TABLE I

COMPARISON OF MUZSKAT AND KIRSON'S IONIZATION POTENTIAL DATA WITH CALCULATED ENERGIES

Compound	Ionization potential,[a] e.v.	θ, deg.	Energy of highest filled π-level[b]
1,3,5-$(C_6H_5)_3C_6H_3$	8.21	20.0	0.726
$(C_6H_5NBH)_3$	8.36	20.0	0.680
		39.6	0.745
		44.2	0.766
$(C_6H_5BNH)_3$	8.92	20.0	0.982
		39.6	0.987
		44.2	0.988
$(C_6H_5NBCH_3)_3$	9.16	71.6	0.925 (0.842)[c]
		72.2	0.929 (0.847)
$(C_6H_5BNCH_3)_3$	?[d]	71.6	0.997 (0.936)
		72.2	0.998 (0.938)

[a] Ref. 1. [b] Calculated for $h_N = -h_B = 0.890$, $k_{B-N} = 0.855$, $k_{B-C} = 0.618 \cos \theta$, and $k_{N-C} = 0.915 \cos \theta$. The latter two parameters refer to inter-ring bonds. These energies are in units of β_{CC}, which is negative, and are referred to α_C (the Coulomb integral for carbon) = 0. [c] Values in parentheses include an inductive parameter for an attached methyl group $\delta h = -0.54$. When the inductive effect is included k_{B-N} is scaled according to the Wolfsberg–Helmholtz approximation (see ref. 2). [d] As noted in the text this ionization potential is probably higher than that of $(C_6H_5NBCH_3)_3$. This inference is based on the lack of a visible charge-transfer band for $(C_6H_5BNCH_3)_3$. It is also possible that the charge-transfer band was not observed because it falls at very low energies, or because a complex was not formed. In view of the widespread occurrence of tetracyanoethylene complex formation and the high energy of the charge-transfer complexes of substituted borazines, the original interpretation is the most reasonable.

drocarbons in calculations with B or N compounds.[4] Therefore, we did one set of calculations for the methyl-substituted compounds in which a change in h of -0.54[5] was made for atoms attached to methyl, and another set with no methyl inductive effect; the results are given in Table I.

Providing we compare similar compounds the Hückel calculations give the correct orders for energies of the highest filled molecular orbitals: $(C_6H_5NBH)_3 > (C_6H_5BNH)_3$ and $(C_6H_5NBCH_3)_3 > (C_6H_5BNCH_3)_3$. Also, calculated energies and observed ionization potentials for the former pair lead to $\beta_{CC} = 2.2 \pm 0.3$ e.v., which is within the range observed for conjugated hydrocarbons.[6] The Hückel MO treatment appears to provide a simple means of interpreting the charge-transfer spectra without invoking Muzskat and Kirson's assumption that the N-phenyl group has a larger electron-donating effect than an N-methyl group. Evidence to the contrary is readily available from Taft σ^* values (CH_3–, 0.00; C_6H_5–, 0.60),[7] empirical electronegativities (CH_3– < C_6H_5–),[7] and semi-empirical orbital electronegativities (2.48 for sp^3 and 2.75 for an sp^2 carbon hybrid orbital).[8]

There is little doubt that an adjustment of molecular orbital parameters could lead to a single correlation series for the MO energies and ionization potentials of triphenylbenzene and all of the substituted borazines, but this parameter fitting cannot be checked with the limited data now available. Furthermore, steric hindrance of complex formation with tetracyanoethylene is probably much different for triphenylborazines than for trimethyltriphenylborazines. The resulting variation in donor–acceptor interaction will be reflected in derived ionization potentials and will probably invalidate comparison of these ionization potentials for the two groups. Hückel MO theory does offer a satisfactory answer to the question: What is the effect of B-phenyl *vs.* N-phenyl substitution on ionization potentials and electron affinities of the borazines? In addition, the MO treatment, like resonance theory, reveals a lower B–N bond order for N-triphenylborazine than B-triphenylborazine, and this is in harmony with results of pyrolysis experiments.[9]

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Book Reviews

Inorganic Thermogravimetric Analysis. Second and Revised Edition. By CLEMENT DUVAL (translated by Ralph E. Oesper). American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1963. xv + 722 pp. 15 × 22.5 cm. Price, $22.00.

This book is the second and revised edition of the earlier classical edition which appeared in 1952. It is now generally agreed that the first edition did much to kindle the interest of analytical and inorganic chemists in the area of thermogravimetry. As a result of this interest, a large number of papers have appeared in this area of research since the first edition. In fact, Professor Duval states in the preface that some 2200 papers in periodicals were read in the preparation for the second edition.

