593. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part I. Boron Trifluoride–Ethyl Ether.*

By N. N. Greenwood, R. L. Martin, and H. J. Emeléus.

The specific electrical conductivity and kinematic viscosity of liquid boron trifluoride–ethyl ether, $BF_3,(C_2H_5)_2O$, have been investigated in the temperature range −10° to +45°. At 25° the conductivity is $\kappa = 2{\cdot}97 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$, and the viscosity, $\nu = 1{\cdot}71$ centistokes. Electrolysis of the pure liquid results in liberation at the cathode of a mixture of hydrogen, ethane, and ethyl ether. No gas is evolved at the anode. The decomposition potential is temperature-dependent and has the value $1{\cdot}2_5$ volts at 25°. These measurements indicate that considerable ionic character is introduced into ethyl ether when co-ordinated to boron trifluoride. The nature of the ions present is discussed and it is concluded that the compound is ethyl ethoxyfluoroborate, $C_2H_5{\cdot}[BF_3{\cdot}O{\cdot}C_2H_5]$.

This paper is the first of a series dealing with some aspects of the electrochemistry of co-ordination compounds of boron trifluoride. An attempt has been made to characterize the pure compounds as completely as possible and measurements have been made of the electrical conductivity, decomposition potential, viscosity, and density over a range of temperatures on these purified liquids. In addition, the gaseous products of electrolysis have been isolated and analysed. These compounds include complexes of boron trifluoride with ethers, esters, alcohols, fatty acids, and certain nitrogen-containing compounds, such as the pyridines and alkylamines. It is hoped in this way to gain a clearer insight into the nature of these compounds and to contribute to the elucidation of the catalytic activity of both boron trifluoride and its co-ordination compounds.

Since Landolph (*Compt. rend.*, 1878, **86**, 1463) first reported the reaction of boron trifluoride in 1 : 1 equivalent proportions with aldehydes, ketones, and other carbonyl compounds, many co-ordination compounds between boron trifluoride and organic molecules, containing donor atoms, have been mentioned in the literature. A comprehensive review of this field has recently been given by Booth and D. R. Martin (" Boron Trifluoride and its Derivatives," John Wiley and Sons, 1949). These compounds have been used extensively as catalysts in condensation, alkylation, and polymerization reactions, and interpretations of this catalytic activity have been based largely on the concept of an increased acidity conferred on the organic molecule when co-ordinated to boron trifluoride. In a few isolated instances, direct physical evidence has been obtained for increased ionic character of the donor molecule from electrical-conductivity measurements. In particular, Klinkenberg (*Chem. Weekblad*, 1937, **34**, 23) has studied the equivalent conductivity of aqueous solutions of boron trifluoride and has reported the specific conductivity of its monohydrate (BF_3,H_2O) and dihydrate ($BF_3,2H_2O$) to be $42{\cdot}0 \times 10^{-3}$ and $105{\cdot}0 \times 10^{-3}$ ohm^{-1}cm.$^{-1}$, respectively, at 25°. The variation of conductivity with composition in the systems boron trifluoride–methyl alcohol and boron trifluoride–phenol has also been investigated (Nieuwland, Vogt, and Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018; Sowa, Hinton, and Nieuwland, *ibid.*, 1933, **55**, 3402) and minima have been observed at concentrations corresponding to the compounds boron trifluoride–di(methyl alcohol), $BF_3,2CH_3{\cdot}OH$ ($\kappa = 22 \times 10^{-3}$ ohm^{-1}cm.$^{-1}$) and boron trifluoride–diphenol, $BF_3,2C_6H_5{\cdot}OH$ ($\kappa = 1{\cdot}1 \times 10^{-3}$ ohm^{-1}cm.$^{-1}$). However, in the last two systems the molecular compounds were not isolated and purified.

Some studies on the conductivities of solutions of boron trifluoride complexes in organic solvents have been made (Meerwein, *Ber.*, 1933, **66**, 411; O'Leary and Wenzke, *J. Amer. Chem. Soc.*, 1933, **55**, 2117), but in such systems the polarizing and solvating effects of the solvent render uncertain any direct interpretation of the results in terms of an increased ionization of the donor molecule owing to co-ordination with boron trifluoride.

Apart from these measurements, no electrochemical data have appeared in the literature, and this series of papers is an attempt to study systematically the electrochemistry of these compounds, and to correlate variations of electrical properties, both with increase in chain length in any one series of compounds and with the nature of the donor atom in each particular series.

