volatilization of salt from the solutions at temperatures approaching its boiling point. However, the presence of a still more substantial error in the previous work would seem necessary to account for the false peritectic halts and larger apparent reaction of metal with the salt, 29% *vs.* 18.5% at the eutectic, for example. This may have been the failure of the Mo coating intended to protect the fused silica containers from the very reactive melt, since they noted that this coating ". . . adhered poorly to the quartz and on cooling came loose here and there . . . ." If so, the results pertain to a far more complex system containing silicide and oxide or oxychloride as well.

Disagreement with these workers has been noted before[10] in connection with the $PrCl_3$–Pr system. A later report of their work[11] does not help in that the alleged intermediate $PrCl_{2.5}$ is shown as separating from a eutectic melt of the same composition, and again there is no indication of the means by which its composition was established. In addition, the metal used contained 18% Nd, more than enough to stabilize the substituted $Pr(Nd)Cl_{2.32}$.[10]

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(10) L. F. Druding, J. D. Corbett, and B. N. Ramsey, *Inorg. Chem.*, **2**, 869 (1963).

(11) G. I. Novikov and O. G. Polyachenok, *Zh. Neorgan. Khim.*, **8**, 1053 (1963).

Correspondence

The Indirect Assessment of a Catalytic Path

Sir:

In a study of the kinetics of formation of ZnL^{-2} from the reaction of NiL^{-2} with Zn^{+2} (L^{-4} = ethylenediaminetetraacetate) Margerum and Bydalek[1] have deduced that the reaction is catalyzed by Cu^{-2} according to the scheme

$$M'L + M'' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M''L + \mathrm{I}$$

$$M'L + M''' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M'''L + M' \qquad (2)$$

$$M'' + M'''L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M''L + M''' \qquad (3)$$

where M′ = Ni(II), M″ = Zn(II), and M‴ = Cu(II). The reaction of NiL^{-2} with Cu^{+2} is much faster than is the reaction with Zn^{+2} and the displacement of Cu^{+2} from CuL^{-2} by Zn^{+2} is also relatively fast. Thus, when Cu^{+2} is present an alternate means of forming ZnL^{-2} is provided.

Because the reaction was followed by spectrophotometrically observing the disappearance of NiL^{-2}, the procedure used by Margerum and Bydalek represents an indirect method of assessing the effect of the catalytic pathway. Catalytic paths analogous to the one proposed by these workers may be important in other systems: in general, the metal ions may be representative of any three competing species and L may represent any other ligand, an electron or reaction product resulting, say, from a condensation.

This indirect approach may be useful in cases where a direct measure of the reaction product is not feasible. Since this type of system is somewhat complicated and an intuitive feeling for the effects of the various parameters is not easily had, we have undertaken a numerical study of the NiL^{-2}–Cu^{+2}–Zn^{+2} system investigated by Margerum and Bydalek to determine what information regarding the catalytic path experiments such as this may furnish.

The integration was performed numerically using the fourth-order Runge–Kutta method.[2a,b] Simulated kinetic runs were made using the values of k_1 and k_2 and the equilibrium constants and concentrations pertaining to the experiments described in ref. 1 with various assumed values of k_3; see the legend of Figure 1 for details.