The contents of the book are divided into two main parts: (a) thermobalances and (b) thermolysis curves. Although practically every thermobalance is mentioned in part a, the contents are now generally of historical interest only because of the recent developments in instrumentation during the past 3 years. A good discussion is presented on the applications of thermobalances (Chapter 4), but kinetic studies are absent. Of even more interest is the list of precautions to be taken in interpreting weight-change curves (Chapter 5), although these seem to be forgotten when discussing the thermolysis curves in part b. Duval does point out, however, that thermogravimetry by itself cannot solve problems of structure or other parameters of the thermal decomposition reaction. Indeed, in most cases a supplementary thermal technique is needed.

Unlike the first edition, the weight-change curves of the many compounds discussed in the contents of part b are not illustrated. The compounds are discussed on an element by element basis, with 78 chapters for the elements from lithium to americium. The coverage is broad and fairly comprehensive but is not very critical, and again, unlike the first edition, the new edition includes the results of other workers in the field, rather than just those of Duval's group.

A large number of errors are present in part b. Duval still maintains that scandium oxalate precipitates from solution as $Sc_2(C_2O_4)_3 \cdot 10H_2O$, rather than the hexahydrate. The latter composition has been confirmed by at least four different independent investigations. Other errors are similar to this example and not simply differences in decomposition temperatures. Many of the temperatures in the weight-change curves have been changed from the earlier edition with no experimental justification.

Concerning mechanical details, some of the pages are misnumbered, decreasing from page 300 to 200, and then increasing from page 203 to 304.

In general, it is felt that the book should be of general interest to inorganic chemists if the proper interpretation is placed upon the results presented.

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Introduction to Physical Inorganic Chemistry. By KENNETH B. HARVEY and GERALD B. PORTER. Addison-Wesley Publishing Co., Inc., Reading, Mass. 1963. x + 437 pp. 16 × 23.5 cm. Price, $9.75.

This well-written book is an excellent example of the modern approach to inorganic chemistry. The book's objective is "to emphasize the principles underlying chemical behavior rather than the phenomena themselves." Study of the phenomena, however, is still the basis for development of theory, and the authors' suggestion that a laboratory course provides adequate descriptive information is an oversimplification.

So also is the statement that the book "attempts to describe the chemical behavior of 103 elements. . ." It does, however, admirably correlate many experimental observations with the current versions of the theories of inorganic chemistry. It is insistent in its emphasis that theories must be questioned and that an awareness of the assumptions and approximations utilized must exist. The authors regularly point out the necessity for care in interpretation and for the avoidance of loose reasoning.

The wide range and amount of material discussed is only partially indicated by the chapter titles: Ionic Crystals, Atomic Structure, Thermochemistry, Molecular Structure, Transition Metal Complexes, Crystal Chemistry, Thermodynamics, Solutions of Electrolytes, and Rates and Mechanisms of Reactions. The chapters which treat of the more classical physical chemistry are introduced at logical intervals. Whether they would be considered adequate by a physical chemist is problematical, but they add much to the intervening topics.

The book uses structure and the process of reaction as the unifying ideas for the presentation of its material. Although it is intended to follow the first university course in chemistry, I would hesitate to recommend it for this purpose without a comment that supplemental lecture material may be needed.

In general, the explanations are clear, pertinently illustrated, and well detailed, although sometimes of a sparseness and precision that requires careful attention to the exact meaning of the terminology. There are indexes of mathematical and chemical symbols and formulas which are most helpful, and an adequate selection of problems and questions, many of which require prediction and estimation. The references are divided into two groups. One is intended to be of the same approximate level as the book, the other of an advanced nature. At times, the distinction between the two is difficult to discern. References to names, without appropriate literature citations, are sometimes used and are not conducive to further searching. The illustrations and graphs are clean and uncluttered and are used primarily for clarification of the textual material. The book is attractive and patently free of typographical errors.

As with any text, one can find items of personal choice over which one can quibble. There is a lack of clarity in the original discussion of unit cells; ν is used instead of $\bar{\nu}$ for wave number; Zachariasen is misspelled; reference is made to the "weight" of covalent and ionic parts; there is inconsistency in the use of K as equilibrium constant, base constant, and ion product; and there is occasional overdependence on the term "determined by."

But these are minor points in a book which has such a bold and stimulating approach to the problem of teaching the principles and correlative theories of inorganic chemistry, and one which I heartily recommend.

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BOOKS RECEIVED

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ALFRED ROMER, Editor. "The Discovery of Radioactivity and Transmutation." Classics of Science, Volume II. Dover Publications, 180 Varick St., New York 14, N. Y. 1964. xi + 233 pp. $1.65.

HARRY B. GRAY. "Electrons and Chemical Bonding." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 10016. 1964. ix + 223 pp. Clothbound, $8; paperbound, $3.95.

H. L. FRISCH and J. L. LEBOWITZ. "The Equilibrium Theory of Classical Fluids." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 10016. 1964. xii + 517 pp. Clothbound, $10; paperbound, $5.95.