[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Equilibria and Reaction Rates in the Disproportionation of Pu(IV)[1]

BY SHERMAN W. RABIDEAU

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The equilibrium quotients and the specific rate constants for the disproportionation of Pu(IV) have been measured as a function of hydrogen and plutonium ion concentrations in perchloric acid solutions of unit ionic strength at 25.00 ± 0.02°. Instead of obtaining the plutonium ion concentrations spectrophotometrically as has been done by previous workers, measurements of the mean oxidation number of the solutions were combined with electromotive force measurements of the Pu(III)–Pu(IV) couple and the total plutonium ion concentrations. From these data it is possible to calculate the concentrations of Pu(III), Pu(IV) and Pu(VI) present in the solutions at any time. The equilibrium quotient for the disproportionation reaction has been found to be directly dependent upon the fourth power of the hydrogen ion concentration, thus supporting the existence of the plutonyl ion, PuO_2^{++}, in these solutions. A weighted mean value of 0.0089 was found for the Pu(IV) disproportionation equilibrium quotient in perchloric acid solutions of unit ionic strength at 25°. The rate of the forward (disproportionation) reaction has been found to exhibit an inverse third power hydrogen ion concentration dependence and the most probable rate-determining step of this reaction is $PuOH^{+++} + Pu(OH)_2^{++} \rightarrow Pu^{+++} + PuO_2^{+} + H_2O + H^{+}$.

Introduction

If the accepted formulas of the ions are used, the net reaction involved in the disproportionation of Pu(IV) in acid solutions is $3Pu^{++++} + 2H_2O \rightleftarrows 2Pu^{+++} + PuO_2^{++} + 4H^{+}$. The equilibrium quotient for this reaction is given by $K = (Pu^{+++})^2(PuO_2^{++})(H^{+})^4/(Pu^{++++})^3$. Although this expression indicates a fourth power hydrogen ion concentration dependence, Kasha[2] reported that his spectrophotometrically derived equilibrium quotients for the disproportionation of Pu(IV) in perchloric acid solutions best fitted a third power hydrogen ion concentration dependence. Since the experimental work of the present paper was completed, Connick and McVey[3] have shown that Kasha's conclusions were in error because he neglected to correct for the effect of α-reduction. Hence, the equilibrium quotient values reported by Kasha[2] in reality corresponded to steady state conditions. With the α-reduction correction applied to the data obtained by Kasha, Connick and McVey found that the equilibrium quotient approximated a fourth power hydrogen ion concentration dependence in perchloric acid solutions.[4]

Specific rate constants have been calculated by Connick and McVey[3] for the disproportionation of Pu(IV) in perchloric acid solutions. The uncertainties of these constants ranged from 16 to 53%; however, the results best fitted an inverse third power hydrogen ion concentration dependence.

Connick[5] has shown that the mechanism of the disproportionation of Pu(V) in 0.5 M hydrochloric acid consists of the steps

$$Pu(V) + Pu(III) \longrightarrow 2Pu(IV) \quad \text{(slow)}$$
$$Pu(V) + Pu(IV) \rightleftarrows Pu(III) + Pu(VI) \quad \text{(fast)}$$

He concluded that the data of Kasha and Sheline[6] strongly support the assumption that the mechanism of the disproportionation of Pu(IV) is essentially the reverse of the disproportionation of Pu(V). No attempt was made by Connick[5] to determine the hydrogen ion dependence of the rate of disproportionation of Pu(V).

In the present work, the equilibrium quotients and the rate constants for the disproportionation of Pu(IV), together with the hydrogen ion concentration dependencies of these quantities, have been evaluated from the variation of the Pu(III), Pu(IV) and Pu(VI) concentrations with time. These concentrations were derived from measurements of the mean oxidation number of solutions of known total plutonium concentration combined with values of the Pu(IV)/Pu(III) ratio obtained from electromotive force measurements of the Pu(III)–Pu(IV) couple.