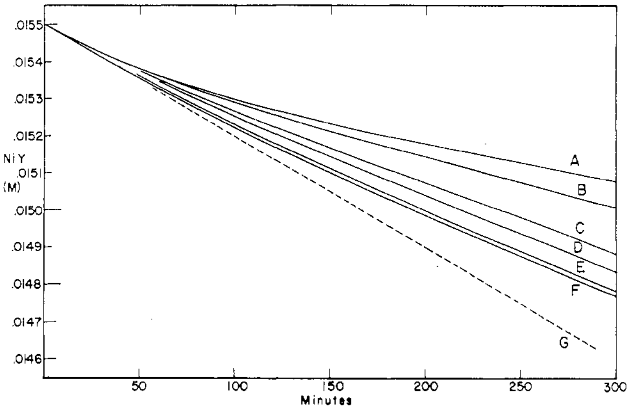

Figure 1.—The rate of disappearance of NiY^{-2}; conditions of ref. 1: $Ni_t = L_t = 0.01550$ *M*; $Zn_t = 0.3945$ *M*; $Cu_t = 0.000134$ *M*; $Q_{ZnL} = 3.2 \times 10^{16}$, $Q_{CuL} = 6.3 \times 10^{18}$, $Q_{NiL} = 4.0 \times 10^{18}$; $k_1 = 2.67 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$; $k_2 = 1.63 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. Values of k_3 (l. mole^{-1} sec.$^{-1}$) × 10^4 are: A, 0; B, 1.67; C, 8.33; D, 16.7; E, 83.3; F, 833, 1667; G, extrapolation of initial curves.

The constants for the back reactions were evaluated from the following relationships (Q_{ML} = the formation constant of ML^{-2}).

$$k_{-1} = k_1 Q_{NiL}/Q_{ZnL}$$

$$k_{-2} = k_2 Q_{NiL}/Q_{CuL}$$

$$k_{-3} = k_3 Q_{CuL}/Q_{ZnL}$$

The computed results are presented in Figures 1 and 2 for the first 300 min. of reaction. In Figure 1

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(1) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

(2) (a) F. B. Hildebrand, "Introduction to Numerical Analysis," McGraw-Hill Book Co., New York, N. Y., 1956, p. 237; (b) I. D. Gay, *J. Am. Chem. Soc.*, **86**, 2747 (1964).

it is seen that as k_3 increases, the shape of the rate curve, NiL^{-2} *vs.* t, changes until a limiting "wall" is reached at $k_3 \sim 0.08$ l. mole^{-1} sec.$^{-1}$. Thus, if the catalytic paths (2) and (3) are operating it is possible, using this indirect approach, either to evaluate k_3 or at least to establish its lower limit.

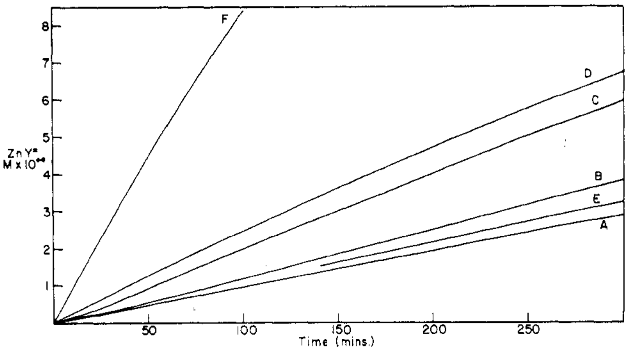

Figure 2.—The rate of formation of ZnY^{-2}: curve A, $k_3 = 0$, $Cu_t = 0$, 1.34×10^{-4} *M;* B, $k_3 = 1.67 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-4}$ *M;* C, $k_3 = 16.7 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-4}$ *M;* D, $k_3 = 833$, 1667×10^{-4}, $Cu_t = 1.34 \times 10^{-4}$ *M;* E, $k_3 = 1667 \times 10^{-4}$, $Cu_t = 1.00 \times 10^{-5}$ *M;* F, $k_3 = 1430 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-3}$ *M;* other quantities the same as in Figure 1.

All the curves shown in Figure 1 have the same initial slope, which is determined by the sum of the initial velocities of the Zn^{+2} and Cu^{+2} reactions with NiL^{-2}. Thus, zero-time data do not experimentally demonstrate catalysis although, if some knowledge of k_3 is had, catalysis may be deduced, as was done in ref. 1.

