423. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part IV.* The Hydrates of Boron Trifluoride.*

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

Boron trifluoride monohydrate, BF_3,H_2O, and boron trifluoride dihydrate, $BF_3,2H_2O$, have been obtained in a highly purified form as colourless, transparent crystals melting at 5·9—6·0° and 6·2° respectively. The monohydrate is unstable to heat and evolves boron trifluoride at temperatures above 15°. The density, dynamic viscosity, and specific conductivity just above the m. p. are $d_4^{10} = 1·7973$, $\eta_{10} = 12·1_0$ centipoises, and $\kappa_{10} = 1·82 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. The corresponding figures for boron trifluoride dihydrate are $d_4^{10} = 1·6458$, $\eta_{10} = 8·25$ centipoises, and $\kappa_{10} = 5·82 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. The temperature dependence of these quantities is also reported, and activation energies are calculated. The decomposition potentials of the monohydrate and dihydrate are $3·2_5$ and $2·8_5$ v. respectively at 10°. Electrolysis of the monohydrate results in the evolution of hydrogen and oxygen, together with considerable quantities of boron trifluoride. The dihydrate also gives hydrogen and oxygen, in the ratio 2 : 1, but only traces of boron trifluoride are evolved. The results confirm that both compounds are highly ionized in the liquid state and should be considered as hydroxytrifluoroboric acid, $H^+[BF_3{\cdot}OH]^-$, and hydroxonium hydroxytrifluoroborate, $[H_3O]^+[BF_3{\cdot}OH]^-$.

This paper describes a series of electrochemical measurements on boron trifluoride monohydrate, BF_3,H_2O, and boron trifluoride dihydrate, $BF_3,2H_2O$. These compounds are liquids at room temperature and may be prepared by absorbing the required amount of boron trifluoride in water. The monohydrate fumes strongly in air and has a marked tendency to evolve boron trifluoride when warmed above room temperature. The dihydrate, on the other hand, does not fume in air and is much more stable to heat. It will be convenient to present first the results obtained on the dihydrate and then to consider those on the monohydrate. These results will then be discussed together and compared with previously published work.

Boron trifluoride dihydrate was prepared by absorbing boron trifluoride in a weighed amount of distilled water and purified by fractional crystallization of the melt. This procedure gave large, colourless transparent crystals melting at 6·1—6·2°. Further recrystallization in a static vacuum, with an apparatus described by Greenwood and Emeléus (*J.*, 1950, 987), gave crystals with a sharp melting point of 6·2°.

Electrical conductivity measurements on the highly purified dihydrate were made by pouring the vacuum-recrystallized compound into a conductivity cell which was then sealed without breaking the vacuum. The conductivity at 1000 cycles A.C. in the temperature range 3—45° is given in Table I and Fig. 1.

Table I.

Conductivity of boron trifluoride dihydrate from 3° *to* 45°.

t.	$\kappa \times 10^2$, ohm^{-1} cm.$^{-1}$.	$\mu = M\kappa/d$, ohm^{-1} cm.^{2}.	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.	*t*.	$\kappa \times 10^2$, ohm^{-1} cm.$^{-1}$.	$\mu = M\kappa/d$, ohm^{-1} cm.^{2}.	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.
2·6°	4·81	3·02	19·6	25·0°	7·79	4·98	17·2
5·0	5·18	3·26	19·5	30·0	8·44	5·41	16·8
8·8	5·66	3·57	18·9	34·5	8·91	5·74	16·2
12·2	6·10	3·86	18·4	40·4	9·80	6·31	15·8 *
17·2	6·69	4·25	17·8	45·5	10·52	6·83	15·5 *
20·0	7·03	4·47	17·4				

* Viscosities for these two temperatures by logarithmic extrapolation.

