

The data indicate two hydrates, the hexadeca and deca as well as anhydrous salt exist at 30°. One hydrate, the deca, and anhydrous salt were found to exist at 80°.

The precision of measurement was limited by the alcohol determination. As no special precautions were taken in these determinations the relative precision of the 30° isotherm is $\pm 2\%$. At 80° difficulty was experienced in the sampling of solutions of high aluminum sulfate concentra-

tion. The relative precision of the 80° isotherm is thus limited to $\pm 3\%$.

Summary

The 30 and 80° isotherms for the system aluminum sulfate-ethanol-water have been determined. Anhydrous salt, hexadecahydrate and decahydrate were found to be present at 30° and anhydrous salt and decahydrate at 80°.

COLLEGE PARK, MD.

RECEIVED AUGUST 26, 1944

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polarographic Characteristics of Vanadium in its Various Oxidation States

BY JAMES J. LINGANE

The first polarographic study of vanadium compounds was carried out by Zeltzer,¹ who investigated the reduction of vanadium trichloride from acid solution, and the reduction of vanadate (+5 vanadium) from acid, strongly alkaline, and ammoniacal media. Unfortunately the vanadium trichloride solutions used by Zeltzer were more or less oxidized and not standardized, so that the polarograms that he obtained cannot be interpreted. Neither is it possible to deduce half-wave potential data for the reduction of vanadate, or to definitely assign oxidation states to the various waves of vanadate, from the incomplete polarograms given by Zeltzer.

The reduction of vanadate at the dropping electrode from acidic, strongly alkaline, and ammoniacal media has since been studied by Stackelberg, *et al.*,² Thanheiser and Willems,³ Voriskova,⁴ and Page and Robinson,⁵ but, since these authors were completely preoccupied with the development of empirical methods for determining vanadium in various materials, very little fundamental information can be gleaned from their papers. Indeed, their conclusions in several respects are bewildering. For example, Stackelberg, *et al.*,² concluded that vanadate ion is reduced to the +3 state from ammoniacal medium, whereas Zeltzer¹ had concluded that reduction proceeds to the +2 state. In the text of his paper Voriskova⁴ assumes reduction to the +2 state, but in an accompanying table he presents an equation showing reduction to the +3 state. Furthermore, although the polarograms of vanadic acid in dilute hydrochloric acid presented by Zeltzer¹ clearly show a double wave, those published by Stackelberg, *et al.*, display only a single wave, and Thanheiser and Willems³ state that they observed only a single wave from slightly

acid solutions (pH 2 to 6) of +5 vanadium at about -0.9 v. vs. the S.C.E.

These latter conclusions are surprising and difficult to reconcile with the fact that +5 vanadium in acid medium is a rather strong oxidant, easily reduced to the +4 state, and with the additional facts that the standard potentials of the $V^{+5} \rightarrow V^{+4}$ and $V^{+4} \rightarrow V^{+3}$ couples in acid medium differ by nearly 0.7 v., and those of the $V^{+4} \rightarrow V^{+3}$ and $V^{+3} \rightarrow V^{+2}$ couples in acid medium are about 0.6 v. apart, so that conditions are very favorable for stepwise reduction.

These contradictory conclusions, and the lack of any information at all on the polarographic behavior of vanadium in its lower oxidation states, prompted the present investigation.

Experimental

Ammonium metavanadate, purified by recrystallization, served as the source of +5 vanadium. An 0.08 *M* stock solution was prepared in 1 *N* sulfuric acid and standardized by the sulfurous acid-permanganate procedure.⁶

A stock solution of vanadyl sulfate in 0.5 *N* sulfuric acid was prepared by reducing a 250-cc. portion of the stock ammonium metavanadate solution with sulfur dioxide gas. The excess sulfur dioxide was expelled by boiling the solution, while a stream of purified nitrogen was swept through it, until the effluent gas ceased to reduce permanganate ion. The solution was cooled and diluted to exactly 500 cc. The concentration of +4 vanadium in this solution, determined by permanganate titration, checked the value expected from the concentration of the ammonium vanadate solution used in its preparation, and the solution remained unchanged over a period of six weeks in contact with air.

A stock solution of vanadic sulfate, 0.01 *M* in respect to V^{+5} , was prepared in 0.1 *N* sulfuric acid from a sample of pure $V_2(SO_4)_3 \cdot 10H_2O$ which was kindly furnished by Professor Grinnell Jones. The preparation and analysis of this salt have been described by Jones and Colvin.⁷ Since vanadic ion is rather easily air-oxidized, care was taken to prepare and store the solution in an atmosphere of purified nitrogen. The concentration of +3 vanadium in this solution determined by permanganometric titration was 0.3% larger than the value computed from the weight of

(1) S. Zeltzer, *Coll. Czechoslov. Chem. Commun.*, **4**, 319 (1932).

(2) M. v. Stackelberg, P. Klinger, W. Koch and E. Krath, *Forschungsberichte Tech. Mitt. Krupp. Essen*, **2**, 59 (1939).