Experimental

Materials.—All plutonium solutions used in this work were prepared by dissolving known weights of oxide-free plutonium metal in standardized Mallinckrodt 71% reagent grade perchloric acid followed by dilution with distilled water to the desired acidity. The ionic strength of the solutions was maintained at unity by the addition of the appropriate weight of recrystallized sodium perchlorate. This salt was prepared by the neutralization of dilute perchloric acid with C.P. sodium carbonate. In the preparation of Pu(III)–Pu(IV) solutions of known composition, a weight aliquot of a freshly prepared Pu(III) stock solution was mixed with the requisite weight of standardized 0.05 N potassium dichromate solution. At the beginning of an experiment a solution of known Pu(VI) concentration was added to the solution of known Pu(IV)/Pu(III) ratio. The Pu(VI) solutions were prepared by oxidizing a weight aliquot of a Pu(III) stock solution with ozone for a period of one to two hours followed by a flushing period of an hour with argon to remove any dissolved ozone. The completeness of the oxidation of Pu(III) to Pu(VI) was checked by measuring the mean oxidation number of a solution containing ions of Pu(III), Pu(IV) and Pu(VI), and it was found that quantitative oxidations of Pu(III) to Pu(VI) could be achieved with ozone.

Apparatus.—The manual apparatus used in the measurement of the cell potentials and the thermostatic assembly have been described in a previous communication.[7] Although the course of the disproportionation reaction was followed in a few cases by measuring manually the cell potentials as a function of time, the remainder of the experiments were made using a "folding-scale" recording potentiometer.[8] This instrument utilizes a modified Brown "Electronik" recording potentiometer to chart the change of electromotive force with time. To permit the recording of voltage differences of as little as 0.02 mv., six scales each of 10 mv. full span were incorporated into the instrument. As the cell voltage diminishes and the pen reaches the

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[1] This work was done under the auspices of the A.E.C.

[2] M. Kasha, Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. 1, 295 (1949).

[3] R. E. Connick and W. H. McVey, UCRL-1687, March, 1952.

[4] In view of the unknown absorption spectrum of $PuOH^{+3}$, Connick and McVey did not correct Kasha's results for the hydrolysis of Pu(IV).

[5] R. E. Connick, Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. I, 268 (1949).

[6] M. Kasha and G. E. Sheline, *ibid.*, 180 (1949).

[7] S. W. Rabideau and J. F. Lemons, THIS JOURNAL, **73**, 2895 (1951).

[8] The "folding-scale" recording potentiometer was designed by V. G. Rexroth of the Los Alamos Scientific Laboratory.

bottom of the chart, a switching arrangement actuated by a relay shifts the pen to the top of the next scale. Since the current drain from the cell is only about 10^{-8} ampere, the cell polarization induced by the recording instrument is negligible. The calibration of each scale of the recorder was made by measuring the potential of the cell first with a Rubicon type B precision potentiometer and then with the "folding-scale" recording potentiometer.

Analyses.—In each of the equilibrium and rate constant experiments, the equilibrium was approached from the disproportionation direction in order that the Pu(V) concentration could be considered to be negligibly small. Kasha[2] has determined the equilibrium quotient for the reaction Pu(III) + Pu(VI) $\rightleftarrows$ Pu(IV) + Pu(V) and obtained a mean value of 9.0 in 0.05 to 0.10 M perchloric acid solutions of unit ionic strength. This equilibrium quotient should be independent of acidity. Accordingly, at disproportionation equilibrium in molar perchloric acid solutions the Pu(V) concentration was calculated to be about 0.3%, and it is considerably less than this amount in the early stages of the disproportionation experiments.

In addition to obtaining the total plutonium concentration, it was necessary to make two additional measurements to state the concentrations of Pu(III), Pu(IV) and Pu(VI) present in the solution at a given time. The two measurements chosen were the Pu(IV)/Pu(III) ratio and the mean oxidation number. The potential of the cell and the Pu(III) and Pu(IV) concentrations were known at the beginning of the experiment. The Pu(IV)/Pu(III) ratio at a given time was obtained from the initial ratio and the change in the potential of the cell

$$\text{Pt; Pu(III), Pu(IV), HClO}_4(c_1)\text{, NaClO}_4(c_2)\text{; HClO}_4(c_1)\text{, NaClO}_4(c_2)\text{; H}_2\text{, Pt.}$$

The mean oxidation number of a solution consisting of ions of Pu(III), Pu(IV) and Pu(VI) is given by the relation

$$\overline{\text{OX}} = [3\text{Pu(III)} + 4\text{Pu(IV)} + 6\text{Pu(VI)}]/\Sigma(\text{Pu})$$

The brackets refer to concentrations and Σ(Pu) represents the total plutonium ion concentration in the solution. In the mean oxidation number determination, use was made of the fact that Pu(IV) is strongly complexed by sulfate ion, and hence the reproportionation reaction is favored in an acid sulfate solution. In the presence of sulfate ion Pu(III) can be quantitatively oxidized to Pu(IV) with permanganate.

