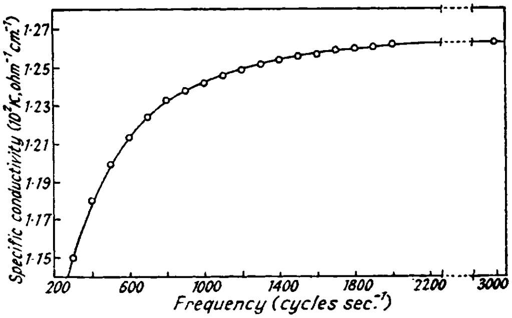


FIG. 2. *The dependence of specific conductivity of* $BF_3,CH_3{\cdot}OH$ *on frequency.*

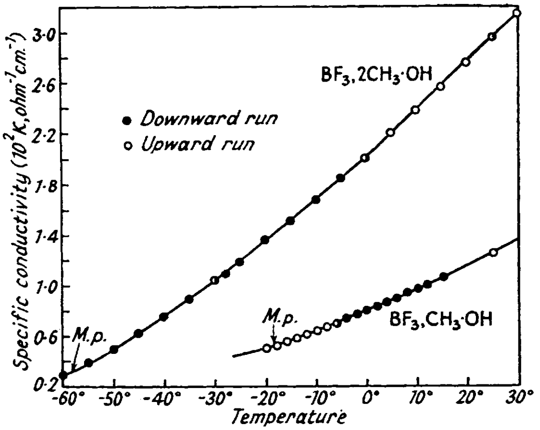


FIG. 3. *Temperature dependence of specific conductivity.*

The specific electrical conductivity of boron trifluoride–monomethanol purified by fractional freezing was studied in the temperature range —20° to +25°. The results are presented in Table 1 and Fig. 3. The value at 25°, $\kappa_{25} = 1{\cdot}240 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$, may be

TABLE 1. *Electrical conductivity of* $BF_3,CH_3{\cdot}OH$.*

t	$10^2\kappa$	μ	$\mathfrak{K}$	t	$10^2\kappa$	μ	$\mathfrak{K}$	t	$10^2\kappa$	μ	$\mathfrak{K}$
—20·0°	0·4944	0·3388	2·22	—6·0°	0·6953	0·4821	2·21	8·0°	0·9249	0·6492	2·26
—18·0	0·5024	0·3572	2·20	—4·0	0·7288	0·5059	2·23	10·0	0·9598	0·6748	2·25
—16·0	0·5478	0·3766	2·20	—2·0	0·7593	0·5283	2·23	12·0	0·9952	0·7009	2·24
—14·0	0·5766	0·3969	2·21	0·0	0·7911	0·5514	2·24	15·2	1·053	0·7435	2·23
—12·0	0·6052	0·4175	2·21	2·0	0·8230	0·5746	2·24	20·0	1·133 †	0·8037 †	2·23
—10·0	0·6334	0·4378	2·22	4·0	0·8561	0·5988	2·25	25·0	1·240	0·8831	2·22
— 8·0	0·6640	0·4596	2·21	6·0	0·8906	0·6238	2·25				

* κ in ohm^{-1} cm.$^{-1}$; molar conductivity $\mu = M\kappa/d$ in ohm^{-1} cm.^{2}; reduced conductivity $\mathfrak{K} = M\kappa\eta/d$ in ohm^{-1} cm.^{2} cp. † Interpolated.

compared with the value $\kappa_{25} = 1{\cdot}371 \times 10^{-2}$ (Topchiev, Paushkin, Vishnyakova, and Kurashov, *Doklady Akad. Nauk, S.S.S.R.*, 1951, **80**, 381), published as an isolated observation during the course of this work. In the 40°-range above the m. p. (−18·6°) the conductivity increases by 130%, and the relative temperature coefficient of conductivity, $(1/\kappa)(d\kappa/dt)$, alters from 2·53% to 1·56%.

