

Burgess and Kahler<sup>9</sup> found that precipitation of sodium amide poisoned a metallic catalyst for the sodium-ammonia reaction.

The slower rate for lithium as compared to potassium was expected. We have studied lithium and potassium reductions of ethanol in ammonia under conditions similar to those used for sodium reductions already reported<sup>10</sup> in the previous paper in this series. In

(9) W. M. Burgess and H. L. Kahler, *J. Am. Chem. Soc.*, **60**, 189 (1938).

(10) E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastham, *ibid.*, **84**, 3611 (1962).

these reaction mixtures at  $-33^{\circ}$ , the rate of the reaction of lithium with the solvent was found to be much slower than the rates of potassium or sodium.

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## BOOK REVIEWS

**Représentation des Équilibres de Solubilités et Utilisation des Diagrammes.** By ROBERT BERTHON, Ingénieur Chimiste (I. C. N.), Docteur es Sciences Physiques, Chef du Service de Recherches des Mines Domaniales de Potasse d'Alsace. Gauthier-Villars et Cie, Quai des Grands-Augustins, 55, Paris (VIe), France, 1963. 269 pp. 16.5 × 24.5 cm. Price, 38 F.

This monograph deals with a special aspect of the representation and application of the quantitative relations in the phase-equilibria of aqueous salt systems. The "representation" is treated purely as a problem in analytical geometry in three dimensions; the mathematical relations are considered graphically, in superposed and juxtaposed combinations of projections, and at the same time and equivalently, they are expressed analytically in the form of vectorial equations. The first 160 pages are given over entirely to a general, systematic, almost excessively elaborate exposition of the modes of plotting and of the interrelation of frames of reference and of systems of units (amount of salt per fixed amount of water, or the reverse, or the percentage of each substance, and with variation between use of moles and use of weights), with most of the relations re-expressed in each set of units.

The point of view is so purely mathematical that the ideas of the phase rule are not used at all; the author decided to do without the phase rule as it would only "introduce complications in the reasoning." Consequently, many relations of equilibrium diagrams which are already known on the basis of the phase rule meaning of these diagrams are elaborately derived as purely mathematical theorems or "rules." Although this seems to be a waste, it is done deliberately for the sake of generality and consistency, and the chemical and physical significance of the diagrams considered is assumed as background on the part of the reader. At the same time even the reader with such background may be disturbed if not annoyed by the arbitrary definitions of otherwise familiar phase rule terms, despite the mathematical consistency of the whole procedure—terms such as variance, degree of freedom, phase, invariance, and pseudo-invariance.

The second half of the book illustrates the application of the unified set of vectorial equations and definitions, using as examples sets of data from the literature pertaining to ternary, quaternary, and quinary aqueous systems. Most of the data are used directly in units such as equivalents or moles for 1000 moles of water. The procedure is explained through diagrams and projections, while the actual numerical calculations are done with impressive ease through general vectorial equations.

Particularly interesting is a chapter on "crystallization through isothermal displacement," as a parallel to "isothermal evaporation." In most treatments of solubility diagrams we customarily place much emphasis on isothermal evaporation not so much as a real or practical process but as a means of explanation and instruction. We consider what can be read from the diagram, qualitatively and quantitatively, as water is imagined to be removed (or added), isothermally, at equilibrium. If we start with a solution saturated with one salt and to it add some other salt of the system, maintaining isothermal equilibrium, a similar sequence of events may be considered. The expression "crystallization through isothermal displacement," for the process, indicates that the added salt causes a sequence of precipitations and transformations, like that caused by evaporation. With his general vectorial and graphical methods, the author gives an instructive example of the process in the fundamental quinary system of the oceanic salts ( $H_2O + Na, K, Mg/Cl, SO_4$ ). He treats in detail and numerically the sequence of events accompanying the addition of the incongruently soluble kainite to water (saturated always with NaCl) until saturation with kainite in addition is attained.

Essentially these are numerical problems in material balance, and further examples are also given for cyclic (polythermal) processes of salt separations and conversions.