At 25° the conductivity is $7·79 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. The relative temperature coefficient of the conductivity is $\frac{1}{\kappa}\cdot\frac{d\kappa}{dt} = 1·9\%$. Table I gives also the values of the molar conductivity μ, and the product $\mu\eta$ (where η is the dynamic viscosity). This function has been termed the reduced conductivity $\mathfrak{K}$ (Part III) and is important in comparing the

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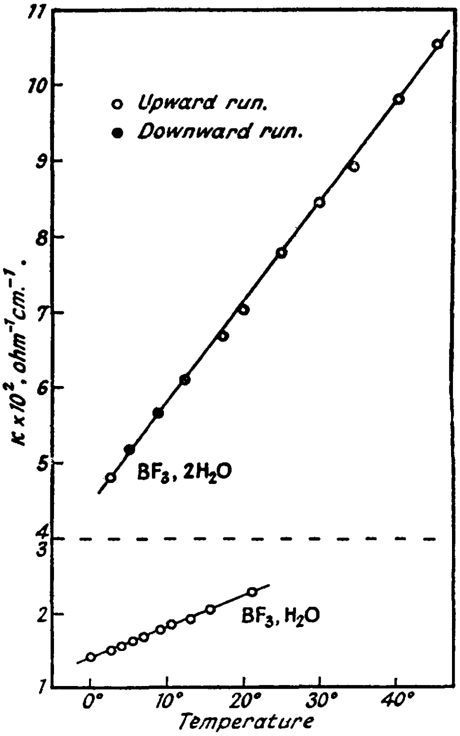
* Part III, *J.*, 1951, 1795.

conductivity of the dihydrate with that of other compounds. This comparison will be discussed in more detail in a subsequent paper.

The electrical conductivity was reproducible below 45°, and showed no alteration with time. Above 45°, bubbles of gas were evolved, but the compound could be heated to at least 60° in a closed system without affecting its conductivity at the lower temperatures. The conductivity of samples exposed to the air was very similar to that given in Table I. Solid boron trifluoride dihydrate, three degrees below its melting point, had a conductivity which was less than that of the liquid by a factor of 5000.

FIG. 1.

Conductivity of boron trifluoride hydrates.



The kinematic viscosity, ν, of boron trifluoride dihydrate, measured with a modified U-tube viscometer as described in Part I (*J.*, 1950, 3030), is shown in Table II, which also gives the dynamic viscosity η, calculated from the relation $\eta = \nu d_4^t$. The kinematic viscosity is plotted in Fig. 2.

TABLE II.

Viscosity of boron trifluoride dihydrate from 5° *to* 35°.

t	5·6°	12·4°	20·0°	25·0°	30·0°	34·7°
ν (centistokes)	5·82	4·73	3·90	3·46	3·10	2·81
η (centipoises)	9·58	7·77	6·36	5·63	5·01	4·54

At 25° the viscosity of the dihydrate is 5·63 centipoises, which is more than six times the value for water itself at the same temperature (0·89 centipoise).

The density of boron trifluoride dihydrate was measured with a Pyrex-glass pyknometer. Its variation with temperature between 5° and 45° is given in Table III. The relation between

TABLE III.

Density of boron trifluoride dihydrate from 5° *to* 45°.

t	5·75°	10·8°	15·0°	20·1°	25·0°	30·0°	35·0°	40·0°	44·9°
d_4^t	1·6521	1·6450	1·6395	1·6328	1·6261	1·6194	1·6132	1·6070	1·6008

density and temperature is accurately represented to within one in the fifth significant figure by the equation :

$$d_4^t = 1{\cdot}6261 - 1{\cdot}31 \times 10^{-3}\,(t - 25) + 2 \times 10^{-6}\,(t - 25)^2$$

The D.C. current–voltage curves obtained on boron trifluoride dihydrate all show well-defined decomposition potentials. On slightly impure samples this potential varied between 3·1 and 3·2 v., but on the highly purified liquid reproducible values may be obtained, and these show a systematic decrease as the temperature is raised (see Table IV).

TABLE IV.

