

selenium oxychloride-sulfuric acid method, while days or even weeks are required by the Marignac method.

It is believed, therefore, that the method proposed for the separation of columbium and tantalum is superior to any other yet proposed.

#### Procedure for the Preparation of Pure Oxides.

To prepare pure columbium pentoxide, the mixed oxides should be extracted with sufficient solvent to dissolve all of the columbium. The boiling should not be prolonged until all of the columbium is dissolved, since the object is to dissolve as little tantalum pentoxide as possible. The dissolved oxide is precipitated with water and ammonia, filtered, and ignited. Some tantalum pentoxide will inevitably be dissolved during the extraction, but by repeating the treatment upon the oxide obtained by the first extraction, very pure columbium pentoxide may be obtained, since the amount of tantalum pentoxide present during the second purification is so small that virtually no tantalum will be dissolved.

To prepare pure tantalum pentoxide, it is only necessary to extract the oxide with the reagent until all of the columbium is dissolved, sacrificing the portion of the tantalum which goes into solution. The complete removal of the columbium may be expedited by increasing the proportion of sulfuric acid in the reagent.

#### Summary.

A method for the separation of columbium and tantalum, both for purposes of analysis and of purification, by means of selenium oxychloride and sulfuric acid, has been described.

This work was performed by the author while acting as research assistant to Professor Victor Lenher.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]  
**THE SEPARATION OF MOLYBDENUM AND TUNGSTEN BY  
MEANS OF SELENIUM OXYCHLORIDE.<sup>1</sup>**

BY HENRY BALDWIN MERRILL.

Received July 22, 1921.

It was found by Lenher<sup>2</sup> that molybdenum trioxide is soluble in selenium oxychloride, while tungstic oxide is insoluble in this reagent. Since none of the methods hitherto known for the separation of molybdenum and tungsten is entirely satisfactory, it was felt that this observation of Lenher's which appeared to afford a new method of separation, should be studied further. The purpose of the present investigation was to determine

<sup>1</sup> Abstract of a portion of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the University of Wisconsin, 1921. This work was financed in part by a grant from the University research fund.

<sup>2</sup> Lenher, *THIS JOURNAL*, 43, 29 (1921).

whether, and with what degree of accuracy, molybdenum trioxide and tungsten trioxide can be separated by means of selenium oxychloride, and to determine the best conditions for the separation.

**Basis of the Separation.**—The solubility of molybdenum trioxide in selenium oxychloride varies with the physical state of the oxide. The freshly precipitated hydrated oxide is readily soluble; the ignited oxide, on the other hand, is soluble only with difficulty, so that complete solution of a given sample cannot be effected in days or weeks. However, the addition of small amounts of sulfuric acid to the selenium oxychloride causes the ignited molybdenum trioxide to dissolve with ease. Hydrated tungsten trioxide, as is well known, is peptized readily by many substances, and as it happens to be peptized by selenium oxychloride, it passes into the colloidal condition. Ignited tungsten trioxide is neither dissolved nor peptized by selenium oxychloride with or without the addition of sulfuric acid. The basis of the separation, is therefore, the extraction of molybdenum trioxide with selenium oxychloride and sulfuric acid from a mixture of ignited molybdenum and tungsten trioxides.

**Method of Attack.**—To determine the best conditions for the separation, preliminary experiments were first conducted with each oxide separately. Weighed samples of molybdenum trioxide were boiled with the reagent in small Erlenmeyer flasks, the mouths of the flasks being covered with small watch glasses to prevent hydrolysis of the selenium oxychloride by the moisture of the air. One g. samples were employed, and the digestion was continued until solution was complete, or until no further action could be detected. The factors varied were the ratio of sulfuric acid to selenium oxychloride, and the volume of the solvent. Control experiments were conducted with tungsten trioxide, 1g. samples being digested with the reagent, the solution filtered through weighed Gooch crucibles with asbestos mats and the undissolved oxide transferred to the crucibles, ignited, and weighed. The amounts dissolved were thus determined by difference.

**Reagents.**—The oxides of molybdenum and tungsten were prepared by ignition of their ammonium salts which had been purified by repeated recrystallizations. Selenium oxychloride was prepared by the interaction of selenium dioxide and selenium tetrachloride,<sup>3</sup> the product being distilled in a vacuum. The purity of the other reagents employed was ascertained by the customary tests.