The molar conductivity (μ), like the specific conductivity, shows an increase (137%) in the same temperature range. The value of 0·804 ohm^{-1} cm.^{2} at 20·0° is of the same order of magnitude as the molar conductivity of several molten salts. That the increase in conductivity is due predominantly to increased mobility rather than to increased ionic dissociation is seen by the constancy of the reduced conductivity, $\mathfrak{K} = \mu\eta = M\kappa\eta/d$, in the last column of Table 1. The function corrects the molar conductivity for changes in mobility by introducing the dynamic viscosity, which is inversely proportional to the mobility in this system (see Greenwood and Martin, *J.*, 1951, 1795). The mean variation in $\mathfrak{K}$ over the whole 45° temperature range is <0·7%, and the maximum deviation from the mean is 1·6%.

The stability of the 1 : 1 complex at 25° was investigated; after 16 days, the specific conductivity had increased by less than 0·1%, after 7 weeks by less than 0·5%, and after >6 months in an imperfectly stoppered cell, during which time the compound developed a pale straw colour and evolved boron trifluoride, the conductivity increased by only 6%. If this increase is ascribed entirely to loss of boron trifluoride owing to thermal dissociation, the value after 6 months would indicate a mole ratio of 0·97. Insofar as the present electrochemical investigation is concerned, there is no significant change in properties at 25° in a fortnight. The reproducibility of the specific conductivity is also indicated in Fig. 3.

TABLE 2. *Electrical conductivity of* $BF_3,2CH_3{\cdot}OH$.*

t	$10^2\kappa$	μ	$\mathfrak{K}$	t	$10^2\kappa$	μ	$\mathfrak{K}$	t	$10^2\kappa$	μ	$\mathfrak{K}$
−60·0°	0·2918	0·296 †	—	−25·0°	1·187	1·241 †	—	5·0°	2·198	2·359	7·74
−55·0	0·3856	0·393	—	−20·0	1·350	1·416	8·73 ‡	10·0	2·379	2·565	7·67
−50·0	0·4940	0·505	—	−15·0	1·503	1·584	8·53 ‡	15·0	2·562	2·775	7·55
−45·0	0·6179	0·635	—	−10·0	1·666	1·764	8·31	20·0	2·754	2·997	7·49
−40·0	0·7516	0·775	—	− 5·0	1·835	1·953	8·08	25·0	2·945	3·220	7·34
−35·0	0·8861	0·918	—	0·0	1·991	2·177	7·95	30·0	3·142	3·451	7·25
−30·0	1·034	1·076	—								

* See first footnote to Table 1. † Densities by extrapolation between −60° and −25°.
‡ Viscosities by extrapolation.

The specific electrical conductivity of boron trifluoride–dimethanol between −60° and +30° is given in Table 2 and Fig. 3. The relative temperature coefficient at 25° is $(1/\kappa)(d\kappa/dt) = 1{\cdot}33\%$. Comparison between Tables 1 and 2 shows that, for any given temperature, the specific and molar conductivities of the 1 : 2 complex are greater than for the 1 : 1 complex; *e.g.*, at 25° the molar conductivity of boron trifluoride–dimethanol is nearly four times that of boron trifluoride–monomethanol. The final column in Table 2 demonstrates that, when the molar conductivity is corrected for varying mobility by reducing conductivity to a standard of unit viscosity, an almost temperature-independent function is obtained.

The presence of traces of water appears to have little effect on the specific conductivity of boron trifluoride–dimethanol. Samples of the complex prepared either from " AnalaR " methanol (<0 2% of water) or from methanol dried by refluxing over magnesium gave essentially the same results. The deliberate addition of 2 moles % of water to the complex increased its specific conductivity by 0·9% at 25°.

Both compounds gave well-defined decomposition potentials. For the 1 : 1 complex at 20°, $D = 2{\cdot}8$ v; for the 1 : 2 complex at 22°, $D = 1{\cdot}3$ v. Electrolysis of the liquids gave rise to copious cathodic evolution of a colourless gas together with minute traces of gas at the anode.