(3) G. Thanheiser and J. Willems, *Arch. Eisenhüttenw.*, **13**, 73 (1939).

(4) M. Voriskova, *Coll. Czechoslov. Chem. Commun.*, **11**, 588 (1939).

(5) J. E. Page and F. A. Robinson, *Analyst*, **68**, 269 (1943).

(6) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 359.

(7) G. Jones and J. H. Colvin, *This Journal*, **66**, 1563, 1573 (1944).

salt taken; this result agrees with the analytical data given by Jones and Colvin.

Polarograms were recorded according to the usual technique⁸ with a calibrated Sargent-Heyrovsky Polarograph. An H-type cell,⁹ with either a saturated calomel electrode or a mercury-mercurous sulfate-1 *N* sulfuric acid electrode, was used. The dropping electrode assembly, which included a stopclock device for measuring the rate of flow of mercury, *m*, automatically, has been described elsewhere.⁹ Nitrogen, purified by passage over copper gauze at 400°, was used to remove air from the solutions. All measurements were made with the cell in a water thermostat at 25.00°.

Results and Discussion

+5 Vanadium.—In agreement with the results of Zeltzer¹ it was found that the reduction of +5 vanadium from acid medium produces a double wave as shown in Fig. 1. Both curves in Fig. 1 were obtained with the same concentration of +5 vanadium (3.87 millimolar as ammonium metavanadate), and 0.005% gelatin was present as a maximum suppressor. Curve a was obtained with a supporting electrolyte consisting of 0.05 *N* sulfuric acid and 0.1 *N* potassium chloride, and curve b from 1 *N* hydrochloric acid.

In both cases the first stage of reduction produces an excellently developed diffusion current which starts from zero applied e. m. f. Since the standard potential of the $V^{+5} \rightarrow V^{+4}$ couple in acid medium is +0.75 v. *vs.* the saturated calomel electrode,^{10,11} and since mercury reduces acid solutions of +5 vanadium to the +4 state, there is no doubt that the first diffusion current corresponds to a 1-electron reduction of the pervanadyl ion, $V(OH)_4^+$, to the vanadyl ion, VO^{++} . Because the true half-wave potential of this reduction is several tenths of a volt more positive than the potential at which anodic dissolution of mercury from the dropping electrode begins, the first wave starts at zero applied e. m. f. and its half-wave potential actually corresponds to the anodic dissolution potential of mercury, and not to the true reduction potential of pervanadyl ion.

The second stage of reduction is seen to be well defined in the presence of 0.05 *M* hydrogen ion (curve a), but in more strongly acid medium (curve b) the second wave is partially masked by the reduction of hydrogen ion, and it is distorted by a pronounced maximum. Conversely, the first wave shows a sharp maximum in the more dilute acid solution, even though gelatin was present, but not in the more strongly acid medium. The maximum in the first wave was observed to disappear after the solutions stood in the cell for about a half hour in contact with a small amount of mercury that had accumulated from the dropping electrode.

Since mercury is oxidized fairly rapidly by acid solutions of +5 vanadium a mercury pool anode

should not be used, and polarograms must be recorded immediately after the dropping electrode is placed in the solution, as otherwise a significant amount of the +5 vanadium will be reduced. This fact was overlooked by Stackelberg, *et al.*, who used a large mercury pool anode and found only a single reduction wave (the second one), and it is quite likely that their solutions were more or less completely reduced to the +4 state at the time that they recorded polarograms.

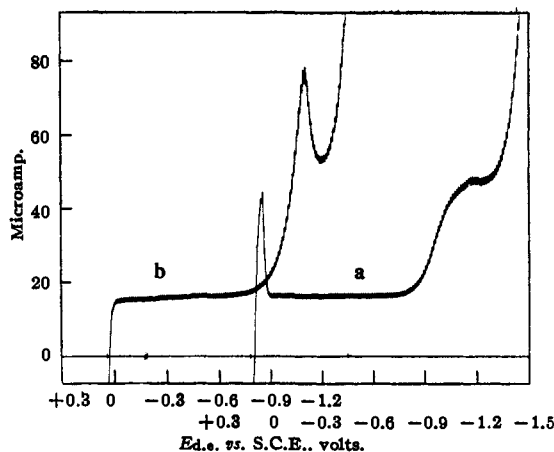


Fig. 1.—Polarograms of +5 vanadium in acid media.

The total second diffusion current is exactly three times the first; the diffusion current constants,¹² $i_d/(Cm^{3/2}t^{1/2})$, in 0.05 *N* sulfuric acid and 0.1 *N* potassium chloride (curve a in Fig. 1) were found to be 1.65 and 4.96 microamp./millimole per liter/mg.^{1/2} sec.^{-1/2} at 25°. It is evident from these data that the second wave corresponds to a 2-electron reduction according to the equation $VO^{++} + 2H^+ + 2e^- = V^{++} + H_2O$.