A weight aliquot of the solution of known total plutonium concentration was taken for analysis. The quantity of plutonium in the sample was about 25 mg. The solution was made about 2 to 3 N in sulfuric acid, three drops of a 0.025 M ferrous-phenanthroline indicator solution was added, and the solution was titrated with standardized 0.01 N potassium permanganate from a micro-buret until the reddish-orange color of the indicator was discharged. If the solution was known to have a mean oxidation number very close to or greater than four, a weight aliquot of a Pu(III) stock solution of known concentration was added in sufficient amount to permit the reproportionation reaction to be complete. The value of the mean oxidation number can be found from the equation

$$\overline{\text{OX}} = 4.000 - \frac{(\text{meq. KMnO}_4 - \text{blank}) + (\text{meq. Pu(III) added})}{\text{millimoles }\Sigma\text{Pu}}$$

If X, Y and Z are the fractions of Pu(III), Pu(IV) and Pu(VI) present in the solution, the composition can be determined by solving the three simultaneous equations.

$$X + Y + Z = 1$$
$$3X + 4Y + 6X = \overline{\text{OX}}$$
$$Y/X = A$$

Results and Discussion

Rate of α-Reduction.—The mean oxidation number of a plutonium solution diminishes with time as a result of α-particle radiation in the solution. The rate of this reduction is of interest in connection with the analyses of plutonium solutions; further, this rate is directly related to the time at which equilibrium is reached in the Pu(IV) disproportionation experiments. If a Pu(IV) solution in molar perchloric acid is allowed to stand until a steady state has been reached, the concentrations of Pu(III), Pu(IV) and Pu(VI) will not in general correspond to the equilibrium concentrations because of the α-reduction effect. A 10^{-2} M solution of Pu(III) in molar perchloric acid was prepared and sufficient potassium dichromate was added to make the final solution 95.53% Pu(IV) and 4.47% Pu(III). This solution has a calculated initial mean oxidation number of 3.955. Two titrations were made on aliquots of the stock solution within an hour of the time of preparation, and identical results of 3.955 were obtained. Analyses were made at frequent intervals over a 10-day period. The results are plotted in Fig. 1. A mean value of 0.0150 equivalent per day was obtained as the rate of α-reduction, and within the limits of experimental error, the reduction rate is linear with time. In each disproportionation experiment mean oxidation analyses were made as a function of time on aliquots of the original plutonium solution. The results obtained for the rate of α-reduction in these solutions closely approximated the value of 0.0150 equivalent per day. From spectrophotometric analyses over an 820-hour period, Kasha[2] obtained an α-reduction rate of 0.0128 equivalent per day in molar perchloric acid solutions.

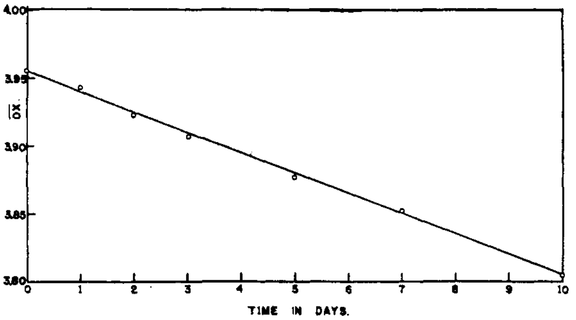

Fig. 1.—Rate of decrease of mean oxidation number as a result of alpha reduction.