Boron trifluoride–dimethanol was electrolysed at room temperature for 7 hours at 9·2 v and 30 milliamp. The cathodic gas was shown to be hydrogen (98·5 mole%) together with boron trifluoride (1·5 mole %). More rapid electrolysis at 75 v and 350 milliamp. gave the same result. The minute trace of anodic gas was insufficient for analysis.

The variation of the density of boron trifluoride–monomethanol with temperature was determined dilatometrically in the range −20° to +20° and is given by the equation $d^t_4 = 1{\cdot}4328 - 1{\cdot}23_3 \times 10^{-3}t$. The precision with which the experimental values approximate to this relation is shown in Table 3.

The density of boron trifluoride–dimethanol in the same temperature range (Table 4) may be represented by the equation $d^t_4 = 1{\cdot}2344 - 1{\cdot}12 \times 10^{-3}t$. In this instance the points for the three lowest temperatures were less satisfactory, experimentally, and this is reflected in the deviations in the final column. For this reason, the least-squares line of best fit, which gives equal weight to all points has not been used. It will be noted that both compounds are considerably denser than methanol itself, the best values for which (see Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier Publ. Co. Inc., N.Y., 1950) can be fitted by the equation $d^t_4 = 0{\cdot}8100 - 0{\cdot}94 \times 10^{-3}t$.

TABLE 3. *Density of* $BF_3,CH_3{\cdot}OH$.

t	d^t_4 (obs.)	d^t_4 (calc.)	$10^4\,\Delta$ (obs.—calc.)	t	d^t_4 (obs.)	d^t_4 (calc.)	$10^4\,\Delta$ (obs.—calc.)
−20·0°	1·4575	1·4575	0	5·0°	1·4265	1·4266	−1
−15·0	1·4513	1·4513	0	10·0	1·4205	1·4205	0
−10·0	1·4449	1·4451	−2	15·0	1·4144	1·4143	+1
− 5·0	1·4386	1·4389	−3	20·0	1·4081	1·4081	0
0·0	1·4326	1·4328	−2				

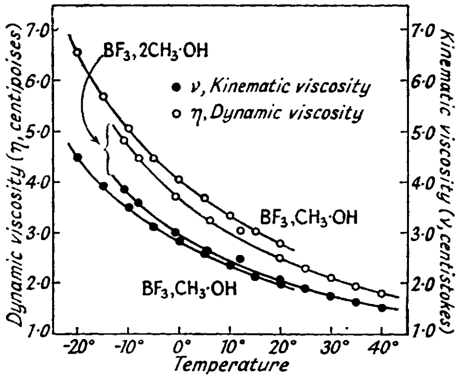


FIG. 4. *Temperature dependence of viscosity.*

TABLE 4. *Density of* $BF_3,2CH_3{\cdot}OH$.

t	d^t_4 (obs.)	d^t_4 (calc.)	$10^4\,\Delta$ (obs.—calc.)	t	d^t_4 (obs.)	d^t_4 (calc.)	$10^4\,\Delta$ (obs.—calc.)
−20·0°	1·2755	1·2568	+7	5·0°	1·2288	1·2288	0
−15·0	1·2515	1·2512	+3	10·0	1·2232	1·2232	0
−10·0	1·2458	1·2456	+2	15·0	1·2176	1·2176	0
− 5·0	1·2400	1·2400	0	20·0	1·2120	1·2120	0
0·0	1·2344	1·2344	0				

The kinematic viscosity (ν, centistokes) was determined in a U-tube viscometer, and a kinetic energy correction made. The dynamic viscosity (η, centipoises) was then calculated by the relation $\eta = d^t_4\nu$. Table 5(*a*) lists the kinematic and dynamic viscosities of boron trifluoride–monomethanol in the temperature range −20° to +20°. Similar results for the 1 : 2 complex in the temperature range −11° to 40° are summarized in Table 5(*b*).

TABLE 5. *Viscosity of* (*a*) $BF_3,CH_3{\cdot}OH$ and (*b*) $BF_3,2CH_3{\cdot}OH$.