Decomposition potential of boron trifluoride dihydrate between 3° *and* 30°.

t	2·5°	10·7°	20·0°	30·7°
D (volts)	2·92	2·83	2·72	2·62

Electrolysis of the complex results in the liberation of hydrogen at the cathode and oxygen at the anode in the molar ratio 2·05 : 1·00. It was further established that, for each equivalent of electricity passed, one equivalent of hydrogen was liberated. At both electrodes a trace of gas condensable in liquid air was evolved. This was presumably boron trifluoride, but the amount liberated was too small to allow positive identification.

FIG. 2.

Kinematic viscosity of boron trifluoride hydrates.

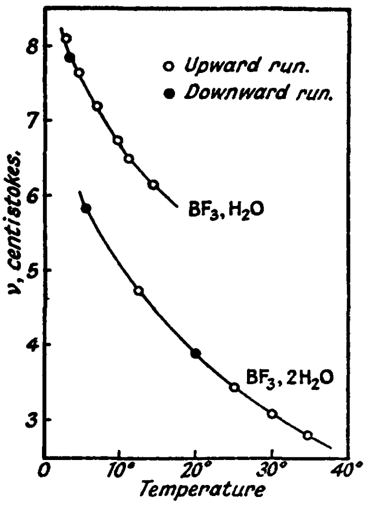
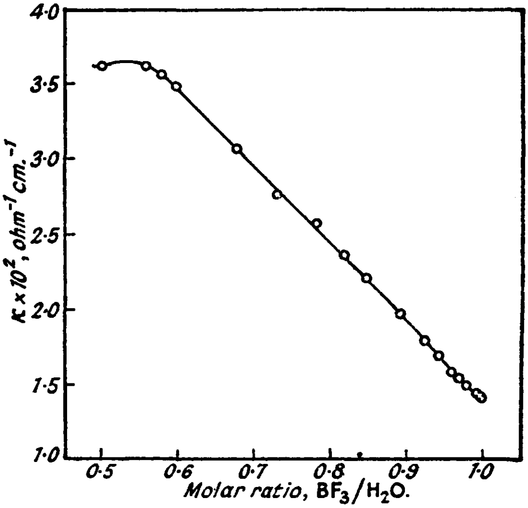


FIG. 3.

Conductivity–composition isotherm at 0·0°.



The variation of conductivity with composition in the system boron trifluoride–water was investigated in the way described in Part II (*J.*, 1951, 1328). However, owing to the appearance of a precipitate of boric acid (cf. McGrath, Stack, and McCusker, *J. Amer. Chem. Soc.*, 1944, **66**, 1263), the conductivity–composition isotherm is not readily interpreted. The system does not constitute a homogeneous phase, so that the composition of the liquid between the electrodes is not a simple function of the weight of boron trifluoride absorbed. The cell constant might also be expected to vary with the amount of suspended solid between the electrodes. Despite this difficulty, it was possible to show that very small additions of either water or boron trifluoride to the highly purified dihydrate increase its conductivity. The stoicheiometric compound is therefore characterized by both a minimum in electrical conductivity and a maximum in melting point. The complex hydrolysis reactions occurring in dilute aqueous solutions of boron trifluoride have recently been fully investigated by Wamser (*J. Amer. Chem. Soc.*, 1951, **73**, 409) and fall outside the scope of the present paper.

Above the molar ratio 0·5, the system is homogeneous and it becomes possible to study the effect of increasing amounts of boron trifluoride on the conductivity. The results of such an experiment at 0·0° are shown in Fig. 3. Boron trifluoride could be rapidly absorbed up to a molar ratio of about 0·90 at this temperature, but further absorption was extremely slow. In no experiment could gas be absorbed above the molar ratio 0·999, and when a liquid of this composition was warmed to room temperature bubbles of boron trifluoride were evolved. Weighings had therefore to be made in a sealed system under pressure to retain all the boron trifluoride in the liquid. At room temperature it was found that water became saturated with boron trifluoride at a molar ratio of 0·95. These observations confirm the report of Meerwein and Pannwitz (*J. pr. Chem.*, 1934, **141**, 123) that the monohydrate exerts a considerable pressure of boron trifluoride at room temperature.

