[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Separation and Determination of Tungsten and Molybdenum

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The precise analysis of materials containing tungsten and molybdenum is complicated by the fact that in separating tungstic acid the precipitate is always contaminated by appreciable quantities of molybdenum,[2] and that in the formation of molybdenum sulfide, a considerable amount of tungsten is precipitated with it. The problem of the separation of molybdenum, both from tungsten and the other metals, is further complicated in that molybdenum sulfide is seldom precipitated quantitatively in one operation, its complete removal demanding two or more repetitions of the treatment with hydrogen sulfide.

A bibliography of the literature on the methods of analysis for tungsten and molybdenum up to the year 1923 is available in the bulletin by Moore.[3] Since that time, new methods for the determination of these elements have appeared making use of organic precipitants, but none of the reagents is suitable for separating the two metals. Among the organic compounds proposed for these determinations are, 8-hydroxyquinoline[4] which forms stable compounds having the composition, $WO_2(C_9H_6ON)_2$[5] and $MoO_2(C_9H_6ON)_2$[6]; and α-benzoin oxime which is serviceable for the direct determination of molybdenum in steels.[7]

The methods for the separation of tungsten and molybdenum come under two general headings. In the first grouping, one of the constituents of the mixture is removed by extraction with a suitable solvent. In this class come the methods of Ruegenberg and Smith,[8] who employed concentrated sulfuric acid to separate the molybdenum from a mixture of hydrated tungstic and molybdic acids; also, the procedure of Merrill,[9] who effected a like separation through the use of selenium oxychloride as the solvent. Under the second classification come precipitation reactions, the mechanism of which, in general, lends itself to more exact separations than are possible by extraction methods. Unfortunately, the properties of the two ions in question are very similar, so that with the exception of the sulfides, salts of the two elements have not been discovered that have a sufficient difference in solubility to effect a quantitative separation of one metal from the other.

The disadvantage of the separation by means of hydrogen sulfide is that the precipitation of molybdenum sulfide is usually incomplete owing to the reduction of part of the molybdenum by the reagent to lower valency states in which the ions can no longer form insoluble sulfides.[2] A further inconvenience of the method is that the subsequent removal of the large quantities of tartaric acid, whose presence is essential for a sharp separation of the two elements, is a very difficult and time consuming operation.

The present investigations were initiated in order to circumvent the described difficulties in the quantitative precipitation of pure molybdenum sulfide. Examination of the law of mass action for the reaction between the hexavalent molybdenum ion and the hydrogen sulfide in an acid medium, reveals that the complete precipitation of the molybdenum sulfide is favored by a low hydrogen-ion concentration and a high concentration of hydrosulfide ion

$$Mo^{6+} + 3HS^- \rightleftharpoons MoS_3 + 3H^+ \qquad (1)$$

$$[Mo^{6+}] = [MoS_3][H^+]^3/k[HS^-]^3 \qquad (2)$$

The hydrogen-ion concentration can be reduced only over a narrow range as, in alkaline media, soluble sulfomolybdates are formed. The concentration of hydrogen sulfide can be increased by conducting the precipitation in a pressure bottle at an elevated temperature. The efficiency of this procedure is doubtful, for the pressure effect is probably nullified by the increased reducing action of the reagent at elevated temperatures.[10]

It occurred to the writers that another means of increasing the concentration of the hydrogen

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(1) J. T. Baker Chemical Co. Research Fellow in Analytical Chemistry, 1935–36.

(2) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, pp. 246–247.

(3) R. B. Moore and collaborators, "Analytic Methods for Certain Metals," *Bur. Mines Bulletin* 212, Washington, D. C., 1923, pp. 125 and 167.

(4) G. Banalescu, *Ann. chim. anal.*, **12**, 259 (1930).

(5) S. Halberstadt, *Z. anal. Chem.*, **92**, 86 (1933).

(6) H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388 (1933).

(7) H. B. Knowles, *Bur. Stds. J. Res.*, **9**, 1 (1932).

(8) M. J. Ruegenberg and E. F. Smith, THIS JOURNAL, **22**, 772 (1900).

(9) H. B. Merrill, *ibid.*, **43**, 2383 (1921).

(10) W. Werz, *Z. anal. Chem.*, **100**, 241 (1935); "Applied Inorganic Analysis," p. 55.

sulfide in the system is to take advantage of the increased solubility of the gas in water at low temperatures. At 0° the solubility of hydrogen sulfide is 7.1 g. per liter, which is more than twice that at 25°.[11] As the concentration of the hydrosulfide ion enters as a cube in equation 2, doubling the concentration of the hydrogen sulfide tends to make an eight-fold effect in diminishing the molybdenum-ion concentration. Also, as the reaction is conducted at a low temperature, the reducing action of the reagent is considerably diminished, a factor which favors the quantitative separation of the sulfide. Experimental investigations revealed that this method was eminently suitable for the separation of molybdenum from tungsten.

