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. ALEXANDER[1]

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 Meloche[2] devised an analytical method, refined by Snyder[3] 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. Feit[5] utilized the slight solubility of potassium perrhenate in a process for the recovery of rhenium from molybdenite concentrates. Melaven and Bacon[6] 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, Snyder[3] 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 *p*H 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 shown[3] 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.

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[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.

Molybdic Acid Adsorption.—The rate of adsorption of molybdic acid (see Table I) was determined by stirring 2.50 g. of Norit with 100 ml. of 1.95 *N* sulfuric acid containing 1.33 millimoles (based on H_2MoO_4) of molybdic acid for timed intervals, filtering, and analyzing the filtrate for molybdenum by the volumetric permanganate method.

TABLE I

RATE OF MOLYBDIC ACID ADSORPTION

Adsorbent, 2.50 g. Norit; adsorbate, 1.33 millimoles H_2MoO_4; solvent, 100 ml. of 1.95 *N* H_2SO_4

Time of contact, hours	Adsorption, %
0.13	35.7
.25	37.9
.5	39.7
1.0	41.6
3.0	43.5
10	46.0
48	46.6
72	48.0

The desorption rate (Table II) was determined by stirring 2.50 g. of Norit, on which 2.20 millimoles of molybdic acid had been adsorbed, with 100 ml. of 1.95 *N* sulfuric acid for a given time, filtering, and analyzing the filtrate. The samples of Norit for desorption studies were prepared by stirring 2.50 g. of Norit with 100 ml. of 1.95 *N* sulfuric acid containing 5.33 millimoles of molybdic acid for three days, then filtering. The filtrates contained 0.0314 ± 0.0003 millimole of molybdic acid per ml. The Norit "held up" approximately 6 ml. of solution containing 0.19 millimole of molybdic acid, hence the total amount of molybdic acid present in the desorption experiments was 2.39 millimoles of which 2.20 millimoles was adsorbed.

TABLE II

RATE OF MOLYBDIC ACID DESORPTION

Adsorbent, 2.50 g. Norit; adsorbed, 2.20 millimoles H_2MoO_4; solvent, 100 ml. 1.95 *N* H_2SO_4

Time of contact, hours	Remaining adsorbed, %
0.08	60.3
.33	58.2
1.0	55.5
4.0	53.2
18	50.3
72	50.0

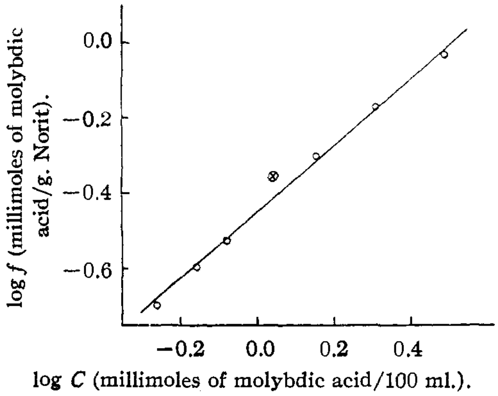

Fig. 1.—The molybdic acid isotherm: ⊗, distribution of molybdic acid after seventy-two hours of desorption (Table II).

The observed slow rates of adsorption and desorption (Tables I and II) indicate that reaction rates will play a predominant role in molybdic acid chromatography. Thus in the formation of a chromatographic band, the front boundary will tend to be broad and diffuse, resulting in premature break-through. During development of the chromatogram, the band will migrate at a slower rate than might otherwise be expected, and the rear boundary will tend to become very diffuse. This condition will necessitate the use of large volumes of developing agent in order to remove the last traces of adsorbed molybdic acid from a column.

The adsorption isotherm (log f = 0.87 log c −0.45) shown in Fig. 1 is based on data obtained by stirring 2.50 g. of Norit with various amounts of molybdic acid in 100 ml. of 1.95 *N* sulfuric acid for three days. Evidence that equilibrium is nearly complete in this time is the fact that a point almost on the isotherm is obtained by approaching equilibrium for seventy-two hours by desorption. (Note that the location of this point is unaffected when either the eighteen- or seventy-two hour reading is taken; see Table II.)

Figure 2 shows the behavior of molybdic acid in a chromatographic process. Two hundred ml. of 1.95 *N* sulfuric acid containing 1.06 millimoles of molybdic acid was passed through a column (19 mm. dia. and 100 mm. high) of 12.0 g. of Norit at a rate of 0.8 ml. per minute. The molybdate band was developed with 1.95 *N* sulfuric acid. Theory predicted[7] break-through after a total of about 450 ml. of solution had passed through the column. In actual experiment, however, 82% of the in-

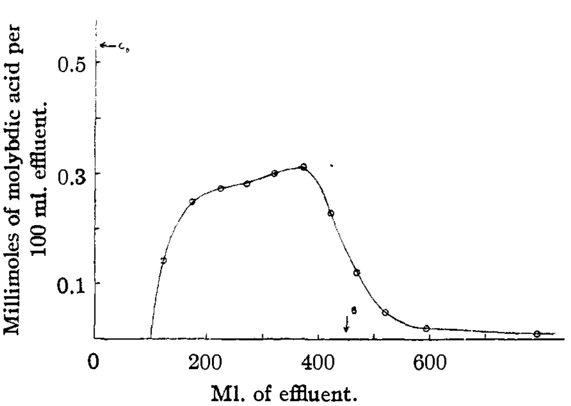

Fig. 2.—The behavior of molybdic acid in a chromatographic process: C_0, concentration of molybdic acid in the influent; B, theoretically predicted break-through.