All that is treated, however, is a highly restricted situation. The calculations appear to be so simple because only straight lines and planes are considered. Solid phases are assumed pure, and solid solution is not mentioned. Solubility surfaces (at least for the cases in the applications) are assumed plane. These two restrictions make all crystallization paths straight lines on all projections. Even the curves for liquid saturated with two or more salts are assumed to be straight lines. In a sense, then, the whole construction is an exercise, applicable only if all these conditions hold, so that we are dealing simply with the problem of the intersections of lines and planes. Also, the only systems considered, even in the general introduction, have water as an additive component, and no background is given for operation on systems in which water itself enters into heterogeneous double decomposition.

Nevertheless there is value in the whole effort. The book may hardly be meaningful to one not familiar with aqueous salt diagrams but the specialist interested in their utilization should find it rewarding, both because of the ingenious and useful graphical and analytical procedures it presents and because of the unified point of view it demonstrates.

There are a few very minor confusions and even one or two numerical slips, but the general result is not disturbed by these.

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**The Analytical Chemistry of Indium.** By A. I. BUSEV, Professor of Analytical Chemistry, Department of Chemistry, Moscow State University. Translated from the Russian by J. T. GRAVES. The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. 1963. 22.5 × 14.5 cm. 288 pp. Price, \$12.50.

This book collects into one volume all of the known methods for the detection, separation, and determination of indium that have been published up to the beginning of 1957. The 476 references cover both Russian and Western literature.

After an introductory chapter outlining the general analytical behavior of indium, the remaining chapters deal with specific methods for indium analysis based upon the use of various reagents or techniques. The author has noted the advantages and limitations of the methods, has included many tables of data to show the reliability of separations and determinations, and has given detailed procedural directions for methods that have been proved most reliable.

Gravimetrically, indium is determined by weighing as oxide, after hydrolytic precipitation of the hydrous oxide; as sulfide; as ferrocyanide; and as 8-quinolinolate and its substituted derivatives. Analytical methods based on halide complexes include solvent extraction separations from hydrohalic acid solutions and chromatographic separations. Instability constants for many of the halide complexes are given. The slightly soluble complex salt,  $[Co(NH_3)_6][InCl_6]$ , has been used for gravimetric determination, and its solution for spectrophotometric determination of indium. The principal titrimetric methods are potentiometric titration with potassium ferrocyanide and complexometric titration with EDTA. Various hydroxyanthraquinones, triphenylmethane dyes, and azo dyes give color reactions with indium, and have been used for detection and spectrophotometric determination of the element. Several organic sulfur compounds,

notably diethylthiocarbamate and alkyl xanthates, are used for gravimetric and for photometric determination of indium.

Methods based on reduction of indium(III) are principally in the field of polarography; in the presence of accompanying elements, laborious prior chemical concentration and separation methods are required. The only satisfactory electrodeposition method is by internal electrolysis.

The text of this work concludes with a chapter on emission spectrographic and X-ray spectrographic methods, and a very brief chapter on radioactive methods.

In his preface, Professor Busev states, "The book is intended for a wide circle of analytical chemists in research and works laboratories and in universities, technical colleges and schools. It may also make it easier to use the results obtained, and may help in formulating and solving new problems in the analytical chemistry of indium." That there are, indeed, new problems in the analytical chemistry of indium may be indicated by the appearance, during the past one or two years, of many articles dealing with this subject. It seems likely that the use of indium arsenide and indium antimonide crystals as current-activated (injection) lasers may be a contributing factor in the increased interest in indium chemistry.

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**Infrared Spectra of Inorganic and Coordination Compounds.** By KAZUO NAKAMOTO, Associate Professor of Chemistry, Illinois Institute of Technology. John Wiley and Sons, Inc., 440 Park Avenue, S., New York 16, N. Y. 1963. 328 pp. 23.5 × 15.5 cm. Price, \$9.50.