Purification of Standards

$Na_2WO_4 \cdot 2H_2O$.—The purification of sodium tungstate was effected by following the procedure developed by Folin.[12] The final product was tested for traces of molybdenum by means of potassium ethyl xanthate.[13] By applying the spot test technique, described by Feigl[14] to solutions of the purified salt to which were added known quantities of sodium molybdate, it was found that the red coloration characteristic of the element was discernible in a mixture containing 0.005% of sodium molybdate. As the solution of the purified salt did not give any visible reaction, the sodium tungstate employed in these investigations probably contained not more than 0.005% of sodium molybdate. Analysis of the product for water of crystallization[15] and tungstic oxide[16] showed that the salt contained 10.91 ± 0.02% water and 70.27 ± 0.02% WO_3, which compares favorably with the theoretical amounts 10.92 and 70.30%, respectively.

$Na_2MoO_4 \cdot 2H_2O$.—This salt was purified by dissolving 50 g. of the best obtainable sodium molybdate in 300 cc. of water; to the solution was added 600 cc. of 95% alcohol. A small crop of crystals separated at this point, these were filtered off after a period of one hour and discarded. The clear filtrate was again treated with 600 cc. of alcohol, the small crystals of sodium molybdate were filtered, washed with 100 cc. of 95% alcohol and permitted to dry at room temperature. The product, weighing 25 g., consists of small pearly-lustered crystals that are completely water soluble.

There is no chemical test for tungsten sufficiently delicate to establish the presence of traces of the element as an impurity in sodium molybdate. Spectrographic examination of the purified salt showed a very faint line in the position where the most persistent line of the arc spectrum of tungsten is located. But, as the other characteristic lines of the optical spectrum of tungsten were not recorded on the plate, appreciable amounts of the element probably are not present in the sample. This is further evident from the chemical analysis in which it was found that the salt contained 14.91 ± 0.01% water[15] and 59.49 ± 0.02% MoO_3,[17] the values closely agreeing with the calculated percentages, 14.89 and 59.50, respectively.

Preparation of Reagents

0° Hydrogen Sulfide Water.—This solution can be prepared by bubbling a stream of the purified gas through a column of water that has been chilled in an ice-bath to 0°. Several methods for preparing this solution were investigated with the object of obtaining rapid saturation and economy in the use of the gas. It was found most convenient to pass the gas through a porous sphere of "Aloxite."[18] This produces an ascending stream of numerous minute bubbles that are almost entirely absorbed by the column of water before they reach the surface. The standard 61 cm. (2-ft.) Kipp gas generators do not supply sufficient pressure to overcome the internal resistance of the porous sphere and the hydrostatic pressure of the column of water above it. The pressure can be augmented easily by compressing the air in the head of the Kipp with the help of an atomizer bulb. Small tanks of liquid hydrogen sulfide, substituted for the Kipp generator, serve the purpose admirably well.

The length of time required to reach the saturation point depends upon the volume of water, its initial temperature and the rate of influx of the gas. The relative rate of absorption, under constant gas pressure, by a column of water at the freezing point is recorded in Table I.

TABLE I

RATE OF ABSORPTION OF HYDROGEN SULFIDE

Volume of water at 0°, 750 cc. Diameter of "Aloxite" sphere, 25 mm. Influx of gas, 150 bubbles per min., as counted in the wash bottle having a conducting tube of 4 mm. inside bore.

Time, min.	10	20	30	45	60	120
G. H_2S/ l. sol.[19]	0.863	2.12	3.53	5.21	6.12	6.59
Molarity	0.0253	0.062	0.104	0.153	0.180	0.193

The point of near saturation can be ascertained visually when it is noted that large bubbles reach the surface of the solution. In one experiment on the absorption of hydrogen sulfide, the undissolved gas was collected, dried over calcium chloride, and its weight ascertained by measuring the increase in weight of a U-tube filled with sodium hy-

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(11) L. W. Winkler, *Math. és Termeszettu-dományi Eresitő*, **25**, 86 (1907).

(12) Otto Folin, *J. Biol. Chem.*, **106**, 311 (1934).

(13) S. L. Malowan, *Z. anal. Chem.*, **79**, 201 (1929).

(14) F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, p. 176.

(15) The water content was determined by drying 1-g. samples of the salt at 120° for several hours in a platinum crucible. To make sure of the complete removal of the water, the anhydrous salt was heated to the point of fusion.

(16) The tungstic oxide was determined by the standard cinchonine–hydrochloric acid method.

(17) The molybdic oxide content was determined by precipitating and weighing lead molybdate.

(18) These aerator stones are manufactured by the Carborundum Company, Niagara Falls.

(19) The concentration of the hydrogen sulfide was determined by transferring a 10-cc. sample to a solution of lead acetate and weighing the resultant lead sulfide.

droxide pellets connected to the train. It was found that in the process of saturating 750 cc. of water only 0.42% of the total hydrogen sulfide escaped absorption.

Formic Acid.—The acid employed in these investigations was a standard product of analyzed purity, of 85–90% strength. Analysis of the material showed that its concentration was 23.7 molar. Dilute 2 *M* formic acid was prepared by diluting 80 cc. of the concentrated acid to one liter.

Ammonium Formate.—A 50% solution of the salt was prepared by dissolving 250 g. of the J. T. Baker Chemical Co. analyzed product in 150 cc. of water, warming the mixture until the crystals dissolved, filtering and diluting to 500 cc. The solution should have a *p*H of 6.7 using bromo cresol purple as the indicator.

Tartaric Acid.—A 50% solution of the acid was prepared from an analyzed grade product. After the procedure for the separation of the two metals was developed, it was found more convenient to use a 30% solution of the acid.