The present paper is concerned with boron trifluoride–ether $BF_3,(C_2H_5)_2O$, which was first reported by Gasselin (*Ann. Chim. Phys.*, 1894, **3**, 5) to be a colourless fuming liquid, b. p. 123°. More recent determinations report boiling points of 123° to 126°, a variation which may be due to a tendency for the complex to dissociate into boron trifluoride and ethyl ether at higher temperatures (Brown and Adams, *J. Amer. Chem. Soc.*, 1942, **64**, 2557). The melting point has been reported as $-50°$ to $-52°$ by Brown and Adams (*loc. cit.*), but more precise determinations have given a value of $-60{\cdot}4°$ (Wiberg and Mäthing, *Ber.*, 1937, **70**, 690; Laubengayer and Finlay, *J. Amer. Chem. Soc.*, 1943, **65**, 884).

The boron trifluoride–ether used was prepared by passing boron trifluoride gas into ethyl ether at room temperature. The product was purified by successive vacuum distillations in the apparatus shown diagrammatically in Fig. 3, and the purified compound was poured directly into the conductivity cell, which was sealed off without breaking the vacuum. The melting point of boron trifluoride–ether so prepared was $-57{\cdot}8°$ to $-57{\cdot}7°$, which is rather higher than the value found by Laubengayer and Finlay (*loc. cit.*).

The electrical conductivity of this liquid was determined in the temperature range $-10°$ to $+45°$ and the results are contained in Table I and Fig. 1. It is seen that the conductivity of the ether complex is $2{\cdot}97 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$ at 25° and that it increases with rise in temperature, the relative temperature coefficient being $(1/\kappa)(d\kappa/dt)_{25°} = 2{\cdot}0\%$. Conductivity measurements were not extended above 45°, for at higher temperatures boron trifluoride–ether shows an irreversible increase of conductivity with time. At 45° the conductivity rose by 3% of its value during 63 hours. At lower temperatures, however, the curve was accurately reproducible, as is shown by the points on Fig. 1. In column 4 of Table I the values of the molar conductivity are tabulated, and the final column gives the values of the function $\kappa\eta/d$, where η is the dynamic viscosity.

TABLE I.

Conductivity of boron trifluoride–ether from −10° *to* +45°.

t.	$\kappa \times 10^4$, ohm⁻¹cm.⁻¹.	d_4^t.*	$100M\kappa/d$.	$10^6(\kappa\eta/d)$, ohm⁻¹g.⁻¹ poise cm.².	t.	$\kappa \times 10^4$, ohm⁻¹cm.⁻¹.	d_4^t.*	$100M\kappa/d$.	$10^6(\kappa\eta/d)$, ohm⁻¹g.⁻¹ poise cm.².
−9·4°	1·344	1·160	1·644	4·60	11·0°	2·222	1·138	2·771	4·86
−5·5	1·490	1·156	1·830	4·67	14·8	2·406	1·134	3·011	4·89
−4·3	1·540	1·155	1·892	4·68	19·7	2·662	1·129	3·347	4·97
−1·0	1·676	1·151	2·066	4·72	24·9	2·952	1·123	3·731	5·01
0·0	1·728	1·150	2·132	4·76	30·3	3·250	1·117	4·130	5·04
+2·3	1·815	1·148	2·244	4·75	34·6	3·497	1·112	4·464	5·07
5·0	1·942	1·145	2·407	4·80	39·9	3·801	1·107	4·874	5·13
8·0	2·074	1·141	2·580	4·81	44·7	4·083	1·102	5·259	5·18

* $d_4^t = 1{\cdot}150 - 0{\cdot}00108t$ (above 0°) (Sugden and Waloff, *J.*, 1932, 1942); $d_4^t = 1{\cdot}150 - 0{\cdot}001105t$ (below 0°) (Wiberg and Mäthing, *loc. cit.*).

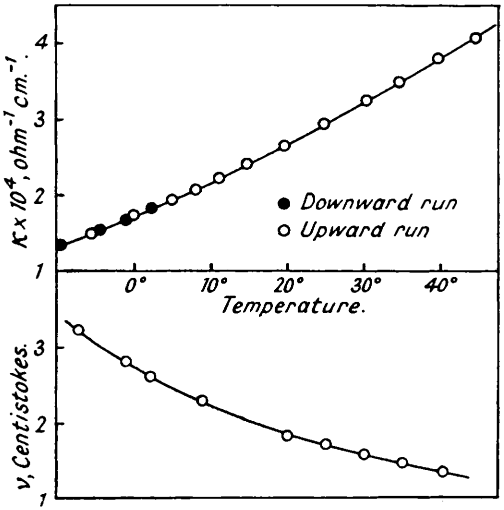


FIG. 1.

