ion concentration. Therefore, exchange will be complete. We now expect G(HD) to increase by a chain propagation sequence consisting of steps 5, 8 and 9 as the pH is lowered. No such increase is found[15,16] and we conclude that HD^+ does not play a role in the water–deuterium exchange reaction.

Owing to the hydration of H_2^+, we expect this ion to have high solubility in water compared to hydrogen atoms. On this basis, more chemical effect will occur at lower pHs. Still the rate of hydrogen atom reduction of ferric ions in 0.01 N sulfuric acid is about the same as the rate of oxidation of ferrous ions in 0.8 N sulfuric acid. And the γ-ray reduction yield of ferric ions by hydrogen atoms is equal to the γ-ray oxidation yield of ferrous ions by hydrogen atoms. Therefore the hydrogen atom concentration is not appreciably altered by pH.

On the basis of the above evidence, we favor reaction 4 involving a triple collision of ferrous ion, a hydrogen atom and a hydrogen ion for explaining the oxidation of ferrous ions by hydrogen atoms.

An alternate mechanism is the reaction of the hydrogen atom with a polarized water molecule in the hydration sphere of the ferrous ion.

$$H + Fe^{++}\cdot(H_2O)_n = H_2 + Fe^{+++}\cdot(H_2O)_{n-1} + OH^-$$

This is consistent with photochemical evidence.[16]

Acknowledgments.—We gratefully acknowledge help from Miss P. D. Walsh for analytical data and from Messrs. Joseph Hodur and Peter Ziegelmeir for glass-blowing and machine work.

[16] M. Lefort and P. Douzou, *J. chim. phys.*, **69**, 536 (1956).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY, INC., A.E.C. RAW MATERIALS DEVELOPMENT LABORATORY]

A Spectrophotometric Investigation of Vanadium(V) Species in Alkaline Solutions[1]

BY LEONARD NEWMAN,[2] WILLIAM J. LAFLEUR, FREDERICK J. BROUSAIDES AND ARTHUR M. ROSS

RECEIVED FEBRUARY 27, 1958

The interpretation of spectrophotometric data has demonstrated that both monohydrogen orthovanadate and pyrovanadate are formed during the first break in the titration of orthovanadate with acid. A constant of 0.097 ± 0.005 has been obtained at 25° for the hydrolysis of orthovanadate to monohydrogen orthovanadate at an ionic strength of 3.0 over the ranges in vanadium concentration of 2×10^{-4} M to 1×10^{-2} M, hydroxide concentration of 0.01 to 3.0 M and wave length of 260 to 360 mμ. A constant of 48 ± 5 has been obtained for the dimerization of monohydrogen orthovanadate to pyravanadate over the ranges in vanadium concentration of 0.01 to 0.1 M and hydroxide concentration of 0.0015 to 0.01 M.

The chemistry of vanadium(V) has been the subject of many investigations over a period of more than fifty years. It has been shown that when a solution of orthovanadate is titrated with acid, three inflections, or breaks, are observed in the plotted curve. All workers in the field agree that the first two breaks appear, respectively, upon the addition of one and two equivalents of acid. However, there is some disagreement as to the number of equivalents required for the third break; some workers report it as 2.5 equivalents, while others report it as 2.6 equivalents.

Of chief interest in the present investigation has been a quantitative understanding of the chemistry of vanadium in highly alkaline media, covering the pH region involved when the first equivalent of acid is added to orthovanadate. No conclusive data were available; some workers postulated that monohydrogen orthovanadate is formed in this pH region, others suggested that pyrovanadate is formed, and still others concluded that both species are formed. Nearly all these workers relied on titrimetric and/or cryoscopic measurements basing their decisions solely on the stoichiometry. It was clearly evident that any effort to enlarge or improve on such measurements would not be likely to provide a singular solution to the problem. The adoption of a different approach was most desirable and accordingly it was decided to study the vanadium species by a spectrophotometric method. The appropriate spectrophotometric equations are derived and utilized in a manner similar to that described by Newman and Hume.[3]

Reagents and Instruments.—Fisher Scientific Company purified sodium orthovanadate was used as a source of vanadium, and Fisher Scientific Company purified sodium perchlorate monohydrate as a source of perchlorate. All other chemicals were reagent grade.