Pure boron trifluoride monohydrate was obtained by repeated fractional crystallisation of an aqueous solution saturated with boron trifluoride at 0°. By melting the compound below 10° and freezing it at 2°, large, colourless, transparent crystals were obtained, having m. p. 5·9—6·0°.

The specific electrical conductivity of boron trifluoride monohydrate at 1000 cycles A.C. is recorded in Table V and Fig. 1.

TABLE V.

Conductivity of boron trifluoride monohydrate from 0° to 20°.

t.	$\kappa \times 10^2$, ohm^{-1} cm.$^{-1}$.	$\mu = M\kappa/d$, ohm^{-1} cm.^{2}.	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.	t.	$\kappa \times 10^2$, ohm^{-1} cm.$^{-1}$.	$\mu = M\kappa/d$, ohm^{-1} cm.^{2}.	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.
0·0°	1·42	0·674	—	9·1°	1·78	0·849	10·5
2·7	1·51	0·701	10·3	10·5	1·85	0·884	10·3
4·0	1·57	0·764	10·7	13·0	1·92	0·918	10·4
5·0	1·63	0·776	10·5	15·6	2·05	0·982	10·6
6·9	1·69	0·805	10·5	21·1	2·29	1·101	—
7·2	1·70	0·810	10·5				

The specific conductivity at 25° (extrapolated) is 2·45 × 10^{-2} ohm^{-1} cm.$^{-1}$, a value which is smaller than that for the dihydrate by a factor of three. At all temperatures the conductivity remained constant for one day, and the values obtained at the lower temperatures could be reproduced even after prolonged heating above 20°. (The conductivity measurements were made in a sealed cell with only a small gas space above the liquid so that at temperatures above about 15° the pressure was greater than one atmosphere and the composition of the liquid did not differ significantly from that of the stoicheiometric 1 : 1 compound.) The values of the molar conductivity μ and the reduced conductivity $\mathfrak{K}$ (Table V) will be discussed later.

The results of measurements on the viscosity of boron trifluoride monohydrate are presented in Table VI and Fig. 2. As it was inconvenient with the apparatus used to measure viscosities at pressures greater than one atmosphere, the investigation was confined to temperatures below 15°. It may be seen that the viscosity is about half as large again as that of the dihydrate.

TABLE VI.

Viscosity of boron trifluoride monohydrate from 0° to 15°.

t	2·9°	4·7°	7·0°	9·8°	11·1°	14·3°	3·3°
ν (centistokes)	8·08	7·64	7·19	6·74	6·49	6·18	7·84
η (centipoises)	14·61	13·78	12·96	12·12	11·65	11·03	14·16

The density of boron trifluoride monohydrate was measured in a sealed pyknometer and the results obtained are summarized in Table VII which represents the overlapping results of three experiments. The figures are reproduced, to within one in the last decimal place, by the equation, $d_4^t = 1{\cdot}8087 - 1{\cdot}14 \times 10^{-3}t$.

TABLE VII.

Density of boron trifluoride monohydrate from 0° to 20°.

	3·5°	4·0°	5·3°	5·8°	6·9°	8·4°
d_4^t	1·8049	1·8043	1·8027	1·8021	1·8008	1·7991
t	8·5°	9·9°	11·4°	15·7°	20·0°	
d_4^t	1·7990	1·7973	1·7956	1·7909	1·7859	

Direct-current experiments at 10° indicated that boron trifluoride monohydrate has a well-defined decomposition potential $D = 3{\cdot}25$ v. Electrolysis at higher voltages results in the liberation of a colourless gas at each electrode. In an experiment on the supercooled liquid the cathodic gas was found to consist of hydrogen and boron trifluoride in approximately equimolar amounts. The anode gas was identified as a mixture of oxygen and boron trifluoride. When a similar experiment was carried out at 15° the hydrogen and oxygen were accompanied by a large excess of boron trifluoride.