The half-wave potential of the second wave in 0.05 *N* hydrogen ion is -0.98 v. *vs.* the S.C.E., From the recent measurements of Jones and Colvin⁷ the reversible standard potential at a platinum electrode of the reaction $VO^{++} + 2H^+ + e^- = V^{+++} + H_2O$ is +0.337 v. and that of the reaction $V^{+++} + e^- = V^{++}$ at a stationary mercury electrode is -0.255 v., both *versus* the standard hydrogen electrode. Jones and Colvin found that both of these systems functioned reversibly so that if the reductions of the vanadyl and vanadic ions both proceeded reversibly at the dropping electrode the second wave in Fig. 1 should be a doublet with half-wave potentials of about +0.09 v. and -0.50 v. *vs.* the S.C.E. From the polarograms in Fig. 1 this is clearly not the case; the fact that the half-wave potential of the second wave in curve a is about 0.9 v. more negative than the reversible potential of the vanadyl-vanadic couple at a hydrogen ion concentration of 0.05 *M*, coupled with the fact that the reduction proceeds directly in one step from the

(12) For a discussion of the theoretical significance of diffusion current constants see Ref. 8 and J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(9) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

(10) C. D. Coryell and D. M. Yost, *This Journal*, **55**, 1909 (1933).

(11) J. E. Carpenter, *ibid.*, **56**, 1847 (1934).

+4 to the +2 state, proves that the reduction of the vanadyl ion does not proceed reversibly at a mercury cathode. It is shown below that the reduction of the vanadic ion (V^{+++}) to the vanadous state (V^{++}) is reversible at the dropping electrode, and hence the large overvoltage required to produce the second wave in Fig. 1 must be associated entirely with the vanadyl-vanadic stage. This conclusion is substantiated by the polarograms of vanadyl solutions discussed in the following section.

Polarograms of +5 vanadium in ammoniacal media are shown in Fig. 2. These three polarograms were obtained with the same concentration of vanadium (1.59 millimolar added as ammonium metavanadate), and the same concentration of ammonium chloride (1 *M*), but with (a) 0.1, (b) 1, and (c) 6 *M* ammonia. In each case 0.005% gelatin was present as a maximum suppressor. With 0.1 *M* ammonia (curve a) a complicated polarogram is obtained and the diffusion current is not well developed, but with a concentration of ammonia 1 *M* or greater very well developed doublet waves result.

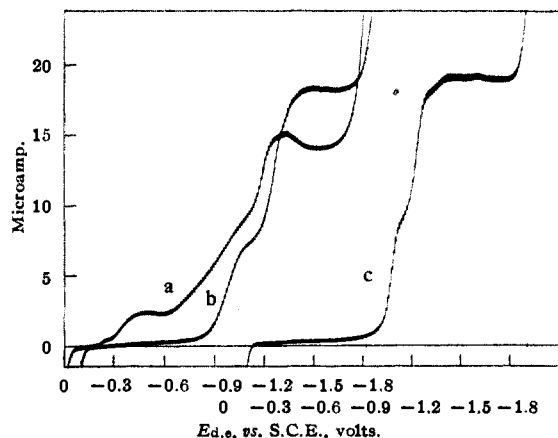


Fig. 2.—Polarograms of +5 vanadium in ammoniacal media.

The stock solution of +5 vanadium in these experiments was prepared by dissolving ammonium metavanadate in 1 *N* sulfuric acid, and it possessed a bright yellow color. When small volumes of this solution were added to large volumes of ammoniacal solutions of ammonium chloride, a more intense yellow color was first produced, but gradually the solutions became completely colorless. The rate of fading of the yellow color was greater the greater the *pH* of the ammoniacal solutions; with 0.1 *M* ammonia in 1 *M* ammonium chloride the color persisted for several hours, but with 1 *M* ammonia it disappeared in an hour or so. The decolorization was found to be accelerated noticeably by sulfite ion, and markedly by heating. Solutions of +5 vanadium are known to be quite complex and to contain a variety of isopoly acids and their anions

whose relative proportions depend on the *pH*,¹³ and the color changes noted above probably result from the slow transformation of the $V(OH)_4^+$ and $H_2V_6O_{17}^-$ which predominate in acid medium to the di- and trivanadate ions, $V_2O_7^{--4}$ and $V_3O_9^{-3}$, which appear to be the chief species in alkaline media. To insure reproducibility in the ionic state of the vanadium the ammoniacal solutions were allowed to decolorize completely before polarograms were recorded.

Zeltzer,¹ Stackelberg, *et al.*,² Voriskova,⁴ and Page and Robinson,⁵ also investigated polarograms of +5 vanadium in ammoniacal media, but none of these authors noted the fact that the wave is double.