(*a*) $BF_3,CH_3{\cdot}OH$						(*b*) $BF_3,2CH_3{\cdot}OH$					
	ν, cs.	η, cp.	t	ν, cs.	η, cp.	t	ν, cs.	η, cp.	t	ν, cs.	η, cp.
−20·0°	4·50	6·56	5·0°	2·59	3·69	−10·8°	3·86	4·82	20·0°	2·06	2·50
−15·0	3·93	5·70	10·0	2·35	3·34	− 8·0	3·60	4·48	25·0	1·89	2·28
−10·0	3·51	5·07	15·0	2·13	3·01	− 0·8	3·00	3·71	30·0	1·75	2·10
− 5·0	3·11	4·48	20·0	1·97	2·77	+ 5·5	2·64	3·24	35·0	1·62	1·94
0·0	2·83	4·06				12·0	(2·48)	(3·03)	40·0	1·51	1·80

Fig. 4 compares the values for the two compounds. The values are considerably greater than those of methanol itself, for which $\eta_{-20°} = 1{\cdot}18$, $\eta_0 = 0{\cdot}82$, $\eta_{20°} = 0{\cdot}597$ cp.

DISCUSSION

Although the most significant conclusions about the nature of the two molten complexes are to be drawn from the conductivity, electrolysis, and viscosity results, the measurements of density are not without interest. It is true that their main use in this investigation lies in the calculation of the molar conductivity from the specific conductivity and of the dynamic viscosity from the kinematic viscosity, but they have a certain intrinsic importance owing to the structural information derivable from molar volumes. This topic is developed in a subsequent paper (in preparation), and, for the present, the density values will merely be compared with existing data.

The density of boron trifluoride–monomethanol is given by Paushkin (*Zhur. Priklad. Khim.*, 1948, **21**, 1199) as 1·416 but neither temperature nor experimental details are recorded. The value may be compared with d_4^{20} 1·4081 found in the present work. The density of boron trifluoride–dimethanol was reported by Meerwein (*loc. cit.*) and Meerwein and Pannwitz (*loc. cit.*) as d_4^{20} 1·3115, which is more than 8% higher than the present value of d_4^{20} 1·2120, but their specimen was " purified " by distillation under conditions which are known to alter the methanol content of the sample. Boron trifluoride–dimethanol used in the present investigation was purified by fractional freezing. The density was determined on three different specimens, prepared from different batches of methanol, both by addition of boron trifluoride to methanol and by addition of methanol to boron trifluoride–monomethanol. The dilatometer was also recalibrated to eliminate this possible source of error.

The activation energies of ionic migration and viscous flow may be estimated from the plot of log κ or log η against the reciprocal of the absolute temperature. The curves so obtained are generally not linear over the whole temperature range, presumably because of the gradual decrease of intermolecular attraction as the temperature rises farther from the m. p. In general, the activation energy decreased with increasing temperature. A comparison between the activation energies of the two complexes and methanol itself is given in Table 6.

TABLE 6. *Activation energies of ionic migration, E_κ, and viscous flow, E_η.*

	E_κ, kcal. mole^{-1}		E_η, kcal. mole^{-1}	
Compound	Room temp.	Low temp.	Room temp.	Low temp.
$BF_3,CH_3{\cdot}OH$	2·95	3·34	3·16	3·16
$BF_3,2CH_3{\cdot}OH$	2·46	4·76	2·90	3·47
$CH_3{\cdot}OH$	—	—	2·47	—

The Table indicates that the activation energies of the 1 : 1 complex at room temperature are slightly greater than those of the 1 : 2 complex and that these, in turn, are somewhat above the activation energy for viscous flow of pure methanol. It may also be noted that the activation energies for viscous flow for both compounds fall within the range of activation energies for ionic migration, and that E_κ and E_η are very similar to each other. This is in marked contrast to many molten salts for which the ratio E_η/E_κ may be as high as 5. The result suggests that similar configurational changes occur in the two processes in the case of the boron trifluoride complexes, and hence that the sizes of the cation and anion are similar. In those instances where there is a large disparity between E_κ and E_η, conduction is unipolar and occurs by the rapid migration of small cations through the interstices of the larger anion network, whereas viscous flow is conditioned by the shear of the anions past each other.

