to the work of Hindman and Kritchevsky[2] who found this couple to be polarographically irreversible in perchloric acid. This phenomenon is not unique. Jones and Colvin[8] found the V(III)-V(IV) couple to behave reversibly at a platinum electrode, while Lingane[9] found this couple to be irreversible at the dropping mercury electrode. This behavior can most probably be attributed to a measurable slowness of the electrode reaction.

The $\Delta\bar{S}$ for the cell reaction of -31.2 e.u. is very close to that found by Connick and McVey[10] (-30.6 e.u.) for the corresponding plutonium reaction.

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(8) G. Jones and J. H. Colvin, THIS JOURNAL, **66**, 1563 (1944).

(9) J. J. Lingane, *ibid.*, **67**, 182 (1945).

(10) R. E. Connick and W. H. McVey, *ibid.*, **73**, 1798 (1951).

CHICAGO 80, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Neptunium(IV)-Neptunium(V) Couple in Perchloric Acid. The Partial Molal Heats and Free Energies of Formation of Neptunium Ions

BY DONALD COHEN AND J. C. HINDMAN

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The formal oxidation potential for the cell reaction (equation 1) has been determined to be -0.7391 ± 0.0010 v. in 1 *m* perchloric acid at 25°. $\Delta\bar{H}$ for this reaction is 35.6 ± 0.3 kcal. and $\Delta\bar{S}$ is 62.3 ± 1 e.u. Based on these and previously reported measurements a potential scheme for the neptunium ions in 1 *m* perchloric acid is given. Calculations have been made of the partial molal heats and free energies of formation of the various neptunium ions. Entropies of these ions are given.

Measurements on the potentials of the neptunium(III)-(IV) and neptunium(V)-(VI) couples in molal perchloric acid have been reported previously.[1] The present communication deals with the potential data on the neptunium(IV)-(V) couple and the calculations of the partial molal heats and free energies of the neptunium ions in this medium.

Prior measurements on this couple were made in molar hydrochloric acid at 25°.[2] The couple was not reversible at a bright platinum electrode; the potential was therefore evaluated from a cell containing an equilibrium mixture of Np(V), Np(IV), Fe(III) and Fe(II). More recently, Magnusson and Huizenga[3] measured the potential of this couple in perchloric acid at several temperatures using this same technique.

Investigation of the overvoltage behavior exhibited in the electrolytic oxidation and reduction of neptunium ions[4] suggested that a direct measurement of the potential of the couple might be feasible at higher temperatures. Actually, a reinvestigation of the couple has shown that a formal potential can be obtained without a mediator at 25° as well as at higher temperatures. The time required for electrode equilibrium to be reached rapidly decreases with increasing temperature.

Experimental

The formal potential of the Np(IV)-Np(V) couple was measured using the cell

$$\mathrm{Pt{:}H_2{:}HClO_4{:}HClO_4,\ Np(IV),\ Np(V){:}Pt}$$

The three temperatures used were 47, 35 and 25°. The ratios of Np(IV) to Np(V) were prepared from stock solutions of the pure oxidation states. Two separate stock solutions of each state were used.

The Np(V) stock solution was prepared by dissolving Np(V) hydroxide in perchloric acid. The Np(IV) stock solution was prepared electrolytically using a potentiostat. Np(V) perchlorate solution was first reduced to Np(III) and this solution was then oxidized to Np(IV). Care was taken to keep the Np(IV) solution under an atmosphere of nitrogen to prevent its slow oxidation by air to the (V) state. The stock solutions were analyzed for neptunium content by radiometric assay.

The measuring cell was an "H" type cell with the two compartments separated by a 10-mm. fine sintered glass disc. The tops of the cell were fitted with standard taper joints, one for the hydrogen electrode and the other for a delivery tube to bubble prepurified nitrogen through the neptunium solution. Twenty-one inches of 51 mil platinum wire in the form of a spiral served as the inert measuring electrode.

The usual electrical measuring circuit was used with a Leeds and Northrup Type K potentiometer. The constant temperature bath was controlled to ±0.03°.