Pu(IV) Disproportionation Equilibrium.—Before the rate laws for the disproportionation reaction can be written, a knowledge of the nature of the α-reduction process is required. In the absence of this specific information, it is assumed that the net result of the α-reduction process is the conversion of Pu(IV) to Pu(III). This conclusion is not invalidated by the conversion of Pu(VI) to Pu(V) since Pu(V) reacts rapidly with Pu(IV) to form Pu(VI) and Pu(III).[3] If the over-all disproportionation reaction is considered to consist of the two steps

$$\text{Pu(IV)} + \text{Pu(IV)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Pu(III)} + \text{Pu(V)} \quad \text{(slow)}$$

$$\text{Pu(V)} + \text{Pu(IV)} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{Pu(III)} + \text{Pu(VI)} \quad \text{(fast)}$$

the rate law for the disproportionation reaction, including the effect of α-reduction is

$$-\,\text{d(Pu(IV))}/\text{d}t = 3k_1\text{Pu(IV)}^2 - 3k_2\text{Pu(III)}^2\text{Pu(VI)}/\text{Pu(IV)} + \alpha$$

The first term in the rate law represents the forward disproportionation reaction, the second represents the reproportionation term and α is the α-reduction correction. The α-reduction term was not taken into consideration either by Kasha[2] or by Kasha and Sheline.[6] This omission led these authors to report steady state concentrations as corresponding to equilibrium concentrations. The α-reduction correction is especially important in perchloric acid solutions of 0.5 *M* and greater. It appears from the results of Kasha and Sheline that the rate of α-reduction is less in hydrochloric acid than in perchloric acid solutions. Consequently, the error introduced as a result of neglecting the α-reduction factor in disproportionations of Pu(IV) in hydrochloric acid solutions should be small.

The method used in obtaining the equilibrium quotient is illustrated in Fig. 2. Plots were made of $-d(\text{Pu(IV)})/dt$ and of the apparent equilibrium quotient *versus* time. The apparent equilibrium quotient is equal to the true equilibrium quotient, $K' = \text{Pu(III)}^2\text{Pu(VI)}/\text{Pu(IV)}^3$, at the time at which $-d(\text{Pu(IV)})/dt$ equals the rate of α-reduction.

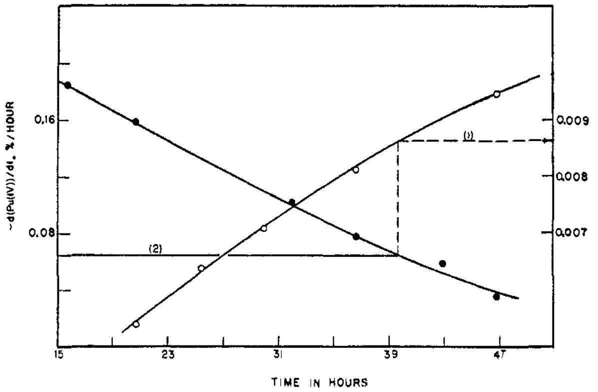

Fig. 2.—Determination of Pu(IV) disproportionation equilibrium quotient from rate data: (1) true equilibrium quotient, (2) observed α-reduction rate, O, apparent equilibrium quotient, ●, $-d(\text{Pu(IV)})/dt$.

Since Pu(IV) is appreciably hydrolyzed in solutions of low acidity, the observed equilibrium quotient, K', cannot exhibit an integral power dependence on the hydrogen ion concentration. In a previous communication[7] a value of 3.1×10^{-2} was reported for the hydrolysis constant of Pu(IV) at 25° in perchlorate solutions of unit ionic strength. The unhydrolyzed species, Pu^{++++}, is related to the total Pu(IV) concentration, $\Sigma\text{Pu(IV)}$, by the relation $\text{Pu}^{++++} = \Sigma\text{Pu(IV)} \times (\text{H}^+)/[(\text{H}^+) + 0.031]$. At the acidities used in these experiments Pu(III) is not hydrolyzed to any significant extent. Values for the equilibrium quotient, $K'' = K'\,\text{Pu(IV)}^3/(\text{Pu}^{++++})^3$, have been calculated and are listed in column four of Table I.

Over a fivefold range in acidity this equilibrium quotient, K'', has been found to be proportional to the fourth power of the hydrogen ion concentration. This result is in agreement with that predicted from the disproportionation reaction. These experiments may be considered to furnish supporting evidence for the existence of the plutonyl ion, PuO_2^{++}, in acid solution. A weighted average value of 0.0089 was obtained for the equilibrium quotient, *K*, of the disproportionation reaction $3\text{Pu}^{++++} + 2\text{H}_2\text{O} \rightleftarrows 2\text{Pu}^{+++} + \text{PuO}_2^{++} + 4\text{H}^+$ in perchlorate solutions of unit ionic strength at 25°. More weight was given to the results in the 0.5 and 1.0 *M* perchloric acid solutions because of the smaller hydrolysis correction.

