The difference between ΔH_a and the corresponding heat of solution of PrO_x yields the heat of oxidation of $PrO_{1.5}$ to give PrO_x. The sum of the heat of formation of $PrO_{1.5}$ and the heat of oxidation gives the heat of formation of PrO_x. These calculated values are shown in Table III.

Acknowledgments.—The authors are grateful to Doctors E. D. Guth and C. L. Siegläff for help in the preparation of some of the calorimeter samples.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Nature of Niobium(V) in Hydrochloric Acid Solution[1]

BY J. H. KANZELMEYER, JACK RYAN AND HARRY FREUND

RECEIVED OCTOBER 31, 1955

The nature and dependency of niobium species in solutions of varying hydrogen ion, chloride ion and hydrochloric acid are studied. Only three soluble chloride species appear to exist to any extent in these systems: $Nb(OH)_2Cl_4^-$ in high chloride and high hydrogen ion; $Nb(OH)Cl_3^+$ in extremely high hydrogen ion and low chloride and $Nb(OH)_2Cl_3$ at hydrogen ion and chloride ion in the range of three molar. Decreasing hydrogen ion at high chloride results in colloid formation.

Niobium and tantalum are unique in the very small number of their water-soluble compounds. In order to produce water-soluble compounds of niobium it is necessary to use complexing agents and one of the more important of these is chloride. It has been found that anhydrous niobium pentoxide dissolves in highly concentrated hydrochloric acid to the extent of about four grams of the pentoxide per hundred milliliters.[2]

Spectrophotometric work on niobium(V) solutions in hydrochloric acid of varying concentration has indicated the presence of several species of niobium.[3] The species present in concentrated hydrochloric acid showing an absorption maximum at 281 mμ was used as the basis of a spectrophotometric method for the determination of niobium. Several species have been postulated for niobium in hydrochloric acid but little work has been done to actually prove the existence of any of these in solution.[4-10] In order to place the colorimetric determination on a firm basis and to further study the effect of chloride ion and hydrogen ion variation on the niobium species a study has been made of the nature of the species of niobium present in systems containing hydrogen ion and chloride ion.

The investigation of this system has been carried out primarily by spectrophotometric methods. The complex ion present in concentrated hydrochloric acid has been identified by comparison of the absorption spectrum of this solution to that of a solution of a salt of this ion in an organic solvent. Other species have been characterized by comparison of absorption spectra, ion exchange work and by quantitative study of the effect of independently varying hydrogen ion and chloride ion activity.

Experimental

Spectral Measurements.—All absorbance measurements were made by use of a Beckman Model DU spectrophotometer using matched 1.00-cm. fused silica cells. A hydrogen discharge lamp was used as the source of radiation for all measurements below 340 mμ. All absorbance measurements were made with a reagent blank in the null cell and net absorbances were recorded. Spectral measurements were made at 5 mμ intervals except in the region of peaks at which narrower intervals were used.

Niobium Solutions.—Niobium pentoxide obtained as "Columbium Pentoxide" from A. D. MacKay, 198 Broadway, New York 7, N. Y., was fused with potassium pyrosulfate in the ratio of 1 gram of the pentoxide to 3 grams of the pyrosulfate. The resulting melt was cooled, ground and taken up in 1:1 sulfuric acid. The resulting milky solution was neutralized with concentrated ammonium hydroxide. The hydrous niobium pentoxide was separated and washed by centrifugation, slurried with concentrated hydrochloric acid and placed in an ice-bath. Hydrogen chloride was passed through the solution for from two to three days in an ice-bath to complete the dissolving of the hydrated pentoxide. The solutions thus prepared contained about 20 g. Nb/liter and were used as stock solutions for more dilute solutions.

Compounds for Spectral Comparison.—The compound reported as Cs_2NbOCl_5 by Weinland and Storz[11] was prepared by their method using solutions saturated with hydrogen chloride at temperatures varying from 45 to −20°. Analysis of the compound agreed with that which was reported but was not considered accurate enough to distinguish between Cs_2NbOCl_5 and $Cs_2Nb(OH)_2Cl_5$.