The results of Bydalek and Margerum[3] obtained for experiments with Cu^{+2} give a straight line having a slope $3.0_8 \times 10^{-6}$ sec. when plotted as $-\ln (NiL^{-2})$ *vs.* time for the first 400 min. The computed values in Figure 1 for the curve $k_3 \geqslant 0.083$ l. mole^{-1} sec.$^{-1}$ plotted similarly give a straight line with a slope 3.0×10^{-6} sec.$^{-1}$. Thus, the data of Margerum and Bydalek conclusively show the effect of a catalytic path with a rate constant k_3 of at least 0.083 l. mole^{-1} sec.$^{-1}$.

A variation of concentrations shows that this indirect method is most sensitive to k_3 when conditions are arranged so that the velocities of the competing paths (1) and (2) are nearly identical: when the rate of either of the paths (1) or (2) becomes dominant over the other the catalytic path (3) exerts a relatively smaller effect on the rate of the NiL^{-2} disappearance. Under these latter conditions the concentration of the product of the catalyzed reaction is best measured directly. The advantage of a direct approach can be seen by comparing the computed curves given in Figure 2, where the effect of a variation in Cu(II) on the rate of ZnL^{-2} formation is also shown. The effect is seen to be quite large, although at both the high and low Cu(II) levels the rate of disappearance of NiL^{-2} is relatively insensitive to k_3.

Acknowledgment.—We wish to thank the staff of the numerical computation laboratory of The Ohio State University for the kind use of their facilities, and Professor Margerum for valuable discussions.

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RECEIVED AUGUST 7, 1964

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[3] Private communication.

Kinetics and Mechanism of the Acid Hydrolysis of Carbonatobis(ethylenediamine)cobalt(III) Ion

Sir:

A paper under the above title appeared in a recent issue of this journal[1] in which an attempt was made to deduce the mechanism of the process from somewhat limited data. The authors found it impossible to choose between two suggested mechanisms based on a protonated intermediate, one involving direct reaction of the intermediate with water, the other with hydronium ion. We wish to report our studies of the same reaction which are now in progress, and which we have extended to the closely similar propylenediamine and trimethylenediamine analogs. These studies developed from our earlier conclusions[2] concerning the acid hydrolysis reaction, which were based on carbonate exchange experiments, and which Tong and co-workers seem to have overlooked. Our new data on the acid hydrolysis reactions embrace the range $1 < pH < 5$ (as compared to the $2.4 < pH < 3$ range of Tong's work), and were obtained by a spectrophotometric technique utilizing phosphate–citric acid buffering. Since (H^+) was effectively kept constant in our work, pseudo-first-order kinetics were observed in individual runs. The mechanism now proposed, which is slightly modified from our previous suggestions,[2] is as follows (L = chelated diamine ligand).

$$CoL_2CO_3^+ + H_2O \rightleftharpoons CoL_2(OH_2)(OCO_2)^+ \qquad (1)$$

$$CoL_2(OH_2)(OCO_2)^+ + H^+ \rightleftharpoons CoL_2(OH_2)(OCO_2H)^{+2} \quad 1/K \qquad (2)$$

$$CoL_2(OH_2)(OCO_2)^+ + H_2O \longrightarrow CoL_2(OH)(H_2O)^{+2} + HCO_3^- \quad k_1 \qquad (3)$$

$$CoL_2(OH_2)(OCO_2H)^{+2} + H_2O \longrightarrow CoL_2(OH_2)_2^{+3} + HCO_3^- \quad k_2 \qquad (4)$$

$$CoL_2(OH_2)(OCO_2H)^{+2} + H_3O^+ \longrightarrow CoL_2(OH_2)_2^{+3} + H_2CO_3 \quad k_3 \qquad (5)$$

This is similar to Tong's suggestions in that, except for our assumption of opening of the carbonato chelate by inclusion of a water molecule in the coordination sphere, his reactions 1a, 2a, and 2b correspond to our reactions 3, 4, and 5. We differ, however, in our inter-

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[1] J. Y. Tong, E. St. A. Kean, and B. B. Hall, *Inorg. Chem.*, **3**, 1103 (1964).

[2] G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).