TABLE I

THE Pu(IV) DISPROPORTIONATION EQUILIBRIUM QUOTIENT IN PERCHLORIC ACID SOLUTIONS AT UNIT IONIC STRENGTH AND 25°

(H^+), mole/l.	ΣPu, mole/l.	K'^a	K''^b	K^c
1.000	1.132×10^{-2}	0.0083	0.0091	0.0091
1.000	1.104×10^{-2}	.0071	.0078	.0078
1.000	6.714×10^{-3}	.0087	.0095	.0095
1.000	6.400×10^{-3}	.0071	.0078	.0078
1.000	5.620×10^{-3}	.0071	.0078	.0078
			Mean	0.0084
0.500	1.275×10^{-2}	0.109	0.131	0.0082
.500	8.833×10^{-3}	.115	.139	.0087
.500	6.085×10^{-3}	.112	.135	.0084
			Mean	0.0084
0.210	5.779×10^{-3}	3.73	5.64	0.0110
.200	8.000×10^{-3}	4.41	6.80	0.0109
			Mean	0.0110

[a] K' is the observed equilibrium quotient, $\text{Pu(III)}^2\text{Pu(VI)}/\text{Pu(IV)}^3$. [b] $K'' = K'\text{Pu(IV)}^3/\text{Pu}^{++++})^3$. It is this quotient which would be expected to exhibit an integral power dependence on the hydrogen ion concentration. [c] $K = K''(\text{H}^+)^4$.

Rates of Pu(IV) Disproportionation.—The values of k_1, the specific rate constant for the forward reaction, can be obtained from the rate law expression in the form $k_1 = [-d(\text{Pu(IV)})/dt - \alpha]/[(1 - K^*/K')\ 3\text{Pu(IV)}^2]$. The quantity K^* is the apparent equilibrium quotient, $\text{Pu(III)}^2\text{Pu(VI)}/\text{Pu(IV)}^3$, at a given time. K' is the equilibrium quotient without acidity or hydrolysis corrections, and α is the rate of α-reduction in the solution. The second power dependence of the Pu(IV) concentration in this rate expression gave much more consistent results than either the

TABLE II

SPECIFIC RATE CONSTANTS FOR Pu(IV) DISPROPORTIONATION IN PERCHLORIC ACID SOLUTIONS OF UNIT IONIC STRENGTH AT 25°

(H^+), mole/l.	ΣPu, mole/l.	k_1, l./mole/hr.	$k_1(\text{H}^+)^3$
1.000	1.132×10^{-2}	0.101	0.101
1.000	1.097×10^{-2}	.088	.088
1.000	6.482×10^{-3}	.107	.107
1.000	6.400×10^{-3}	.093	.093
1.000	5.676×10^{-3}	.102	.102
		Mean	0.098
0.500	1.275×10^{-2}	0.897	0.112
.500	8.833×10^{-3}	.857	.107
		Mean	0.110
0.210	5.779×10^{-3}	13.9	0.129
.200	8.000×10^{-3}	14.4	.115
		Mean	0.122

first or third powers. Thus it would appear that the disproportionation of Pu(IV) is essentially the reverse of the disproportionation of Pu(V) as proposed by Connick.[5] The results of the rate constant measurements as a function of hydrogen ion concentration are given in Table II. In column 4 of Table II are found the products of the specific rate constants and the cubes of the hydrogen ion concentration. The good agreement of this product over a fivefold change in acidity is evidence for the inverse third power hydrogen ion concentration dependence of the specific rate constants for the disproportionation reaction.

