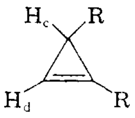
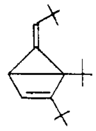
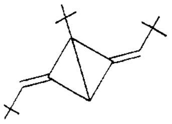
of structures loosely accommodating the above data can be entertained. Of these, save for the [2.2.0]-bicyclohexa-2,5-diene system, all feature one or two three-membered rings; and except for two cases (alkylidenecyclopropanes VII and VIII), all are cyclopropene types (VI). Other investigators[10]



VI



VII



VIII

have measured the chemical shifts of various hydrogens on the latter ring system, with the finding that a proton (H_c) on the saturated ring carbon appears at 8.6–8.7 τ, while a hydrogen (H_d) on the double bond falls at 3.0–3.4 τ. The proton resonances of the photo hydrocarbon lie distinctly outside these ranges and, beyond that, are reasonable for the proposed structure (V) (cyclobutene exhibits an olefinic proton peak at 4.03 τ and methylene resonance at 7.46 τ, $J = 0 \pm 0.2$ cps.).[8] As a possibility, structure VII is photochemically sound[5] and might be considered consistent with the physical data described above; however, thermal conversion to starting benzenoid material of VII or of its valence tautomer, tri-*t*-butylfulvene, seems unlikely.[11] Structure VIII appears even less plausible, both on the grounds of photochemical improbability as well as expected non-reversion to aromatic precursor. Thus anticipated structure V remains as the most acceptable of the various candidates.

Experiments on the preparation and detection of Dewar benzene itself will be presented later.

Acknowledgment.—The authors are grateful to Dr. C. Hoogzand, European Research Associates, Brussels, for a gift of one gram of tri-*t*-butylbenzene; to the Petroleum Research Foundation for financial support; and to Dr. A. Storni for valuable assistance.

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(10) For example, G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961), and personal communications from Prof. Closs.

(11) J. H. Day, *Chem. Rev.*, **53**, 179 (1953).

(12) National Institutes of Health Predoctoral Fellow.

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BOOK REVIEWS

Crystallometry. By P. TERPSTRA, D. Sc., Sometime Professor of Crystallography and Mineralogy in the University of Groningen, and L. W. CODD, M.A. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 420 pp. 18.5 × 25.5 cm. Price, $12.00.

Crystallometry is the quantitative examination of crystals with an optical goniometer to determine the angles between the faces. The data are then summarized in the form of projections and face pole figures. Terpstra and Codd have prepared a detailed volume on this topic written in a textbook style. However, the authors also intended that the book prove useful in a self teaching program. The present English version constitutes a second edition of an earlier Dutch version, first published in 1954.

Crystallometry is presented in great detail. The authors appear to have taken scrupulous care not to stray into adjacent disciplines even when these techniques are closely related to crystallometry and in fact may be considered as extensions of the optical technique. The style is easy to follow, it is almost chatty in many places. There are numerous excellent figures (273). The book seems to have been very carefully edited; the authors made good use of bold-face type in calling attention to significant conclusions. They also prepared many tabular summaries, and worked out selected problems in detail to illustrate the techniques which could be used at the different stages of the development of the subject. There is no overabundance of reference. However, those which have been included were carefully selected and should prove useful to the reader; references to literature include some papers which appeared in 1960. At the end of the book, the authors have assembled a chapter of significant questions and included the answers. The typography of the book is excellent and the paper and binding are of high quality. The English edition has been modernized in several respects. W. L. Bond's technique, based on matrix algebra, for reducing crystallographic data to a form required for plotting projections has been included. Detailed descriptions are given of modern goniometers. In Chapter 4 the elements of crystal symmetry are described and a useful compilation of the various notations is presented. No proofs were included.

The basic limitation of this book is that it is so narrow in scope. The authors sing the praises of crystallometry with evangelical fervor, although they recognize this narrowness. In several places (p. 129 and p. 162) they call attention to the limitation of the method but nonetheless laud a preoccupation with one aspect of the optical examination of crystals. Why is the goniometer to be preferred to the polarizing microscope for the identification of crystals? If one is concerned with the symmetry of a crystal, why not establish whether it is optically isotropic and why not attempt to measure the indices of refraction? The book would have been much more useful were some of the excessive details of crystallometry replaced by brief discussions of methods for the determination of crystal densities and simple tests for judging whether a crystal is piezo or pyroelectric. The authors do mention these techniques as additional and helpful devices which occasionally must be "dragged in" to establish the crystal symmetry. One concession to other techniques is a final chapter of ten pages on the use of Laue diagrams for plotting stereographic projections. The question remains whether it is proper to give students such a distorted impression.

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Thermodynamics. Second Edition. By GILBERT NEWTON LEWIS and MERLE RANDALL. Revised by KENNETH S. PITZER, Professor of Chemistry, University of California, Berkeley, and LEO BREWER, Professor of Chemistry, University of California, Berkeley. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1961. xii + 723 pp. 16.5 × 23.5 cm. Price, $12.50.

The first edition of Lewis and Randall was many books in one. It was a text book, a guide book, a prospectus to lure both the young and the adult chemist, a hand-book for setting up and for using a system of bookkeeping, a table of all entries in the book, and a case book of the authors' 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 $(F^0 - H^0_0)/T$ and $(F^0 - H^0_{298})/T$, 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; Nonisothermal 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 $\log \gamma$, ϕ_H and ϕ_{cp}; lists properties of KCl. As functions which vary only slightly with concentration, $B^{\cdot} = [\log \gamma_{\pm} + A_{\gamma}m^{1/2}/(1 + m^{1/2})]/m$, $dB^{\cdot}/dT$ and $d^2B^{\cdot}/dT^2$ are chosen for KCl and for other 1–1 electrolytes, $\Delta B^{\cdot} = B^{\cdot}_{MX} - B^{\cdot}_{KCl}$ and the temperature derivatives of $\Delta B^{\cdot}$. For bi-univalent and uni-bivalent salts they use $CaCl_2$ as standard.

They find that at 0.1 M, $-\log \gamma_{KCl}$ i 0.0004 too small and ϕ 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 ϕ at all higher concentrations. This is proper for $-\log \gamma$ which is determined by integration, but for ϕ, 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 θ_D/T for Debye solids.

App. 7. "Tables of Thermodynamic Properties." Tables are given of $-(F^0 - H^0_{298})/T$ or $-(F^0 - H^0_0)/T$ at 298.15, 500, 1000, 1500 and 2000°K. and the corresponding ΔH^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 nonelectrolyte 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. DREISBACH, 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