A Beckman model DU quartz spectrophotometer equipped with a hydrogen lamp was used for all spectrophotometric measurements. Matched one-centimeter cells were used throughout.

A Beckman Model G pH meter was used equipped with a Beckman Type E-2 glass electrode to avoid pH errors in the highly alkaline region.

Data and Results

Hydrolysis of Orthovanadate.—When sodium orthovanadate is dissolved in water, about half of it hydrolyzes.[4] Two equally possible hydrolysis reactions can be postulated

$$VO_4^{-3} + H_2O = HVO_4^{=} + OH^-$$

and

$$2VO_4^{-3} + H_2O = V_2O_7^{-4} + 2OH^-$$

The basis of the present method of investigation has been to add first a sufficiently great excess of hydroxide to repress the hydrolysis so that less than 5% of the orthovanadate is hydrolyzed, then to decrease slowly the hydroxide concentration to permit further hydrolysis to take place. From a meas-

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[1] This work was done under U. S. Atomic Energy Commission Contract No. AT(49-6)-924 and was presented at the 133rd Meeting of the American Chemical Society in San Francisco, Calif., April, 1958.

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[3] L. Newman and D. N. Hume, THIS JOURNAL, **79**, 4571, 4576, 4581 (1957).

[4] H. T. S. Britton and R. Robinson, *J. Chem. Soc.*, 1261 (1930); 1955 (1932); 512 (1933).

ure of the change of the absorbance of the solution as a function of the hydroxide concentration, it should be possible to ascertain which of the hydrolysis reactions is taking place. In order to obtain constant activity coefficients, the ionic strength was maintained at a high and constant value of 3.0 with sodium perchlorate. The derivations leading to the equations relating the absorbance of orthovanadate solutions to hydroxide concentration are appended. These equations were derived, one on the basis of the hydrolysis to monohydrogen orthovanadate (Appendix A) and the other on the basis of hydrolysis to pyrovanadate (Appendix B). Both expressions (equations A6 and B6) describe the absorbance as a linear function of the hydroxide ion concentration.

To ascertain which expression is valid, data for the absorbance of vanadium solutions as a function of hydroxide concentration were obtained. Aliquots of a solution containing the vanadium concentration under investigation plus 3.0 *M* sodium perchlorate were mixed with aliquots of a carbonate-free 3.0 *M* sodium hydroxide solution containing vanadium of the same concentration. The three vanadium concentrations investigated were 2.04×10^{-4} *M*, 1.01×10^{-3} *M* and 1.04×10^{-2} *M*. The range in hydroxide ion concentration covered was 0.008 to 3.0 *M*. To attain equilibrium the mixed solutions were quickly brought to a boil and cooled to 25°.[4] Since the sodium hydroxide concentration was always in large excess over the vanadium, the free hydroxide ion concentration was equal to the molar concentration of sodium hydroxide added.

The absorbances at seventeen wave lengths covering the range of 260 to 360 mμ were measured at a constant slit width of 0.5 mm. against a blank containing everything except the vanadium. From these data, the extrapolated absorbance values, A_0, corresponding to the absorbance of pure orthovanadate, were obtained. The data were applied to equations A6 and B6 to ascertain which of the two reactions is valid. The results indicate conclusively that only equation A6 is satisfied, and that accordingly, orthovanadate first hydrolyzes to form monohydrogen orthovanadate.

When the data were applied to equation B6, nonlinear plots were obtained. In some cases, these plots show initial linearity, but the "hydrolysis constants" calculated from the intercepts of these linear portions are not found to be constant but roughly proportional to the reciprocal of the vanadium concentration.

When equation A6 was tested, the plots were found to be linear in all cases. The slopes of the lines yield the reciprocal of the hydrolysis constant, K_h, and the intercepts yield the product of the analytical concentration of vanadium and the extinction coefficient for monohydrogen orthovanadate. The calculated values of the hydrolysis constant may be found in Table I. The average value of the hydrolysis constant is 0.097 ± 0.005.