### Behavior of the Pure Oxides.

Preliminary experiments seemed to show that ignited tungsten trioxide was slightly soluble in selenium oxychloride and sulfuric acid. The losses, when 1g. samples were treated with 30 cc. of the solvent, amounted to several milligrams and their magnitude appeared to be independent of the composition or the volume of the reagent, and of the time of di-

<sup>3</sup> Lenher, *THIS JOURNAL*, 42, 2498 (1920).

gestion. Examination of the selenium oxchloride filtrate and of the wash-water employed in transferring the undissolved oxide from the flask to the crucible showed that all of the dissolved oxide was contained in the latter. The losses were therefore due to peptization of the tungsten trioxide by the wash-water. It was found to be impractical to transfer the oxide to the crucible with a jet of selenium oxychloride, due to the rather high viscosity of the latter. Various solutions of electrolytes were employed for this purpose, and good results were obtained with a hot, 10% solution of ammonium nitrate. When this solution was employed the amount of tungsten trioxide dissolved was only a few tenths of a mg.

The experiments with tungsten trioxide having shown that this oxide is insoluble under all conditions in selenium oxychloride and sulfuric acid, the conditions for the separation could be adjusted solely with reference to dissolving the molybdenum trioxide. It was found that both the amount of solvent and the time required to effect the complete solution of a given sample of molybdenum trioxide decreased with increasing concentration of sulfuric acid in the reagent. Thus the time required to dissolve 1 g. of molybdenum trioxide in 30 cc. of solution containing 15 cc., 5 cc., and 2 cc. of sulfuric acid, was 30 minutes, 45 minutes, and 60 minutes, respectively. When the reagent contained less than 2 cc. of sulfuric acid per 30 cc. of solution, complete solution of 1 g. of oxide in 30 cc. of solvent could not be effected. It was found desirable to keep the sulfuric acid concentration low, as the viscosity of the reagent increases with increasing concentration of the acid. The reagent which was found to be most satisfactory, taking all factors into consideration, was a mixture of 1 part of sulfuric acid and 5 parts of selenium oxychloride. Thirty cc. of this reagent will dissolve 1 g. of molybdenum trioxide in 45 minutes at the boiling point of the solvent.

#### Separation of Mechanical Mixtures.

The separation of mechanical mixtures of molybdenum and tungsten trioxides was next attempted. One-g. samples of known composition were boiled with 30 cc. of the reagent for an hour, the solution decanted through weighed Gooch crucibles, the residues washed several times with small portions of selenium oxychloride, and finally brought on the filter with hot, 10% ammonium nitrate solution. The crucible was ignited and weighed, the gain in weight representing tungsten trioxide. Molybdenum trioxide was determined by difference. The results of a few of these experiments, chosen at random from the large number of separations performed, are given in Table I.

It will be seen that the errors are in all cases small, which shows that the separation for molybdenum and tungsten with this reagent is a very accurate one.

TABLE I.  
SEPARATION OF MECHANICAL MIXTURES OF MOLYBDENUM AND TUNGSTEN  
TRIOXIDES.

| Expt.                       | 1.     | 2.     | 3.     | 4.     | 5.     | 6.     | 7.     | 8.     |
|-----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| WO <sub>3</sub> taken.....  | 0.0034 | 0.3330 | 0.2071 | 0.3506 | 1.4238 | 0.7500 | 0.7333 | 0.5065 |
| WO <sub>3</sub> found.....  | 0.0032 | 0.3337 | 0.2074 | 0.3501 | 1.4224 | 0.7449 | 0.7327 | 0.5068 |
| MoO <sub>3</sub> taken..... | 0.4967 | 1.5443 | 0.7437 | 0.7594 | 0.9435 | 0.2500 | 0.0856 | none.  |
| MoO <sub>3</sub> found..... | 0.4969 | 1.5436 | 0.7434 | 0.7599 | 0.9449 | 0.2501 | 0.0862 | none.  |