The following procedure was used to measure the potential for this couple. A mixture of Np(IV) and Np(V) was added to the thermostated cell and nitrogen was bubbled through this solution. The other compartment of the measuring cell containing a hydrogen electrode of conventional design was filled with the stock molal perchloric acid. Both the hydrogen and the nitrogen were first bubbled through molal perchloric acid solutions which were kept in the constant temperature-bath. E.m.f. readings were taken until a constant potential was attained after which the neptunium ratio was changed and again, e.m.f. measurements were taken until the potential became constant.

As a check on the effect of electrode surface compositions on the cell potentials, measurements were also made using platinized platinum and gold for the inert electrode.

Results and Discussion

Magnusson and Huizenga[3] have shown the fourth power hydrogen ion dependence of the Np(IV)-Np(V) couple. These data, combined with other evidence[5] that Np(IV) exists as Np^{+4} in acid solution leads to the cell reaction

$$\mathrm{Np^{+4}(aq) + 2H_2O \rightleftarrows NpO_2^{+}(aq) + 3H^{+} + {}^{1}/_{2}H_2(g)} \qquad (1)$$

The e.m.f. for this reaction is given by equation (2)

$$E = E' - \frac{RT}{F}\ln\,[\mathrm{H^+}]^3[\mathrm{H_2}]^{1/2}\,\frac{[\mathrm{Np(V)}]}{[\mathrm{Np(IV)}]} \qquad (2)$$

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(1) D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679 (1952).

(2) J. C. Hindman, L. B. Magnusson and T. J. La Chapelle, *ibid.*, **71**, 687 (1949).

(3) L. B. Magnusson and J. R. Huizenga, paper presented before the Division of Nuclear Chemistry, XII International Congress of Pure and Applied Chemistry, New York, September, 1951.

(4) D. Cohen and J. C. Hindman, manuscript in preparation.

(5) J. C. Sullivan and J. C. Hindman, manuscript in preparation.

where E' is defined by

$$E' = E^\circ - \frac{RT}{F} \ln \gamma^3{}_{\mathrm{H}^+}\gamma^{1/2}{}_{\mathrm{H}_2} \frac{\gamma\mathrm{Np(V)}}{\gamma\mathrm{Np(IV)}} + E_\mathrm{L} \quad (3)$$

E_L is the unknown liquid junction potential which is assumed to be small. The total neptunium concentration in the cell was approximately 0.01 molar. E', as defined by equation (3), is the formal potential of the cell with the hydrogen gas at one atmosphere pressure, the hydrogen ion concentration at unity and the two neptunium ion concentrations equal and small.

The vapor pressures of molal perchloric acid used are listed in a previous paper.[1]

The results of the first series of measurements are shown in Table I. The couple was found to be reversible at the platinum electrode at the three temperatures, 25, 35 and 47°. At 47°, equilibrium was reached in about 15 minutes, just about the time necessary for the cell to come to temperature equilibrium in the bath. At 35° equilibrium was reached in an hour, and at 25°, it took approximately four hours for equilibrium to be established. Once equilibrium was reached, the potential held constant for 15 hours. These equilibrium times are those required for the initial mixtures to come to equilibrium. As additional aliquots were added the time required for equilibrium to be established was approximately cut in half. This is shown in Fig. 1 which is a plot of e.m.f. against time for the first four neptunium ratios at 25°. The time required for equilibrium to be reached was independent of whether the neptunium mixtures were freshly prepared or had been left to stand for some weeks before insertion into a cell. This suggests that a surface reaction at the electrode is involved.