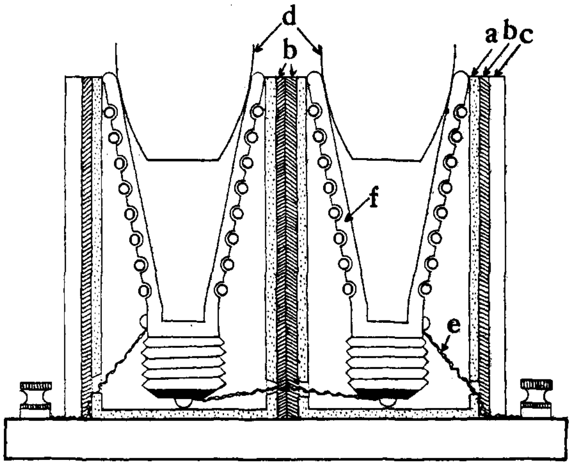

Fig. 1.—Crucible furnace for igniting MoS_3: a, porous clay cup 11 cm. high and 5.5 cm. diam. (inside meas.); b, a 3-mm. layer of thin asbestos paper; c, a 5-mm. layer of heavy asbestos paper; d, protective nickel crucibles; e, connecting wires of standard nichrome; f, 660-watt conical heating units.

Quantitative Precipitation of Molybdenum Sulfide

Molybdenum sulfide can be precipitated from solutions acidified with hydrochloric, sulfuric or formic acid. If the filtrate is to be reserved for the analysis of tungsten, it is desirable that the acidifying agent be readily volatile. Complete precipitation in hydrochloric acid media is a difficult matter[2]; it was therefore decided to investigate the claims of Sterba-Böhm[20] concerning the precipitation of molybdenum sulfide in solutions acidified with formic acid, who concludes that the sulfide can be precipitated completely over a range of acidity varying from 5–20% of the acid. To check this, six samples of sodium molybdate were each dissolved in 125 cc. of 10% formic acid and the solutions were saturated at room temperature with hydrogen sulfide. On examination of the filtrates, all were found to contain minute amounts of molybdenum, averaging 0.10 ± 0.03 mg. of the metal.[21]

A series of analyses was then made using hydrogen sulfide water saturated at 0° as the precipitant. The sodium molybdate was dissolved in 10 cc. of water, 100 cc. of the hydrogen sulfide reagent was added to each sample and the solutions were acidified with measured volumes of 24 *M* formic acid. The mixtures were heated on a hot-plate; when the temperature reached 36° the molybdenum sulfide coagulated, and settled to the bottom of the beakers in the form of bulky deep black precipitates. After digestion for thirty minutes at 40–50° the sulfides were filtered and washed with 5% formic acid. All the filtrates were colorless and perfectly clear[22] and on analysis were found to contain only traces of molybdenum. The results from twelve experiments showed that on the average only 0.04 to 0.01 mg. of the metal failed to be precipitated by following this procedure. This loss is entirely negligible in the gravimetric determination of the element.

Determination of Molybdenum as Molybdic Oxide

After the molybdenum is separated as the sulfide, it is convenient to convert the molybdic sulfide to molybdic oxide and weigh the element in that form. The early investigators of this process[3] concluded that it was difficult to roast the sulfide to the oxide owing to the volatile nature of molybdic oxide. Recent work by Brinton,[23] Hartmann[24] and Knowles[7] proves that the moist sulfide can be converted to the oxide, at temperatures below 600°, without any appreciable loss; and that the process is quite rapid at temperatures above 500°. As the temperatures must be carefully controlled, it is best to ignite the molybdenum sulfide in an electric furnace. The simple heating unit described in Fig. 1, which can be readily assembled from standard laboratory stock, proved to be very useful in executing this process.

The improvised furnace reaches thermal equilibrium in about thirty minutes. With two 660-watt conical heating coils connected in series and insulated as shown in the diagram, the surfaces of the nickel crucibles reach a maximum temperature of 550°. At this temperature the furnace draws a current of 2.75 amp. at 120 volts. By removing part of the wiring from the heating coils, the temperature reaches 750° and the unit can then be employed for igniting precipitates of tungstic acid to the oxide. It is recommended that the crucible containing the precipitate be protected by a nickel crucible, as shown in the figure, in order to prevent its being scratched by the rough walls of the cone shaped heater.

During the progress of the work on the quantitative conversion of molybdenum sulfide to oxide, it was found

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(20) Sterba-Böhm and J. Vostrebal, *Z. anorg. allgem. Chem.*, **110**, 81 (1920).

(21) The molybdenum content was determined colorimetrically by evaporating the solution to dryness and testing the residue by the thiocyanate reaction: L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 396 (1935).

(22) As the solutions warm up to room temperature, the excess hydrogen sulfide escapes from solution. The resultant gas bubbles probably play an important part in flocculating the molybdenum sulfide. See Henry Bassett, "Theory of Quantitative Analysis," New York, 1925, p. 102.

(23) P. H. Brinton and A. E. Stoppel, THIS JOURNAL, **46**, 2454 (1924).