The compound $(C_2H_5)_4NNb(OH)_2Cl_4$ was prepared by mixing 1.0 g. of tetraethylammonium chloride dissolved in a minimum amount of 0° saturated hydrochloric acid with a solution containing 0.5 g. Nb in 25 ml. also in 0° saturated hydrochloric acid. The compound precipitated in the form of fine white crystals which were filtered and washed with 0° saturated hydrochloric acid on a sintered glass filter. The compound was dried over anhydrous magnesium perchlorate and analyzed for niobium, chloride and nitrogen. For niobium the compound was moistened, ignited and weighed as Nb_2O_5. Nitrogen was determined by the micro Dumas method, and chloride was determined by Volhard titration. The rest of the formula of the compound was determined by difference and valence requirements.

Niobium oxychloride ($NbOCl_3$) was prepared by two methods. The first method was the thermal decomposition

---

[1] Presented before the Northwest Regional Meeting of the American Chemical Society, Eugene, Oregon, June, 1955. Published with the Approval of the Monographs Publication Committee, Oregon State College, as Research Paper 294, School of Science Department of Chemistry.

[2] Josef Wernet, *Z. anorg. allgem. Chem.*, **267**, 213 (1952).

[3] J. H. Kanzelmeyer and Harry Freund, *Anal. Chem.*, **25**, 1807 (1953).

[4] R. E. Elson, U. S. Atomic Energy Commission Report No. UAC-712 (1953).

[5] J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, *Anal. Chem.*, **26**, 1045 (1954).

[6] G. Gruben and Hans L. Gruben, *Z. Elektrochem.*, **44**, 771 (1938).

[7] E. H. Huffman, G. M. Iddings and R. C. Lilly, THIS JOURNAL, **73**, 4474 (1951).

[8] E. H. Huffman and G. M. Iddings, *ibid.*, **74**, 4714 (1952).

[9] K. A. Kraus and G. E. Moore, *ibid.*, **71**, 3855 (1949).

[10] K. A. Kraus and G. E. Moore, *ibid.*, **73**, 2900 (1951).

[11] R. F. Weinland and Ludwig Storz, *Z. anorg. allgem. Chem.*, **54**, 223 (1907).

TABLE I

ANALYSIS OF TETRAETHYLAMMONIUM COMPOUND

	Nb, %	Cl, %	N, %
Theoretical for			
$(C_2H_5)_4NNb(OH)_2Cl_4$	23.30	35.54	3.51
$(C_2H_5)_4NNb(O)Cl_4$	24.39	37.22	3.67
$(C_2H_5)_4NNb(OH)Cl_5$	22.26	42.48	3.35
Experimental for			
Sample 1	23.66	35.03	3.40
2	23.62	35.05	
3	23.51	34.92	
Averages	23.59	35.00	3.40

of the cesium salt under reduced pressure. The second was the direct chlorination of niobium pentoxide mixed with carbon. The chlorinating agent was chlorine gas and the chlorination mixture consisted of sugar charcoal and excess niobium pentoxide.

Organic Solvents.—Diethyl ether was dried and stored over freshly cut sodium metal.

1,4-Dioxane was dried by refluxing with sodium metal, distilling, and storing over freshly cut sodium metal.

Electromigration.—The electromigration was carried out on filter paper strips 15 cm. long and 1.5 cm. wide held in the shape of an inverted V over a glass rod support. The ends of a paper dipped in a solvent reservoir and the entire setup was enclosed in a glass cover to keep a constant vapor pressure of hydrogen chloride and water. Potential was applied by means of a regulated 300 volt power supply through a voltage divider. Two niobium spots were placed equidistant from the center of the paper to eliminate the effect of capillary action brought about by the evaporation of solvent from the paper. The algebraic difference between the movement of the two spots was then taken as a measure of the actual migration of the niobium. In all cases of niobium in concentrated hydrochloric acid the niobium was found to migrate toward the positive electrode.

Ion-exchange Columns.—All ion-exchange columns were 30 cm. in length. Cation-exchange resin was Dowex 50 and the anion-exchange resin was Amberlite IRA 400.

Dependence of Absorption Spectra on Hydrogen Ion and Chloride Ion Activities.—For most spectrophotometric investigations experimental conditions are so adjusted that ordinary concentration units may be used in place of activities. The stabilities of the complexes under consideration here require high effective concentrations of hydrochloric acid for existence and the reacting particles make up too large a fraction of the solution to follow ideal behavior predicated upon their relative isolation. Thus the system is best described in terms of the activities and not concentrations of hydrogen and chloride ions.