Specific conductivity and kinematic viscosity of boron trifluoride–ether from −10° *to* +45°.

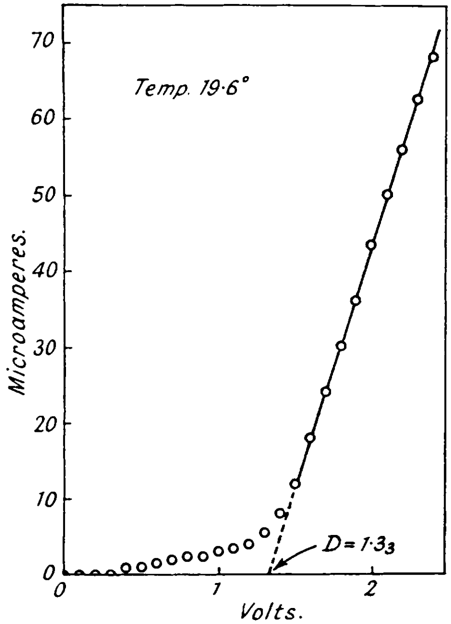


FIG. 2.

Decomposition potential of boron trifluoride–ether.

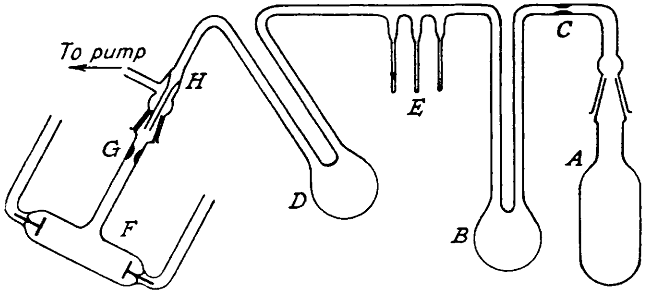


FIG. 3.

Vacuum purification apparatus.

TABLE II.

Viscosity of boron trifluoride–ether from —10° *to* +40°.

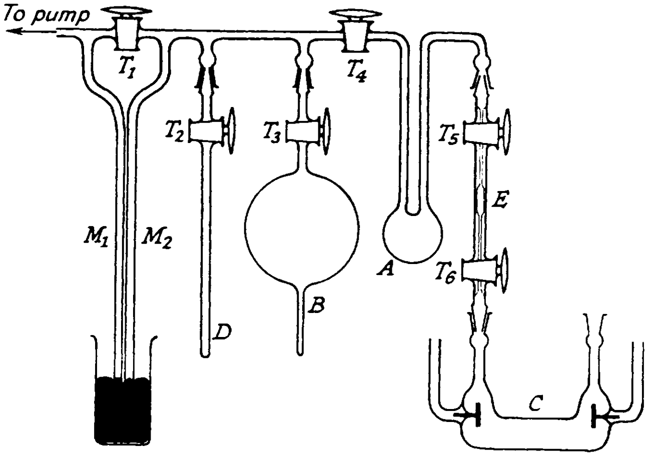
t	$-7{\cdot}1°$	$-1{\cdot}0°$	$+2{\cdot}3°$	$8{\cdot}9°$	$20{\cdot}0°$	$25{\cdot}0°$	$30{\cdot}0°$	$35{\cdot}0°$	$40{\cdot}3°$
ν, centistokes	3·22	2·81	2·61	2·29	1·82	1·71	1·58	1·47	1·35
d_4^t *	1·158	1·151	1·148	1·140	1·128	1·123	1·118	1·112	1·107
η, centipoises	3·72	3·24	3·00	2·61	2·05	1·93	1·77	1·65	1·50

* Densities by interpolation from Sugden and Waloff, and Wiberg and Mãthing (*locc. cit.*).