(24) W. Hartmann, *Z. anal. Chem.*, **67**, 152 (1926).

that the most concordant results were obtained when the sulfide was filtered through Gooch or porous bottom porcelain crucibles. Under these conditions the sulfide is deposited in a layer that is quite uniform in depth, and this promotes rapid conversion to the oxide. It was also noted that during the roasting process there was at times mechanical loss of oxide due to the sputtering of the burning sulfur. It is possible to avoid this loss and make the oxidation process quiescent by mixing the precipitate with a small amount of ashless filter paper fibers before conducting the filtration. In general, it takes fifteen to twenty minutes to convert 150 mg. of molybdic sulfide to the oxide. It was found by experiment that a sample of the oxide weighing 120 mg. could be heated for one hour at 550° without any detectable loss in weight. When the temperature was increased to 750°, 0.0036 g. was volatilized during a period of thirty minutes.

The results recorded in Table II show that the oxidation process is suitable for the quantitative determination of molybdenum. The sulfide was precipitated from solutions containing weighed samples of sodium molybdate, by the method previously described, using 100 cc. of the hydrogen sulfide reagent and 10 cc. of 24 *M* formic acid as the acidifying agent.

TABLE II

DETERMINATION OF MOLYBDENUM AS MoO_3

Grams of $Na_2MoO_4 \cdot 2H_2O$	Weight of molybdic oxide		
	Recov.	Calcd.	Diff.
0.2547	0.1513	0.1515	−0.0002
.2030	.1203	.1208	− .0005
.1543	.0920	.0918	+ .0002
.1515	.0899	.0901	− .0002
.1208	.0721	.0719	+ .0002
.1021	.0605	.0608	− .0003

If facilities are lacking for igniting the sulfide by the described method, then it is preferable to determine the element by precipitating and weighing lead molybdate.[25] Solution of molybdenum sulfide can be effected by the action of nitric acid and bromine,[26] or a mixture of ammonium hydroxide and hydrogen peroxide.[27] These solvents oxidize the sulfide, producing appreciable amounts of sulfuric acid, so that it is necessary to separate the lead molybdate in the presence of ammonium acetate in order to prevent the precipitation of lead sulfate.[2] The recent work by McCay[28] shows that molybdates can be precipitated quantitatively by silver nitrate and the molybdenum determined by weighing the silver molybdate. The presence of sulfate ion does not interfere with this reaction and the method should prove useful under the present circumstances.

The Precipitation of Molybdenum Sulfide in the Presence of Tungsten

When a solution of sodium tungstate is treated with hydrogen sulfide and then acidified with dilute acid, no insoluble sulfide is formed. However, when molybdenum sulfide separates from a solution containing both metals it carries down with it part of the tungsten. The degree of contamination varies with the amount of molybdic sulfide formed, the concentration of tungsten in the solution and with the acidity of the medium. Koppel[29] claims that in the presence of formic acid the molybdenum sulfide separates free from tungsten; the writers have not been able to duplicate these results.

Table III is a compilation of analyses of sodium tungstate and molybdate in which the sulfide was separated from solutions containing different concentrations of formic acid. Experiments 2 and 3 correspond to the conditions recommended by Koppel for the separation of the two elements. The results obtained show that the molybdenum sulfide carries down with it large quantities of tungsten, the degree of contamination increasing with the acidity of the solution.

The next matter investigated was whether the results obtained in dilute formic acid media could be improved upon by decreasing the hydrogen-ion concentration of the solution by means of the buffer action of ammonium formate. Under these conditions it was found that a brown colored variety of molybdenum sulfide separated from the solution in a finely divided granular form. After digesting the mixture at 50–60° for one hour the brown sulfide darkens in color, and is then capable of being filtered and washed without encountering any difficulties.

The precipitation of molybdenum sulfide was studied in buffered systems over a range of *p*H from 5.0 to 3.0. As the *p*H increased, the sulfide precipitated in purer form, and it was found that tungsten did not co-precipitate when the *p*H of the solution exceeded 4.5. Under these conditions, however, the hydrogen-ion concentration of the solution is not sufficient to decompose all of the soluble sulfomolybdate, with the result that part of the molybdenum remains unprecipitated. The data obtained from these experiments are summarized in Table IV.

A further attempt was made to render the above processes quantitative by precipitating the molybdenum sulfide in two stages, the idea being to precipitate the bulk of the sulfide in a pure form at a *p*H of 5.0, and then to complete the precipitation by a secondary addition of formic acid. Since the quantity of tungsten that coprecipitates is proportionate to the amount of molybdenum sulfide formed, the mechanism suggested that only a negligibly small amount of the metal would be carried down during the formation of the residual molybdic sulfide upon further acidification.

The experimental data assembled in Table V were obtained by dissolving the weighed salts in 10 cc. of water, 10 cc. of 50% ammonium formate and 100 cc. of hydrogen sulfide water saturated at 0°. Precipitation was initiated in solutions 1–5 by the addition of 5 cc. of 2 *M* formic acid and digesting the mixtures at 60° for one hour. The decomposition of the sulfomolybdate was completed by the further addition of 10 cc. of 2 *M* formic acid. The treatment given to samples 6 and 7 differed from that received from the others only in that the dilute and concentrated formic acids were added at approximately the same time. Comparison of the results obtained in experiments 4 and 5 with those from 6 and 7 shows that though the two-stage decomposition of the ammonium sulfo-

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[25] T. M. Chatard, *Am. J. Sci.*, [3] **1**, 416 (1871).