### Separation of Intimate "Chemical" Mixtures.

The mixtures which were separated in the above experiments are not strictly comparable to those which are met with in actual practice. The samples which were separated in the experiments reported in Table I were simply mechanical mixtures of the ignited, finely ground oxides, while in actual practice the oxides would be obtained in a much more intimate state of admixture. Mixtures of tungsten and molybdenum trioxides are usually obtained by the ignition of their mercurous salts, precipitated together; by ignition of their ammonium salts, crystallized together; or by the decomposition of a mineral with aqua regia. When the separation of such mixtures (which may be called "chemical") prepared by dissolving known amounts of the oxides in ammonia, evaporating to dryness and igniting to oxide, was attempted, it was found that the separation proposed is of somewhat limited applicability. When the mixture contains more than about 10% of tungsten trioxide, complete extraction of the molybdenum cannot be effected, no matter how long the digestion is continued, or how much sulfuric acid is added to the selenium oxychloride. The molybdenum and tungsten trioxides apparently form a solid solution, the tungsten trioxide preventing the solution of the molybdenum trioxide unless the latter is present in large excess. When less than 10% of tungsten trioxide is present, the molybdic oxide can be completely extracted. In this case, however, the small amount of tungsten trioxide which was dispersed through the predominant molybdenum trioxide is left in a very fine state of division, and tends to run through the filter, causing serious losses. This difficulty was overcome by dissolving the mixed oxides in ammonia, and adding enough nitric acid to precipitate most of the tungsten, which thus had a chance to segregate from the molybdenum trioxide. The solution was then evaporated to dryness, and the residue ignited at dull red heat. Weighed samples of the mixed oxides so prepared were separated with selenium oxychloride and sulfuric acid as previously described. The results of these experiments are given in Table II.

TABLE II.  
SEPARATION OF CHEMICAL MIXTURES OF MOLYBDENUM AND TUNGSTEN  
TRIOXIDES.

| Expt.                       | 1.     | 2.     | 3.     | 4.     |
|-----------------------------|--------|--------|--------|--------|
| WO <sub>3</sub> taken.....  | 0.0717 | 0.0417 | 0.0233 | 0.0156 |
| WO <sub>3</sub> found.....  | 0.0720 | 0.0409 | 0.0243 | 0.0163 |
| MoO <sub>3</sub> taken..... | 0.6177 | 0.7439 | 0.7264 | 0.8570 |
| MoO <sub>3</sub> found..... | 0.6174 | 0.7447 | 0.7254 | 0.8563 |

These experiments show that the separation of these two oxides is possible by means of selenium oxychloride and sulfuric acid.

### Summary.

A new method has been described for the separation of molybdenum and tungsten, consisting in the extraction of molybdenum trioxide from a mixture of the ignited oxides by means of selenium oxychloride.

This work was performed by the writer while acting as research assistant to Professor Victor Lenher, whom the writer takes this occasion to thank for all his help and kindness.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

## THE SPEED OF REACTION IN CONCENTRATED SOLUTIONS AND THE MECHANISM OF THE INVERSION OF SUCROSE.

BY GEORGE SCATCHARD.

Received July 27, 1921.

### Introduction.

Although the speed of inversion of sucrose in acid solutions has been studied more than the kinetics of any other reaction,<sup>1</sup> there are two anomalies which were discovered by the earliest workers, but which have not yet received an adequate explanation. According to the accepted theories of chemical kinetics, the speed of reaction ought to be independent of the concentration of sucrose and proportional to the concentration of the hydrogen ion. Experimentally, the speed increases more rapidly than the concentration of the hydrogen ion when that of the sugar is kept constant; and when the concentration of acid is unchanged the speed increases rapidly with increasing sugar concentration.

There have been three types of explanation of these anomalies offered. The one most generally accepted at the present time explains only the abnormal increase with increased acid concentration or on the addition of a salt. This theory assumes that the non-ionized acid exerts a catalytic effect, which may be even greater than that of the hydrogen ion itself.<sup>2</sup> However, this theory alone is not sufficient as is shown by the facts that it will not explain the change in speed with changing sugar concentration, and that different values are calculated for the activity of the non-ionized

<sup>1</sup> A good bibliography up to 1906 is given by R. J. Caldwell, *Brit. Assoc. Rep.*, (York), 1906, pp. 267-92.

<sup>2</sup> The following references are typical of a voluminous literature in this field.  
H. C. S. Sneath, *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 211 (1913).

S. F. Acree, *Am. Chem. J.*, **49**, 345 (1913).

H. S. Taylor, *Medd. K. Vetenskapsakad. Nobelinst.*, **1913**; *Z. Elektrochem.*, **20**, 201 (1914).