

computation of each entry. Although the authors did not specifically say so, it was also a thermodynamic bible for many of Lewis' students and for some of us who were not so fortunate.

Religion makes conformity a virtue, and bookkeeping makes it a necessity. One strength of the book was that it was always overtly directed to the systematic determination of chemical equilibria. The chief weaknesses arose from this same emphasis on book-keeping—an over emphasis on standard states and "partial molal quantities," and an inelasticity which made it very difficult to extend the treatment to a problem very different from one solved in the book.

Although the treatment of electrolyte solutions was obsolete the year the book was published, and much on other solutions within a few years, it is probable that it could not have been revised by any of Lewis' older colleagues, or much before the thirty-eight years which elapsed before this second edition.

The second edition contains much more material than the first, but it has only about ten per cent more pages, with perhaps another ten per cent gained by a different format. The omission of most of the case-book saves about twenty per cent more. Much of the sales talk for fugacity and activity is now omitted as unnecessary, and some elementary treatment is dropped. A notable exception is the discussion of weak electrolytes in Chapter 22. This should have been cut much more. The arrangement of chapters is changed to that used at Berkeley even before the first edition was published.

Many naive and provincial details have been deleted, but much of the discussion of the fundamentals is left in the words of Lewis. In the revised and new chapters the writing is usually simple and clear and the perspective is good, particularly in the more general sections.

The treatment of solutions, except for the introductory chapters, is completely revised, including the chapter on galvanic cells. So is the treatment of real gases, and the discussion of entropy and the third law of thermodynamics.

The chapters and appendices which I would call new are:

15. "Standard Free-Energy Functions and Equilibrium Calculations". Discussion of  $(F^0 - H_{298}^0)/T$  and  $(F^0 - H_{298}^0)/T$ , which are tabulated in Appendix 4 as slowly varying functions of the temperature for interpolation.

27. "Thermodynamic Properties of Ideal Gases Calculated from Spectroscopic and Other Molecular Data." Extremely condensed presentation of formulas.

28. "Irreversible Processes Near Equilibrium; Non-isothermal Systems; Steady States." Excellent introduction to subject.

29. "Surface Effects." Simple discussion with good perspective.

30. "Systems Involving Gravitational or Centrifugal Fields." Good discussion, but does misrepresent Gibbs.

31. "Systems Involving Electric or Magnetic Fields." Standard presentation with emphasis on magnetic depolarization and very low temperatures.

32. "Estimations of Entropy and Other Thermodynamic Quantities." Methods of determining what species may be important by rough estimation when exact calculations are inconvenient or impossible.

33. "Vaporization Processes." Very interesting examples of worth-while results retained by pushing the roughness of estimation to the limit.

34. "Multicomponent Systems." Mostly discussion of solid alloys and of aqueous electrolyte solutions, with a little on fused salts and on aqueous solutions of electrolyte plus non-electrolyte, and the determination of the ionization constants of weak acids.

35. "Hydrogen and Helium at Low Temperatures." Good standard presentation.

App. 1. "Properties of Normal Fluids." Concise presentation of Pitzer's extension of corresponding state treatment to include the acentric factor.

App. 2. "Properties of Gaseous Solutions." Treatment of gas mixtures through pseudocritical constants, including the acentric factor.

App. 3. "Translational Entropy of an Ideal Gas."

App. 4. "Data for Aqueous Electrolyte Solutions." Develops Debye-Hückel equations for special case of  $a = \sqrt{I}$  and tabulates limiting slope factors for  $\log \gamma$ ,  $\phi_H$  and  $\phi_{EP}$ ; lists properties of KCl. As functions which vary only slightly with concentration,  $B' = \{\log \gamma_{\pm} + A_1 m^{1/2}/(1 + m^{1/2})\}/m$ ,  $dB'/dT$  and  $d^2B'/dT^2$  are chosen for KCl and for

other 1-1 electrolytes,  $\Delta B' = B'_{MX} - B'_{KCl}$  and the temperature derivatives of  $\Delta B'$ . For bi-univalent and uni-bivalent salts they use  $\text{CaCl}_2$  as standard.

They find that at 0.1  $M$ ,  $-\log \gamma_{KCl}$  is 0.0004 too small and  $\phi$  is 0.0020 too small in Robinson and Stokes. They therefore add 0.0004 to the values of  $-\log \gamma$ , and 0.002 to the values of  $\phi$  at all higher concentrations. This is proper for  $-\log \gamma$  which is determined by integration, but for  $\phi$ , which is measured directly, and more precisely at higher concentrations, their correction is unjustified and probably incorrect. A correction of 0.0002/ $m$  would give a more probable fit. The results for higher valence salts require more specific corrections.