[26] J. C. Evans, *Western Chemist and Metallurgist*, **3**, 218 (1907).

[27] C. A. Mitchell, "Recent Advances in Analytical Chemistry," Philadelphia, 1931, Vol. II, p. 287.

[28] LeRoy W. McCay, THIS JOURNAL, **56**, 2548 (1934).

[29] I. Koppel, *Chem.-Z.*, **48**, 801 (1924).

TABLE III

SEPARATION OF MOLYBDENUM SULFIDE FROM TUNGSTEN IN FORMIC ACID MEDIA

Expt. no.	Mol. of soln.	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide			Tungstic oxide		
				Recov.	Calcd.	Diff.	Recov.	Calcd.	Diff.
1	0.27	0.1003	0.1000	0.0749	0.0597	+0.0152	0.0528	0.0703	−0.0175
2	1.1	.1008	.1003	.0778	.0600	+ .0178	.0543	.0705	− .0162
3	1.1	.1052	.1512	.0839	.0626	+ .0213	.0873	.1063	− .0190
4	1.8	.1054	.1004	.1107	.0627	+ .0480	.0253	.0706	− .0453
5	1.8	.0533	.3014	.0928	.0317	+ .0611	.1495	.2119	− .0624

TABLE IV

SEPARATION OF MOLYBDENUM SULFIDE FROM TUNGSTEN IN BUFFERED MEDIA

System A: 25 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System B: 10 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System C: 5 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System D: 5 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 25 cc. of 2 *M* formic acid.

System	*p*H[30]	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide			
				Recov.	Calcd.	Diff.	Color
A	5.0	0.2032	....	0.1087	0.1209	−0.0122	White
		.3006	0.3020	.1677	.1789	− .0112	White
B	4.5	.0524	....	.0272	.0312	− .0040	White
		.2029	.2040	.1272	.1207	+ .0065	Faint yellow
		.2011	.2027	.1283	.1197	+ .0086	Faint yellow
C	3.9	.2030	....	.1203	.1208	− .0005	White
		.2008	.2022	.1324	.1195	+ .0129	Yellow
		.1990	.1034	.1279	.1184	+ .0095	Yellow
		.1012	.1030	.0621	.0602	+ .0019	Faint yellow
D	3.5	.2484	....	.1475	.1478	− .0003	White
		.2488	.3017	.1662	.1480	+ .0182	Yellow

TABLE V

TWO-STAGE SEPARATION OF MOLYBDENUM SULFIDE

Expt.	$Na_2MoO_4 \cdot 4H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide		
			Recov.	Calcd.	Diff.
1	0.1592	....	0.0947	0.0947	0.0000
2	.0558	....	.0330	.0332	− .0002
3	.1252	.3086	.0906	.0745	+ .0161
4	.1700	.4000	.1198	.1012	+ .0186
5	.1694	.4000	.1193	.1008	+ .0185
6	.1710	.4000	.1376	.1017	+ .0359
7	.1703	.4000	.1398	.1013	+ .0385

molybdate produces a less contaminated sulfide than that precipitated from a solution whose *p*H is adjusted to 3.0 from the very beginning of the reaction, the mechanism is not able to produce a quantitative separation of the two elements.

Since molybdenum sulfide can be precipitated free from tungsten in solutions containing tartaric acid,[31] experiments were made to determine whether the amount of tartaric acid required for the quantitative separation of the two metals could be diminished by conducting the reaction in solutions buffered by ammonium formate.

Weighed samples of sodium molybdate, of approximately the same mass, were dissolved in 10 cc. of a standardized solution of sodium tungstate containing 4 g. of $Na_2WO_4 \cdot 2H_2O$ per 100 cc. To these solutions were added varying volumes of 50% tartaric acid and 50% ammonium formate, 100 cc. of hydrogen sulfide reagent and 10 cc. of 24 *M* formic acid. The mixtures were kept at 60° for ninety minutes, a small quantity of filter paper pulp was added, the precipitates were permitted to settle, and then filtered through porous bottom porcelain crucibles. The sulfides were washed with five 10-cc. portions of a solution consisting of 5 cc. of 50% ammonium formate, 5 cc. of 24 *M* formic acid and 100 cc. of water; then ignited to oxides at 550° and weighed. The difference between the weights of the recovered oxides and the theoretical weight of molybdic oxide equivalent to the sodium molybdate put into the solution is a measure of the amount of tungstic oxide carried down by the molybdenum sulfide. The degree of co-precipitation can also be judged from the color of the resultant oxide. Pure molybdic oxide is white, and when it is contaminated, it is colored yellow by the tungstic oxide. The yellow coloration becomes quite pronounced when the impure oxide contains more than 4% of tungsten.

The results obtained from these experiments, recorded graphically in Fig. 2 show that in the absence of ammonium formate the molybdenum sulfide carries down with it appreciable amounts of tungsten even though the solution contains a high concentration of tartaric acid. The sulfide that separates under these conditions is black and non-crystalline, and filters and washes with great difficulty. Hence, part of the error observed in experiments 1–8 may be due to the presence of sulfotungstate in the incompletely washed precipitate, as is also indicated by the erratic disposition of the points in curve A of Fig. 2. In solutions buffered with ammonium formate, the tartaric acid is more effective in producing a complete separation

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(30) The *p*H values of the solutions were estimated by the use of suitable indicators and standard buffer mixtures. Because of the bleaching action of the hydrogen sulfide, the measurements had to be made on independent systems in which an equal volume of water was substituted for the 100 cc. of the hydrogen sulfide reagent.