From the values of the extinction coefficients and the hydrolysis constant, theoretical absorbance curves were determined. The agreement between calculated and experimental values is remarkably good. The resolved absorption spectra of orthovanadate and monohydrogen orthovanadate are presented in Fig. 1, in which the calculated extinction coefficients are plotted logarithmically as a function of wave length.

TABLE I

HYDROLYSIS CONSTANT FOR ORTHOVANADATE TO MONOHYDROGEN ORTHOVANADATE

Ionic strength = 3.0; temperature = 25°; slit width = 0.5 mm.

Vanadium concn., *M*	Wave length, mμ	Hydrolysis constant
2.04×10^{-4}	260	0.098
2.04×10^{-4}	265	.095
2.04×10^{-4}	270	.095
2.04×10^{-4}	275	.097
2.04×10^{-4}	280	.10
2.04×10^{-4}	285	.099
2.04×10^{-4}	290	.10
2.04×10^{-4}	295	.10
2.04×10^{-4}	300	.095
1.01×10^{-3}	310	.098
1.01×10^{-3}	315	.096
1.01×10^{-3}	320	.097
1.01×10^{-3}	325	.096
1.04×10^{-2}	345	.10
1.04×10^{-2}	350	.095
1.04×10^{-2}	355	.096
1.04×10^{-2}	360	.10
	Av.	0.097 ± 0.005

The constancy of the calculated value of the hydrolysis constant over the entire range of vanadium concentration and wave length studied demonstrates that initially only one reaction is taking place, namely

$$VO_4^{-3} + H_2O = HVO_4^{=} + OH^-$$

Dimerization of Monohydrogen Orthovanadate to Pyrovanadate.—It having been shown that orthovanadate hydrolyzes to form monohydrogen orthovanadate, an investigation was carried out to determine whether or not the monohydrogen orthovanadate ion dimerizes to form pyrovanadate

$$HVO_4^{-2} + HVO_4^{-2} = V_2O_7^{-4} + H_2O$$

If dimerization occurs, equation C6 (derived in Appendix C) would describe the relationship between the dimerization constant K_d and the extinction coefficient for pyrovanadate, $\epsilon_{V_2O_7^{-4}}$. This equation involves the total vanadium concentration, the free hydroxide concentration and the absorbance. From the absorbance measured at a particular hydroxide concentration for two vanadium concentrations, equation C6 can be used to construct two simultaneous relationships from which K_d and $\epsilon_{V_2O_7^{-4}}$ can be calculated. Necessary to this calculation is the hydrolysis constant of orthovanadate and the extinction coefficients of orthovanadate and monohydrogen orthovanadate. The determination of these constants has been described in the previous section.

The absorbance of solutions 0.115 and 0.0111 *M* vanadium was measured at 360 mμ for seven hydroxide concentrations covering the range 0.010 to 0.0016 *M*. The first series was made by mixing aliquots of a solution containing 0.115 *M* sodium orthovanadate with aliquots of a solution contain-

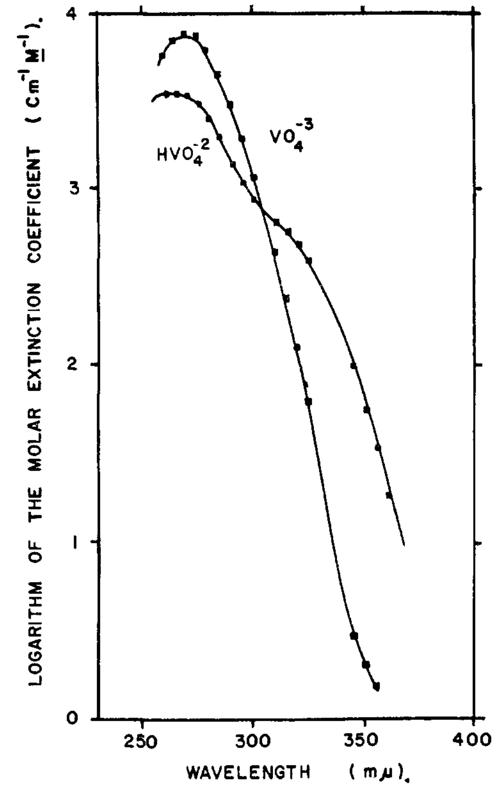

Fig. 1.—Resolved absorption spectra of orthovanadate and monohydrogen orthovanadate: ionic strength = 3.0, temperature = 25°, slit width = 0.5 mm.