Two series of solutions were prepared at an ionic strength of 10.5 ± 0.1. By using lithium chloride–hydrochloric acid mixtures the chloride level was held constant while the hydrogen ion activity varied. The data of Hawkins[12] suggest that activity coefficients in lithium chloride and hydrochloric acid of the same concentration should be similar. This would only be approximately true at the high ionic strengths since HCl is associated to a higher degree than LiCl.

By using hydrochloric acid–perchloric acid mixtures a second series of solutions were prepared in which the hydrogen ion activity was held constant while the chloride activity varied. The only data available on the variation of activity coefficients in such solutions is at an ionic strength of one.[13] Under these conditions a change from approximately 0.1 to 0.5 M caused a negligible effect on its activity coefficient.

The activity of solutions containing varying amounts of H^+ and Cl^- was carried out by measuring the e.m.f. developed by the cell

$$\text{Pt, } H_2 \text{ (1 atm.) } H^+ \, Cl^- \, \text{AgCl, Ag}$$

The temperature was maintained at 25.0° and the ionic strength at 10.5 ± 0.1 using the series of solutions described above. Under these conditions it was assumed in the first case the hydrogen ion and in the second case the chloride ion activities remained essentially constant. Then by calculating the mean ionic activity of HCl at 25° and ionic strength 10.5 from the data of Akerlof and Teare,[14] and measuring the cell potentials the apparent activities of Cl^- and H^+ could be evaluated. While these absolute activities are in gross error their relative value should be meaningful.

The same solutions used for the activity measurements were employed as solvents for the spectrophotometric work. A standard solution of niobium was prepared which analyzed 6.59 mg. Nb/ml. An aliquot of 0.04 ml. of this solution was introduced into 50.00-ml. volumetric flasks in a standardized manner from a 0.1-ml. pipet and diluted to the mark with the previously mentioned LiCl-HCl and $HClO_4$-HCl solutions. Spectral absorption measurements were made at 5 mμ intervals from 215 to 300 mμ and at 310, 320, 340 and 360 mμ. A portion of each sample was conserved for subsequent analysis of the ion whose concentration was varied. Chloride was determined argentometrically, using a potentiometric end-point. Acid concentrations were determined by titration with dilute standardized sodium hydroxide to the phenolphthalein end-point. The absorption curves are shown in Figs. 1 and 2.

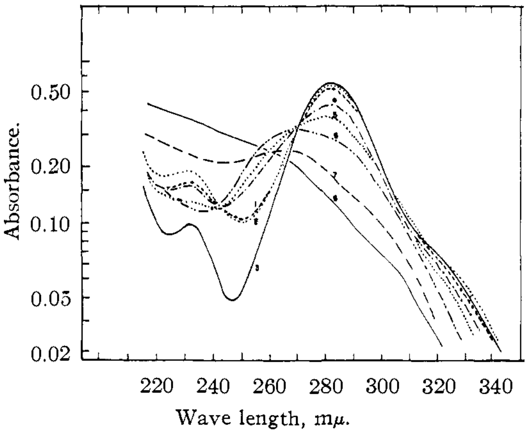

Fig. 1.—Absorption curves for niobium (5.68×10^{-5} M) at various chloride levels (M). Hydrogen ion maintained at 10.5 M with $HClO_4$: (1) 8.62; (2) 5.81; (3) 1.56; (4) 0.217; (5) 0.109; (6) 0.047; (7) 0.0054; (8) 0.0038.

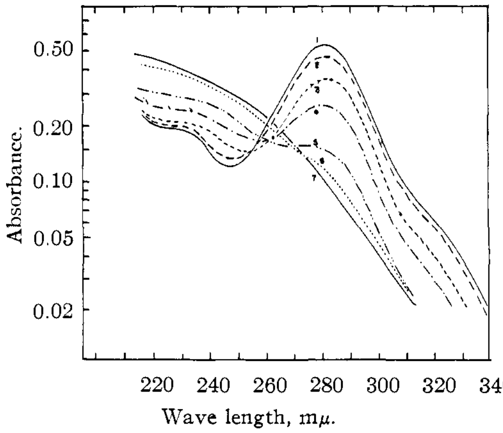

Fig. 2.—Absorption curves for niobium (5.68×10^{-5} M) at various hydrogen ion levels (M). Chloride maintained at 10.5 M with LiCl: (1) 9.86; (2) 1.826; (3) 0.5579; (4) 0.2777; (5) 0.1002; (6) 0.0595; (7) 0.01823.