TABLE I

E.M.F. OF THE CELL: Pt:H_2:$HClO_4$:$HClO_4$, Np(IV), Np(V):Pt 1.0 *m* $HClO_4$ AT VARIOUS TEMPERATURES

	25.05°		35.35°		47.40°	
Np(V)/ Np(IV)	$-E$, volt	$-E'$, volt	$-E$, volt	$-E'$, volt	$-E$, volt	$-E'$, volt
0.3896	0.7154	0.7387	0.6863	0.7108	0.6516	0.6780
.7801	.7329	.7383	.7075	.7111	.6707	.6780
1.171	.7444	.7394	7163	7116	6825	6785
1.560	.7518	.7396	.7237	.7124	.6911	.6792
2.117	.7581	.7379	.7318	.7116	.6990	.6787
2.498	.7631	.7386	.7367	.7121	.7042	.6793
3.120	.7689	.7389	.7419	.7113	.7099	.6789
E' Av.	0.7388 ±0.0005		0.7115 ±0.0005		0.6786 ±0.0005	

It is of some interest to note that the behavior of the Np(IV)–Np(V) couple is not markedly different from other systems in which there is a change in the number of oxygens attached to the cations. Extensive work[6–9] has been done on the vanadium couples. Coryell and Yost[6] have reported that a trace of ferric chloride had to be added to the system in order to obtain reproducible results for the potential of the VO^{++}–VO_2^+ couple in hydrochloric acid at acid concentrations above 0.25 *M*. Carpenter[7] studied this couple in perchloric acid and found his potential measurements to be constant and reproducible. Hart and Partington[8] studied this couple in both sulfuric and hydrochloric acids. They reported that equilibrium values were reached in two to four hours without the use of a potential mediator. With their more dilute vanadium solutions, equilibrium was reached only after the second day of measurements. Their vanadium concentrations ranged from 0.03 to 0.0007 molar. From their sketch of the apparatus one can estimate that the inert platinum electrode is fairly large, about 10 to 20 sq. cm. Neither Yost nor Carpenter gave any information as to the size of the inert electrode.

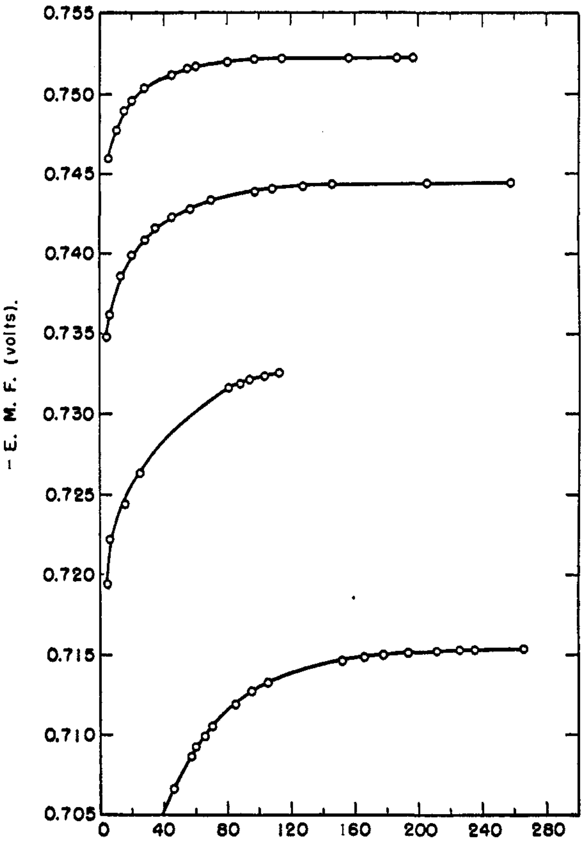

Fig. 1.—Plot showing time required for equilibrium to be established after addition of successive aliquots of neptunium (V) to a Np(IV)–Np(V) mixture. Lower curve is initial mixture.

Jones and Colvin[9] measured the V^{+++}–VO^{++} couple in sulfuric acid, and at vanadium concentrations of 0.2 molar they obtained constant and reproducible potential readings within an hour. However, with cells containing lower concentrations of vanadium, they had more difficulty in obtaining reproducible potential readings. It is possible that this was caused by the small measuring electrode they used; only 0.5 cm.^{2}.

The oxidation potential of the MoO^{+++}–MoO_2^{++} couple was studied by Tourky and El Shamy,[10] who used a measuring cell similar to the one described by Hart and Partington.[8] They obtained a constant potential at 30° within a few hours.

It appears probable that a large inert measuring electrode is necessary for measuring the potentials of couples in which there is a change in the number of oxygens attached to the cations.