App. 5. "Debye Functions for the Thermodynamic Properties of Solids." Tables of  $C_v/3R$ ,  $(E - E_0)/3RT$ ,  $(A - E_0)/3RT$  and  $S/3R$  as functions of  $\theta_D/T$  for Debye solids.

App. 7. "Tables of Thermodynamic Properties." Tables are given of  $-(F^0 - H_{298}^0)/T$  or  $-(F^0 - H_{298}^0)/T$  at 298.15, 500, 1000, 1500 and 2000°K. and the corresponding  $\Delta H^0$  for most of the substances for which these quantities are known.

App. 8. "Electromagnetic Work."

App. 9. "Symbols." A convenient collection.

For thirty years or more this reviewer has differed fundamentally with the Lewis school in two respects. I think they over-emphasize partial molal quantities and pay too little attention to total energy change, etc. For practical applications to equilibria, the partial quantities are necessary; but for understanding and teaching, the total quantities are superior. I also think that they make too little use of analytical expressions, preferring graphs or tables. Approximate results are obtained most quickly and easily from graphs, and next from tables, but many thermodynamic properties are known precisely enough to require analytical expression. For understanding and teaching the analytical method is again much preferable.

The present authors have yielded somewhat in both respects, particularly where the other approaches have come into general use, such as for non-electrolyte mixtures. However, they missed the applications to multicomponent systems where they are especially useful, particularly the Redlich-Küster rule which permits the calculation of the free energies of mixing, etc., for a system of any number of components from these functions for the component binary systems. For mixed electrolyte solutions they accept analytical expressions for changes of composition at constant ionic strength, but not for the closely related changes at constant concentrations of all components but one. For both non-electrolyte and non-electrolyte multicomponent systems they become involved in complicated discussions of details of integration which have not much importance for practical purposes and less for understanding thermodynamics.

On the whole, Pitzer and Brewer are to be heartily congratulated for bringing Lewis and Randall up to date and expanding it greatly while still retaining the virtues of the first edition, particularly the philosophy and spirit of Lewis.

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Physical Properties of Chemical Compounds III. Advances in Chemistry Series Number 29. By ROBERT R. DREIBACH, Dow Chemical Company, Midland, Michigan. American Chemical Society, 1155 Sixteenth Street, N. W., Washington 6, D. C. 1961. v + 489 pp. 16 × 23.5 cm. Price, \$6.50.

Years ago, Robert R. Dreisbach of the Dow Chemical Company began a systematic compilation of values of the physical properties of chemical compounds. His first volume on this subject was published in 1955, the second volume in 1959, and now the third volume has appeared, in 1961. These tabulations cover a continuous lot of compounds. The first volume dealt with 511 organic cyclic compounds, the second volume with 476 organic straight-chain compounds, and the third volume with 434 aliphatic compounds and 22 miscellaneous compounds and elements. The total number of compounds covered is now 1443. There are fourteen physical properties for which values are given: freezing point, vapor pressure, liquid density, vapor density, refractive index, rate of change of boiling point

with pressure, latent heat of fusion, latent heat of evaporation, critical values, compressibility, viscosity, heat content, surface tension, solubility. The tables of compounds are grouped according to Cox-Chart families. Means are provided for interpolation and reasonable extrapolation, based on the systematic way in which the properties vary within a given homologous series. This third volume contains a cumulative index applicable to all three volumes. This volume is a necessary reference book for all scientists and engineers whose work requires knowledge of the properties of organic compounds. The technical world owes Dreisbach a debt of gratitude for this valuable work.

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**Struktur und Eigenschaften der Materie in Einzeldarstellungen. Band XXIII. Gruppentheorie der Eigenschwingungen von Punktsystemen.** By FRANK MATOSI, Ord. Professor für Physikalische Chemie an der Universität Freiburg i. Br. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1961. viii + 191 pp. 16 × 23.5 cm. Price, DM 39.—.

In a field where books tend to run to several hundreds of pages, Professor Matossi has written a short and concise little monograph. Though the text is in German, the two subject indices serve also as brief German-English, English-German technical dictionaries, and were found to be most useful by the reviewers. There is in addition also a name index, which seems quite thorough.

The author has aimed his book at the experienced researcher in the field as well as at the advanced student. He has, therefore, attempted to give not only the formulas, but also to present the fundamentals systematically for those with a background training in physics and physical chemistry, in the hope that he may provide the tools for fruitful and original applications of group theory methods in the treatment of molecular vibrations.

In this ambitious project the author has made a commendable job. The presentation of the point groups commonly encountered in dealing with molecules and crystalline solids is suitably detailed and small oscillation theory is developed completely from first principles. The treatment of space groups is brief, but adequate, and in keeping with the aims of the author.