In 1 *M* ammonia and 1 *M* ammonium chloride, and in the presence of 0.005% gelatin, the half-wave potential of the first wave is -0.97 v. and that of the second is -1.26 v. *vs.* the S.C.E. When the concentration of ammonia is increased to 6 *M* the half-wave potential of the first stage of reduction is shifted to a more negative value (-1.07 v.), whereas that of the second stage becomes more positive (-1.22 v.), so that the separation of the two stages is less distinct (curve c in Fig. 2). This may account for the failure of Zeltzer,¹ Stackelberg, *et al.*,² and Page and Robinson⁵ to observe the doublet character of the wave, since these authors employed solutions in which the ratio of the concentration of ammonia to that of ammonium ion was even greater than 6 to 1. Also Page and Robinson employed an unusually large concentration of gelatin as a maximum suppressor (0.05%), and they apparently did not remove air from the solutions; both of these conditions tend to obscure the true character of the wave. However, Voriskova did not observe the double wave with solutions of ammonium metavanadate in 1 *M* ammonia and 1 *M* ammonium chloride, corresponding to curve b in Fig. 2. Since Voriskova added sodium sulfite to his solutions to remove oxygen, the writer also recorded polarograms with sulfite present (0.2 g. of sodium sulfite per 20 cc.). As shown in Fig. 3 the wave obtained in the presence of sulfite (curve b) is also double and identical in every respect with that obtained without sulfite ion present (curve a).

Although the diffusion current of the first reduction stage is not completely developed before the second stage begins, it is evident that the first waves in curves b and c in Fig. 2 are one-third the height of the total double waves. The diffusion current constant, $i_d/(Cm^{2/3}t^{1/6})$, of the total double wave in 1 *M* ammonia and 1 *M* ammonium chloride was found to be 4.72. and that of the first wave is 1.6 ± 0.1 . In 6 *M* ammonia and 1 *M* ammonium chloride the total diffusion current constant is 4.99. These values are so nearly the same as the values in acid medium (1.65 and 4.96 in 0.05 *N* sulfuric acid) that, even making allow-

(13) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 242.

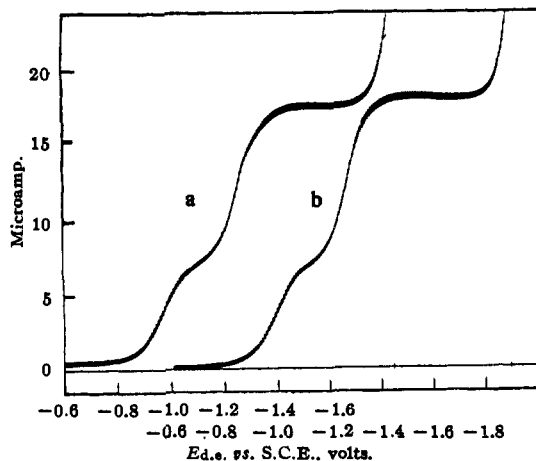


Fig. 3.—Polarograms of 1.59 millimolar +5 vanadium in 1 *M* ammonium chloride and 1 *M* ammonia, (a) without sulfite present, and (b) with 0.08 *M* sodium sulfite.

ances for a possible small difference in the diffusion coefficients of the +5 vanadium in acid and basic solutions, it is evident that the first wave in ammoniacal medium corresponds to reduction of the +5 vanadium to the +4 state, and the second to reduction to the +2 state. The conclusion of Stackelberg, *et al.*, that +5 vanadium is reduced only to the +3 state in ammoniacal medium is evidently erroneous.

+4 Vanadium.—In spite of the fact, recently demonstrated by Jones and Colvin, that the reaction $\text{VO}^{++} + 2\text{H}^+ + e^- = \text{V}^{+++} + \text{H}_2\text{O}$ is reversible at a platinum electrode with a standard potential of +0.09 v. *vs.* the S.C.E., neither the reduction of vanadyl ion nor the oxidation of vanadic ion proceeds reversibly at the dropping mercury electrode. The reduction of vanadyl ion from acid solutions requires an overvoltage of about 0.8 v., and from solutions that are 1 *M* in respect to hydrogen ion the reduction wave occurs so slightly in advance of the discharge of hydrogen ion that a well-defined diffusion current plateau is not produced. However, from solutions containing only 0.1 *M* hydrogen ion it is possible to obtain a fairly well developed wave. Some typical polarograms of various concentrations of vanadyl ion in 0.1 *N* sulfuric acid in the presence of 0.005% gelatin are shown in Fig. 4. The half-wave potential in this medium is -0.85 v. *vs.* the S.C.E., whereas if the reduction proceeded reversibly to the +3 state the half-wave potential should be about -0.03 v.