The most probable mechanism of disproportionation of Pu(IV) in acid perchlorate solutions is

$$\mathrm{Pu^{++++} + H_2O \rightleftharpoons PuOH^{+++} + H^+}$$

$$\mathrm{PuOH^{+++} + H_2O \rightleftharpoons Pu(OH)_2^{++} + H^+}$$

$$\mathrm{PuOH^{+++} + Pu(OH)_2^{++} \longrightarrow Pu^{+++} + PuO_2^{+} + H_2O + H^+} \quad \text{(slow step)}$$

$$\mathrm{PuO_2^{+} + Pu^{++++} \rightleftharpoons Pu^{+++} + PuO_2^{++}}$$

Since the equilibrium quotient has been shown to be dependent upon the fourth power of the hydrogen ion concentration, and the rate of the forward reaction dependent upon the inverse third power, the reproportionation reaction should exhibit a first power dependence upon the acidity.

In the two experiments at unit ionic strength and at comparable hydrogen ion concentrations, namely, 0.5 and 1.0 *M* perchloric acid, the rate constants found in the present work are in excellent agreement with the results obtained by Connick and McVey's correction of Kasha's data.

Acknowledgments.—The author wishes to express his appreciation to Drs. J. F. Lemons and T. W. Newton of the Los Alamos Scientific Laboratory for helpful discussions pertaining to this research. Private communications have also been exchanged with Dr. Robert E. Connick concerning portions of this paper.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Absorption of Inorganic Salts from Organic Solvents onto Anion Exchange Resins[1]

BY LEONARD I. KATZIN AND ELIZABETH GEBERT[2]

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The solutes hydrochloric acid, lithium chloride, lithium nitrate, cobaltous nitrate, cupric chloride and nickelous nitrate have been found to absorb onto anion exchange resins (Dowex A-1) from their solutions in acetone. The absorption is characterized by the molecule as a whole disappearing from the liquid phase, rather than by ions being exchanged. At least the following factors are involved: (a) nature of the anion associated with the cation in solution; (b) nature of the anion associated with the resin; (c) the water content of the starting resin or of the total system. Some discussion is presented of possible mechanisms.

The concentration of inorganic ions from aqueous solutions onto ion exchange resins is a well-known phenomenon. The movement of and separation of inorganic ions in paper chromatography, with the aid of an organic solvent, is also known.[3–5] The only literature on the absorption of salts from organic solutions by ion exchange resins of which the authors are aware was called to their attention during the course of their experimental work, and consists of patents covering the absorption of copper (presumably in organic combination) from petroleum hydrocarbons.[6,7]

In the work to be described, electrolytes such as hydrochloric acid, lithium chloride, lithium nitrate, cobaltous chloride, cobaltous nitrate, cupric chloride and nickelous nitrate have been absorbed from organic solution (principally acetone solution) onto anion exchange resins (principally Dowex A-1). The characteristic feature of the absorption is that one is dealing not with anion exchange, such as characterizes the behavior in water medium, but with removal of the molecule as a whole from the solution onto the resin. This is graphically illustrated in the case of the colored salts by the decrease in color of the solution and the progressive coloration of the solid resin with which it is in contact.

Procedure

Commercial Dowex A-1 resin, chloride form, 250–500 mesh, was treated with aqueous HCl, NaCl or $NaNO_3$, as appropriate, to give a stock resin. The resulting material was washed exhaustively with water and then dried in air to the degree desired. The water content was determined by titration with Karl Fischer reagent with a standard procedure.[8] The chloride content of the resins was determined by bomb ignition, and in the case of the chloride resin, amounts to about 3.1 millimoles per gram of resin.

Stock solutions of cupric chloride and nickelous nitrate in chemically pure acetone were made by dissolving weighed portions of the hydrated salts. The concentrations of lithium salt solutions were determined by analysis of the solution with the Beckman flame photometer. Solutions of the cobaltous salts were analyzed for cobalt by standard electrodeposition procedures. We are indebted to Mr. Ralph Bane for chloride and lithium analyses, and to Mr. John Ferraro for water and cobalt analyses.

Two milliliters of a salt solution was equilibrated with 0.2 g. of the resin in a glass-stoppered tube for 24–72 hours. In the case of the quantitative studies with the cobaltous

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(1) Presented at Cleveland Meeting of American Chemical Society, April 8–10, 1951.

(2) We are indebted to James C. Sullivan for certain preliminary experiments.

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(4) A. Lacourt, G. Sommereyns, E. de Geyndt, J. Baruh and J. Gillard, *Mikrochem. ver. Mikrochim. Acta*, **34**, 215 (1949).

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(8) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).