(31) Heinrich Rose, "Ausführliches Handbuch der analytischen Chemie," Vol. I, Part 2 (1851), pp. 356–357.

of the molybdenum sulfide from the tungsten, as can be seen by comparing the curves in Fig. 2.

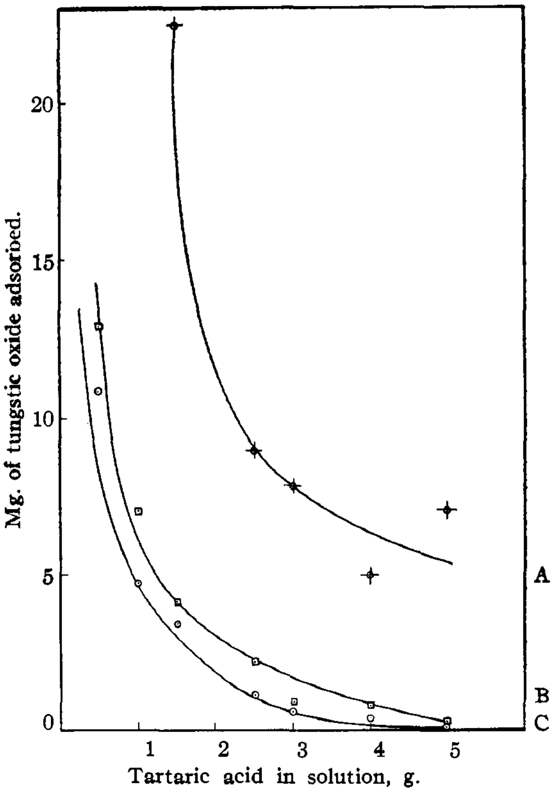

Fig. 2.—Contamination of MoS_3 by tungsten: ⊕, ammonium formate absent; ⊡, 2.5 g. of ammonium formate; ⊙, 5.0 g. of ammonium formate.

On the basis of the evidence presented in Table V and Fig. 2 the following procedure was developed for the separation and determination of molybdenum in the presence of tungsten.

Procedure A.—Dissolve the two salts in 10–15 cc. of water in a 250-cc. Erlenmeyer flask, add 10 cc. of 50% ammonium formate, 10 cc. of 30% tartaric acid, 100 cc. of hydrogen sulfide water saturated at 0° and 10 cc. of 2 *M* formic acid.[32] Heat the mixture on a water-bath to 60° and maintain the temperature for one hour. At the end of the digestion, add a small quantity of filter paper pulp, suspended in about 10 cc. of water, and complete the precipitation of the molybdenum sulfide by adding 10 cc. of 24 *M* formic acid. Keep the mixture in the water-bath for a period of thirty minutes, allow the precipitate to settle, and filter through a porous bottom or a Gooch crucible which has been heated to about 500°. Wash the precipitate with five 10-cc. portions of a solution made by diluting 5 cc. of 50% ammonium formate and 5 cc. of 24 *M* formic acid with 100 cc. of water. Ignite the precipitate in the oven described in Fig. 1 for twenty to thirty minutes until conversion to the oxide is complete; cool and weigh. Reheat the crucible over fifteen-minute intervals until it attains constant weight. Usually the conversion is complete at the end of the first ignition.

TABLE VI

SEPARATION OF MoS_3 FROM TUNGSTEN

Expt.	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	White molybdic oxide		
			Recov.	Calcd.	Diff.
1	0.0513	....	0.0304	0.0305	−0.0001
2	.0516	0.0516	.0300	.0307	− .0007
3	.0509	.5013	.0298	.0303	− .0005
4	.0524	.5031	.0303	.0312	− .0009
5	.1698	....	.1013	.1010	+ .0003
6	.1704	.2026	.1012	.1014	− .0002

The results obtained following this procedure are recorded in Table VI. The small differences between the calculated and the observed values, together with the white color of the oxides, indicates that a fairly sharp separation of the two elements has been effected.