Although not too well developed, the limiting current is directly proportional to the concentration of vanadyl ion, and hence is diffusion controlled. The average value of the diffusion current constant, $i_d/(Cm^{1/2}t^{1/2})$, is 3.2 ± 0.2 , which is just two-thirds the value 4.96 observed in the 3-electron reduction of +5 vanadium from a similar acid solution. This indicates that the reduction of the vanadyl ion under these conditions involves two electrons and proceeds to the vanadous (+2)

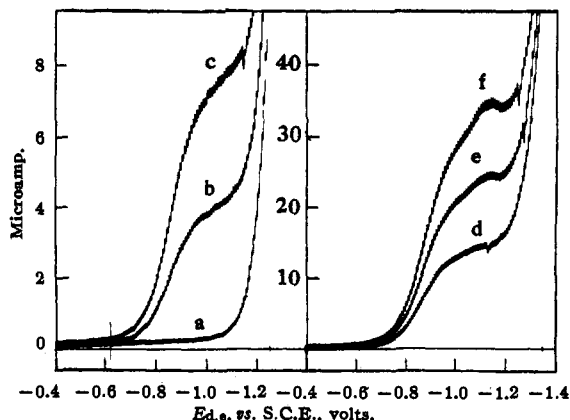


Fig. 4.—Vanadyl ion in 0.1 *N* sulfuric acid in the presence of 0.005% gelatin. Concentrations of +4 vanadium were (a) 0, (b) 0.472, (c) 0.922, (d) 1.76, (e) 2.88, and (f) 4.02 millimolar.

state. Proof of this conclusion is found in the fact, discussed in the following section, that the half-wave potential of the reversible reduction of the vanadic ion to the vanadous state is -0.55 v., and hence vanadic ion could not possibly be the reduction product of vanadyl ion at a potential more negative than this value.

From its solutions in 1 *N* potassium or sodium hydroxides +4 vanadium (probably present as a polyvanadate ion such as $\text{V}_4\text{O}_6^{=}$) is so difficultly reducible that no indication of a reduction wave is observable before the reduction of potassium or sodium ion. However, an excellently developed anodic wave is obtained, corresponding to the oxidation of vanadite ion to the +5 state. Some typical polarograms of various concentrations of

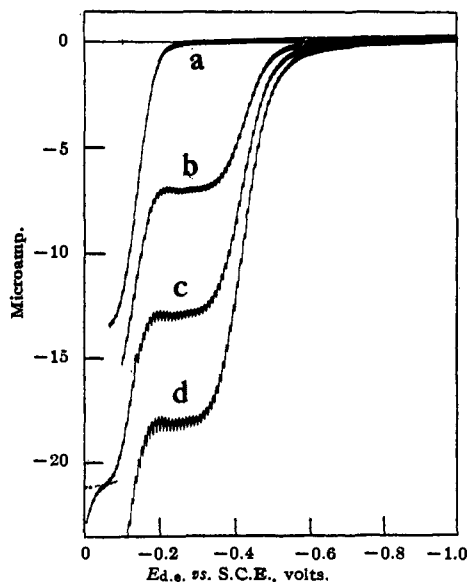


Fig. 5.—Polarograms of +4 vanadium in 1 *N* sodium hydroxide containing 0.08 *M* sodium sulfite. Concentrations of +4 vanadium were (a) 0, (b) 1.84, (c) 3.52, and (d) 5.05 millimolar.

+4 vanadium in a supporting electrolyte composed of 1 *N* sodium hydroxide and 0.08 *M* sodium sulfite (0.2 g. of Na₂SO₃ per 20 cc.) are shown in Fig. 5.

Vanadite ion in strongly alkaline medium is rapidly oxidized by atmospheric oxygen, and hence dissolved air must be removed from the supporting electrolyte before the addition of the vanadium. In the present experiments air was removed from the solutions with nitrogen, and 0.2 g. of sodium sulfite per 20 cc. was also added to ensure the complete absence of oxygen. An idea of the rapidity of the air oxidation is obtained from the fact that a 1.5 millimolar solution of vanadite ion in 1 *N* potassium hydroxide underwent complete oxidation (complete disappearance of the anodic wave) after air was bubbled through the solution for fifteen minutes. By the device of adding a small volume of an acidic vanadyl solution to a relatively large volume of the alkaline supporting electrolyte, which is protected by both nitrogen and sulfite, air oxidation is completely and conveniently eliminated.

In a supporting electrolyte composed of 1 *N* sodium hydroxide and 0.08 *M* sodium sulfite the anodic half-wave potential is -0.42 v. vs. the S.C.E., and it is independent of the concentration of the +4 vanadium. The slope of the wave approximates quite closely to the expected value for a reversible 1-electron oxidation. This is demonstrated by the polarogram in Fig. 6 of a 1.55 millimolar solution of +4 vanadium in 1 *N* sodium hydroxide containing 0.08 *M* sodium sulfite, which was recorded with "magnified" voltage scale. The dashed curve superimposed on the wave has been drawn in according to the theoretical equation of the wave of a reversible 1-electron reaction,⁸ $E_{d.e.} = E_{1/2} - 0.0591 \log i/(i_d - i)$, with the same values of $E_{1/2}$ and i_d as the experimental wave. The discrepancy between the observed and theoretical wave forms is seen to be quite small; hence the oxidation of vanadite ion to

