

ACTION OF HYPOPHOSPHOROUS ACID UPON MOLYBDIC ACID.

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It seemed to us a matter of some interest to learn to what degree molybdic acid could be reduced by hypophosphorous acid. With that end in view, 17.5 grams of very pure ammonium molybdate were dissolved in a liter of water, thus making an approximately tenth-normal solution of the trioxide. However, the real molybdenum content of this solution was ascertained by reducing a known volume of the liquid with zinc and sulphuric acid, and then reoxidizing with a standardized potassium permanganate solution. A one per cent. solution of hypophosphorous acid was employed to effect the reductions.

It was observed that when a concentrated solution of hypophosphorous acid acted upon a concentrated solution of molybdic acid, the liquid assumed at first a yellow and subsequently a brown color. If the solutions were, however, diluted no change in color was noticed in the cold, but upon the application of heat a deep blue color made its appearance. Upon adding a solution of potassium permanganate to this hot liquid the end-reaction was not well defined. If, however, the blue solution was cooled and then treated with permanganate, the end-reaction (complete decolorization) became sharp. The slightest excess of oxidant then occasioned the usual purple tinge. On standing, the liquid slowly regained a blue color, because, doubtless, of the reducing effect of traces of excessive hypophosphorous acid.

The titrations were conducted in solutions (*a*) made acid by a definite excess of hypophosphorous acid, (*b*) acidulated with sulphuric acid, and (*c*) neutralized with an excess of barium carbonate. Barium hypophosphite caused no reduction in the molybdate solution even when it was boiled. In one instance the cold, reduced solution was poured into a measured excess of potassium permanganate acidulated with sulphuric acid, and titrated back with a ferrousulphate solution. The most satisfactory results were obtained in titrating the cold solutions, acidulated with sulphuric acid. They are recorded in the following table:

TABLE.

1.0 cc. solution = 0.01256 gram molybdenum trioxide.

I. MoO ₃ .	II. Weight MoO ₃ .	III. KMnO ₄ .	IV. 1 cc. KMnO ₄ = 0.006523 gram O We O represented by KMnO ₄ .	V. Weight Mo.	VI. Weight Mo ₂ O ₅ (subtract IV from II).	VII. H ₂ PO ₂ (One per cent.)	VIII. Time boiled.	IX. Mo in VI.	X. O in VI.	XI. Ratio of Mo to O.
cc.	Gram.	cc.	Gram.	Gram.	Gram.	cc.	Min-utes.	Per cent.	Per cent.	
25	0.31399	25.5	0.01663	0.20933	0.29736	5	15	70.39	29.61	
25	0.31399	20.5	0.01337	0.20933	0.30062	5	15	69.63	30.37	Mo ₂ O _{5.2}
25	0.31399	26.2	0.01709	0.20933	0.29690	5	30	70.50	29.50	
25	0.31399	29.1	0.01898	0.20933	0.29501	5	30	70.95	29.05	
25	0.31399	28.7	0.01872	0.20933	0.29527	5	60	70.89	29.11	
25	0.31399	28.5	0.01859	0.20933	0.29540	5	60	70.86	29.14	
20	0.25120	20.3	0.01324	0.16747	0.23796	4	60	70.37	29.63	
30	0.37680	31.0	0.02022	0.25120	0.35658	6	60	70.44	29.56	
						Mean		70.48	29.52	Mo ₂ O ₅
								70.59	29.41	
								0.11	0.11	

1.0 cc. solution = 0.012836 gram molybdenum trioxide.

20	0.25671	24.2	0.01579	0.17114	0.24092	4	—	71.07	28.93	
20	0.25671	24.2	0.01579	0.17114	0.24092	8	—	71.07	28.93	
30	0.38506	30.1	0.01963	0.25671	0.36543	6	—	70.25	29.25	
30	0.38506	35.1	0.02289	0.25671	0.36217	10	—	70.89	29.11	
25	0.32089	31.4	0.02048	0.21293	0.30041	6	35	70.87	29.13	
25	0.32089	35.6	0.02322	0.21293	0.29767	10	35	71.53	28.47	
35	0.44925	44.5	0.02903	0.29950	0.42022	8	37	71.27	28.73	
35	0.44925	50.3	0.03281	0.29950	0.41644	10	40	71.91	28.09	
20	0.25671	25.8	0.01683	0.17114	0.23988	4	45	71.34	28.66	
20	0.25671	26.5	0.01728	0.17114	0.23942	8	45	71.49	28.51	
20	0.25671	27.0	0.01761	0.17114	0.23900	8	45	71.58	28.42	
30	0.38506	43.0	0.02805	0.25671	0.35701	10	75	71.95	28.05	
30	0.38506	38.3	0.02498	0.25671	0.36008	10	60	71.29	28.71	
30	0.38506	40.1	0.02616	0.25671	0.35090	10	60	71.25	28.75	
20	0.25671	29.1	0.01898	0.17114	0.23773	10	60	71.94	28.06	
20	0.25671	32.3	0.02107	0.17114	0.23564	10	75	72.62	27.38	Mo ₂ O _{4.52}
						Mean		71.39	28.61	
								70.59	29.41	
								0.80	0.80	
25	0.32089	26.5	0.01729	0.21293	0.30360	10	60	70.35	29.65	
25	0.32089	33.8	0.02205	0.21293	0.29884	10	60	71.25	28.75	
25	0.32089	28.5	0.01859	0.21293	0.30230	6	60	70.43	29.57	
25	0.32089	27.2	0.01742	0.21293	0.30315	6	60	70.23	29.77	
						Mean		70.56	29.44	Mo ₂ O ₅
								70.59	29.41	
								0.03	0.03	
								70.59	29.41	

Mo₂O₅ requires theoretically

In carrying out the determinations a measured quantity of the molybdic acid solution was introduced into an Erlenmeyer flask. This was followed with a definite volume of hypophosphorous acid of known strength. The mixture was then diluted to 150 cc. with water, and boiled on a stove plate for a definite period. After this the solution was chilled and immediately titrated with the permanganate solution.

An examination of the results warrants the conclusion that hypophosphorous acid reduces molybdic acid to the pentoxide (Mo_2O_5), and further that the method can not be regarded as applicable for trustworthy quantitative determinations of molybdenum.

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ON THE CONSTITUTION OF BARYTOCELESTITES.¹

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ON a former occasion² I presented the result of analytical work and investigations on barium and strontium minerals occurring in the crystalline limestone of Eastern Ontario. I now have the honor to report on the analysis of a fourth species of these minerals from the same locality.

In the previous report, I have described the analytical methods. The principal interest may be found in the deductions and conclusions which follow the chemical work.

To judge from current literature, opinions seem to be uncertain as to the composition or existence of barytocelestites. Rammelsberg³ states that Thomson's barytocelestites from the Lake Huron district was found by Professor Hunt to be free from barium. Dana, in his system,⁴ is of the same opinion, and in the sixth edition⁵ mentions merely the analyses, showing celestites with varying amounts of barium sulphate.

The celestite from Lansdowne, Eastern Ontario, reported from my analysis in 1891 as containing over three per cent. of barium sulphate, was likewise found by the analyst of the Canadian Geological Survey to be pure strontium sulphate, with only

¹ Read at the New York meeting of the American Chemical Society, December 28, 1898.

² This Journal, 13, 290 (1897).

³ Rammelsberg, *Mineralchemie*, 2d edition, p. 255.

⁴ Dana's System, V, p. 620.

⁵ Dana's System, VI, p. 906.