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(6) C. D. Coryell and D. M. Yost, THIS JOURNAL, **55**, 1909 (1933).

(7) J. E. Carpenter, *ibid.*, **56**, 1847 (1934).

(8) A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1532 (1940).

(9) G. Jones and J. H. Colvin, THIS JOURNAL, **66**, 1563 (1944).

(10) A. R. Tourky and H. K. El Shamy, *J. Chem. Soc.*, 140 (1949).

In an effort to throw some light on the effect of the electrode surface a few preliminary experiments were carried out with different measuring electrodes; bright platinum, platinized platinum and gold. The data are summarized in Table II.

TABLE II

E.M.F. OF THE CELL: Pt:H_2:$HClO_4$:$HClO_4$, Np(IV), Np(V):Pt 1.0 *m* $HClO_4$ AT 25° WITH DIFFERENT MEASURING ELECTRODES

	Np(V)/ Np(IV)	$-E$, volt	$-E'$, volt
Bright platinum	1.852	0.7561	0.7395
	2.778	.7664	.7394
	3.704	.7741	.7396
Platinized platinum	0.463	.7203	.7392
	0.926	.7380	.7391
Gold	1.852	.7557	.7389
	3.704	.7749	.7404
	4.630	.7808	.7406
	5.556	.7860	.7412

Bright and platinized platinum electrodes gave essentially the same results, indicating that if it were an effect of surface area the bright platinum electrode was sufficiently large. The gold electrode (of approximately the same surface area as the bright platinum electrode) gave somewhat different results. As can be seen from Table II the formal potential is somewhat dependent on the ratio of Np(V) to Np(IV). The average values are, however, in general agreement with those obtained at platinum surfaces. In the case of the gold electrode, however, the potential equilibrium was established more rapidly. The initial mixture was at equilibrium within two hours and successive mixtures came to equilibrium very rapidly; within five to ten minutes. Although these experiments support the view that the condition of the electrode surface is important, further investigation is required before the factors involved can be definitely determined.

Attempts were made to measure the couple at lower neptunium concentrations. At a total neptunium concentration of 0.0025 molar, precise measurements could not be made although even at this low concentration the equilibrium potentials were within a few millivolts of one another. At neptunium concentrations of 0.007 molar or above highly reproducible results were obtained.

From the data in Tables I and II, the formal potential for this couple is -0.7391 volt at 25°, with an average deviation of 0.5 millivolt. The value for the change of potential with temperature is 0.00265 volt/degree for the 25 to 35° temperature interval and 0.00273 volt/degree for the 35 to 47° interval. From the 25° value of the formal potential and its temperature dependence one calculates for reaction (1) that $\Delta\bar{H}$ is 35.6 ± 0.3 kcal. and $\Delta\bar{S}$ is 62.3 ± 1 e.u. The uncertainties in these values are assigned on an estimated limit of accuracy of ±1 millivolt for the formal potential. The value for the partial molal heat change obtained by Magnusson and Huizenga[3] was 35.3 ± 0.3 kcal., in very good agreement with the value obtained in the present work. The agreement for the formal potential of the couple is not as good. Changing their molar potential to the molal value, one gets -0.7422 v., a difference of three millivolts from the value obtained in the present work.

TABLE III

VALUES OF ΔF, ΔH AND ΔS, AT 25° IN 1.0 *m* $HClO_4$ FOR THE GIVEN REACTION

Reaction	$\Delta\bar{F}$, kcal.	$\Delta\bar{H}$, kcal.	$\Delta\bar{S}$, e.u.
$Np^{+3}(aq) + H^+ \rightleftarrows Np^{+4}(aq) + {}^1/_2H_2$	3.58	− 5.7	−31.2
$Np^{+4}(aq) + 2H_2O \rightleftarrows NpO_2^+(aq) + 3H^+ + {}^1/_2H_2$	17.04	35.6	62.3
$NpO_2^+(aq) + H^+ \rightleftarrows NpO_2^{++}(aq) + {}^1/_2H_2$	26.23	28.1	6.4

The Partial Molal Heats and Free Energies of Formation of Neptunium Ions.—Combining the present measurements with those previously reported[1] values of $\Delta\bar{S}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ for the reactions involving the neptunium ions have been calculated. These are summarized in Table III.