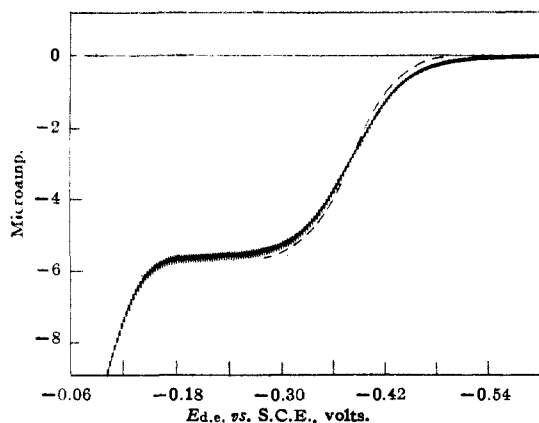


Fig. 6.—Comparison of observed and theoretical (dashed curve) wave forms of +4 vanadium in 1 *N* sodium hydroxide and 0.08 *M* sodium sulfite. Note the extended voltage scale.

vanadate ion proceeds practically reversibly in 1 *N* sodium hydroxide, and the observed half-wave potential (-0.42 v. vs. the S.C.E.) must be quite close to the standard potential of this couple. However, vanadate ion in 1 *N* sodium hydroxide is not reduced reversibly, its half-wave potential being in the neighborhood of -1.6 v., and hence the vanadite-vanadate couple cannot be regarded as being truly reversible in a thermodynamic sense at the dropping electrode.

The data in Table I demonstrate that the anodic diffusion current in 1 *N* sodium hydroxide is accurately proportional to the concentration of +4 vanadium over a large concentration range. The maximum concentration of +4 vanadium that is stable in this particular supporting electrolyte is between 5 and 8 millimolar. Solutions that were 5 millimolar or less in +4 vanadium were light brown in color and perfectly clear, but with 8 millimolar vanadium a pale brown turbidity appeared a few minutes after the solution was composited. The character of this precipitate was more suggestive of a sodium polyvanadate than of hydrated vanadyl oxide.

TABLE I
ANODIC DIFFUSION CURRENT CONSTANT OF VANADITE ION

The supporting electrolyte comprised 1 *N* sodium hydroxide and 0.08 *M* sodium sulfite, and measurements were made at 25.00°. The diffusion currents were measured at -0.2 v. vs. the S.C.E., and correction has been applied for the residual current (compare Fig. 5). $m^2/4t^{1/2} = 2.50 \text{ mg.}^2/\text{sec.}^{-1/2}$.

C, millimolar	i_d , microamp. (cor.)	$\frac{i_d}{Cm^2/4t^{1/2}}$
0.094	0.35	1.49
.278	0.98	1.41
.506	1.78	1.41
.860	3.09	1.44
1.548	5.63	1.45
1.84	6.96	1.51
3.52	12.85	1.46
5.05	18.13	1.44
8.05	(27.6) ^a	(1.37)

Av. 1.45 ± 0.03

^a Light brown turbidity.

The excellent development of the anodic vanadite wave in 1 *N* sodium hydroxide should be of value in practical analytical work, and its application to the determination of vanadium in steel and various vanadiferous minerals is being investigated.

Polarograms of +4 vanadium in ammoniacal media display both a cathodic and an anodic wave as shown in Fig. 7. Curve a in Fig. 7 is the residual current curve of a supporting electrolyte composed of 1 *M* ammonium chloride, 1 *M* ammonia and 0.08 *M* sodium sulfite. Curve b was obtained after adding 1.76 millimolar vanadyl sulfate. The half-wave potential of the anodic wave is -0.32 v. and that of the cathodic wave is -1.28 v. vs. the S.C.E. in this particular support-

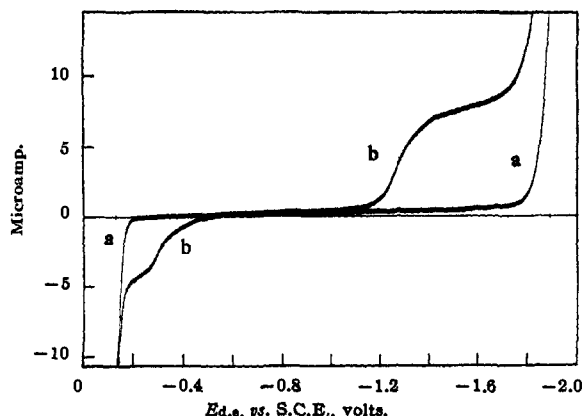


Fig. 7.—Polarogram of +4 vanadium in ammoniacal medium.

ing electrolyte. The diffusion current constants, $i_d/(Cm^{2/3}t^{1/2})$, are 0.94 ± 0.05 for the anodic wave and 1.82 ± 0.05 for the cathodic wave. Since the anodic wave can only correspond to oxidation to the +5 state, and since the cathodic diffusion current constant is just twice that of the anodic wave, it is clear that the cathodic wave results from a 2-electron reduction to the +2 state. The relatively large slopes of both waves in Fig. 7 show that neither reaction proceeds reversibly at the dropping electrode from ammoniacal medium.