ing 0.115 *M* sodium orthovanadate and 0.1 *M* perchloric acid. In the second series of experiments, the vanadium and perchloric acid concentrations were reduced to 0.0111 *M*. In the second series data for the higher hydroxide concentrations was obtained by adding various amounts of solid sodium hydroxide to aliquots of the 0.0111 *M* sodium orthovanadate solution. The ionic strength was maintained at 3.0 with sodium perchlorate.

In all cases, prior to measurement, the solutions were quickly brought to a boil and cooled to 25°. The absorbances were read *versus* appropriate vanadium-free blanks at a constant slit width of 0.5 mm. Immediately following this, the *p*H measurements were made.

The *p*H meter was standardized with a *p*H 10 buffer. All *p*H measurements were made at 25°. The outer solution of the reference electrode was changed to sodium chloride in order to prevent precipitation of potassium perchlorate at the tip of the electrode.

Since the hydroxide concentration was not in large excess over the vanadium, it was necessary to relate the measurement of *p*H to the free hydroxide concentration. The *p*H values of hydroxide solutions between 0.4 × 10^{-3} and 50 × 10^{-3} *M* were read in an ionic strength of 3.0 ($NaClO_4$). The hydroxide solutions were made carbonate free and nitrogen was passed over them during the *p*H measurements. A linear relationship was obtained on semi-logarithm coördinates between the actual hydroxide concentration and the *p*H of the solution. From this plot, the free hydroxide concentrations of the solutions were determined from the *p*H measurements in the dimerization experiment. Having obtained absorbance data for both vanadium concentrations at the same free hydroxide concentration, we were able to apply equation C6. The data and results are presented in Table II.

TABLE II

THE DIMERIZATION CONSTANT AND EXTINCTION COEFFICIENT FOR PYROVANADATE

Ionic strength = 3.0; temperature = 25°; slit width = 0.5 mm.; $\epsilon_{VO_4^{-3}}$ = 0.96; $\epsilon_{HVO_4^{-2}}$ = 18.3; K_h = 0.097; λ = 360 mμ.

Free hydroxide, *M*	Absorbance 0.0111*M* V	Absorbance 0.115 *M* V	$\epsilon_{V_2O_7^{-4}}$ cm.$^{-1}$ *M*$^{-1}$	K_d
0.010	0.158	1.39	21	48
.0060	.166	1.47	22	50
.0053	.167	1.48	22	48
.0040	.169	1.51	23	50
.0030	.173	1.55	24	44
.0023	.176	1.58	25	54
.0016	.179	1.66	26	44
		Av.	23	48

A dimerization constant of 48 ± 5 was obtained, and an extinction coefficient for pyrovanadate of approximately 23 (360 mμ) was found. The slight increase in the value of the extinction coefficient as the hydroxide concentration is decreased might be caused by the further polymerization of the pyrovanadate ion in the low hydroxide region.

Distribution of Vanadium.—From the value of the dimerization constant of monohydrogen orthovanadate and the hydrolysis constant of orthovanadate, the distribution of vanadium among the three species has been calculated as a function of the free hydroxide concentration. For simplicity of calculation, the constants were assumed to be 50 and 0.1, respectively. Due to the dimerization of vanadium, it is necessary to present a curve for each vanadium concentration of interest. The curves for 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} *M* vanadium are presented in Fig. 2. As can be seen, the importance of the pyrovanadate diminishes as the vanadium concentration is decreased and the hydroxide concentration increased.