The temperature-dependence of the kinematic viscosity (ν) was determined by using a modified Ostwald U-tube viscometer in accordance with British Standard 188:1937. The results are presented in Table II and Fig. 1. The values of η, which is related to ν by the equation $\eta = \nu d_4^t$, are also included in Table II. It may be seen that the viscosity at 25° is $\eta = 1{\cdot}93$ centipoises, which is about twice the value for water at the same temperature. The plot of log η against the reciprocal of the absolute temperature is approximately linear with a slope corresponding to an activation energy of 3·1—3·3 kcals.mole^{-1}. These results will be discussed later.

FIG. 4.

Apparatus for examination of electrode gases.



To obtain some information on the nature of the electrode processes occurring in liquid boron trifluoride–ether, D.C. measurements were carried out. The current–voltage curves gave well-defined decomposition potentials which varied slightly with temperature as shown in the following table; Fig. 2 shows a typical plot. At higher voltages a colourless gas was evolved at the cathode, and there was a slow colour change in the liquid through pale yellow to brown; at the anode the only visible reaction was a colour change similar to that observed at the cathode. The cathodic gas was collected and analysed in an apparatus shown in Fig. 4, and was found to be mainly hydrogen with smaller amounts of ethane and ether, in the mole ratios, hydrogen 4·4, ethane 1, ether 0·3.

Decomposition potential of boron trifluoride–ether.

t	$10{\cdot}9°$	$19{\cdot}6°$	$30{\cdot}6°$
D, volts	$1{\cdot}4_0$	$1{\cdot}3_3$	$1{\cdot}2_2$

DISCUSSION.

The only reference to the conductivity of boron trifluoride–ether in the literature is by Bowlus and Nieuwland (*J. Amer. Chem. Soc.*, 1931, **53**, 3835), who observed that the conductivity was " very low in comparison with that found for the ethyl alcohol compound." Unfortunately, the value of the conductivity of the ethyl alcohol compound was not published; their reference to Nieuwland, Vogt, and Foohey (*loc. cit.*) appears to concern the conductivity of the system methyl alcohol-boron trifluoride (see above). The present investigation gives the conductivity of highly purified boron trifluoride–ether as $\kappa_{25°} = 2{\cdot}97 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$, which is smaller by a factor of 10^2 than the published figure for boron trifluoride–di(methyl alcohol) ($\kappa_{25^\circ} = 2{\cdot}2 \times 10^{-2}$ ohm^{-1}cm.$^{-1}$).

The conductivity of ethyl ether itself is $<3 \times 10^{-13}$ ohm^{-1}cm.$^{-1}$ at 25° and measurements on liquid boron trifluoride at -120° (Woolf and Greenwood, *J.*, 1950, 2200) give a conductivity of $<5 \times 10^{-10}$ ohm^{-1}cm.$^{-1}$. The much higher conductivity of the co-ordination complex arises from ionization caused by the electron displacement involved in the formation of the oxygen–boron donor–acceptor bond.

The molar conductivity, which is equal to the product of the specific conductivity and the molar volume, is tabulated in col. 4 of Table I. The value $(M\kappa/d)_{25^\circ} = 3{\cdot}75 \times 10^{-2}$ may be used to compare the conductivity of the complex with that of other liquids at the same temperature. Such a comparison shows that the molar conductivity of boron trifluoride–ether is considerably larger than that of most other compounds which are liquid at this temperature.

The steady increase in conductivity with rising temperature is caused by an increase in both the number and the mobility of the ions in the liquid. As mobility is inversely proportional to viscosity, the function $\kappa\eta/d$ given in the final column of Table I should compensate for increased conductivity arising from this cause, and the increase of 10% in the value of this function over the temperature range investigated is a measure of the enhanced ionization of the complex effected by rise in temperature.

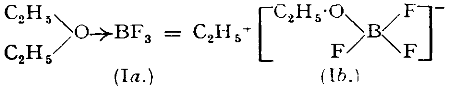
When log κ is plotted against the reciprocal of the absolute temperature, a curve is obtained which is slightly convex to the temperature axis. An accurately linear plot is not to be expected for, in addition to the activation energy of ionic migration, a term reflecting the changing number of ions with temperature will be involved. However, it is possible to obtain some idea of the activation energies from the slope of the curve, and these have been calculated to vary systematically between the limits 3·72 kcals.mole^{-1} at lower temperatures and 2·32 kcals.mole^{-1} at higher temperatures.

