

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, PRINCETON UNIVERSITY]

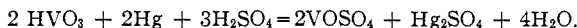
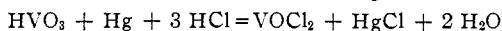
THE REDUCTION OF VANADIC ACID SOLUTIONS WITH MERCURY

By LEROY W. MCCAY AND WILLIAM T. ANDERSON, JR.

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Theoretical

When a hydrochloric or sulfuric acid solution of a vanadate is shaken vigorously in the presence of mercury the solution becomes pure blue in color, the vanadium being reduced to the quadrivalent state.



If the sulfuric acid solution of the vanadate, before shaking it with mercury, be mixed with a solution of a little more sodium chloride than that equivalent to the mercurous sulfate formed, as indicated in the above equation, all the mercury oxidized during the reaction will be precipitated as mercurous chloride, which can be filtered off and a clear liquid obtained suitable for titration with potassium permanganate. The removal of the mercury present in the lower state of oxidation is necessary, for solutions of mercurous salts are oxidized by permanganate. A solution of potassium permanganate acts upon one of a vanadyl salt heated to about 80° in the following manner.



One cc. of 0.1 *N* permanganate solution is equivalent to 0.0051 g. of vanadium. The results are very accurate, for the small amount of chloride remaining in the solution has no perceptible action on the permanganate. Fifty cc. of 0.1 *N* permanganate solution shows the presence of 0.255 g. of vanadium, which is equivalent to 1.003 g. of mercury as mercurous salt, and to react with this quantity 0.2925 g. of sodium chloride is required. Assuming then that in making a determination of vanadium not more than 50 cc. of 0.1 *N* permanganate solution will be required, 0.3 g. of sodium chloride should be dissolved in the sulfuric acid solution prior to reducing it with mercury.

Experimental

The sulfuric acid solution of vanadic acid, containing the necessary amount of sodium chloride and diluted to about 100 cc., was placed in a bottle of convenient size provided with a well fitting ground-glass stopper, 20 cc. (272 g.) of mercury was added, the bottle stoppered and the whole shaken vigorously for 5 minutes. The liquid above the slate-colored mixture of finely divided mercury and mercurous chloride was decanted into a small beaker, from which it was poured through a suction filter.

The residue in the bottle was washed four times by decantation, 20 cc. of water being used for each washing, and the washings were severally decanted into the beaker and then through the filter. The procedure here followed is identical with that described in a recent paper,¹ where directions for the recovery of the mercury are also given. The filtrate was then diluted to 250 cc., heated to 80–90° and titrated with permanganate to the faintest pink. Since the mixture of mercury and mercurous chloride remaining in the bottle is as active as pure mercury, the bottle after each determination was stoppered and placed aside so as to be ready at any moment for further reductions. To reduce a solution, filter it, carry out the necessary washings, heat to 90° and titrate requires about half an hour.

A solution of crystallized sodium vanadate, containing somewhat more sulfuric acid than that necessary to inhibit the separation of any metavanadates, was standardized by the sulfur dioxide² and then examined by the mercury method.

Sulfur Dioxide Method			Mercury Method		
No.	Using 0.1 <i>N</i>	Using 0.05 <i>N</i>	No.	Using 0.1 <i>N</i>	Using 0.05 <i>N</i>
	KMnO ₄ and 25 cc. of solution	KMnO ₄ and 10 cc. of solution		KMnO ₄ and 25 cc. of solution	KMnO ₄ and 10 cc. of solution
	V G.	V G.		V G.	V G.
1	0.1033	0.0410	1	0.1033	0.0411
2	0.1033	0.0411	2	0.1039	0.0411
3	0.1035	0.0411	3	0.1036	0.0410
			4	0.1033	

Another solution, prepared as above outlined and standardized carefully by the sulfur dioxide method by M., was examined according to the mercury method by A. to whom the concentration of the solution was unknown. Fifty cc. of this solution was taken in each case and an approximately 0.1 *N* potassium permanganate solution was employed.

No.	Sulfur Dioxide Method (M)	Mercury Method (A)
	Found V G.	Found V G.
1	0.1379	0.1375
2	0.1373	0.1373
3	0.1376	0.1375
4	0.1373
5	0.1374
Av.	0.1376	0.1374

The results obtained by the two methods are practically identical.

Since hydrochloric and sulfuric acid solutions of arsenic acid are not reduced when shaken with mercury, the method may be employed for the

¹ THIS JOURNAL, 43, 2372 (1921).

