

reaction vessel I was filtered through the filter tube into the previously weighed vessel 2 connected with an ice cooled trap. After having exchanged the filter tube for a gas inlet tube, the vessel was immersed in a water-bath at 20° and evaporated at about 5 mm. in a slow stream of nitrogen. After the evaporation the trap was exchanged for one filled with phosphorus pentoxide, and evacuated at less than 0.5 mm. to constant weight.

For analysis the content of the weighed vessel was dissolved in water and decomposed by slow addition of neutral 10% hydrogen peroxide, boiling finally until the iron tetracarbonyl formed had disappeared completely. To prevent loss by volatilization of iron carbonyl the vessel was connected with a wash bottle containing 0.2 *N* alcoholic potassium hydroxide and a small quantity of hydrogen peroxide. The solution filtered from the iron oxide contains the potassium as carbonate. The carbonate was determined by acidimetric titration. The iron was determined in the residue on the filter and in the contents of the washing bottle.

Fe(CO)₄K₂.—The solution was prepared from 1 ml. = 0.0074 mole Fe(CO)₅ and 40 ml. of a solution containing exactly 0.0074 mole of Ba(OH)₂ and 0.0148 mole of KOH. *Anal.* Calcd. for Fe(CO)₄K₂: Fe, 22.70; K, 31.78. Found: Fe, 22.89, 23.30, 22.73; K, 31.3, 31.45. 1.316 g. of the dry salt was dissolved in 50 ml. of water freed from air and poured under nitrogen into a saturated solution containing 5 g. of mercuric chloride. The mixture was shaken for thirty minutes to complete the reaction, then filtered, washed with water, dilute hydrochloric acid, alcohol and ether (to remove small quantities of iron tetracarbonyl) and dried *in vacuo*, giving 3.4484 g. of the

yellow Fe(CO)₄Hg₂Cl₂. *Anal.* Calcd.: Fe, 8.72; CO, 17.51. Found: Fe, 8.65, 8.63; CO, 17.08, 16.98. Calculating the amount of pure mercuric salt from the found CO value the relation Fe(CO)₄K₂:Fe(CO)₄Hg₂Cl₂ is 1:0.98.

Fe(CO)₄KH.—Prepared from 1.5 cc. of Fe(CO)₅ (excess) and 40 cc. of a solution containing exactly 0.0074 mole of Ba(OH)₂ and 0.0074 mole of KOH. *Anal.* Calcd. for Fe(CO)₄KH: Fe, 26.85; K, 18.80. Found: Fe, 27.35, 26.87; K, 18.89.

The reaction of 0.845 g. of this salt with HgCl₂ yields 2.5716 g. of the mercuric salt. *Anal.* Found: Fe, 8.54; CO, 17.05. In the filtrate from the mercuric salt we determined the HCl by acidimetric titration. The relation Fe(CO)₄KH:Fe(CO)₄Hg₂Cl₂:HCl is 1:0.97:0.92 if the salt is calculated as pure Fe(CO)₄KH. As the salt contains about 5% Fe(CO)₄K₂ this relation is still about 1% nearer to the theoretical amount.

Summary

The dissociation constants of iron tetracarbonyl hydride at 17.5° have been determined to $K_1 = 4 \times 10^{-5}$ and $K_2 = 4 \times 10^{-14}$.

The molar solubility of iron carbonyl hydride at 17.5° is about 1.8×10^{-3} .

The anhydrous salts Fe(CO)₄K₂ and Fe(CO)₄KH (the latter containing about 5% of Fe(CO)₄K₂) have been prepared.

RECEIVED OCTOBER 21, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Disperse Structure of Manganese Oxides and a Magnetic Method for Studying Depolarizer Action in the Leclanché Cell¹

BY P. W. SELWOOD, R. P. EISCHENS,² MARYLINN ELLIS AND KATHRYN WETHINGTON

The object of this work was to explore the possibility of using magnetic methods for the study of chemical changes occurring *in situ* in the dry cell. Manganese is the only paramagnetic constituent in the cell, and the number of unpaired electrons increases as tetravalent manganese is reduced. Consequently it was considered possible to follow the valence changes of the manganese during cell discharge and recovery by observing changes of magnetic susceptibility.

