k, m and n are calculated from equation (2) by measuring S for three independent mixing ratios CO_2/O_2 at one temperature.

TABLE 1.—DATA FOR CO_2/O_2 EXCHANGE EXPERIMENTS

T (°C)	k $\times 10^5$	m coeff. CO_2	n coeff. O_2
900	2·37	0·78	1·21
850	0·87	0·76	1·08
820	0·33	0·65	1·10

In testing the heterogeneous wall reaction the vessel was packed full of short sections of crushed quartz giving an increase in the surface to volume ratio of 17 times. The error of this value is of the order of 20 per cent.*

TABLE 2.—RATE CONSTANTS FOR PACKED (k_p) AND UNPACKED (k_u) VESSEL

T (°C)	k_u $\times 10^5$	k_p $\times 10^5$	Ratio k_u/k_p
900	2·37	4·3	1·8
850	0·87	5·8	6·7
820	0·33	4·6	13·9

When the ratios of k-values from Table 2 are compared, we immediately see that the rate of the heterogeneous reaction decreases with increasing temperature. At 820°C the ratio k_u/k_p is approximately equal to the increase in surface to volume ratio within experimental error, suggesting that up to this temperature the reaction is predominantly heterogeneous. At higher temperatures the decrease in the ratio indicates the increasing importance of the homogeneous reaction.

A detailed account of work in progress will be published in the near future.

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* This determination has been done at the Centraal Laboratorium van de Staatsmijnen te Geleen.

The chloride ion catalysed solvolysis of boron trichloride in liquid sulphur dioxide†

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THE reaction $2BCl_3 + 3SO_2 \rightarrow 3SOCl_2 + B_2O_3$ was indicated by HECHT *et al.*,⁽¹⁾ who observed the first signs of reaction after five years at room temperature and tentatively identified the products after ten years. Recent thermochemical data⁽²⁾ indicate that $\Delta H^\circ = -24$ kcal for the liquid phase reaction; and ΔF° also should be favourable.

† Abstracted from the Master of Science thesis by ERNEST R. BIRNBAUM, University of Southern California Libraries, 1958 (available on microfilm).

(1) H. HECHT, R. GREESE and G. JANDER, *Z. anorg. Chem.* **269**, 265 (1952).

(2) *National Bureau of Standards.* Circular No. 500 (1952).

We now find that this reaction is strongly catalysed by either sodium chloride or potassium chloride. For example, 1·303 g (11·1 mmole) of boron trichloride and 1·995 g (31·2 mmole) of sulphur dioxide, in a well dried bomb tube with 299 mg of vacuum-baked potassium chloride, changed to a plastic mass during two days at room temperature and after seven days seemed to be all solid. The volatile components were partially separated by high-vacuum fractional condensation. Each fraction was analysed by hydrolysis and titration for boron, chloride, strong acid, and sulphur (IV): (Found: 2·64 mmole BCl_3, 11·4 mmole $SOCl_2$, and 18·4 mmole SO_2). Thus 95·5 per cent of the sulphur was recovered in volatile form; and qualitative tests failed to disclose any sulphide, sulphite, or sulphate in the nonvolatile white solid.

This solid was investigated (with the aid of Mr. K. I. HARDCASTLE) by X-rays, giving a pattern which included lines characteristic of potassium chloride and boron oxide. It contained 8·55 mmole of boron (total recovery, 100·8 per cent) and 6·02 mmole of chloride—implying 2·01 mmole of chloride assignable to B–Cl bonds. The corresponding strong acid titration gave 1·83 mmole. This excess chloride (beyond the KCl) would represent an incomplete disproportionation of BOCl units, which could exist as mutually isolated components in the boron oxide polymer.

When ionic chlorides were absent, control experiments showed no reaction between sulphur dioxide and boron trichloride within a reasonable time.

The catalytic effect of chloride can be understood in terms of formation of a SO_2Cl^- ion,* which may well be a sufficiently strong base to bond to boron trichloride through oxygen. Loss of chloride from boron in the resulting complex, $\mathrm{Cl\overset{O}{S}OBCl_3^-}$, would be a reasonable expectation; and a displacement of the $OBCl_2^-$ unit from sulphur by chloride also is possible. Thus one would have $SOCl_2$ and $KOBCl_2$, and the dissociation of the latter into KCl and the disproportionation products of BOCl would be expected.

This research began with an attempt to determine whether the hypothetical BCl_4^- ion is present sufficiently in the NaCl–BCl_3 solution in liquid sulphur dioxide(4) for transference of boron to the anode during electrolysis. The conductance was fairly high, but the solvolysis reaction prevented a decision concerning the transference. In any case, the specific ion BCl_4^- need not have been present, in view of alternative explanations of the solubility of sodium chloride in the presence of boron trichloride.

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* Presumably far less stable than SO_2F^-.(3)

(3) F. SEEL and H. JONAS, *Angew. Chem.* **67**, 32 (1955).

(4) D. M. GARDNER, Thesis, University of Pennsylvania (1955).

The back-extraction of uranyl nitrate from tributyl phosphate solution

THE optimum conditions for extraction of uranyl nitrate from nitric acid solutions by TBP were investigated in a preceding paper.(1) Back-extraction studies were made with a separated organic phase of 19 % TBP in kerosene containing uranyl nitrate extracted at 20°C from 5 g/l. aqueous uranyl nitrate containing 6 M HNO_3. Backwashing was carried out in similar manner to that of the extraction, 50 ml portions of the organic phase and of the backwashing solution being put into 100 ml stoppered conical flasks and shaken for 10 min in a thermostat at 20°C. The uranium content of the backwash phase was then determined and the percentage back-extracted calculated from $(x_2/x_1) \times 100$, where x_1 is the uranium concentration of the original organic phase and x_2 that of the backwash phase.

Sulphuric, hydrochloric, acetic and oxalic acids and their ammonium and sodium salts, and additionally ammonium and sodium carbonate, were chosen as back-extraction agents; 1, 5 and 10 w/w per cent solutions were employed, and the results compared with those from water backwash. The effect of backwashing with water alone was examined with varying volumes and also successive

(1) T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).