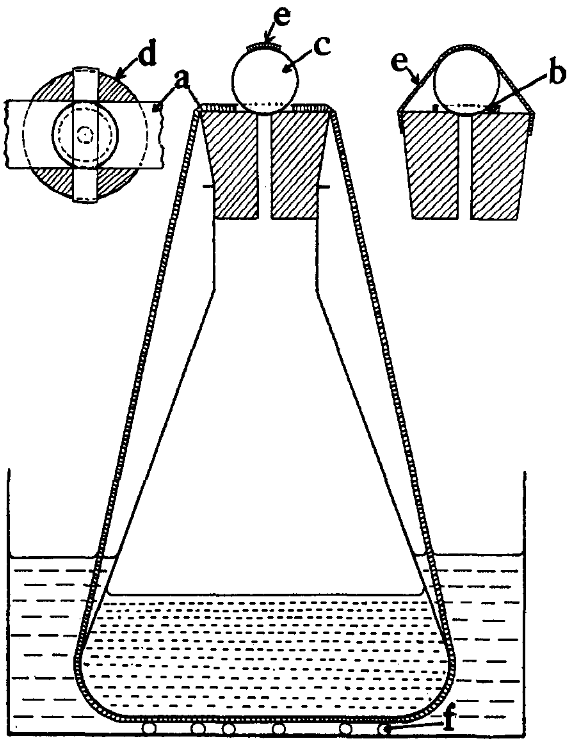

Fig. 3.—Safety pressure flask: a, large endless rubber band 1.4 mm. thick, 1.6 mm. wide and 25 cm. peripheral length at rest; b, 1.3 cm. diam. hole in rubber band; c, 1.6 cm. diam. sphere of glass or "marble"; d, semi-hard rubber stopper with 3-mm. hole in center; e, rubber band 6.4 mm. wide and 0.8 mm. thick; f, glass beads.

During the progress of this work recourse was made to the precipitation of molybdenum sulfide in pressure bottles. Difficulty was encountered in transferring the precipitate quantitatively from the pressure bottle of usual design owing to its narrow mouth and the dangling of the capping device when pouring the contents. Efforts were therefore made to convert Erlenmeyer flasks into pressure

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[32] At this point the solution has a *p*H of 3.9; after the addition of the concentrated formic acid the *p*H drops to 2.9. Crystals of ammonium hydrogen tartrate may separate on the addition of the cold hydrogen sulfide solution, but these redissolve during the subsequent warming of the mixture.

bottles by closing the neck with a rubber stopper, the latter being kept in place by stretching rubber bands around it and the base of the flask. On warming the hydrogen sulfide mixture to 60°, the pressure developed by the liberated gases usually popped the stopper and on two occasions broke the bottom out of the flask.

To prevent such accidents, the safety pressure flask illustrated in Fig. 3 was designed. When the pressure inside the flask becomes sufficiently high, the sphere covering the opening in the stopper loosens and permits some of the gas to escape until the restoring force of the rubber band that keeps it in position is sufficient to balance the internal pressure. The equilibrium pressure varies with the tension in the band supporting the sphere. By closing a suction flask with these valves, maximum pressures above atmospheric of 46–80 cm. of mercury were recorded on a manometer attached to the side-arm.

The construction of the stoppering device is apparent from the figure. The accessory rubber bands are secured to the stopper by means of rubber cement. The band holding the sphere in place is best made by cutting the necessary length from a piece of 6-mm. rubber tubing. The semi-circular cross section of the tubing hugs the surface of the sphere and prevents side slippage.

TABLE VII

PRECIPITATION OF MOLYBDIC SULFIDE UNDER PRESSURE

Pressure, atm.	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	White molybdic oxide Recov.	Calcd.	Diff.
1.0	0.1693	....	0.1007	0.1007	0.0000
1.5[33]	.1709	....	.1017	.1017	.0000
1.0	.0534	....	.0314	.0318	− .0004
1.5	.0498	....	.0295	.0296	− .0001
1.0	.0498	....	.0290	.0296	− .0006
1.5	.0498	....	.0295	.0296	− .0001
1.0	.0523	0.5019	.0308	.0311	− .0003
1.5	.0501	.5022	.0296	.0298	− .0002

The results obtained by conducting the precipitation of the molybdenum sulfide in the safety pressure flasks, recorded in Table VII, show that the negative errors in the determination of molybdenum are slightly decreased. In general, little advantage is gained by conducting the precipitation under pressure. The use of the pressure flasks is recommended when the sample of tungsten contains only small amounts of molybdenum, or in the absence of adequate ventilation, to minimize the odor of the gas in the laboratory during the long digestion period.

The Determination of Tungsten

The filtrate and washings resulting from the separation of the molybdenum sulfide contains the tungsten in solution combined as a tartaro complex, together with the excess hydrogen sulfide, ammonium formate and formic acid. Evaporating the solution down to near dryness effects the removal of the hydrogen sulfide, formic acid and part of the ammonium formate. Treatment of the residue with 12 *M* hydrochloric acid and cinchonine precipitates after prolonged boiling the greater part of the tungstic acid in the form of a hard crystalline mass that adheres tenaciously to the surface of the beaker. The yield is not quantitative, as shown by the figures below.

$Na_2WO_4 \cdot 2H_2O$	Tungstic oxide Recov.	Calcd.	Diff.
0.2033	0.1385	0.1429	−0.0044
.1013	.0488	.0712	− .0224

Procedure B.—Treatment of the concentrated filtrate with 25 cc. of 16 *M* nitric acid produces a much better recovery of the tungsten. The acid facilitates the completion of the reaction by the removal of the ammonium salts, the presence of which retards the precipitation of tungstic acid,[2] (pp. 119 and 552), and also in that the simultaneous evolution of gases during the decomposition prevents the precipitate from adhering to the walls of the vessel. When the removal of the ammonium salts is completed the mixture is diluted with 100 cc. of water and 5 cc. of cinchonine reagent,[34] digested on a hot-plate for two hours and then filtered through an ashless filter paper. The precipitate is washed, ignited at 750° and the tungstic oxide weighed. The results obtained by following this procedure are not strictly quantitative except when only a small quantity of tartaric acid is present. For a given amount of tartaric acid the amount of tungsten remaining unprecipitated is remarkably constant, and by applying the necessary correction factor, the method is recommended for rapid routine analyses.