The partial molal heats of formation of the neptunium ions can be computed from the data in Table III and the partial molal heat of formation of Np^{+4} (aq) calculated by Westrum and Eyring[11] from the heat of solution of neptunium metal in 1.5 *M* HCl. The data given in Table IV were calculated on this basis after applying a small correction (0.3 kcal.) to convert from HCl to $HClO_4$.[12]

TABLE IV

PARTIAL MOLAL HEATS AND FREE ENERGIES OF FORMATION FOR NEPTUNIUM IONS IN 1.0 *m* $HClO_4$ AT 298°K.

Reaction	$\Delta\bar{H}$, kcal./mole	$\Delta\bar{F}$, kcal./mole
$Np° + 3H^+ = Np^{+3}(aq) + 3/2\ H_2(g)$	−126.9	−126.3
$Np° + 4H^+ = Np^{+4}(aq) + 2H_2(g)$	−132.6	−122.7
$Np° + 2H_2O(l) + H^+ = NpO_2^+(aq) + 5/2\ H_2(g)$	− 97.0	−105.7
$Np° + 2H_2O(l) + 2H^+ = NpO_2^{++}(aq) + 3H_2(g)$	− 68.9	− 79.5

In order to calculate the partial molal free energies of formation for the ions, it is necessary to estimate values for the entropy of the metal and the entropy of one of the ions. In the absence of experimental data, the entropy of neptunium metal will be taken as equal to that of uranium metal[13] (12 e.u.). Estimates of entropies of the ions of these heavy elements have in general been based either on the value of the entropy of Gd^{+++} or on the value of the entropy of the uranyl ion,[14] UO_2^{++}, (−17 e.u.). Extrapolation from the uranyl entropy would appear to be less satisfactory than from the Gd^{+++} entropy in view of the complex nature of the uranyl ion. The entropy of Gd^{+3} as reported by Powell and Latimer[15] is −43 e.u. Using this value and making appropriate corrections

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(11) E. F. Westrum, Jr., and L. Eyring, THIS JOURNAL, **74**, 2045 (1952).

(12) L. Brewer, L. Bromley, P. W. Gilles and N. Lofgren, Paper 6.40, "The Transuranium Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(13) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 146-147.

(14) L. V. Coulter, K. S. Pitzer and W. M. Latimer, THIS JOURNAL, **62**, 2845 (1940).

(15) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

for mass difference, radius difference,[12] and magnetic entropy difference, we calculate $S_{\mathrm{Np}^{+3}} = -37$ e.u. The entropy change in going from 1 *m* perchloric acid to the infinitely dilute solution is neglected. Combining these entropies with the entropy for hydrogen[16] we obtain

$$\mathrm{Np}^{\circ} + 3\mathrm{H}^{+} = \mathrm{Np}^{+3}(\mathrm{aq}) + 3/2\mathrm{H}_2 \quad \Delta S = -2.2 \text{ e.u.} \quad (4)$$

corresponding to a free energy change for the reaction of −126.3 kcal. per mole of neptunium. This corresponds to an E' for the Np^0–Np^{+3} couple of +1.83 volts. The partial molal free energies of formation of the other neptunium ions are given in Table IV.

Entropies of Neptunium Ions.—Entropy values for the neptunium ions, calculated using the entropy of Gd^{+3} to be −43 e.u. are given in Table V. Also, included in this table for comparison are the published entropies for uranium and plutonium ions.[17] These plutonium entropies are corrected for $S_{\mathrm{Gd}^{+3}} = 43$ and for estimated magnetic entropy difference.

The entropies for the Np^{+3}(aq) and Np^{+4}(aq) ions fit smoothly into the general scheme. The entropies of the ions of the +5 and +6 oxidation states, however, vary considerably more than would be expected from, for example, the small differences in crystallographic radius found in isomorphous compounds of the $\mathrm{XO_2}^{++}$ ions. The entropy of $\mathrm{PuO_2}^{+}$ estimated by Brewer[12] from entropy differences of simple +1 and +2 ions must be too positive. These observations emphasize the fact that the oxygenated ions of these heavy elements cannot be treated as simple singly and doubly charged ions.