Co-ordination to boron trifluoride increases the viscosity of ethyl ether from 0·224 to 1·93 centipoises at 25°, and the activation energy of viscous flow from 1·63 kcals.mole^{-1} to 3·20 kcals.mole^{-1}. The latter value is just that which would be predicted from the latent heat of vaporization ($L_{\text{vap.}}$) on the basis of Eyring's theory of absolute reaction rates. According to this theory, the activation energy of viscous flow for liquids having unsymmetrical molecules is $\frac{1}{4}L_{\text{vap.}}$, and, a value of 13·1 kcals.mole^{-1} being used for the latent heat of vaporization (Laubengayer and Finlay, *loc. cit.*), this gives a calculated activation energy of 3·27 kcals.mole^{-1}, which agrees well with the observed value of 3·20.

The discussion so far has dealt only with the results of viscosity and A.C. conductivity measurements. The results of D.C. measurements are now considered. The decomposition potentials in the last table cannot be used directly to calculate the free-energy change associated with the electrode processes occurring in the complex because of the disturbing influence of irreversible phenomena. Back-e.m.f. measurements are free from this disadvantage, but preliminary experiments showed that the e.m.f was so transient that measurements of its equilibrium value were impracticable. The current densities used in the decomposition potential measurements were of the order of 10^{-5} amp.cm.$^{-2}$, and at these low values Bowden and Rideal (*Proc. Roy. Soc.*, 1928, *A*, **120**, 59) have shown that the hydrogen overvoltage on platinum is 0·03—0·05 v. If this were so, the present measurements could be used to estimate the free-energy change involved but it is by no means certain that overvoltage measurements on 0·2N-aqueous sulphuric acid would be applicable to liquid boron trifluoride–ether. The observed dependence of the decomposition potential on temperature may be due to changes in both the free energy of the electrode process and the hydrogen overvoltage.

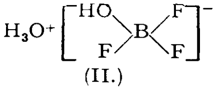
Electrolysis of boron trifluoride–ether at potentials between 50 and 100 v. results in the liberation of a mixture of hydrogen, ethane, and ethyl ether at the cathode in the molar ratios 4·4 : 1 : 0·3. In addition, there is a marked colour change at both electrodes from colourless to brown. It is significant that no boron trifluoride was evolved at either electrode but remained in the electrolyte, presumably still co-ordinated to the oxygen-containing residue. Any proposed scheme of ionization for the complex must be in accordance with these facts.

It is possible to consider boron trifluoride–ether (I*a*) as the ethyl derivative (I*b*) of ethoxytrifluoroboric acid :



$$(C_2H_5)_2O\rightarrow BF_3 = C_2H_5^+\left[(C_2H_5O)BF_3\right]^-$$

(I*a*.) (I*b*.)



$$H_3O^+\left[(HO)BF_3\right]^-$$

(II.)

Although no direct analogy can be made, it is relevant that Klinkenberg and Ketelaar (*Rec*·

Trav. chim., 1935, **54**, 959), on the basis of *X*-ray diffraction measurements, have established the structure of boron trifluoride dihydrate as hydroxonium hydroxytrifluoroborate (II). Further, the methoxytrifluoroborate ion is known in such compounds as mercuric methoxytrifluoroborate, $Hg(BF_3{\cdot}O{\cdot}CH_3)_2$, which is derived from the acid $H^+[BF_3,O{\cdot}CH_3]^-$, boron trifluoride–mono-(methyl alcohol) (O'Leary and Wenzke, *loc. cit.*). The ionization now postulated is esentially the same as that assumed by Price and Ciskowski (*J. Amer. Chem. Soc.*, 1938, **60**, 2499) to explain the alkylation of organic compounds by ethers or alcohols in the presence of boron trifluoride. Although no direct evidence for the nature of the ionic species was available at that time, it would now seem that this ionization is consistent with the results of the present electrolysis experiments. At the cathode the primary reaction would be the discharge of the ethyl ion to give hydrogen and ethylene :

$$C_2H_5^+ + e^- \longrightarrow C_2H_4 + \tfrac{1}{2}H_2$$

The ethylene would then be subject to two competing reactions, first, polymerization to higher olefins, and secondly, hydrogenation to ethane. The relative amounts of ethylene undergoing each reaction will depend on the rate of electrolysis (current density) and on the rate of agitation of the electrolyte. The ratio may also be dependent on the applied voltage, which affects the hydrogen overpotential on platinum and hence its efficiency as a reducing agent. Such a variation of electrolysis products with current density and applied voltage is well known from the classical work of Haber and others.