The fact that the cathodic half-wave potential in Fig. 7 is virtually identical with the half-wave potential of the *second* wave in the reduction of +5 vanadium in the same ammoniacal medium (compare Figs. 2 and 3) serves as additional confirmation of the previous conclusion that the second wave in the latter case is the result of reduction of +4 vanadium to the +2 state.

The addition of sulfite ion was found to be essential when investigating +4 vanadium in ammoniacal media. When it was not added a yellowish-brown precipitate appeared immediately on the addition of vanadyl sulfate solution, even though air had been removed with nitrogen. Even with sulfite present the solutions were not very stable. With 1 to 2 millimolar +4 vanadium in 1 *M* ammonium chloride, 1 *M* ammonia, and 0.08 *M* sodium sulfite, the freshly prepared solutions were brownish-yellow and perfectly clear, but after an hour (under nitrogen) a light brown turbidity developed. Oxidation seems unlikely with the solutions protected by both nitrogen and sulfite, and it seems most logical to conclude that +4 vanadium in ammoniacal medium is actually in a thermodynamically metastable state. The stabilizing effect of sulfite ion is peculiar and warrants further investigation.

+3 and +2 Vanadium.—It was found that vanadic ion, V^{+++} , is reduced reversibly to vanadous ion, V^{++} , and the latter is oxidized reversibly to vanadic ion, at the dropping electrode in dilute acid solutions.

Typical polarograms of various concentrations

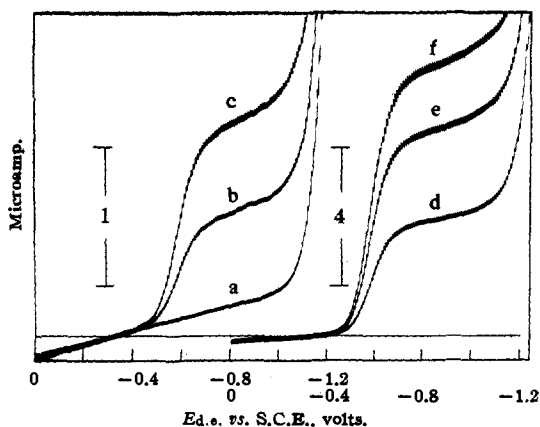


Fig. 8.—Polarograms of vanadic ion in 1 *N* sulfuric acid. Concentrations of V^{+++} were (a) 0, (b) 0.196, (c) 0.386, (d) 0.913, (e) 1.67, and (f) 2.20 millimolar.

of vanadic ion in 1 *N* sulfuric acid are shown in Fig. 8. The wave is well developed with a half-wave potential of -0.55 v. *vs.* the S.C.E. The data in Table II show that the diffusion current is accurately proportional to the concentration of vanadic ion after proper correction is applied for the residual current.

TABLE II

DIFFUSION CURRENT CONSTANT OF VANADIC ION

The supporting electrolyte comprised 1 *N* sulfuric acid and 0.005% gelatin. Diffusion currents were measured at 25.00° at -0.8 v. *vs.* the S.C.E., and correction has been applied for the residual current (compare Fig. 8). $m^2/s^{1/2} = 2.48$ mg./s. sec.^{-1/2}.

V^{+++} millimolar	i_d microamp. (cor.)	$\frac{i_d}{Cm^{2/3}t^{1/2}}$
0.196	0.69	1.42
.386	1.34	1.40
.913	3.16	1.40
1.673	5.85	1.41
2.196	7.64	1.41

Av. 1.41 \pm 0.01

The half-wave potential of vanadic ion in 1 *N* sulfuric acid (-0.55 v. *vs.* the S.C.E.) agrees quite well, as such data go, with the standard potential (-0.51 v. *vs.* the S.C.E.) of the reaction $V^{+++} + e = V^{++}$ determined by Jones and Colvin⁷ by the ordinary potentiometric method with a large stationary mercury electrode.

The practical reversibility of the vanadic ion-vanadous ion couple at the dropping electrode is demonstrated conclusively by the polarograms in Fig. 9. Curve a is the residual current curve of the 1 *N* sulfuric acid supporting electrolyte, and curve b is a polarogram of a 4.64 millimolar solution of vanadous ion in 1 *N* sulfuric acid. This solution was prepared by reducing a 4.64 millimolar solution of ammonium metavanadate in 1 *N* sulfuric acid with amalgamated granulated zinc in the same apparatus and by the same general technique previously used in the study of reduced