The method of symmetry co-ordinates is adopted to factor the F and G matrices corresponding to the potential and kinetic energy functions respectively. A more fundamental approach, however, and one that can be applied to a wider class of problems, can be based directly on the methods of I. Schur (originally published in the Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften, Berlin, 1905 and 1906) and would surely have deserved at least a mention by Professor Matossi. Examples of computing the F and G matrices are given in unusually great detail for three molecular structures (two-dimensional and one three-dimensional), for the Wurzite lattice and for a linear chain, and should be of value to anyone attempting these difficult calculations for the first time. Selection rules are also discussed and employed to determine active and inactive Raman spectra for several cases.

Perhaps the main criticism that may be leveled at the book is that only selected aspects of group theory are presented so that the theory appears to become a rather specialized and restricted mathematical tool. Thus the student will gain considerable facility in performing analyses closely similar to those treated by the author, but he will not become sufficiently familiar with the standard group theoretical methods to perform new analyses, nor will he understand clearly the extent to which the results of his method depend on the group theory involved.

Tables are presented where possible to summarize results, and a total of 25 diagrams are included to advantage. Not out of place, however, would have been a Table listing the symbols adopted and used throughout the text. References are included in many places to original papers where either different or more extensive accounts are given of special topics treated necessarily rather briefly in the text, though no mention appears to be made of the very complete compilation of symmetry groups to be found, for example, in Vol. 1 of the "International Tables for X-ray Crystallography."

However, in spite of some minor shortcomings, the book by Prof. Matossi (who also has one on the Raman effect to his credit) is a welcome addition, not so much to group theory, as to studies in the application of symmetry co-ordinates to the determination of characteristic vibrations of point groups. For such studies we can confidently recommend the book, which is well produced with good type and paper, and seemed free of any obvious typographical errors, though perhaps priced rather high (\$9.75).

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**Preparativní Reakce V Organické Chemii. Díl VI. Reakce Organokovových Činidel.** By Inž. DR. KAREL BLÁHA. Publishing House of the Czechoslovak Academy of Sciences, Vodičková 40, Praha 2, Czechoslovakia. 1961. 954 pp. 18.5 × 24 cm. Price, Kčs. 105, —.

"Reactions of Organometallic Reagents" is the sixth volume of the encyclopedic series "Preparative Reactions in Organic Chemistry" published by the chemical section of the Czechoslovak Academy of Sciences.<sup>1</sup> The present volume is an attempt at a systematic description of the reactions of organometallic compounds containing magnesium, cadmium, zinc, mercury, alkali metals, alkaline earths and aluminum. Emphasis is placed on the use of organometallic reagents in the synthesis of organic substances, but information is also included concerning the analytical aspects and chemical bonding problems.

Three-quarters of the book is devoted to the discussion of the preparation, properties and synthetic uses of the organic compounds of magnesium. A brief historical introduction is followed by detailed treatment of the direct and indirect methods for the preparation of Grignard reagents. The structure and analytical estimation of these reagents receive attention in two separate sections. The synthetic utilization of Grignard reagents is treated in subsequent chapters with attention to all known variants of the Grignard reaction. The discussion is arranged according to the various modes of reaction of the organomagnesium halides, *i.e.*, reactions involving cleavage of bonds, addition to double bonds, addition to triple bonds and "anomalous" reactions of Grignard reagents. The vast amount of descriptive material is thoroughly documented by references to thousands of original publications and, in many instances, conveniently summarized in tabular form. The text contains numerous illustrative experimental procedures which can be used by the experienced experimenter in the laboratory without having to consult the original sources in every instance. Every attempt has been made to achieve a thorough, up-to-date coverage of the subject matter. Sections on the preparation and reactions of Grignard reagents of the fluorocarbon and cyclopentadiene series illustrate this endeavor.

The remaining one-quarter of the book is devoted to the treatment of the organic compounds of the remaining Group I and Group II elements and of aluminum. Among these, the organolithium compounds receive the greatest amount of attention in view of their increasing synthetic importance. The subject matter dealing with organolithium compounds is arranged and treated similarly to the corresponding material on magnesium derivatives. Modern aspects of the chemistry of organic lithium compounds, such as dehydroaromatic (benzyne) compounds and "ylids," are included. The organic compounds of the other alkali metals, zinc, cadmium, mercury, the alkaline earths and aluminum are dealt with in the several remaining shorter chapters. The discussion of mercury and zinc compounds is largely restricted to areas where the corresponding organometallic reagents have still retained sufficient importance in the synthesis of organic compounds. Among the other organometallic compounds included in the book, the sodium, cadmium and aluminum derivatives are steadily gaining in importance and are, therefore, treated in greatest possible detail.

"Reactions of Organometallic Reagents" is a treatise conceived on a large scale and, in the opinion of the reviewer, successfully executed. The broad coverage of the field,

(1) Cf. *J. Am. Chem. Soc.*, **83**, 2969 (1961), for a review of the fifth volume of this series.