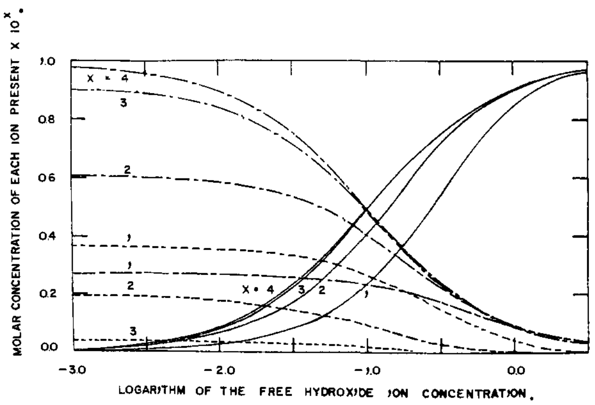

Fig. 2.—Distribution of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} *M* vanadium. Ionic strength = 3.0; temperature = 25°. Full drawn curves are VO_4^{-3}. Alternate short and long dashed curves are HVO_4^{-2}. Short dashed curves are $V_2O_7^{-4}$.

Discussion

The interpretation of spectrophotometric data has demonstrated that both monohydrogen orthovanadate and pyrovanadate must be formed during the first break in the titration of orthovanadate. At 25° in a perchlorate medium of ionic strength 3.0, the hydrolysis constant

$$K_h = \frac{[HVO_4^{-2}][OH^-]}{[VO_4^{-3}]}$$

was determined as 0.097, and the dimerization constant

$$K_d = \frac{[V_2O_7^{-4}]}{[HVO_4^{-2}]^2}$$

was determined as 48. In all calculations, the hydroxide ion was expressed as concentration and therefore the constants are "concentration constants" where all terms are in the form of concentration and not "mixed constants"[5] where one or more terms are expressed as activities.

In a potentiometric study, Britton[4] calculated a "mixed constant" of ~0.003 for the hydrolysis of orthovanadate. The value is of doubtful validity since he neglected the formation of pyrovanadate. In fact, the constant decreased as the *p*H decreased. The value of the constant can be questioned further since there was an inconsistency in using *p*H both as a measure of the hydroxide ion *activity* and as a measure of the *concentration* of the monohydrogen orthovanadate formed by hydrolysis.

In a cryoscopic study, Souchay and Schaal[6] obtained a value of 0.15 for the hydrolysis constant of orthovanadate. The agreement with our value is very good considering their investigation was conducted in sulfate media of approximately 3 *M* (ionic strength equal to 9).

On the assumption that metavanadate exists as a trimer in solution, Souchay and Carpeni[7] derived a relationship between the dimerization constant of monohydrogen orthovanadate with the *p*H and vanadium concentration. By successive approximations they selected a value of 6.7 as a best fit to the data. Comparing the predicted changes in *p*H with the observed changes, the value of 6.7 yields an average error of 25%. Using our constant of 48, a comparable average error of 34% is obtained. Therefore, the method that they adopted of expressing the data has become insensitive to large changes in the constant selected.

In general, the changes in *p*H predicted by the constant chosen by Souchay and Carpeni are too small for the lower vanadium concentrations and too large for the higher concentrations, whereas the value obtained in this work applied to their data would predict consistently low changes in *p*H. However, if the metavanadate exists as a tetramer or larger polymer, the changes in *p*H predicted by our constant would become greater and more nearly equal to the observed changes.

The data obtained by Souchay and Carpeni do not, therefore, conclusively demonstrate that metavanadate exists as a trimer in solution; in fact our constant applied to their data indicates that the metavanadate exists as a series of polymers. This view is corroborated by Hazel, McNabb and Santini[8] who postulate by analogy to phosphate that dihydrogen pyrovanadate dimerizes to a tetrametavanadate. However, if the analogy to phosphate is pursued completely, the possibility of higher polymers must be considered.[9] The view of higher polymers is further corroborated by the fact that in the solid state sodium metavanadate exists as long chain polymer.[10-12]

It now appears that there are two neutralization reactions occurring during the addition of the first equivalent of acid to orthovanadate

$$VO_4^{-3} + H^+ = HVO_4^{-2}$$

and

$$2VO_4^{-3} + 2H^+ = V_2O_7^{-4}$$

At the start of the second break, there is the possibility of two new neutralization reactions

$$HVO_4^{-2} + H^+ = H_2VO_4^- =\square= VO_3^- + H_2O$$

and

$$V_2O_7^{-4} + 2H^+ = H_2V_2O_7^{-2} =\square= (VO_3^-)_2 + H_2O$$

Both these reactions are in accord with the second break occurring after the addition of one more equivalent of acid. It should be recognized that both species formed cannot be differentiated from the analogous metavanadates, plus a molecule of water. The reaction of dihydrogen pyrovanadate with itself or dihydrogen orthovanadate would account for the existence of the tri- and tetra-metavanadates. Further condensation of these species could produce larger polymers.