Results

The chloride species of niobium in concentrated hydrochloric acid was found to follow Beer's law very well in the range of 1–10 μg. Nb/ml.[3] This and

---

[12] J. E. Hawkins, THIS JOURNAL, **54**, 4480 (1932).

[13] P. C. Murdock and R. C. Barton, *ibid.*, **75**, 4074 (1953).

[14] Gosta Akerlof and J. W. Teare, *ibid.*, **59**, 1855 (1937).

the high solubility of niobium in this solvent in contrast to many other aqueous solvents indicate the presence of an ionic complex. Electromigration studies indicated that this was an anion. Further work showed that niobium was removed completely from concentrated hydrochloric acid solution by an anion-exchange column but was unaffected by passage through a cation-exchange column.

In a study of the chloride complex of iron(III) in concentrated hydrochloric acid[15] the complex ion was shown to be $FeCl_4^-$ by comparison of the absorption spectrum of the acid solution to that of $KFeCl_4$ dissolved in an organic solvent. In the same manner antimony(V) in concentrated hydrochloric acid[16] was shown to be in the form $SbCl_6^-$ by comparison of the absorption spectrum to that of $H_3OSbCl_6 \cdot H_2O$ in an organic solvent. In this study a similar procedure was used to characterize the chloride complex of niobium present in concentrated hydrochloric acid.

No inert solvent could be found for the cesium compound which had been prepared, but dissolving of the compound in hydrochloric acid of varying concentration and measuring of the absorption curves immediately indicated very rapid establishment of equilibrium between species. The compound $(C_2H_5)_4NNb(OH)_2Cl_4$ was found to be soluble in 1,4-dioxane and the absorption curve was measured in this solvent. Figure 3 is a comparison of the absorption curve of this solution to that of a solution of niobium in concentrated hydrochloric acid showing the same species to be present. Log absorbance is plotted in Fig. 3 so that concentration will not affect the shape of the curves. It also appears that the molar extinction coefficient is about the same for niobium in the form of the salt dissolved in dioxane as in the solution in concentrated hydrochloric acid. Thus the niobium complex present in concentrated hydrochloric acid solution is presumed to be $Nb(OH)_2Cl_4^-$ and is the ion responsible for the absorption peak at 281 mμ on which the ultraviolet spectrophotometric method for the determination of niobium is based.

The curves in Fig. 2 show the disappearance of the 281 mμ peak as the hydrogen ion concentration is lowered. If the curves are analyzed in a manner similar to the method used by Neumann[16] it is possible to gain insight into species other than $Nb(OH)_2Cl_4^-$. Since the absorption curve of niobium in strong hydrochloric acid in the range of 11 to 13.4 molar showed no change and was essentially the same as for curve 1, Fig. 2, the assumption was made that the absorption is due to the pure $Nb(OH)_2Cl_4^-$. Further it was assumed that under any circumstance it would be the only species absorbing at 330 mμ. The subtraction of the absorbance due to $Nb(OH)_2Cl_4^-$ as measured by the absorbance at 300 mμ, yields net curves for the spectra of other species. A marked similarity exists between the net absorbance curve (plotted as log absorbance *vs.* wave length) and the absorption curve of a slightly basic solution containing niobium in the form of a colloid and showing a slight Tyndall effect. This suggests strongly that a colloid is being formed as the hydrogen ion is decreased.