² Treadwell-Hall, "Quantitative Analysis." John Wiley and Sons, New York, 1908, p. 501.

determination of vanadium in the presence of arsenic acid.³ That the results obtained are very accurate will be evident from those given below. Sulfuric acid solutions containing the amount of sodium chloride specified were employed in all cases.

No.	Vanadium Taken ^a G.	KH ₂ AsO ₄ G.	Vanadium Found G.
1	0.1376	0.2391	0.1375
2	0.1376	0.1564	0.1375
3	0.1376	0.3008	0.1377

^a 50 cc. of standardized sodium vanadate solution (one above employed) = 0.1376 g. of vanadium.

The presence of uranic acid or a uranyl salt does not interfere with the determination of the vanadium, for when 0.1376 g. of vanadium was taken in the presence of 0.1974 g. of monopotassium orthoarsenate and 0.2103 g. of uranyl nitrate hexahydrate, 0.1376 g. of vanadium (the amount taken) was found. Two check determinations gave 0.1374 and 0.1379 g. of vanadium. The average is 0.1376 g.

While the method has no advantages over the sulfur dioxide process so far as accuracy is concerned, it is shorter and requires less oversight than the latter. The use of sulfur dioxide and hydrogen sulfide as reducing agents is always more or less objectionable, and to expel these gases from the reduced solutions by boiling them in a current of carbon dioxide requires considerable time. It frequently happens, too, that the gases must be especially prepared when a determination of vanadium is called for, whereas the bottle containing the mercury, or mixture of mercury and mercurous chloride, is always ready, and the reduction with it complete in 5 minutes.

Summary

1. The vanadium in a sulfuric acid solution of vanadic acid containing a relatively small amount of sodium chloride is completely reduced to the quadrivalent state when shaken in the presence of mercury for 5 minutes. Since the quantity of chloride remaining in solution after the reduction is extremely small, the method is well adapted for preparing solutions of vanadium prior to titrating them with potassium permanganate.

2. By this method vanadium can be accurately determined in the presence of arsenic and uranic acids which are not reduced by similar treatment with mercury.

³ Some preliminary experiments indicate that iron also, provided the ferric sulfate solution contain the prescribed quantity of sodium chloride, may be determined rapidly and accurately in the presence of arsenates and uranyl salts. Thus, when 0.1177 g. of iron was taken in the presence of 0.2131 g. of monopotassium orthoarsenate and 0.3157 g. of uranyl nitrate hexahydrate, 0.1180 g. of iron was found. Two other determinations, made under like conditions, gave 0.1174 and 0.1186 g. of iron. The average of the three is 0.1180 g.

3. The method is shorter, more convenient, and requires less oversight than that involving the use of sulfur dioxide, and the results are fully as accurate as those obtained by the latter process.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
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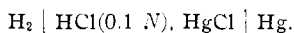
THE EFFECT OF HYDROGEN PRESSURE ON THE ELECTRO- MOTIVE FORCE OF A HYDROGEN-CALOMEL CELL. I

BY WILLIAM R. HAINSWORTH AND DUNCAN A. MACINNES

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Introduction

This investigation is concerned with the effect of pressure of gaseous hydrogen on the potential of a cell consisting of a hydrogen electrode and a calomel electrode, both in 0.1 *N* hydrochloric acid, *i. e.*, a cell of the type



The main interest of the experiments is, of course, the effect of varying the hydrogen pressure on the potential of a reversible hydrogen electrode. In a series of investigations, the results of which have appeared in *THIS JOURNAL*, one of the authors, with his associates, has endeavored to explain the irreversible overvoltage effects occurring when hydrogen gas is formed from its ions. It became evident during these researches that equilibrium measurements, such as will be described below, are essential for a more complete knowledge of the phenomena of hydrogen overvoltage. A discussion of this relation will be reserved for another paper. The measurements are, however, of interest outside of this connection.

Lewis and Randall,¹ Loomis and Acree² and Ellis³ have studied the effect of pressure on a reversible hydrogen electrode. They found that the usual equation

$$\Delta E = \frac{RT}{2F} \ln p \quad (1)$$

(in which ΔE is the change of the e.m.f. of the cell produced by changing the pressure from 1 atmosphere to p atmospheres) is applicable within the experimental error. The range of Ellis' experiments was, however, only from 1 to 1.5 atmospheres and this was considerably greater than the ranges of pressures covered by the other investigators. In this research the pressure range was extended to 400 atmospheres.

This article will discuss the apparatus used for the measurements,

¹ Lewis and Randall, *THIS JOURNAL*, **36**, 1969 (1914).

² Loomis and Acree, *ibid.*, **38**, 2391 (1916).

³ Ellis, *ibid.*, **38**, 737 (1916).