Magnetically dilute tetravalent manganese has three unpaired electrons and a well established, spin-only, magnetic moment of about 3.9 Bohr magnetons. Similarly, manganese in the oxidation states of three and two has magnetic moments of 4.9 and 5.9, respectively. With adequate magnetic dilution the susceptibility at any one temperature is virtually linear with oxidation state.

Unfortunately, the crystalline transition group oxides are so magnetically concentrated that large interactions occur between adjacent paramagnetic ions. Thus, the susceptibility at 25° for crys-

talline *pyrolusite* is 27×10^{-6} , that for the crystalline sesquioxide (*bixbyite*) is 89×10^{-6} , but for the monoxide (*manganosite*) it is only 67×10^{-6} . Furthermore, all these substances show large and uncertain values for the Weiss constant, and, at lower temperatures, wide deviations from the Curie-Weiss law.

These effects eliminate the possibility of using crystalline *pyrolusite* as depolarizer in quantitative magnetic studies. Attention was, therefore, turned to supported oxides, which have been shown to approach high magnetic dilution at moderately low concentration.³

A series of studies on manganese oxides on various supports showed that the oxidation state of supported manganese was determined in part by the crystal structure of the support, and this observation led to the general principle of valence inductivity, as previously described.⁴ It was established that the experiment on the dry cell could be carried out if the manganese depolarizer were supported on high-area titania, in the *rutile* modification.

At this point in the work it was discovered that many laboratory prepared samples of manganese

(1) This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

(2) Present address: The Texas Company, Beacon Laboratories, Beacon, N. Y.

(3) Selwood, Hill and Boardman, *THIS JOURNAL*, **68**, 2055 (1946).

(4) Selwood, *ibid.*, **70**, 883 (1948).

dioxide and practically all natural and commercial samples of manganese dioxide had an astonishing magnetic difference from pure highly crystalline *pyrolusite*. These samples all have high magnetic susceptibilities and are properly considered as magnetically dilute substances. The effect must be related to the attenuated structure possessed by these oxides. The effect has been observed in various other inorganic solids, and appears to offer promise for the structural study of many so-called gels of transition group oxides.

This observation eliminated the necessity for work with supported oxides, fruitful though that study had been. Cells were made with the gel-like manganese dioxides as depolarizers and the magnetic study of such cells was rapidly completed. There are described below, first the magnetic observations on gel-like oxides as compared with highly crystalline samples; and second, the magnetic changes occurring during dry cell discharge. Those oxides of a highly crystalline, magnetically concentrated form we shall continue to designate as "massive" solids in accordance with the terminology used in our earlier papers on supported oxides. Those oxides of an attenuated gel-like structure, as shown by magnetic dilution effects, we shall designate as "disperse" solids.

Preparative Methods⁵

Analytical Methods.—Analyses were performed for total manganese and for active oxygen. Manganese was determined by reaction with standard ferrous sulfate after all of the manganese had been oxidized to permanganate. Solution of the sample was effected by treatment with dilute sulfuric acid containing ferrous sulfate. Oxidation of the manganese from a valence of two to seven was accomplished by sodium bismuthate in nitric acid.

Active oxygen was found by using a known excess of standard ferrous ammonium sulfate in dissolution of the sample. The excess was then titrated with standard permanganate. Active oxygen is then eight times the number of equivalents of ferrous ion oxidized in the dissolution process.

Pyrolusite.—Massive *pyrolusite* was prepared by thermal decomposition of manganous nitrate in accordance with well known procedures.⁶ "Reagent grade" manganous nitrate was recrystallized from water and the crystals were heated to 120–125° until the whole mass appeared on the verge of solidifying. A stream of air was directed over the open evaporating dish to facilitate the removal of oxides of nitrogen and of water vapor. Water was added to the mass, and it was stirred

(5) Magnetic and X-ray methods have been described in earlier papers from this Laboratory.

(6) A comparison of preparations and properties for the solid oxides and hydroxides of manganese will appear in a forthcoming paper by Moore, Selwood and Ellis.

and filtered. The solid was dried at 110° for twenty-four hours in air. It was ground to pass through a 150-mesh sieve and reheated at 150° in air for twenty-four hours. The crystals were next washed with 1:1 nitric acid and finally with water to remove the nitric acid. The acid and wash water should both be boiling for best results. Final drying was done at 160° in air for fifty-two hours. The product was dark gray in color.