DISCUSSION.

The reaction between boron trifluoride and water was first reported by Gay-Lussac and Thénard in 1811, and the early history of the compounds formed has been summarized by Booth and D. R. Martin ("Boron Trifluoride and its Derivatives," John Wiley and Sons, 1949, pp. 53 and 158 *et seq.*). In 1933 Meerwein (*Ber.*, **66**, 411) showed that two compounds were formed and to these he assigned the formulæ BF_3,H_2O and $BF_3,2H_2O$. A detailed study of the properties of these compounds was published by Meerwein and Pannwitz (*loc. cit.*) who described the monohydrate as a colourless, fuming liquid, f. p. 5·4—6°, which decomposed on attempted distillation. These observations were confirmed in the present work, although the melting point was found to be rather sharper, 5·9—6·0°. The dihydrate was reported as a colourless, non-fuming liquid, stable to distillation, b. p. 58·5—60°/1·2 mm., m. p. 4·5—5°. McGrath, Stack, and McCusker (*loc. cit.*) pointed out, however, that the dihydrate suffers some decomposition on attempted distillation, with the formation of, *inter alia*, dihydroxydifluoroboric acid $HBF_2(OH)_2$. They found that the melting point of carefully prepared, undistilled samples, purified by fractional crystallization, was 5·9—6·1°, which is significantly higher than Meerwein and Pannwitz's value. In the present work, boron trifluoride dihydrate was found to melt sharply at 6·2°.

The density of boron trifluoride monohydrate was reported by Klinkenberg (Thesis, Leiden, 1937) as $d_4^{25} = 1{\cdot}760$, but in view of the thermal instability of the compound it is doubtful whether, at 25°, the molar ratio BF_3/H_2O in Klinkenberg's sample was as high as 1·000. This conclusion is supported by the fact that the density, calculated by a 5° extrapolation of the present results, is $d_4^{15} = 1{\cdot}780_2$, which is appreciably higher than Klinkenberg's value. Meerwein and Pannwitz's value of $d_4^{25} = 1{\cdot}777$ for the monohydrate is also lower than the present value of $d_4^{15} = 1{\cdot}7916$, obtained in a sealed system under pressure to prevent evolution of boron trifluoride on warming.

Boron trifluoride dihydrate is a much more stable compound and the published values of its density at 20°, 1·6315 (McGrath, Stack, and McCusker) and 1·6319 (Meerwein), are similar to the value 1·6327 calculated from the density equation obtained in the present work.

The chemical behaviour of the liquid boron trifluoride hydrates is of considerable interest in relation to the results presented in this paper. Meerwein, and Meerwein and Pannwitz (*locc. cit.*), have shown that the dihydrate has strongly acidic properties and dissolves metals, metallic oxides, and carbonates. Attempts to obtain salts by treating ethereal solutions of boron trifluoride dihydrate with alkali or pyridine were unsuccessful, but they were able to isolate "salts" with dioxan and cineole, $BF_3,2H_2O,C_4H_8O_2$ and $BF_3,2H_2O,2C_{10}H_{18}O$. Meerwein argued that these compounds indicated that the dihydrate functioned as a dibasic acid. However, unpublished observations in this Laboratory have shown that boron trifluoride readily combines with dioxan alone to give a stable addition product, so that the constitution of the above "salts" is by no means certain. For the same reason, dioxan should not be used as an inert solvent for cryoscopic measurements on boron trifluoride complexes. The low molecular weight of boron trifluoride dihydrate when measured in dioxan has been ascribed to decomposition of the dihydrate (McGrath, Stack, and McCusker, *loc. cit.*). However, the present investigations have shown that the solution conducts electricity, so that the low molecular weight must be due, at least in part, to ionic dissociation.