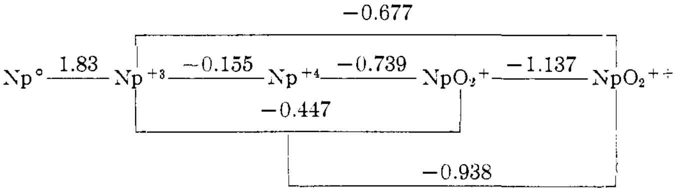
TABLE V

ENTROPIES OF URANIUM, NEPTUNIUM AND PLUTONIUM IONS AT 25°

Ion	Uranium	Neptunium	Plutonium
X^{+3}	-31^a	−37	-39^a
X^{+4}	-78^a	−84	-87^a
$\mathrm{XO_2}^{+}$		− 4	$+6^c$
$\mathrm{XO_2}^{++}$	-17^b	−13	-26^a

[a] Connick and McVey,[17] corrected. [b] Coulter, Pitzer and Latimer.[14] [c] Brewer, *et al.*[12]

Oxidation Potential Scheme.—The results of the measurements on the three neptunium couples[1] can be summarized by giving a formal potential scheme for the ions in 1.0 *m* $\mathrm{HClO_4}$ at 25°. The calculated value of the Np^0–Np^{+3} couple is included to complete the scheme.



CHICAGO 80, ILLINOIS

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(16) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(17) R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

The Preparation and Some Properties of Chromic Phosphate[1]

BY ARTHUR T. NESS, ROBERT E. SMITH AND ROY L. EVANS

RECEIVED SEPTEMBER 27, 1951

Chromic phosphate hexahydrate is best prepared using violet solutions of chromic salts. Complete dehydration of the hexahydrate is attained after ignition for one hour at 800° or above. Heating hydrated or anhydrous chromic phosphate in air or oxygen at temperatures of 300–800° resulted in appreciable decomposition with oxidation to form chromium trioxide; no oxidation occurred on heating *in vacuo*.

An *in vivo* study of the phagocytic function of the reticuloendothelial system led to the choice of chromic phosphate[2] for a chemically inert and non-toxic[3] substance to be administered to animals as a radioactive (P^{32}) colloidal aqueous suspension.

The conditions for the synthesis of pure chromic phosphate have been investigated sparsely[4] and without attention to the well known and singularly strong tendency of trivalent chromium to form complexes in aqueous solution. Our first attempts to prepare chromic phosphate[2] gave products of uncertain composition and yield; the commercial samples of the chromic nitrate and chromic sulfate used were both green, friable, non-crystalline materials which dissolved slowly in water by a process of gradual disintegration and dispersion to give apparently homogeneous green solutions. The nitrate contained 30.3% chromium as compared to 13.0% Cr in the violet, crystalline $\mathrm{Cr(NO_3)_3{\cdot}9H_2O}$. Aged, green solutions of chrome alum also were unsatisfactory for the preparation of chromic phosphate.

Aqueous solutions of violet chrome alum and chromic sulfate gradually become green, violet chromic chloride and chromic nitrate solutions remain violet, and green chromic chloride solutions become violet. The color changes are accompanied by *p*H variations, and the green solutions contain chromium in the form of ionic and non-ionic com-

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 119th Meeting, Cleveland, Ohio, April, 1951.

(2) H. B. Jones, C. J. Wrobel and W. R. Lyons, *J. Clin. Invest.*, **23**, 783 (1944).

(3) K. Akatsuka and L. T. Fairhall, *J. Ind. Hyg.*, **16**, 1 (1934).

(4) (a) H. T. S. Britton, *J. Chem. Soc.*, 614 (1927); (b) A. F. Joseph and W. N. Rae, *ibid.*, **111**, 196 (1917); (c) L. J. Cohen, THIS JOURNAL, **29**, 1194 (1907); (d) H. Schiff, *Z. anorg. Chem.*, **43**, 304 (1905).