Analysis gave the following: Calcd. for MnO_2 : Mn, 63.19; active oxygen, 18.4. Found: Mn, 63.1; active oxygen, 18.3. The X-ray diffraction pattern agreed in detail with the ASTM index cards. The sample appeared to be as pure as any heretofore obtained.

γ (I) Manganese Dioxide.—The preparation so designated was based on the first of three methods given by Glemser.⁷ To a solution of manganous sulfate (50 g. hydrate in a liter of water) there was added 100 ml. of 2 *N* sulfuric acid. The resulting mixture was heated to boiling and 113 g. of ammonium persulfate was added slowly. A black precipitate formed and the supernatant liquid was decanted. Washing was by decantation with temperature of wash liquid 70–80°. This was continued until tests showed that the precipitate was free of sulfate. The precipitate was now filtered and washed with hot water and dried for two days at 60°. Analysis gave Mn, 60.7; "active" oxygen, 16.8. Apparent formula $MnO_{1.95} \cdot 0.25H_2O$. The X-ray diffraction pattern for this preparation was in reasonably satisfactory agreement with that reported by Glemser, as shown.

Reported	<i>d</i> (Å.)	Found	<i>I</i> / <i>I</i> _{max.} Found
3.88		4.03	0.5
2.42		2.42	1.0
2.11		2.12	0.6
..		2.06	.3
1.80		1.83	.1
1.62		1.62	.9
1.42		1.40	.5
1.30	

γ -II Manganese Dioxide.—The second of the three methods given by Glemser was used for a preparation designated by us as γ -(II) MnO_2 . A solution of 36 g. of manganous sulfate hydrate and 24 g. of potassium nitrate in 2.5 l. of water was heated to boiling. Approximately 1 l. of 2% potassium permanganate solution was now added (until the solution acquired a pink color). The supernatant liquid was decanted and the solid was washed four times with 3-l. portions of water. The product was filtered through asbestos, and washed free of sulfate. The brown product was dried for two days at 60°. Analysis yielded a formula $MnO_{1.96} \cdot 0.81H_2O$. The X-ray diffraction pattern was very similar to that for the γ -(I) preparation, although quite diffuse.

(7) Glemser, *Ber.*, **73B**, 1879 (1939).

Gel(I) Manganese Dioxide.⁸—Preparation of a gel form of manganese dioxide was attempted by the hydrolysis of manganese(IV) sulfate. The sulfate was prepared by oxidizing a 55% sulfuric acid solution of manganous sulfate with potassium permanganate. The temperature was kept below 80° because the sulfate decomposes above that temperature in a 55% acid solution. The product was filtered and washed, and hydrolysis was carried out with sodium acetate. The resulting hydrous oxide was filtered, washed and dried at 70° for three days in air. It was very hard, black and shiny, and gave no X-ray pattern. Analysis showed the product to be $\text{MnO}_{1.88} \cdot 0.83\text{H}_2\text{O}$.

Gel II Manganese Dioxide.⁷—Dilute sulfuric acid (1:4) and a 50% solution of sodium permanganate were added slowly to a concentrated solution of manganous sulfate until no more oxide precipitated. The temperature of the solution was kept at about 60° during the reaction. The precipitate was washed by decantation, then filtered and washed free from permanganate and sulfate ion. The product was dried for three days at 60° under vacuum. The sample was brown and soft, and gave only a diffuse X-ray pattern. Analysis showed $\text{MnO}_{1.97} \cdot 0.33\text{H}_2\text{O}$.

Results on Oxides

Magnetic susceptibility data on the several gel-like hydrous oxides and on massive pyrolusite are shown in Table I. Results are shown also on two natural ores. The results on the natural materials are, however, less reliable because these materials always contain a trace of ferromagnetic impurity for which correction must be attempted.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF MASSIVE AND DISPERSE OXIDES

(The data are given in the following order: sample, %Mn, susceptibility $\times 10^6$ at indicated temperature, and susceptibility per gram-atom of Mn at 25°)

Massive *pyrolusite*, 63.1% Mn; $\chi = 27$ (25°), 31 (-80°), 44 (-185°); $\chi_M = 2360$ (25°).

γ -(I), 60.7% Mn; $\chi = 34.8$ (86°), 35.8 (61°), 37.7 (37°), 38.0 (25°), 42.6 (-26°), 46.2 (-56°), 49.0 (-87°); $\chi_M = 3440$ (25°).

