ART. XXXVII.—*The Determination of Vanadic and Molybdic Acids in the Presence of One Another*; by GRAHAM EDGAR.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxii.]

A METHOD has been recently proposed by Glasmann* for the estimation of vanadic and molybdic acids in the presence of one another, based on the different reducing action of zinc and magnesium upon the hydrochloric acid solution of these acids. In a previous paper from this laboratory† it has been shown that the action of magnesium is irregular and not adapted to an accurate quantitative method. Vanadic acid, however, is reduced to the state of dioxide by a column of amalgamated zinc and may be estimated by titration with potassium permanganate, if the receiver be charged with a solution of ferric alum to anticipate the oxidizing action of the air.‡ That molybdic acid is under the same conditions reduced to the state of Mo_2O_3 has been shown by Dudley§ and, independently by Randall.¶ The ease with which vanadic acid is reduced to the state of tetroxide by sulphur dioxide and the difficulty, as has been found, with which this reagent attacks molybdic acid under proper conditions of acidity and concentration, suggest its use in one of two processes of differential action for the determination of these acids. To determine the conditions under which molybdic acid is unaffected by sulphur dioxide, a series of experiments was made in which solutions of molybdic acid of varying concentrations, acidified with varying amounts of sulphuric acid, were heated to boiling and treated with a current of sulphur dioxide for varying lengths of time. The excess of sulphur dioxide was then removed by boiling the solution, a current of carbon dioxide being meanwhile passed into it, and the degree of reduction was determined by titration with nearly N/10 potassium permanganate. The solution of molybdic acid was standardized by the method of Randall¶ and by evaporating a portion to dryness and igniting at low red heat. The results of the experiments are given in Table I.

The results show that if the concentration be not greater than 0.2 gm. of MoO_3 in 50^{cm^3} of solution, and the acidity not less than 1^{cm^3} of sulphuric acid (sp. gr. 1.84) in the same volume, the molybdic acid is not reduced, and that if the acidity be increased to 5^{cm^3} of sulphuric acid, reduction does not occur at even a concentration of 0.4 gm. in 25^{cm^3} .

* Ber. Dtsch. chem. Gesellsch., xxxviii, 600.

† Gooch and Edgar, this Journal, xxv, 233.

‡ Gooch and Edgar, loc. cit.

§ Unpublished, but privately communicated by Professor Henry Fay.

¶ This Journal, xxiv, Oct. 1907.

¶ Loc. cit.

TABLE I.

Volume of solution cm ³ .	MoO ₃ grm.	H ₂ SO ₄ sp. gr. 1.84 cm ³ .	Time of treatment with SO ₂	N KMnO ₄ 10 × 1.004 cm ³ .	Color of solution
25.0	0.200	faintly acid	10 min.	0.15	light blue
35.0	0.200	0.5 ^{cm³}	10 "	0.05	faint blue
50.0	0.200	1.0 ^{cm³}	10 "	0.0	colorless
75.0	0.200	2.0 ^{cm³}	10 "	0.0	"
50.0	0.200	2.0 ^{cm³}	30 "	0.0	"
25.0	0.200	5.0 ^{cm³}	10 "	0.0	"
25.0	0.400	5.0 ^{cm³}	10 "	0.0	"
50.0	0.400	5.0 ^{cm³}	10 "	0.0	"
50.0	0.400	10.0 ^{cm³}	10 "	0.0	"
50.0	0.400	15.0 ^{cm³}	10 "	0.0	"

A series of experiments was then made in which solutions containing vanadic and molybdic acids were diluted to 75^{cm³}, acidified with 2 to 3^{cm³} of strong sulphuric acid, heated to boiling and subjected to a current of sulphur dioxide for a few minutes until the clear blue color indicated the complete reduction of the vanadic acid to the state of tetroxide. The boiling was continued for some time, a current of carbon dioxide being passed into the liquid until the last traces of sulphur dioxide had been removed. Titration was then effected by nearly N/10 potassium permanganate and the vanadic acid was calculated from the equation,

The solution, preceded by 100^{cm³} hot water, and 125^{cm³} of dilute (2½ per cent) sulphuric acid, and followed by 100^{cm³} dilute sulphuric acid and 200^{cm³} of hot water, was passed slowly through a column of amalgamated zinc in a Jones reductor,* the receiver containing a solution of ferric alum. The hot solution was then titrated with nearly N/10 potassium permanganate, a little phosphoric acid being added to decolorize the ferric salt.

Since the reduction of vanadic acid is in this case to the condition of dioxide, V₂O₃, if the number of centimeters of permanganate used in the titration of the tetroxide be multiplied by three and the product subtracted from the total number of centimeters of permanganate used in the final titration, the result is the number of centimeters used in oxidizing Mo₂O₃ to MoO₃, from which the amount of molybdic acid present may be easily calculated. The results, given in Table II, show that molybdic acid and vanadic acid may be accurately estimated in the presence of one another by two processes of reduction and oxidation, the reduction being made first by sulphur dioxide and last by amalgamated zinc.

* The Chemical Analysis of Iron, Blair, page 225.

TABLE II.

Ferric alum 10% cm ³ .	Phos- phoric acid syrup cm ³ .	KMnO ₄ $\frac{N}{10} \times 1.052$ cm ³ .	KMnO ₄ $\frac{N}{10} \times 1.052$ cm ³ .	V ₂ O ₅ taken as NaVO ₃ gram.	MoO ₃ taken as (NH ₄) ₂ MoO ₄ gram.	V ₂ O ₅ found gram.	MoO ₃ found gram.	Error on V ₂ O ₅ gram.	Error on MoO ₃ gram.
50	8	11.95	74.15	0.1144	0.1930	0.1146	0.1934	+ .0002	+ .0004
50	8	11.95	74.00	0.1144	0.1930	0.1146	0.1926	+ .0002	— .0004
50	8	11.94	74.20	0.1144	0.1930	0.1145	0.1936	+ .0001	+ .0006
25	4	5.97	37.10	0.0572	0.0965	0.0572	0.0965	.0000	.0000
25	4	5.97	37.05	0.0572	0.0965	0.0572	0.0962	+ .0000	— .0003
25	4	5.98	37.12	0.0572	0.0965	0.0573	0.0963	+ .0001	— .0002
35	6	11.95	55.0	0.1144	0.0965	0.1146	0.0967	+ .0002	+ .0002
35	6	11.95	55.0	0.1144	0.0965	0.1146	0.0967	+ .0002	+ .0002
35	6	11.96	54.86	0.1144	0.0965	0.1147	0.0958	+ .0003	— .0007
65	10	17.92	92.0	0.1716	0.1930	0.1719	0.1931	+ .0003	+ .0001
65	10	17.94	92.05	0.1716	0.1930	0.1720	0.1931	+ .0004	+ .0001
65	10	17.92	92.02	0.1716	0.1930	0.1719	0.1932	+ .0003	+ .0002

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