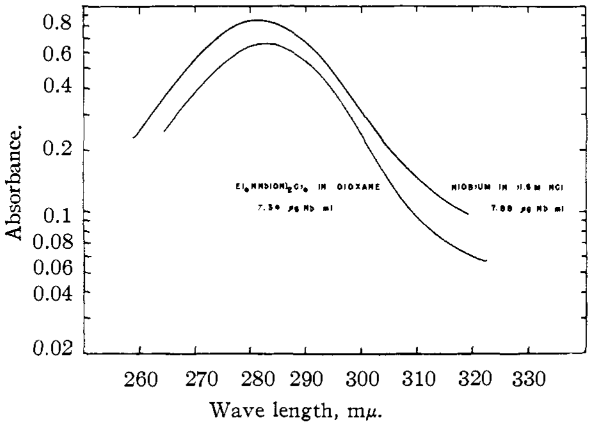

Fig. 3.—Comparison of spectrum of niobium in hydrochloric acid with the tetraethylammonium salt in dioxane.

The reaction involved in the formation of the $Nb(OH)_2Cl_4^-$ from lower species may be considered as

$$Nb(OH)_{2+m}Cl_{4-n}^{-1+n-m} + mH^+ + nCl^- \longrightarrow Nb(OH)_2Cl_4^- + mH_2O$$

If the activities of the niobium species are considered equal to the concentrations and if the activity of water is taken as unity the following is obtained

$$\log K_o = \log [Nb(OH)_2Cl_4^-] - \log [Nb(OH)_{2+m}Cl_{4_{4-n}}^{-1+n-m}] - m \log [a_{H^+}] - n \log [a_{Cl}^-]$$

Since the chloride ion concentration was held constant this may be included in the constant term leaving three variables. If it is assumed that only two species are present, a plot of log $([Nb(OH)_2Cl_4^-]^- - \log [Nb(OH)_{2+m}Cl_{4-n}^{-1+n-m}])$ can be made *versus* log (apparent activity of hydrogen ion) to give a slope of m. In doing this the absorption at 281 mμ, corrected for the absorbance of the other species, is a measure of the amount of $Nb(OH)_2Cl_4^-$ present. The amount of the other species was then obtained by difference since the total niobium was known. This type of plot gives a slope of 1.24. If, as has been shown, the species being formed as the hydrogen ion is decreased is a colloid, then this is not the proper method of plotting. Since the activity of a solid remains constant a plot of log $[Nb(OH)_2Cl_4^-]$ *versus* a log a_{H+} should be made. Such a plot proves to be a good straight line with a slope equal to 0.93, thus indicating a change of one hydrogen ion. Since holding the chloride ion concentration constant does not prevent loss of chloride ions, the reaction forming an insoluble colloid is probably

$$Nb(OH)_2Cl_4^- + H_2O \longrightarrow Nb(OH)_3Cl_2 + H^+ + 2Cl^-$$

below about two molar hydrogen ion concentrations when the chloride ion is held at 10.5 molar.

A similar study was made of the effect of chloride variation at high hydrogen ion concentration. In this the hydrogen ion concentration was maintained at 10.5 molar and the ionic strength held constant by means of perchloric acid. Subtraction of the contribution of the $Nb(OH)_2Cl_4^-$ from the total absorption curve results in curves showing an absorption peak at 260 mμ. These are shown in Fig. 4.

---

[15] H. L. Friedman, THIS JOURNAL, **74**, 5 (1952).

[16] H. M. Neumann, *ibid.*, **76**, 2611 (1954).

A plot of ($\log[Nb(OH)_2Cl_4^-] - \log[II]$) *versus* log (apparent chloride activity) also yields a good straight line with a slope of 0.95. The loss of one chloride is thus indicated. One would expect that $Nb(OH)_2Cl_3$ would be the species formed. This could be considered a hydrate of $NbOCl_3$ and as such would be expected to show an absorption curve similar to that of $NbOCl_3$. Comparison of these 260 mμ peaks to the absorption curve of $NbOCl_3$ in diethyl ether showed no similarity.

It was then postulated that this species showing an absorption peak at 260 mμ might be a cation such as $NbOHCl_3^+$. This appears reasonable in that the extremely high hydrogen ion activity present in 10.5 molar perchloric acid might allow the reaction to be $Nb(OH)_2Cl_4^- + H^+ \rightarrow NbOHCl_3^+ + Cl^- + H_2O$ on decrease of chloride ion activity. In order to show that such a reaction was taking place a cation-exchange column was used to show the presence of a positive ion. Since both the anion $Nb(OH)_2Cl_4^-$ and the other species are present in the same solution it is not to be expected that all of the niobium would be removed from the solution even if the second species were a cation.