γ -(II), 55.0% Mn; $\chi = 45.0$ (25°), 74.3 (-87°), 109 (-171°); $\chi_M = 4490$ (25°).

Gel(I), 55.3% Mn; $\chi = 37.2$ (25°), 46.3 (-87°), 58.2 (-171°); $\chi_M = 3690$ (25°).

Gel II, 59.1% Mn; $\chi = 41.4$ (25°), 62.7 (-87°), 79.1 (-171°); $\chi_M = 3840$ (25°).

African Ore, 56.6% Mn; $\chi = 43$ (25°); $\chi_M = 4160$ (25°).

Brazilian Ore, 47.3% Mn; $\chi = 34$ (25°); $\chi_M = 3960$ (25°).

These results all show the surprising and gratifying result that natural and synthetic manganese dioxides are often magnetically dilute,

(8) Weiser, "Inorganic Colloid Chemistry," Vol. II, "The Hydrous Oxides and Hydroxides," John Wiley and Sons, Inc., New York, N. Y., 1935, pp. 323-333.

and that in this respect they have the character of attenuated inorganic gels. In some cases the molal susceptibility of the manganese is almost twice what it is in the massive pyrolusite.

The sample γ -(I) is seen to follow the Curie-Weiss law, hence it is possible to calculate the magnetic moment. The moment for the manganese in this substance is 3.9, compared with a theoretical moment of 3.87. The Weiss constant has the value of 210°.

Similar calculations of Gel(II) show that the manganese has a moment of 3.7. The other hydrous oxides show small deviations from the Curie-Weiss law, hence calculations of the moment for these cases were not attempted.

All these results are in sharp contrast to data on the massive *pyrolusite* which show the typical behavior of a magnetically concentrated substance. The results on the disperse oxides show that some of these are well suited for the experiment on the dry cell. It is anticipated that this property of gel-like oxides in showing magnetic dilution will be no less useful than the corresponding property has been in structural studies of supported transition group oxides.⁹

The Dry Cell Experiment

Magnetic Measurements.—The horizontal displacement Gouy method was used. The cell was placed on a brass holder suspended by two fine copper wires. The wires were about 2 meters long and served the double purpose of suspension and electrical conduction. The cell was placed so that one end was in a region of maximum magnetic field intensity and the other end in a negligible field. The field was supplied by a large Alnico permanent magnet.¹⁰ The field was about 9000 gauss over a 1-inch gap, with 4-inch diameter poles cut to truncated cones having 2-inch faces. This magnet gave complete satisfaction. All measurements were made at room temperature.

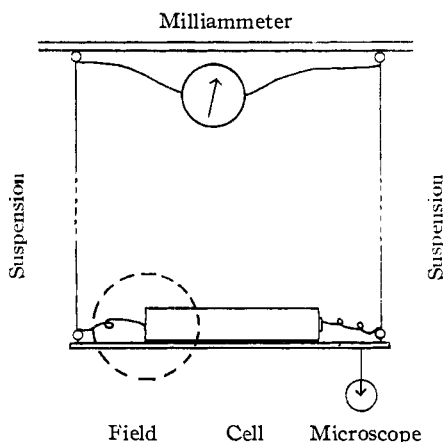


Fig. 1.—Diagram of the apparatus used in finding relative magnetic susceptibility as a function of cell discharge.

The object of the experiment was to obtain relative magnetic susceptibility measurements as a function of

(9) Eischens and Selwood, *THIS JOURNAL*, **69**, 1590 (1947).

(10) Obtained from the Indiana Steel Products Corporation, Valparaiso, Indiana.

time. Displacements of the cell from its initial position were observed with a micrometer microscope. These displacements may be shown to be linear with average susceptibility. The cell was connected through the copper suspension wires directly to a milliammeter. The cell, suspensions, and ammeter provided adequate resistance. For obvious reasons no measurements could be made while the current was flowing, but equilibrium was attained within a few seconds after the circuit was opened. The apparatus had excellent sensitivity.

Preparation of Cells.—Cells used in this experiment were constructed in general according to a modified standard procedure.¹¹ In order to have the cells of sufficient length to extend from high to negligible magnetic fields the following procedure was adopted. The zinc containers from two small commercial cells were combined to make a cell about 9 cm. long. Commercial carbon rods were used for the positive electrode, and acetylene black was used for internal conduction. It was desired to analyze the constituents of the cells before and after each run. Small muslin sacks were therefore used to hold the carbon and the depolarizer. This procedure made accurate weighing possible. The full sacks were then dipped in 10% ammonium chloride solution, and fitted into the zinc containers. Preliminary magnetic measurements on container and contents showed them to be free from ferromagnetism.