The *X*-ray pattern of solid boron trifluoride dihydrate was interpreted by Klinkenberg and Ketelaar (*Rec. Trav. chim.*, 1935, **54**, 959) on the basis of an analogy to ammonium tetrafluoroborate, and they formulated the compound as hydroxonium hydroxytrifluoroborate, $[H_3O]^+[BF_3{\cdot}OH]^-$. On the other hand, Sowa, Kroeger, and Nieuwland (*J. Amer. Chem. Soc.*, 1935, **57**, 454) have pointed out that the compound may be regarded as hydrofluoronium dihydroxydifluoroborate, $[H_2F]^+[BF_2(OH)_2]^-$. The present electrolysis experiments indicate that the former ionization occurs in the liquid, as there is no evidence for evolution of fluorine or hydrogen fluoride at the cathode. Electrolysis results in the liberation of hydrogen at the cathode and oxygen at the anode in the ratio 2 : 1. The electrode processes may thus simply be represented by the scheme :

$$\text{cathode}: H_3O^+ + e^- \longrightarrow H_2O + \tfrac{1}{2}H_2$$

$$\text{anode}: 2BF_3{\cdot}OH^- \longrightarrow 2e^- + BF_3,H_2O + BF_3 + \tfrac{1}{2}O_2$$

The boron trifluoride generated at the anode is immediately absorbed by the dihydrate to give the monohydrate. The relative mobilities of the ions could therefore be determined in principle by careful analysis of the liquid in each electrode compartment, for the cathode liquid becomes progressively more diluted with water whilst the anode liquid becomes steadily more concentrated in boron trifluoride. In this way it is seen that electrolysis effects not only decomposition of the dihydrate into hydrogen and oxygen, but also its disproportionation into water and the monohydrate.

The nature of the ions present in liquid boron trifluoride monohydrate may also be inferred from electrolysis experiments, which result in the liberation of hydrogen and oxygen together with variable amounts of boron trifluoride. The compound may be considered as hydroxytrifluoroboric acid $H^+[BF_3{\cdot}OH]^-$, and although the proton will certainly be solvated by a further molecule (or ion pair) of the monohydrate, the primary electrode processes may be written :

$$\text{cathode}: H^+ + e^- \longrightarrow \tfrac{1}{2}H_2$$

$$\text{anode}: 2BF_3{\cdot}OH^- \longrightarrow 2e^- + BF_3,H_2O + BF_3 + \tfrac{1}{2}O_2$$

As the monohydrate represents a system already saturated with boron trifluoride, the boron trifluoride generated at the anode will be evolved with the oxygen. In addition, depending on the temperature, variable amounts of boron trifluoride are evolved at each electrode. This may be due, in part, to slight local heating of the electrolyte, and also to evolution induced by the passage of hydrogen and oxygen bubbles through the liquid. Such evolution causes only slight changes in composition, for it will be remembered that the monohydrate constitutes a system in which 100 ml. of water have absorbed 125 l. of (gaseous) boron trifluoride. The temperature variation of the amount of boron trifluoride evolved during electrolysis is a further indication of the thermal instability of the monohydrate.

The acidic nature of boron trifluoride monohydrate is confirmed by its chemical properties (Meerwein, and Meerwein and Pannwitz, *locc. cit.*), but the compounds it forms with dioxan and cineole should not be regarded as evidence that it is a dibasic acid (see discussion above on the dihydrate).

The electrical conductivity of boron trifluoride monohydrate was determined at 25° by Klinkenberg (*loc. cit.*). The disadvantage of using so high a temperature on a thermally unstable compound has already been emphasized and indeed the low density of Klinkenberg's samples indicates that the stoicheiometric ratio 1·000 had not been reached. He reports the conductivity as $\kappa_{25} = 4{\cdot}19 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ which is rather higher than the value obtained from the present work by a 4° extrapolation from measurements made under pressure, namely, $\kappa_{25} = 2{\cdot}44 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. Reference to the conductivity–composition isotherm in Fig. 3 shows that this high conductivity again indicates a molar ratio below that of the 1 : 1 compound.