Under the conditions of the present experiments the greater proportion of ethylene appears to undergo polymerization rather than reduction, for, although the primary reaction produces twice as much ethylene as hydrogen, the observed ratio of hydrogen to ethane in the cathode gas is 4·4 : 1. This implies that, for each molecule of ethylene reduced to ethane, ten molecules undergo polymerization.

The final constituent of the cathode gas was ethyl ether itself. This comprised about 5 moles % of the total gases evolved, equivalent to approximately 0·1 millimole. As the amount of complex undergoing electrolysis was approximately 0·2 mole, the liberated ether may represent a stoicheiometric excess of 1 part in 2000 or, more probably, it may arise from contact of the ether complex with traces of water vapour while the electrolysis cell was being loaded :

$$BF_3,(C_2H_5)_2O + H_2O \longrightarrow BF_3,H_2O + (C_2H_5)_2O$$

Such a reaction would explain the tendency of the complex to fume in moist air. This possibility detracts in no way from the accuracy of the measurements of the specific electrical conductivity which were made under much more rigorous conditions.

The reactions occurring at the anode are less amenable to discussion as no gaseous products are evolved. However, it is suggested that the discharged anion may disproportionate according to the reactions :

$$(BF_3,O{\cdot}CH_2{\cdot}CH_3)^- \longrightarrow [BF_3,O{\cdot}CH_2{\cdot}CH_3] + e^-$$
$$2[BF_3,O{\cdot}CH_2{\cdot}CH_3] \longrightarrow BF_3,CH_3{\cdot}CHO + BF_3,CH_3{\cdot}CH_2{\cdot}OH$$

Boron trifluoride–acetaldehyde has been reported by Landolph (*loc. cit.*) and confirmed by Brown, Schlesinger, and Burg (*J. Amer. Chem. Soc.*, 1939, **61**, 673) ; under the present conditions of formation the aldehyde may be polymerized. Boron trifluoride–mono(ethyl alcohol) has been reported by Bowlus and Nieuwland (*loc. cit.*) and will itself be ionized to some extent. Disproportionation of the anion in this way explains the absence of gaseous anodic products and the fact that all the boron trifluoride and oxygen are retained in the electrolyte.

EXPERIMENTAL.

Boron Trifluoride–Ether.—This compound was prepared by passing boron trifluoride gas through ethyl ether in an apparatus kept at room temperature by means of a water-cooler. Boron trifluoride was generated according to the method of Booth and Willson (*Inorg. Synth.*, Vol. I, p. 21) by heating a mixture of concentrated sulphuric acid (300 ml.), boric anhydride (50 g.), and sodium fluoroborate (300 g.) in an all-glass apparatus. The gas was bubbled through two towers containing concentrated sulphuric acid saturated with boric anhydride and then passed directly into a weighed absorption tube containing the ether which had been freshly distilled from sodium. When absorption was complete the product, contained in the tube, *A*, was transferred to the purification apparatus, Fig. 3. The latter had been thoroughly dried by flaming under a vacuum. The vapour pressure of boron trifluoride–ether has been given by Laubengayer and Finlay (*loc. cit.*) as $\log p_{\text{mm.}} = -2845/T + 10{\cdot}02$, which corresponds to a value of about 2 mm. at 20° ; vacuum-distillation could therefore be conveniently carried out at room temperature. The apparatus was evacuated, and after a short time the distillation rate became constant at about 10 ml. per hour. A first fraction was allowed to pass through the apparatus, and then about

30 ml. were condensed by cooling trap *B* in liquid air, after which the bulb *A* was drawn off at the constriction *C*. A similar process resulted in a middle fraction being condensed in trap *D*, the tubes *E* retaining samples for m. p. and carbon and hydrogen determinations. The purified compound in *D* was melted and poured directly into the conductivity cell *F*, which was then sealed at the constriction *G* without breaking the vacuum. The internal seal *H* prevented contamination of the liquid as it flowed through the ground joint.

Carbon and hydrogen analyses confirmed the identity of the compound as $BF_3,(C_2H_5)_2O$ (Found : C, 33·3; H, 7·5. Calc. : C, 33·8; H, 7·1%). The m. p. was $-57{\cdot}7°$ to $-57{\cdot}8°$. In a separate experiment, the m. p. of the impure compound, as prepared, was found to be $-58{\cdot}7°$ to $-59{\cdot}5°$; after a first vacuum-distillation this rose to $-57{\cdot}7°$ to $-57{\cdot}8°$ and successive vacuum fractionations effected no further change in this value. Temperatures were measured by means of a calibrated ammonia thermometer.