Results of Cell Experiment

A total of ten cells was prepared for this study. All gave results in general agreement. One typical set of results will be given in detail, and the remaining results will be described in more general terms.

A cell was prepared using 4.08 g. of $MnO_{1.97}$, $0.33H_2O$ (gel II as previously described), and 1.03 g. of acetylene black.

A plot of deflection against coulombs is shown in Fig. 2.

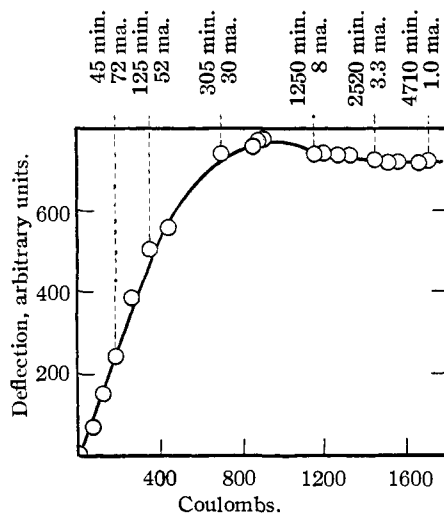


Fig. 2.—Deflection in the magnetic balance as a function of coulombs withdrawn from the cell. Time and discharge rate are given at the top.

During discharge the cell became more paramagnetic as would be expected for a decreasing oxidation state of the manganese. It is reasonable to suppose that the deflection is roughly

(11) Circular 79, U. S. Bureau of Standards, Washington, D. C.

linear with oxidation state for a cell containing gel-like manganese dioxide.

It will be noted that the deflection finally became virtually constant, although current continued to flow from the cell. The amperage fell steadily with increasing paramagnetism, but when the deflection became constant the amperage also became nearly constant. When this "steady" condition was reached the cell had already lost all its useful voltage, but nevertheless it could still yield a large number of coulombs.

Our conclusions from these observations are that the magnetic method is a very useful tool for following chemical changes in the depolarizer without in any way opening or disturbing the cell. The method gives the expected result of a linear relation between oxidation state and coulombs withdrawn over the useful life of the cell. Then, however, it is clearly indicated that there is a second depolarization mechanism. This second mechanism only comes into observation when the cell has lost its useful life, but presumably it is going on from the start of discharge. It is possible that the second depolarization mechanism may be produced by air. It is, of course, of no significance in sealed conventional cells.

A series of five cells was now made for the purpose of comparing the chemically determined oxidation state of the manganese with the magnetic data. All cells were made with 3.10 g. of a mixture prepared by adding 4.35 g. of acetylene black to 13.11 g. of Gel(II), as used in the first cell. Despite all precautions these cells differed considerably in starting amperage, total deflection, and rate of discharge. Nevertheless the deflection *vs.* coulombs curves for all cells had the same general shape.

The initial oxidation state of the manganese was, of course, 3.94, found as described above by chemical analysis. Two cells were completely discharged, and the final oxidation state was found to be 3.54 in each case. (This relatively high final oxidation state simply means that a considerable fraction of the depolarizer was not reached by continuous carbon filaments.) Three cells were run to the point where deflection stops. The final oxidation states were 3.32, 3.44 and 3.42. One cell was run to roughly two-thirds of the discharge at which deflection would have stopped. The oxidation state was then found to be 3.58.

These results support the magnetic data and serve as a rough calibration from which the oxidation state at any discharge point may be found. There is some evidence that the oxidation state of the manganese may actually increase very slightly during the period of air-depolarization, and this observation seems to be supported by the magnetic data.

One cell was discharged intermittently to answer an old question. This question is: does the oxidation state of the manganese change during discharge or during recovery? The cell had an

initial discharge rate of 0.210 ampere. It was discharged for two minutes during which time the rate fell to 0.0180 ampere, and a deflection of 40 units was produced. The cell now stood for twenty minutes after which the discharge rate was 0.200 ampere, but the deflection was still exactly 40 units.