The deduction of similarly sized ions is supported by the electrolysis results (see below), which establish the ions present in the 1 : 2 complex as $[CH_3{\cdot}OH_2]^+$ and $[BF_3{\cdot}OCH_3]^-$. It may be concluded that the 1 : 1 complex, which has been shown to be methoxytrifluoroboric acid, $H(BF_3{\cdot}OCH_3)$, ionizes with solvation of the proton by a further molecule to give $[BF_3,CH_3{\cdot}OH_2]^+$ and $[BF_3{\cdot}OCH_3]^-$.

In order to stress the dependence of viscosity on free volume, an alternative relation to the exponential one just considered in connection with activation energies has been developed by Batschinski (*Z. phys. Chem.*, 1913, **84**, 643) and Macleod (*Trans. Faraday Soc.*, 1923—4, **19**, 6). They propose an equation, $\eta = B/(v - b)$, where B and b are constants and v is the specific volume. The term $(v - b)$ represents the " free volume " in the liquid, and the constant B can be related to the size of the flow units (see Harrap and Heymann, *Chem. Reviews*, 1951, **48**, 45). The experimental test of Batschinski's equation is linear dependence of fluidity ($\phi = \eta^{-1}$) on specific volume : $v = B\phi + b$, and this has been verified for the present compounds. Table 7 lists the values of the constants B and b for the two complexes and for methanol. It will be noted that the values of B for the two complexes

TABLE 7. *Batschinski's constants* B *and* b.

Compound	B, cm.^{3} cp. g.$^{-1}$	b, cm.^{3} g.$^{-1}$	Compound	B, cm.^{3} cp. g.$^{-1}$	b, cm.^{3} g.$^{-1}$
$BF_3,CH_3{\cdot}OH$ ...	0·109	$0{\cdot}670_8$	$BF_3,2CH_3{\cdot}OH$	0·117	$0{\cdot}778_1$
$CH_3{\cdot}OH$	0·063	$1{\cdot}16_0$			

are similar and nearly twice that for methanol itself. This demonstrates the expected increase in the size of flow units consequent on complex formation, and is a further result consistent with the ionization schemes discussed in the following paragraph.

Electrolysis liberates hydrogen at the cathode, together with 1·5 moles % of boron trifluoride. There is only a minute trace of anodic gas; the oxygen in the system remains in the liquid phase, presumably still co-ordinated to boron trifluoride. Although complete analyses of the catholyte and anolyte have not been carried out, the results find a ready explanation in the following reactions :

Ionic dissocation :

$$2BF_3,CH_3{\cdot}OH \rightleftharpoons [BF_3,CH_3{\cdot}OH_2]^+ + [BF_3{\cdot}OCH_3]^- \quad . \quad . \quad . \quad . \quad (1)$$

$$BF_3,2CH_3{\cdot}OH \rightleftharpoons [CH_3{\cdot}OH_2]^+ + [BF_3{\cdot}OCH_3]^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Cathodic discharge :

$$[BF_3,CH_3{\cdot}OH_2]^+ + e^- \longrightarrow \tfrac{1}{2}H_2 + BF_3,CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$[CH_3{\cdot}OH_2]^+ + e^- \longrightarrow \tfrac{1}{2}H_2 + CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Anodic discharge :

$$[BF_3{\cdot}OCH_3]^- \longrightarrow e^- + [BF_3{\cdot}OCH_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$2[BF_3{\cdot}OCH_3] \longrightarrow BF_3,CH_3{\cdot}OH + BF_3,H{\cdot}CHO \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The overall electrolysis reactions are therefore simply represented by