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[7] DeVault, THIS JOURNAL, **65**, 532 (1943).

fluent molybdic acid was present in the effluent at the 450-ml. stage; break-through occurred at the 100-ml. stage. Moreover, the front boundary was not sharp. This behavior is probably due to the slowness with which equilibrium is established.

Perrhenic Acid Adsorption.—The rate of adsorption of perrhenic acid is shown in Table III. After stirring the adsorbent and solution for a given time, the slurry was filtered; rhenium in the filtrate was precipitated as the sulfide and determined by the Nitron method. It is impossible to compare rigorously the reaction rates of perrhenic and molybdic acids, since the structure of the polymolybdic acid which is adsorbed is not known. However, from Tables I and III it would appear that the reaction rates are such that adsorption of perrhenic acid will be favored in the formation of a chromatogram.

TABLE III

RATE OF PERRHENIC ACID ADSORPTION

Adsorbent, 1.00 g. Norit; adsorbate, 0.349 millimole of $HReO_4$; solvent, 100 ml. 1.95 N H_2SO_4

Time of contact, hours	Adsorption, %
0.07	84.0
.25	85.4
1.0	87.1
2.0	89.8
5.0	90.9
30	91.7

Figure 3 shows the chromatographic adsorption of perrhenic acid. In this experiment a 4.0-g. Norit column (19 mm. dia. and 30 mm. high) was treated with 2.44 millimoles of perrhenic acid in 350 ml. of 1.95 N sulfuric acid at a rate of 1.6 ml. per minute. Thereafter the band was developed with 1.95 N sulfuric acid. The capacity of the column before break-through was 1.74 millimoles of perrhenic acid (*i. e.*, 109 mg. of $HReO_4$ per g. of Norit), break-through occurring after 250 ml. of solution had passed through the column. Theory[7] predicts break-through at the 425-ml. stage. (The prediction is based on the isotherm, $\log f = 0.33 \log c - 0.08$. This isotherm was determined in the usual manner; however, only three concentrations of perrhenic acid were studied.)

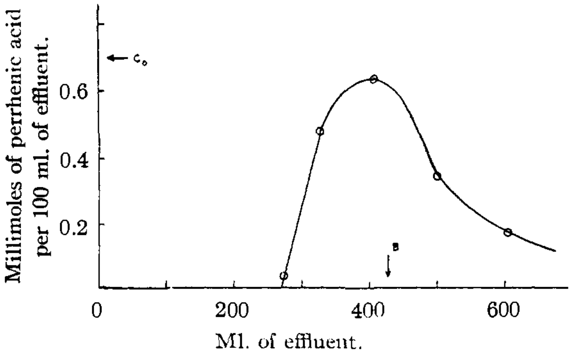

Fig. 3.—The behavior of perrhenic acid in a chromatographic process: C_0, concentration of perrhenic acid in the influent; B, theoretically predicted break-through.

A comparison of the molybdic and perrhenic acid chromatographic experiments shows that despite the fact that a slower rate (0.8 compared with 1.6 ml./min.) and a longer column (100 mm. compared with 30 mm.) were used in the former case, the latter more closely approaches the theoretical behavior. Thus the ratio of experimental to theoretical capacity of the columns at break-through was 0.58 in the perrhenic acid case and was only 0.22 in the case of molybdic acid. Moreover, the maximum concentration of perrhenic acid in the effluent was 90% of that of the influent, while for molybdic acid the maximum was 60% of the original. The better agreement of theory and experiment with perrhenic acid substantiates the conclusion reached from the comparison of Tables I and III, *i. e.*, that reaction rates will favor the chromatographic separation of the two acids.

Rhenium–Molybdenum Equilibrium Adsorption.—The exchange adsorption equilibrium between perrhenic and molybdic acids was determined by stirring different amounts of these compounds in 100 ml. of 1.95 N sulfuric acid with 1.00 g. of Norit for three days. The filtrate from this slurry was analyzed; after precipitation as sulfides, molybdenum was determined by 8-hydroxyquinoline and rhenium by Nitron.[8] The results of this experiment which are found in Table IV, and Fig. 4, indicate that the adsorption of

TABLE IV

RHENIUM–MOLYBDENUM ADSORPTION EQUILIBRIUM

Adsorbent, 100 g. Norit; solvent, 100 ml. 1.95 N H_2SO_4; units, millimole

Perrhenic acid Taken	Perrhenic acid % Adsorbed	Molybdic acid Taken	Molybdic acid % Adsorbed
1.57	43	0.43	14
1.31	47	1.08	14
0.88	58	2.16	15
.43	79	3.24	19
.17	Samples lost	3.90	23

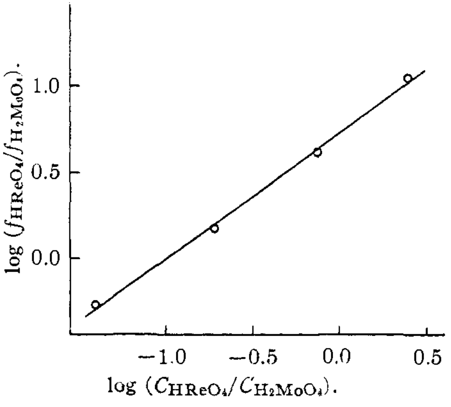

Fig. 4.—Rhenium–molybdenum exchange isotherm.