Klinkenberg (*loc. cit.*; *Chem. Weekblad*, 1937, **34**, 23) has also studied the conductivity of aqueous solutions of boron trifluoride monohydrate, and at a composition corresponding to the dihydrate the conductivity was $\kappa_{25} = 10{\cdot}5 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. However, such a procedure may not give the conductivity of the pure dihydrate, owing to the possibility of partial hydrolysis to hydroxyfluoroboric acids (see Wamser, *loc. cit.*; *J. Amer. Chem. Soc.*, 1948, **70**, 1209). The conductivity of highly purified boron trifluoride dihydrate observed in the present work was $\kappa_{25} = 7{\cdot}79 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$.

The temperature dependence of the electrical conductivity, viscosity, and density of the hydrates of boron trifluoride are here reported for the first time. The activation energies for the conduction process may be obtained from the logarithmic plot of conductivity against the reciprocal of the absolute temperature. Neither curve is quite linear, but approximate values of the activation energies E_κ may be obtained; the corresponding values for the activation energies of viscous flow E_η are also given :

$$BF_3,H_2O: E_\kappa = 3{\cdot}6 \text{ kcals. mole}^{-1};\ E_\eta = 3{\cdot}8 \text{ kcals. mole}^{-1}$$

$$BF_3,2H_2O: E_\kappa = 3{\cdot}1 \text{ kcals. mole}^{-1};\ E_\eta = 4{\cdot}1 \text{ kcals. mole}^{-1}$$

It is noteworthy that the activation energy for viscous flow of both compounds is very close to the value for water itself, 4·0 kcals. mole^{-1}. Further discussion of these activation energies and of the reduced conductivity $\mathfrak{K}$ given in Tables I and V will be deferred until a subsequent paper, when the properties of several co-ordination compounds of boron trifluoride will be compared.

EXPERIMENTAL.

Boron trifluoride was supplied by courtesy of Imperial Smelting Corporation Ltd. and its purity checked as described in Part II (*loc. cit.*). The gas was passed through a trap at the temperature of melting toluene (−97°) and passed directly into the water-cooled reaction vessel. The water used to prepare the hydrates was either conductivity water, re-distilled from potassium permanganate in an all-silica apparatus, or was obtained from an ion-exchange resin column.

Electrical circuits and thermostatic control were the same as those described previously. Conductivity–composition isotherms were obtained with the apparatus specified in Part II. Density was measured pyknometrically as reported in the preceding paper and was corrected for buoyancy and thermal expansion of the glass. The technique for viscosity measurements has also been previously outlined (Part I, *loc. cit.*). The time of outflow for the monohydrate was between 791 and 1066 seconds, and for the dihydrate between 369 and 762 seconds.

Boron trifluoride dihydrate was electrolysed at 40 milliamps. and 5·5 v. The current passed was measured by a copper coulombmeter in series with the electrolysis cell. The gases were collected and analysed as described in Part II. The cathode gas was non-condensable in liquid air and had *M* $1{\cdot}9_7$ (Calc. for H_2 : *M*, 2·0). The gas was sparked in a Hempel apparatus and confirmed as hydrogen. The anode gas was also non-condensable in liquid air and had *M* 32·3 (Calc. for O_2 : *M*, 32·0). Its identity was confirmed by complete absorption in alkaline pyrogallol. The ratio of cathode to anode gases, as measured in a constant-volume manometer was 2·05 : 1·00. At each electrode there was a small amount ($<1\%$) of gas condensable in liquid air. Boron trifluoride monohydrate was electrolysed at 40 milliamp. and 10 v. and analysed similarly. The non-condensable cathode gas was shown to be hydrogen (Found : *M*, 2·1), and the condensable fraction to be boron trifluoride (Found : *M*, 68·2. Calc. for BF_3 : *M*, 67·8). The non-condensable anode gas was identified as oxygen (Found : *M*, 33), and the condensable fraction as boron trifluoride (Found : *M*, 68·6). The ratio of condensable to non-condensable gas at each electrode was determined in a constant-volume manometer and shown to be strongly dependent on temperature.

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