

acid ($10^{-2} M$) or thiourea ($10^{-2} M$)—red light was over one hundred. No polymerization occurred in the presence of oxygen.

It is felt that these systems might be of practical importance in the preparation of polymers and also help to elucidate some of the difficult problems in the photochemistry of chlorophyll, such as the nature of reversible bleaching.

A more detailed account of this work will be published when it is more complete.

The photosynthesis studies were aided by a contract between the Office of Naval Research, Department of the Navy, and the University of Chicago (NR 119-272).

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A NEW SUB-CHLORIDE OF BORON, B_4Cl_4

Sir:

In the spontaneous decomposition of tetrachlorodiborane (B_2Cl_4) at 0° , as well as in its preparation by the procedure of Wartik, Moore and Schlesinger (THIS JOURNAL, 71, 3265 (1949)), very small quantities of volatile, yellowish crystals are obtained by evaporation of the tetrachlorodiborane. Although the decomposition of tetrachlorodiborane is accelerated somewhat by rise in temperature or by exposure to ultraviolet radiation, no significant improvement in yield has been achieved thereby.

The formula, B_4Cl_4 , was established for the crystals by analysis of a 0.057 g. sample (24.2% B and 78.9% Cl) and by vapor density measurements, made at 65° and giving a molecular weight of 188 (average of two determinations at 17.9 and 30.1 mm., respectively). Vapor tensions are as follows:

t°	23.0	30.0	40.8	52.4	57.4	67.7
$p_{mm. obs.}$	1.60	3.15	7.05	13.0	17.7	34.3
$p_{mm. calcd.}$	1.94	3.16	6.42	13.2	17.8	31.2

The calculated values were obtained from the equation

$$\log_{10} p_{mm.} = -2719/T + 9.464$$

The very small quantities of the compound thus far accumulated have limited investigation of its chemical properties to exploratory experiments,

which have disclosed striking differences in the properties of the two sub-chlorides. Both inflame spontaneously in air, but the reaction of B_4Cl_4 is so much more vigorous that the inflammability of tetrachlorodiborane may be due to unavoidable traces of B_4Cl_4 . In the absence of air, the former decomposes moderately rapidly at 0° ; B_4Cl_4 , even at 70° , undergoes no appreciable decomposition.

Tetrachlorodiborane reacts very rapidly with hydrogen even considerably below 0° to give chiefly boron trichloride and diborane; B_4Cl_4 does not react with hydrogen or does so only very incompletely. Tetrachlorodiborane, with alkylating agents such as alkyls of boron, aluminum or zinc, produces non-volatile black solids presumably impure boron; B_4Cl_4 does not react with trimethyl boron at temperatures up to -10° , but with trimethyl aluminum produces colorless, volatile liquid and solid materials, which may be methyl derivatives of B_4Cl_4 since they give decomposition products similar to those of the latter. These products have not yet been obtained in quantities or purity adequate for identification.

Methanol converts tetrachlorodiborane to tetramethoxydiborane and generates hydrogen chloride, but no hydrogen; with B_4Cl_4 , methanol produces no hydrogen chloride but generates 6 gram equivalents of hydrogen per mole of B_4Cl_4 . With 6 moles of methanol per mole of B_4Cl_4 , the major other volatile product appears to be methyl chloride, though identification of the latter is still incomplete. A white solid is also observed. With excess methanol, the major products appear to be methyl chloride, the methanol-methyl borate azeotrope and the 6 gram equivalents of hydrogen.

The liberation of 6 gram equivalents of hydrogen per mole of B_4Cl_4 suggests that the latter contains 6 equivalent boron to boron bonds, as would be the case if the boron atoms were situated at the corners of a tetrahedron and were each associated with one chlorine atom. This supposition is in agreement with results of X-ray diffraction, communicated to us by Professor W. N. Lipscomb in advance of publication.

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GRANT URRY
THOMAS WARTIK
H. I. SCHLESINGER

RECEIVED OCTOBER 9, 1952

BOOK REVIEWS

Thermodynamics of Alloys. By JOHN LUMSDEN, Research Department, Imperial Smelting Corporation, Ltd., Avonmouth. The Institute of Metals, 4 Grosvenor Gardens, London, S. W. 1, England. 1952. xv + 384 pp. 15 × 22.5 cm. Price, \$5.50.

This book will undoubtedly be welcomed by many metallurgical departments since it presents under one cover much material that has never before been set together in form suitable for the metallurgist or metallurgical chemist. The chemistry or science of metals is a field which has too long been neglected not only by authors and publishers but even by the American Chemical Society which has no division for this science. Any reasonably meritorious contri-

bution to this field must be gratefully received. The present work (not to be confused with an excellent recent book of identical title by Carl Wagner) cannot, in this reviewer's opinion, be classed as that of genius—and certainly cannot be classed as that of a hack rewrite.

The dust jacket claims that "The theory is developed from first principles with the mathematics kept as simple as possible. . . ." As pertaining to elementary chemical thermodynamics this optimistic viewpoint is not shared by your reviewer who notes that after many pages bristling with equations sufficient to thoroughly discourage the beginner, temperature is finally defined on p. 36 by the relation $(\partial\rho/\partial E)_V = 1/kT$; and later on p. 42 pressure is defined by the relation $(\partial E/\partial V)_S = -P$. In fact we are told that "Tem-