$$BF_3,CH_3{\cdot}OH \longrightarrow H_2 + BF_3,H{\cdot}CHO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$BF_3,2CH_3{\cdot}OH \longrightarrow H_2 + BF_3,H{\cdot}CHO + CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Reactions (5) and (6) would account for the absence of anodic gas. The compound boron trifluoride–formaldehyde has not been reported in the literature although its homologue boron trifluoride–acetaldehyde is known (Landolph, *Compt. rend.*, 1878, **86**, 1463; Brown, Schlesinger, and Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673); this is considered to be formed by an analogous disproportionation of the ethoxytrifluoroborate radical at the anode when boron trifluoride–ethyl ether, $C_2H_5^+[BF_3{\cdot}OC_2H_5]^-$, is electrolysed (Greenwood, Martin, and Emeléus, *J.*, 1950, 3030).

The ionization schemes indicated by the electrolysis results are consistent with the general chemical properties of both compounds. Meerwein (*loc. cit.*) has shown that boron trifluoride–dimethanol is a strong acid, dissolving metal oxides and carbonates and decomposing diazoacetic ester explosively. It is, however, strange that, although Meerwein (*loc. cit.*) showed that boron trifluoride–dimethanol is a good conductor of electricity in nitrobenzene solution, Meerwein and Pannwitz (*loc. cit.*) found a normal molecular weight for the complex in this solvent.

Acidic properties have also been noted for boron trifluoride–monomethanol (Bowlus and Nieuwland, *loc. cit.*) and its mercuric salt has been isolated (O'Leary and Wenzke, *loc. cit.*) :

$$HgO + 2H^+[BF_3{\cdot}OCH_3]^- \longrightarrow Hg(BF_3{\cdot}OCH_3)_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In confirmation of this work it has now been found that electrolysis of a solution of mercuric oxide in methoxytrifluoroboric acid at 6 v and 16 milliamp. gives rise to both mercury and hydrogen at the cathode but no gas at the anode. This suggests that the water liberated in reaction (9) is subsequently involved in hydroxonium-ion formation. The overall reaction should therefore be formulated as

$$HgO + 3BF_3,CH_3{\cdot}OH \longrightarrow Hg^{++} + H_3O^+ + 3[BF_3{\cdot}OCH_3]^- \quad . \quad . \quad . \quad . \quad (10)$$

The extent to which these ionizations occur, and the relation of the electrochemical properties of boron trifluoride co-ordination compounds to their catalytic activity will be discussed subsequently.

EXPERIMENTAL

The methods employed were very similar to those described in earlier papers. Methanol was of " AnalaR " quality in which the only impurity was water ($<0{\cdot}2\%$). In some experiments the alcohol was dried by refluxing over magnesium, and then distilled in a closed system. Thermometers in the range $-20°$ to $+40°$ were graduated in 0·1° and calibrated directly against N.P.L. standards. Low temperatures were measured with an ammonia vapour-pressure thermometer. Thermostatic control above room temperature was obtained to ±0·015° by a contact thermometer and electronic relay in a large oil-bath. Below room temperature a large, transparent, vacuum flask was used, with acetone or toluene as bath liquid; temperatures were controlled manually to ±0·02° with use of solid carbon dioxide.

Electrical conductivity was measured on a conventional Wagner-earthed A.C. network using the output of a Muirhead variable-frequency oscillator, type A-706-B, with a Muirhead amplifier detector, type D-161-A. Unless otherwise stated, measurements were made at 1000 cycles sec.$^{-1}$. For low resistances a measured 1000-ohm resistance was included in series with the conductivity cell. The conductivity was determined to 1 part in 1000.

Other details of conductivity cells, conductivity–composition cells, viscometers, and dilatometers, as well as of the D.C. circuits and electrolysis apparatus, were as described previously.

With regard to Parts V and VI, the authors thank the Atomic Energy Research Establishment for the award of a Senior Harwell Fellowship (N. N. G.) and the Royal Commission for the Exhibition of 1851 for the award of a Senior Studentship (R. L. M.). These papers are published by permission of the Director, A.E.R.E.

ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL, DIDCOT, BERKS.
UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, October 6th*, 1952.]