

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.

**Acknowledgment.**—We thank the National Science Foundation for financial support through Grants G-14596 and GE-345.

DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF TENNESSEE  
KNOXVILLE 16, TENNESSEE

DAVID Y. P. CHOU  
MARY JO PRIBBLE  
DONALD C. JACKMAN  
CHARLES W. KEENAN

RECEIVED AUGUST 28, 1963

## 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.

DEPARTMENT OF CHEMISTRY  
NEW YORK UNIVERSITY  
NEW YORK, N. Y.

JOHN E. RICCI

**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,