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 tetrachlorodiborine (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 tetrachlorodiborine. Although the decomposition of tetrachlorodiborine 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 tetrachlorodiborine 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.

Tetrachlorodiborine 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. Tetrachlorodiborine, 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 tetrachlorodiborine to tetramethoxydiborine 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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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 $(\partial p/\partial E)_v = 1/kT$; and later on p. 42 pressure is *defined* by the relation $(\partial E/\partial V)_s = -P$. In fact we are told that "Tem-

perature is a conception that acquires significance only in respect of a property, randomness (ρ)." Although it is stated (p. 9) ". . . there are two alternative methods of correlating observed facts; we can relate them to universally valid (!), directly verifiable (!) physical laws, or we can explain them in terms of atomic properties," Lumsden leans heavily on the second alternative. As a result classical thermodynamics suffers, but the viewpoint adopted is of value to the student who already has a firm foundation in chemical thermodynamics. There are many points, particularly in the early chapters, where the reader may disagree with the general philosophy espoused; as another example we find (p. 16) the definition "it is the province of thermodynamics to enunciate the laws governing the restrictions imposed on the convertability of heat into work"—fortunately the author gets far beyond this province, perhaps too far. This reader found only one passing mention of Gibbs; his name does not occur in the index—nor does that of Le Chatelier, Trouton, van't Hoff, Clausius, Clapeyron, Hess, Einstein, Nernst, Boyle, Charles, Gay Lussac, Mendelejeff, Avogadro (except under Avogadro's number), Kelvin (except under degree Kelvin), Dulong and Petit, Maxwell, Duhem or Margules. Of the present day exponents of metallurgical thermodynamics John Chipman is mentioned only once, Friedrich Körber and F. D. Richardson not at all; although four entries occur in the index under Carl Wagner, they all refer to a single experimental paper; his theoretical work is not mentioned.

The major part of this book is devoted to commendable thermodynamic treatment of specific systems. Most of the calculations are original—that is, not reproduction of other published calculations. The calculations are usually carried through carefully and systematically, and serve as excellent examples for the advanced student in this field.

In keeping with the general tenor, entropy (p. 298) is regarded as a sum of thermal entropy and configurational entropy. The third law of thermodynamics is not mentioned by name (nor is it indexed). The statement that "The entropy which a system still possesses at zero temperature may be referred to as its configurational entropy, which is to be regarded as a property of a solution of fixed configuration and independent of temperature," is rather confusing, in comparison with the third law. Loose use of causality is also encountered, for example (p. 304–5)—". . . differences between entropies . . . are due to differences between the compressibilities . . .."

The author is to be congratulated particularly for clearly pointing out the inadequacy of theories of "regular" solutions. However this reviewer has less enthusiasm than the author for the four parameter equation by which he represents the free energy of formation of a binary liquid solution. In fact Lumsden might profitably express doubt about his own conclusions much more frequently than he does—particularly since he has departed so far from Lewis and Randalls' famous "safest and surest . . . broad highway of thermodynamics."

In the semi-final chapter (which is followed by a chapter, perhaps properly an appendix, of tables) on "Imperfect Crystals and Liquids" some excellent points are made relative to lattice distortion, vacant sites in crystals and heat of fusion, but again it seems that some of these are stated too definitely. To find that "the balance of the entropy of fusion could be well accounted for as the configurational entropy to be expected in a glass" (p. 352) is somewhat disconcerting.

In summary it can be said that this book can hardly serve well as a text for students with no background in thermodynamics, but that it furnishes many specific excellent examples of thermodynamic and statistical treatment of one and two component metallic systems. Classical chemical thermodynamics is slighted at the expense of statistical mechanics. The emphasis is definitely on the author's views rather than on a summary or review of the field.

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Valence. By C. A. Coulson, Rouse Ball Professor of Mathematics in the University of Oxford. Oxford University Press, 114 Fifth Avenue, New York 11, N. Y. 1952. x + 338 pp. 15 × 22.5 cm. Price, $5.00.

When one of the acknowledged leaders in any field writes a book dealing specifically with that field, the reader can usually expect to find an authoritative and stimulating exposition of the subject. In this respect, "Valence" by C. A. Coulson measures up to all reasonable hopes. If, in addition, such an author can express the fundamental ideas so simply and so clearly that they can be readily grasped by a person who is not himself an expert in the field, then the reader should be doubly grateful. In this respect also, the book by Professor Coulson can be highly recommended.

An idea of the extent to which all the varied aspects of valence have been covered can be gained from the following list of the titles of the twelve chapters: Theories of Valence; Atomic Orbitals; Wave-Mechanical Principles; Diatomic Molecules, Molecular-Orbital Theory; Diatomic Molecules, Valence-Bond Theory; Preliminary Comparison of Molecular-Orbital and Valence-Bond Theories; Polyatomic Molecules; Hybridization; Conjugated and Aromatic Molecules; Non-Metallic Solids; Metals; The Hydrogen Bond and Other Miscellaneous Topics. The "other miscellaneous topics" in the last chapter include hyperconjugation, hindered rotation about a single bond, electron-deficient molecules, and meso-ionic compounds.

As can be seen from the above list, the viewpoint is quantum-mechanical throughout, and the molecular-orbital and valence-bond approaches are used side by side. This method for dealing with the rather complex subject of valence has here been quite successful, and it makes the present treatment the best rounded and most nearly complete one that is now available. Thus, by going sufficiently into the quantum-mechanical background, Professor Coulson has been able to show that his conclusions are entirely logical, and not at all arbitrary; and, by employing both the molecular-orbital and valence-bond methods, he has been able to make clear the relations between them and to show that they are not conflicting, but complementary. In these several respects, the book is more convincing, as well as more up to date, than is Pauling's "The Nature of the Chemical Bond" which, of all the older treatments of valence, is doubtless the one most closely analogous to it.

In spite of the quantum-mechanical viewpoint, which has been adopted, no great demands upon the mathematical prowess of the reader are made. Indeed, the author says in the preface that "almost everything in this book should be understandable to the chemist with no mathematical attainments." Even though this statement is doubtless somewhat overenthusiastic, it does nevertheless reflect an obvious, and generally successful, effort to keep the mathematics down to the absolute minimum. The reader who has only a bowing acquaintance with calculus should have no difficulty in following the argument. An unfortunate, but unavoidable, result of this simplification has of course been that most of the interesting and important recent work in the field by Professor Coulson and his associates has had to be completely omitted. One may hope that a second volume, in which this missing material is collected and described in detail, will soon be forthcoming.

No review is ever complete unless the reviewer can call attention to at least one misprint, or more serious error. Such lapses, however, are particularly hard to find in this book, since both the Oxford University Press and the author have again maintained their well-known high standards. Diligent search has, in fact, uncovered only one mistake which need be mentioned: it is not correct that, as is stated at the top of page 173, there is "no exchange energy between one orbit and a lone pair." The pertinent exchange integral here enters with a coefficient of $-1/2$, and so Professor Coulson's argument leading to the conclusion that this coefficient must instead be zero is, of course, fallacious.

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