Electrical Conductivity.—A conductivity cell of the conventional type in soda glass, with platinum electrodes, was found quite suitable for conductivity determinations; the value of the conductivity remained unaltered at room temperature during several months. The cell constant was 2·359 $cm.^{-1}$, and the volume of liquid required was approx. 5 ml.

Conductivity was measured by using the amplified output of a 1000-cycle beat frequency oscillator in a Wheatstone-type network, and the balance point was detected electronically by means of a cathode-ray oscilloscope (Haszeldine and Woolf, *J. Soc. Chem. Ind.*, in the press). For temperatures above that of the room, thermostatic control was obtained to $\pm 0{\cdot}05°$ by means of a contact thermometer and " Sunvic " relay in a large water-bath. Lower temperatures were maintained by circulating cooled ethylene glycol from an American Instrument Co. " Aminco " thermostat through metal coils in a large bath of the same liquid. With this arrangement the temperature could be controlled to $\pm 0{\cdot}05°$ over periods of one hour.

D.C. measurements were made by means of a standard circuit which incorporated a microammeter, and potential differences were measured by using an " Avometer."

Identification of Cathode Gases.—The apparatus used for the generation and identification of gaseous electrolysis products is represented in Fig. 4. About 20 ml. of boron trifluoride–ether in cell *C* were electrolysed at 30 ma. during 12 hours. The applied potential was varied between 50 and 100 v. in order to maintain an approximately constant current density. The gas evolved under these conditions was passed into the vacuum system through the lock *E*. With taps T_1 and T_2 closed, and trap *A* cooled in liquid oxygen, the non-condensable fraction of the cathodic gas accumulated in the molecular-weight bulb *B* of 125 ml. capacity, and its pressure was measured in the manometer, M_2, by means of a cathetometer. When approximately 3 millimoles of gas had been collected, taps T_3 and T_4 were closed, and the bulb was weighed. The molecular weight was calculated to be 2·7. Samples of this gas were sparked with air in a Hempel apparatus, and the contraction was noted. There was no further contraction on treatment with aqueous sodium hydroxide solution. In duplicate experiments 19·0 ml. and 15·5 ml. of the gas were found by analysis to be 18·6 ml. and 14·8 ml. of hydrogen, respectively.

The fraction condensable in liquid oxygen constituted approx. 22 moles % of the gases evolved, and had a molecular weight of 39·7. This gas was subjected to further fractionation at the temperature of a melting-alcohol bath, $-112°$, and resolved into two components : (*a*) volatile, *M* 30·1 (Calc. for ethane : 30·1); (*b*) non-volatile, *M* 74·2 (Calc. for ethyl ether : 74·1). The vapour pressure of the volatile fraction was measured manometrically between $-120°$ and $-140°$ and found to correspond to the published figures for ethane. Temperatures were measured by means of an ethylene thermometer. These vapour-pressure results, in conjunction with the molecular-weight determination, unambiguously establish the identity of the component (*a*) as ethane. In a similar way the vapour pressure of component (*b*) was measured over the temperature range $-20°$ to $-78°$ and all the values were found to be in accord with the vapour pressure of ethyl ether. In this instance temperatures were measured with a mercury or an ammonia thermometer.

Viscosity.—The kinematic viscosity (ν) was measured by using a British Standard No. 1 U-tube viscometer constructed in " Pyrex " glass with a capilliary diameter of 1·2 mm. and an efflux volume of 6·5 ml. The limbs of the viscometer were fitted with silica drying-tubes to prevent access of moisture to the liquid under investigation. The time of efflux (t) varied between 180 and 420 secs. and was related to the viscosity by the equation $\nu = Ct - ct^{-1}$. The constant C was determined by direct calibration with distilled water and had a value of $7{\cdot}662 \times 10^{-3}$ centistokes $sec.^{-1}$. Kinetic-energy corrections were effected by the term containing the constant c, which had a value 2·4 centistokes sec. for the instrument used. Thermostatic control was the same as that used in electrical conductivity measurements.

Two of the authors (N. N. G. and R. L. M.) thank the Commissioners of the Exhibition of 1851 for the award of Overseas Studentships during the tenure of which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, May 4th,* 1950.]