

In a nonhydroxylic solvent such as benzene several hours of refluxing were required to carry out the conversion.

This observation was of value in the examination of the thermal equilibrium process  $\text{III} \rightleftharpoons \text{IV}$ . Thus, while the thermal equilibration between I and II sets in, albeit slowly, even at room temperature,<sup>8</sup> the pyrylium oxide (III) in methanol at 150° for 5.5 hr. failed to yield a detectable amount of the pyrone (V). The pyrylium oxide (III) must, therefore, not be thermally isomerized to the epoxyketone (IV), since the latter would have rapidly rearranged under these conditions.

Interestingly, the much higher activation energy for the thermal reaction  $\text{III} \rightarrow \text{IV}$  compared to that for the reaction  $\text{II} \rightarrow \text{I}$  is reflected in the photochemical process. Thus, while photochemical interconversion between I and II and conversion of the epoxyketone (IV) to the pyrylium oxide (III) occur readily in a hydrocarbon glass at 77°K., visible light fails to reconvert III to IV under these conditions. We tentatively interpret these results as indicative of a photochemical tautomerization process involving a vibrationally excited ground state. The excited singlet state of III is of considerably lower energy than that of IV and thus cannot be thermally converted to it. A mechanism involving a temperature-dependent interconversion of excited singlet states at least for the process  $\text{III} \rightarrow \text{IV}$  therefore is unlikely. However, temperature dependence may be explained if the vibrationally excited ground state of III arising from internal conversion of excited singlet III (or an excited nonspectroscopic singlet common to III and IV) has an energy lower than the thermal transition state barrier between III and IV, for no photoreaction could then occur without additional thermal activation. Alternatively, thermal interconversion of similarly energetic triplet states cannot be excluded, although intervention of triplet states appears unlikely because of the absence of phosphorescence and of quenching by heavy metals.

Additional evidence concerning these questions will be described in a later publication.

(8) W. A. Henderson, Jr., and E. F. Ullman, unpublished observation.

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#### Reactions of Metal-Ammonia Solutions. IV. Kinetics of Potassium-Liquid Ammonia Reaction at Room Temperature

Sir:

As a prelude to the study of the kinetics of reactions in liquid ammonia at room temperature between alkali metals and certain organic reductants, we have examined the rate of the reaction of potassium with liquid ammonia in Pyrex. The sodium reaction has been studied under similar conditions by Ebert,<sup>1</sup> the potassium reaction by Stirand.<sup>2</sup> Our findings appear to differ considerably from those of Stirand, who reported that the reaction was not first order, but that indeed the rate (as measured by the time for half the metal to react) increased as the initial concentration of metal decreased over the range 0.2 to 0.04 *M*.<sup>3</sup> By an extrapolation from Stirand's data, the half-time of reaction for solutions in our concentration range is calculated to be of the order of 5 min. and less. We find it to be

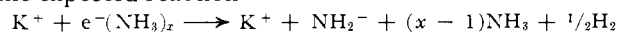
over 100 times this long, and we find the reaction to be first order, with a rate constant of  $0.065 \pm 0.012 \text{ hr.}^{-1}$ .

A plot of our data shows the reaction to be first order until approximately 75% of the metal has reacted. Initial concentrations and half-times for four runs at  $23 \pm 1^\circ$  are, respectively:  $1.13 \times 10^{-3} \text{ M}$ , 11 hr.;  $7.5 \times 10^{-4} \text{ M}$ , 10 hr.;  $3.7 \times 10^{-4} \text{ M}$ , 13 hr.; and  $2.0 \times 10^{-4} \text{ M}$ , 9 hr.

We have used a two-compartment Pyrex reaction cell, one end being a 1-cm.  $\times$  1-cm.  $\times$  4-cm. optical cuvette, the other end being a 3.2-cm. i.d. round tube about 10 cm. long. These ends were separated by an internal fragile glass diaphragm. The cells were cleaned with aqua regia, rinsed, and baked at 400° and  $<1 \times 10^{-5} \text{ mm.}$  for 24 hr. prior to filling *in vacuo*.<sup>4</sup> According to Warshawsky, even this treatment may leave water on the cell wall, but we have been able to detect no evidence of adsorbed water to date.

With triply-distilled potassium *in vacuo* in one end and about 35 ml. of purified liquid ammonia and a heavy glass breaker in the other, the cells were shaken to break the diaphragms and initiate the reactions. Details of construction of a cell<sup>5</sup> and its steel sheath will be published later.

The progress of the reaction was followed with a Cary Model 14 spectrophotometer by making periodic scans of the spectrum from 8000 to 3000 Å. The absorbance at 6500 Å. was taken as a measure of the unchanged metal,<sup>6</sup> while the peak that developed at about 3520 Å. was taken as a measure of the amide ion concentration. During much of the reaction, a plot of one of these absorbance values *vs.* the other is linear. This indicates that Beer's law holds over the range of concentrations and that the electron is being used in the expected reaction



It was noted that, on standing prior to periodic mixing during a run, the reaction appeared to be taking place slightly more rapidly in the cuvette than in the body of the cell. This behavior indicates that the reaction is taking place at the cell wall; if so, reactions in different cells and in cells of different sizes would have different rates. Differences in cell treatment,<sup>7</sup> type of glass, and wall-to-volume ratios may account for the differences between Stirand's results and ours.

We have made one run with lithium. The initial concentration was approximately 0.001 *M*; the reaction was first order for 75 hr., with a calculated half-life of about 120 hr. After 75 hr., the rate of reaction decreased<sup>8</sup>; for the next 140 hr., the half-life was about 140 hr. At about the same time the rate of the reaction changed, the plot of absorbance at 6500 Å. *vs.* amide peak showed a deviation from linearity which indicated the amount of dissolved amide was remaining constant. It is possible that the precipitation of lithium amide on the glass affected the reaction rate;

(4) In this work we have striven to maintain standards of purity and procedure similar to those of J. F. Dewald and G. Lepoutre, *J. Am. Chem. Soc.*, **76**, 3369 (1954); I. Warshawsky, *J. Inorg. Nucl. Chem.*, **25**, 601 (1963).

(5) We are indebted to Labglass of Tennessee, Kingsport, Tennessee, for perfecting the breakable diaphragm and for helping us design our reaction cells.

(6) At lower temperatures Beer's law is reported to hold for alkali metal-ammonia solutions at this wave length by M. Gold and W. L. Jolly, *Inorg. Chem.*, **1**, 818 (1962); under similar conditions, negative deviation from Beer's law for potassium solutions was reported by R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, **82**, 4472 (1960).

(7) Stirand's solutions were made up in equipment described by J. Moc and M. Podlaha, *Cesk. casopis. fys.*, **10**, 534 (1960). These authors state that their cells were simply heated for 6 to 8 hr. in an oven, then evacuated to  $10^{-5} \text{ mm.}$  prior to being filled *in vacuo* with potassium solutions.

(8) It is doubtful that precipitation of lithium amide on the walls of the cuvette caused an increase in absorbance to begin at this point. The absorbance of the solution at 6500 Å. at the conclusion of the reaction was the same as for pure ammonia.

(1) G. Ebert, *Z. anorg. allgem. Chem.*, **294**, 129 (1958).

(2) O. Stirand, *Czech. J. Phys.*, **B**, **12**, 207 (1962).

(3) See also the theoretical treatment of Stirand's data by M. Podlaha, *ibid.*, **B**, **11**, 627 (1961).

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,