In attempting to evaluate any book, the reviewer should ask himself for whom the volume will be most useful. With respect to Dr. Nakamoto's book, the answer to such a question is less than obvious even though the volume was written to fill a well defined and too-long-neglected lack in the literature of inorganic vibrational spectra. The first section begins with the Bohr frequency condition and works very quickly through symmetry and group theory to normal coordinate analysis and band assignments. The organization here is good and the section will serve as a satisfactory review for the practicing spectroscopist. By the same token, however, the apparent simplicity is deceptive and the newcomer to the field may easily find himself more glib than adept. This difficulty is compensated for by extensive referencing to a rather solid bibliography along with a good group of appendixes. These include: (1) the usual point group and character tables, (2) 7.5 pages of questionable value containing results from a simple arithmetic equation, (3) the F and G matrix elements of some typical molecules, (4) some detailed group frequency charts for metal complexes and inorganic groups and ions, and (5) a detailed normal coordinate analysis of a complex molecule. The unique collection of these latter three into one volume is probably well worth the price of the entire volume.

The main purpose for which this book is written is fulfilled by the remaining half, an extensive compilation of infrared studies of inorganic and coordination compounds. This literature survey strikes a very nice balance between the detail necessary for accuracy and the brevity necessary for clarity. The majority of the nearly 900 references listed is from the English language publications, but this apparently was not a restriction in the work and many significant articles in foreign language journals are included for completeness.

Trivial points could be made in criticism. For example, it is disconcerting to find a typographical error in the sixth line of the book—one's confidence in the proofreading of the more technical sections is shaken by such a thing. Mathematical notation (*e.g.*, Eq. 3.1 of Section I) could be made more in accord with the usual practices. But, generally speaking, these things do not detract from the clarity of thought or lucidity of style and organization which characterize the book.

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**Biochemical Systematics.** By RALPH E. ALSTON and B. L. TURNER. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1963. 404 pp. 15.5 × 23.5 cm. Price, \$13.25 trade.

The authors in their preface state, "Although hundreds of thousands of words have already been written about biochemical systematics its actual impact upon formal systematics is still trivial. So far, no significant taxonomic dispositions of higher plants rest primarily upon biochemical criteria. We consider that an important objective of this book is to develop more fully an appreciation of the diversity of applications of biochemistry to systematics." It can be stated that their objective certainly seems to have been achieved. This volume is divided into sixteen chapters in which numbers 5 to 15 inclusive treat of the role that chemical constituents of plants play and may play in plant classification. It is evident that the authors, who are taxonomists by training, have an awareness of chemistry which is still rare in men devoted to the biological disciplines.

Following an introductory chapter which outlines the broad goals, there is one devoted to "Taxonomic Principles" which should be studied by all chemists who hope to make a contribution to "Plant Taxonomy"—which is the title of the next chapter. These two chapters deserve the attention of even those taxonomists who are primarily interested in morphology.

The chapters which treat of the chemical constituents point to the useful aspects as well as to the limitations of their use in taxonomy. Virtually all classes of organic components that can conceivably have a bearing on the subject are discussed. With the possible exception of the beta-cyanins no class of compounds has yet emerged which can be regarded as giving unquestionable answers to present taxonomic difficulties. Nevertheless, the pertinent literature is adequately reviewed and hints and suggestions for further work abound. Nor is the review restricted to higher plants but even algae and pteridophytes are not overlooked where relevant.

To cover so much territory in one volume requires a certain amount of abbreviation, but since at all events there is no finality or pretence thereto it may serve as a basis for future work.

If criticism there be at all, it could be about documentation. Even so, the important references are given and from these it is easy to find many more.

The book is well written, the printing and the diagram and figures are well done, and the volume is highly recommended, even to those chemists who have no ambition to solve taxonomic problems.

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RESEARCH LABORATORIES  
GUELPH, ONTARIO

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## BOOKS RECEIVED

September 1, 1963–October 1, 1963

D. V. BANTHROPE. "Reaction Mechanisms in Organic Chemistry." "Elimination Reactions." American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. 215 pp. \$8.00.

J. H. BEYNON and A. E. WILLIAMS. "Mass and Abundance Tables for use in Mass Spectrometry." American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. 570 pp. \$15.00.

MICHAEL LEDERER, Editor. "Chromatographic Reviews." "Progress in Chromatography, Electrophoresis and Related Methods." Volume 5. American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. 244 pp. \$11.00.