TABLE VIII

SEPARATION OF TUNGSTEN IN THE PRESENCE OF TARTARIC ACID USING 16 *M* NITRIC ACID

Tart. acid, g.	$Na_2WO_4 \cdot 2H_2O$[34]	Tungstic oxide Recov.	Calcd.	Diff.
3.0	0.5046	0.3489	0.3547	−0.0058
3.0	.2081	.1406	.1463	− .0057
3.0	.2026	.1366	.1424	− .0058
3.0	.2004	.1352	.1409	− .0057
3.0	.1032	.0668	.0726	− .0058
3.0	.0559	.0334	.0393	− .0059
1.0	.2033	.1418	.1429	− .0011
1.0	.2014	.1403	.1416	− .0013
0.52	.2137	.1497	.1502	− .0005
.51	.2031	.1425	.1428	− .0003
...	.2020	.1417	.1420	− .0003

The precise determination of tungsten in the filtrate resulting from the separation of the molybdenum sulfide

TABLE IX

SOLUBILITY OF AMMONIUM HYDROGEN TARTRATE AT 29°

Ratio water: alcohol	95% alcohol by volume	$NH_4HC_4H_4O_6$ per cc. of solution, g.	Equiv. tart. acid, g. per cc.
1:0	...	0.0343	0.0308
1:1	50.0	.0048	.0043
1:2	66.7	.0018	.0016
0:1	100.0	.00005	.000045

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(33) This pressure is small compared with the total pressure obtainable by heating the mixture in a standard pressure flask at 100°. The partial pressure of the hydrogen sulfide, however, is probably comparable in both cases.

(34) The samples were dissolved in 100 cc. of water, to which was added the weighed quantities of tartaric acid, 10 cc. of 50% ammonium formate and 10 cc. of 24 *M* formic acid. These solutions were evaporated to 15 cc., and when cool, 25 cc. of 16 *M* nitric acid was added. The precipitate was then further treated as described in procedure B.

TABLE X

SEPARATION AND DETERMINATION OF TUNGSTEN AND MOLYBDENUM

$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide			Tungstic oxide		
		Recov.	Calcd.	Diff.	Recov.	Calcd.	Diff.
0.1703	....	0.1010	0.1013	−0.0003	0.0004	0.0000	+0.0004
....	0.5018	.0002	.0000	+ .0002	.3522	.3528	− .0006
.1725	.1718	.1031	.1026	+ .0005	.1210	.1207	+ .0003
.0539	.0531	.0320	.0321	− .0001	.0365	.0373	− .0008
.0505	.3020	.0300	.0301	− .0001	.2118	.2123	− .0005

necessitates the removal of the greater part of the tartaric acid contained in it. Treatment with oxidizing acids is not recommended, as the process requires many repetitions in order to complete the destruction of the organic matter, and is subject to loss of material due to spattering.

During the later stages of the evaporation of the filtrate, ammonium hydrogen tartrate crystallizes from the solution. The greater part of the organic matter can be removed by taking advantage of the small solubility of this salt in mixtures of alcohol and water.

The solubility of ammonium hydrogen tartrate in water–alcohol systems was approximated by evaporating measured volumes of the saturated solutions and weighing the dry residues. From the solubility data in Table IX it can be seen that by evaporating the filtrate down to a volume of about 25 cc. and adding 50 cc. of alcohol to the concentrate, only about 120 mg. of tartaric acid will remain in solution. This small amount of tartrate no longer interferes with the quantitative separation of tungstic acid, as is demonstrated by the preceding experiments in Table VIII. After being washed with 50% alcohol, the crystals still occlude small quantities of tungsten. This is readily recovered by charring the filter paper containing the ammonium hydrogen tartrate in a platinum crucible containing about 500 mg. of sodium carbonate[2] (p. 61), extracting the residue with water, filtering off any carbonaceous matter, and adding the filtrate to the solution containing the bulk of the tungsten. The resultant solution is evaporated to a small volume to effect the removal of the alcohol, and the tungstic acid is precipitated by the addition of 25 cc. of 16 *M* nitric acid. From this point the precipitate is treated as described in procedure B.

In the table above are recorded the results of several analyses of mixtures of sodium tungstate and molybdate, arrived at by following procedure A for the separation of the sulfides in the presence of ammonium formate, tartaric and formic acids. The close agreement between the recovered and theoretical weights of the oxides shows that the method is satisfactory for the separation of the two metals in the absence of interfering elements. The application of these methods to the analysis of steels and minerals containing tungsten and molybdenum is in the process of investigation.

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Summary

A new technique is described for precipitating metallic sulfides, using a saturated solution of hydrogen sulfide in water at 0° as the reagent. Molybdenum sulfide can be precipitated quantitatively in formic acid media by initiating the reaction at a low temperature and maintaining a high concentration of hydrogen sulfide in the solution. A quantitative separation of the sulfide in the presence of tungsten can be effected in a solution whose *p*H is adjusted to 2.9 by a buffer mixture consisting of ammonium formate, tartaric and formic acids. The article contains descriptions of a simple electric furnace for igniting precipitates at a constant temperature, and of an improved pressure bottle.

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