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[8] Geilmann and Weibke, *Z. anorg. allgem. Chem.*, **199**, 347 (1931).

perrhenic and molybdic acids approaches the exchange isotherm[9]

$$\log (f_{HReO_4}/f_{H_2MoO_4}) = 0.72 \log (c_{HReO_4}/c_{H_2MoO_4}) + 0.73$$

over the range studied. The rhenium–molybdenum equilibrium adsorption experiments show that perrhenic acid is preferentially adsorbed.

Chromatographic Separation Run 1.—In the first experiment a solution containing 0.349 millimole of perrhenic acid (65.0 mg. of rhenium) and 0.43 millimole of molybdic acid (41 mg. of molybdenum) in 100 ml. of 1.95 *N* sulfuric acid was passed through a 19 mm. dia. and 50 mm. high column of 6.0 g. of Norit at a rate of 1.2 ml. per minute. The chromatogram was developed with 1.95 *N* sulfuric acid until the concentration of molybdenum in the effluent had dropped below 0.1 mg. per 100 ml.; this required a total of 700 ml. of developing agent. Tests for rhenium in the effluent fractions were negative. (The limit of detection of rhenium was 50 micrograms per 100 ml. of effluent.) The adsorbent was removed from the column and the remaining adsorbate was eluted by two treatments of 600 ml. of boiling 0.1 *N* sodium hydroxide solution.[3] On analysis, the combined hydroxide solutions were found to contain 63 mg. of rhenium and less than 0.2 mg. of molybdenum. The summary of Run 1, found in Table V, shows that a quantitative separation of rhenium and molybdenum was obtained in this experiment.

TABLE V

THE CHROMATOGRAPHIC SEPARATION OF RHENIUM AND MOLYBDENUM, RUN 1

Adsorbent, 6.0 g. Norit; flow rate, 1.2 ml. per minute; developing agent, 700 ml. 1.95 *N* H_2SO_4; molybdenum used, 41 mg.; rhenium used, 65 mg.

Fraction effluent, ml.	Molybdenum recovered	Rhenium recovered
100	13.5	0
100	22.7	0
100	2.0	0
100	1.4	0
100	0.8	0
100	.5	0
100	.2	0
100	.0	0
Alkaline eluate	.0	63
Total	41.1	63[a]

[a] Incomplete recovery of rhenium may have been due to incomplete elution of rhenium. In Run 2, a third treatment with sodium hydroxide eluted 1 mg. of rhenium.

Run 2.—In the second experiment 100 ml. of 1.95 *N* sulfuric acid solution containing 0.232 millimole of perrhenic acid and 2.90 millimoles of molybdic acid was passed through an 8.0-g. Norit column (19 mm. dia. and 65 mm. high) at a flow rate of 1.2 ml. per minute; this was followed by 2100 ml. of developing agent Analysis revealed 2.90 millimoles of molybdic acid and no perrhenic in the effluent, 0.23 ± 0.01 millimole of perrhenic acid and 0.04 millimole of molybdic in the column after development. Thus a sample which originally contained 0.080 millimole of perrhenic acid for each millimole of molybdic acid was fractionated into: one fraction containing 98.4% of the total molybdic acid recovered and no perrhenic acid; a second fraction containing 6 millimoles of perrhenic acid for each millimole of molybdic.

Conclusion.—There is sufficient difference in the adsorption characteristics of perrhenic and molybdic acids to permit a quantitative chromatographic separation of these compounds—using 1.95 *N* sulfuric acid as the solvent and developing agent and Norit as the adsorbent. It is possible that a chromatographic process similar to those described above might be applied in the separation of rhenium from samples containing molybdenum prior to analysis or for the extraction of rhenium from molybdate concentrates.

Summary

1. Equilibrium for the adsorption of molybdic or perrhenic acid from 1.95 *N* sulfuric acid on Norit requires several days. The Freundlich isotherms for the adsorption of these acids are $\log f = 0.87 \log c - 0.45$, and $\log f = 0.33 \log c - 0.08$, respectively.
2. As expected from the slow reaction rates, the chromatographic behavior of molybdic acid does not agree with the equilibrium theory. The agreement is a little better in the case of perrhenic acid.
3. The equilibrium adsorption of perrhenic and molybdic acids on Norit approaches the exchange isotherm behavior in the range studied.
4. Rhenium and molybdenum may be effectively separated chromatographically.

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[9] Rothmund and Kornfeld, *Z. anorg. allgem. Chem.*, **103**, 129 (1918).