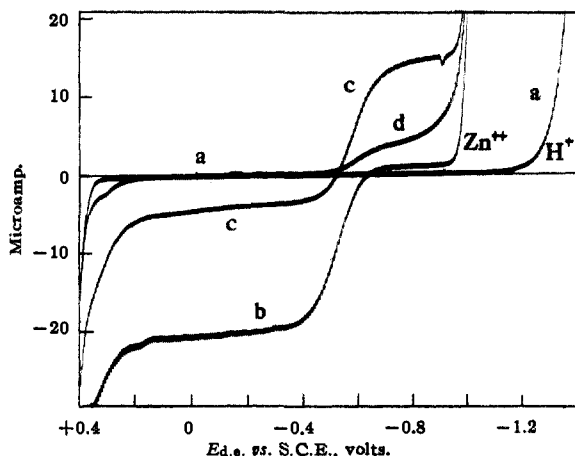


Fig. 9.—Comparison of the anodic wave of vanadous ion with the cathodic wave of vanadic ion in 1 *N* sulfuric acid.

rhenum solutions.¹⁴ The reduction was carried out in a nitrogen atmosphere at room temperature. The polarogram (curve b in Fig. 9) of this solution displays an excellently developed anodic wave with a half-wave potential of -0.50 v. *vs.* the S.C.E. Since polarograms of solutions of vanadic ion in 1 *N* sulfuric acid do not show an anodic wave, it follows that the oxidation of vanadous ion at the dropping electrode proceeds only to the +3 state in this medium.

The small discrepancy between the cathodic half-wave potential of vanadic ion (-0.55 v.) and the anodic half-wave potential of vanadous ion (-0.50 v.) may be caused by a small degree of irreversibility in one or both directions of the reaction, or it may be due simply to the oppositely directed ohmic potential drop (iR) through the cell in the two cases. Since the cell resistance was known to be less than 500 ohms, and the total difference in current between the two half-wave potentials was only about 20 microamp., the iR difference could not have been greater than about 0.01 v., and hence the first postulate appears to be the correct one. From the very good agreement of the anodic half-wave potential with the reversible standard potential, the slight irreversibility (if it actually is real) would seem to be associated with the reduction of vanadic ion rather than with the oxidation of vanadous ion.

The small cathodic diffusion current discernible in curve b shows that either reduction to the +2 state by the amalgamated zinc was not quite complete, or else that the vanadous ion underwent a slight oxidation after its transfer from the reductor to the cell. The latter interpretation is the most likely one, since vanadous ion in acid medium is in a metastable condition with respect to oxidation by hydrogen ion according to $2V^{++} + 2H^+ = 2V^{+++} + H_2$.

Curve c in Fig. 9 was recorded after passing air through the vanadous solution for ten minutes,

and then removing the air with nitrogen. The character of curve c demonstrates that the oxidation of the vanadous ion to vanadic ion was 80% complete after this short exposure to oxygen. The solution was then allowed to stand in the cell for twenty-four hours protected by nitrogen, after which it was exposed to air for ten minutes, the air was displaced by nitrogen, and curve d was recorded. Curve d shows that most of the vanadic ion, as well as all of the vanadous ion, was oxidized by this treatment.

It is evident from the curves in Fig. 9 that the polarographic method can be employed advantageously for studying the reactions of vanadic and vanadous ions, and for investigating the influence of *pH*, complex formation, and various other factors on the potential of the vanadic-vanadous couple.

Summary

From both acid and ammoniacal media +5 vanadium undergoes stepwise reduction at the dropping electrode, first to the +4 state and finally to the +2 state. In 0.05 *N* sulfuric acid the diffusion current of the first stage of reduction starts at zero applied e. m. f., and the half-wave potential of the second stage is -0.97 v. *vs.* S.C.E. In ammoniacal medium the first stage of reduction is only slightly in advance of the second stage, the two half-wave potentials in 1 *M* ammonium chloride containing 1 *M* ammonia being -0.97 v. and -1.26 v. *vs.* the S.C.E., but the total diffusion current is very well defined.

In 0.1 *N* sulfuric acid +4 vanadium is reduced irreversibly to the +2 state; the resulting wave is rather poorly developed and its half-wave potential is -0.85 v. *vs.* the S.C.E. From solutions containing 1 *M* hydrogen ion the reduction of vanadyl ion is practically completely masked by the reduction of hydrogen ion.

From its solutions in 1 *N* sodium or potassium hydroxide +4 vanadium shows no indication of a reduction wave, but an excellently developed anodic wave is obtained, corresponding to oxidation to the +5 state, with a half-wave potential of -0.42 v. *vs.* the S.C.E. The anodic diffusion current is accurately proportional to the concentration of +4 vanadium, and the shape of the wave corresponds closely to a reversible 1-electron oxidation.

Both the reduction of vanadic ion to the vanadous state, and the oxidation of vanadous ion to vanadic ion, proceed practically reversibly at the dropping electrode from an acid medium. In 1 *N* sulfuric acid both waves are very well developed, with an average half-wave potential of -0.52 v. *vs.* the S.C.E.

No indication of reduction of vanadium below the +2 state was obtained with any of the solutions investigated.

(14) I. J. Lingane, *THIS JOURNAL*, **64**, 2182 (1942).