A solution of niobium 10.5 molar in perchloric acid and 0.025 molar in chloride was passed through a cation-exchange column which had first been washed with this solvent. Such a solution had a strong absorption maximum at 260 mμ, which was removed almost completely by the cation exchange resin Dowex-50. These results support the postulated cationic nature of the species absorbing at 260 mμ.

As yet no explanation has been given for the absorption curves obtained for solutions of niobium in hydrochloric acid of about 4–6 molar. These solutions show no absorption maxima in the range which can be studied, but they definitely do not appear to be colloidal. Anion-exchange studies[7] show the anion-exchange distribution coefficient to decrease from about 1200 to about 20 in going from 12 to 6 molar hydrochloric acid. From this it appears that the species present in 6 molar hydrochloric acid has a zero or positive charge since a minus one charged species is present in 12 molar hydrochloric acid. It is to be expected then that the species formed in decreasing hydrochloric acid concentration below 12 molar might be $NbOCl_3$ or a hydrate of it. This is sustained by the marked similarity of the spectrum of $NbOCl_3$ in diethyl ether to those of niobium in 4.2 and 6.1 molar hydrochloric acid.

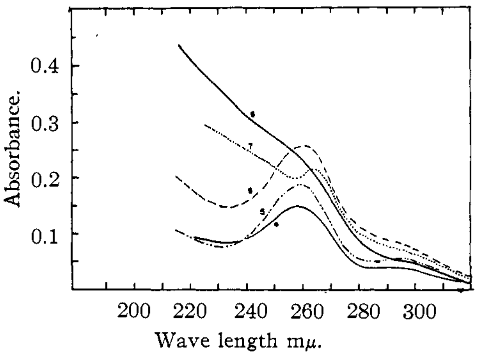

Fig. 4.—Net absorbance curves after subtracting species I, 281 mμ from curves in Fig. 1. Curve numbers are the same as Fig. 1.

The over-all mechanism can now be shown. When chloride is decreased by decreasing hydrochloric acid below 12 molar the reaction $Nb(OH)_2Cl_4^- \rightarrow Nb(OH)_2Cl_3 + Cl^-$ takes place but at high hydrogen ion activity, $Nb(OH)_2Cl_3 + H^+ \rightarrow NbOHCl_3^+ + H_2O$. Lowering of hydrogen ion below about 2 molar at high chloride ion concentration causes colloid formation probably of the type $Nb(OH)_3Cl_2$. It appears that only three soluble chloride containing species of niobium exist to any appreciable extent in the systems studied. These are $Nb(OH)_2Cl_4^-$ in both high chloride and high hydrogen ion concentration, $NbOHCl_3^+$ at extremely high hydrogen ion concentration and low chloride ion concentration, and $Nb(OH)_2Cl_3$ at hydrogen ion and chloride ion concentrations which are both in the range of about 3 molar up to where the $Nb(OH)_2Cl_4^-$ predominates.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Solubility of Silver Sulfate in Sulfuric Acid Media at High Temperatures. Effects on the Silver, Silver Sulfate Electrode[1]

BY M. H. LIETZKE AND R. W. STOUGHTON

RECEIVED FEBRUARY 15, 1956

The solubility of Ag_2SO_4 has been determined in water and in 0.1, 0.5 and 1.0 *m* H_2SO_4 to above 250° in order to evaluate the useful range of the Ag, Ag_2SO_4 electrode in acid solutions. The effects of the increase in solubility with increasing temperature and H_2SO_4 concentration are discussed. Calculated solubilities in H_2SO_4 media based on the decrease in the HSO_4^- acid constant with temperature are compared with the observed values.

In a previous paper[2] the behavior of saturated Ag, Ag_2SO_4 and Hg, Hg_2SO_4 electrodes at high temperatures in H_2SO_4 solutions was described. It was shown that in acid concentrations high enough to repress hydrolysis of the Hg_2SO_4 electrode potentials predicted on the basis of thermodynamic calculations were obtained. However, no attempt was made to define the useful range of either the silver or mercury electrode as limited by the solubility of silver or mercurous sulfate in H_2SO_4 solutions of various concentrations. If, at a given tem-

---

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) M. H. Lietzke and R. W. Stoughton, THIS JOURNAL, **75**, 5226 (1953).