Discharge of this cell intermittently was continued with relatively long recovery periods, until discharge was virtually complete. The results were the same throughout the whole experiment, namely, that the manganese oxidation state changes during discharge and not during recovery. This view is contrary to that often expressed. The final oxidation state in this particular cell was 3.42, and the deflection *vs.* coulombs curve was similar to that already presented.

During the course of this work some cells were studied containing as depolarizers supported manganese (+4) on γ -alumina, and supported-

iron (+3 and +4) on alumina and titania, respectively. The results on these cells will be described in forthcoming papers dealing with the preparation and properties of supported oxides.

Our thanks are due to Dr. T. E. Moore for invaluable assistance in some of the early phases of this work.

Summary

Preparations of manganese dioxide show widely varying magnetic dilution. This effect will be useful in studying the degree of attenuation in solid inorganic gels formed by oxides of the transition elements.

Disperse manganese dioxide showing high magnetic dilution has been used as depolarizer Leclanché cells. In this way it has been possible to make magnetic susceptibility measurements on discharging cells *in situ*.

EVANSTON, ILLINOIS

RECEIVED AUGUST 4, 1948

[CONTRIBUTION NUMBER 81 FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF UTAH]

The Chromatographic Separation of Perrhenic and Molybdic Acids

BY GUY B. ALEXANDER¹

The problem of separating rhenium from samples containing large amounts of molybdenum has been investigated in connection with the analytical determination of rhenium and in connection with the extraction of rhenium from molybdenite concentrates. Hiskey and Meloche² devised an analytical method, refined by Snyder³ and Alexander,⁴ for the determination of rhenium in molybdenite minerals; the procedure was based on the separation of rhenium from the other components of the mineral by distilling from sulfuric acid solution. Feit⁵ utilized the slight solubility of potassium perrhenate in a process for the recovery of rhenium from molybdenite concentrates. Melaven and Bacon⁶ have reported a method for extracting rhenium from molybdenite roaster flue dust by (a) a water leaching, (b) precipitation of crude potassium perrhenate, and (c) the purification of this crude product.

In the course of an experiment in which it was attempted to recover rhenium by roasting a molybdenite concentrate at a controlled temperature, Snyder³ discovered that perrhenic acid was adsorbed by Norit. Following this discovery, Snyder studied several of the variables of the adsorption of rhenium and molybdenum compounds on

Norit, including the effect of the concentration of hydrochloric and sulfuric acids on adsorption, and the effect of temperature and *pH* on desorption. Although Snyder's work was limited to the equilibrium or batch technique, his results suggest that a chromatographic process might be useful in separating compounds of rhenium and molybdenum.

The purpose of this paper is to show that a quantitative separation of rhenium and molybdenum can be made by the chromatographic method with Norit as the adsorbent. The basis of the separation is the fact that, from a sulfuric acid solution of perrhenic and molybdic acids, perrhenic acid is more strongly and more rapidly adsorbed on Norit.

Experimental

In order to provide a basis for predicting the behavior of perrhenic and molybdic acids in a chromatographic process, the adsorption of each adsorbate was studied before attempting a chromatographic separation. All adsorption studies were carried out in 1.95 *N* sulfuric acid, since it has been shown³ that there is a difference in the adsorption of perrhenic and molybdic acids from this solvent.

Reagents.—Stock solutions of molybdic acid were prepared by dissolving reagent grade ammonium molybdate in 1.95 *N* sulfuric acid. The molybdenum content of these solutions was determined by titrating with standardized potassium permanganate after passage through a Jones reductor.

A perrhenic acid solution was prepared by dissolving a weighed amount of recrystallized potassium perrhenate in 1.95 *N* sulfuric acid. The rhenium content of this solution was checked by precipitating the perrhenate with Nitron and weighing the dried product.

Norit A, technical decolorizing carbon, from the Fisher Scientific Co. was used as the adsorbent.

(1) Present address: E. I. du Pont de Nemours and Co., 3092 Broadway, Cleveland, Ohio.

(2) Hiskey and Meloche, *Ind. Eng. Chem., Anal. Ed.*, **12**, 503 (1940).

(3) Snyder, Ph.D. Thesis, University of Wisconsin, 1945.

(4) Alexander, Ph.D. Thesis, University of Wisconsin, 1947.

(5) Feit, *Z. angew. Chem.*, **43**, 459 (1930).

(6) Melaven and Bacon, paper presented at the 105th Meeting of the ACS, Detroit, Michigan, 1943.