Appendix

Derivation of the Spectrophotometric Equations

The method adopted is similar to the one described by Newman and Hume.[3] A somewhat modified approach is used to account for the possibility of dimer formation (pyrovanadate). The derivation is based upon the fact that the absorbance (optical density) of a mixture of species is a function of their individual extinction coefficients ϵ, equilibrium constant K, ligand concentration (OH^-) and total central atom concentration V_T. Various functions of the extinction coefficients, complex constants, ligand concentrations and experimentally determined absorbances, are plotted to evaluate the unknown terms and coefficients.

A. Hydrolysis of Orthovanadate to Monohydrogen Orthovanadate.—If we consider the hydrolysis reaction to be

$$VO_4^{-3} + H_2O = HVO_4^{-2} + OH^-$$

and the corresponding equilibrium constant to be

$$K_h = \frac{[HVO_4^{-2}][OH^-]}{[VO_4^{-3}]} \qquad (A1)$$

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(5) R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1069 (1954).

(6) P. Souchay and Scbaal, *Bull. soc. chim. France*, **20**, 819, 824 (1950).

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(8) J. F. Hazel, W. M. McNabb and R. Santini, Jr., *J. Phys. Chem.*, **57**, 681 (1953).

(9) T. Moeller, "Inorganic Chemistry," 1st Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 645.

(10) H. Sorum, *Kgl. Norske Videnskab. Selskab. Forh.*, **16**, 39 (1943).

(11) J. Lukesh, *Acta Cryst.*, **3**, 476 (1950).

(12) C. L. Christ, J. R. Clark and H. T. Evans, *ibid.*, **7**, 801 (1954).

the absorbance of a solution containing both species is

$$A = \epsilon_{VO_4^{-3}}[VO_4^{-3}] + \epsilon_{HVO_4^{-2}}[HVO_4^{-2}] \qquad (A2)$$

where ϵ represents the molar extinction coefficient for one cm. cells.

The total concentration of vanadium, analytical concentration, is

$$V_T = [VO_4^{-3}] + [HVO_4^{-2}] \qquad (A3)$$

The absorbance (for one-centimeter cells) when all the vanadium is in the form of orthovanadate is

$$A_0 = \epsilon_{VO_4^{-3}}(V_T) \qquad (A4)$$

Solving A2, A3 and A4 for orthovanadate and monohydrogen orthovanadate and substituting into A1, we obtain

$$K_h = \frac{(A_0 - A)[OH^-]}{(A - \epsilon_{HVO_4^{-2}})(V_T)} \qquad (A5)$$

Upon rearranging, we obtain

$$A = \frac{1}{K_h}(A_0 - A)[OH^-] + \epsilon_{HVO_4^{-2}}(V_T) \qquad (A6)$$

A plot of A *versus* $(A_0 - A)$ $[OH^-]$ yields a straight line with a slope of $1/K_h$, and $\epsilon_{HVO_4^{-2}}$ (V_T) as the intercept.

B. Hydrolysis of Orthovanadate to Pyrovanadate.—If we consider the hydrolysis reaction to be

$$2VO_4^{-3} + H_2O = V_2O_7^{-4} + 2OH^-$$

and the hydrolysis constant to be

$$K_h = \frac{[V_2O_7^{-4}][OH^-]^2}{[VO_4^{-3}]^2} \qquad (B1)$$

the absorbance of a solution containing both species becomes

$$A = \epsilon_{VO_4^{-3}}[VO_4^{-3}] + \epsilon_{V_2O_7^{-4}}[V_2O_7^{-4}] \qquad (B2)$$

and the total concentration of vanadium becomes

$$V_T = [VO_4^{-3}] + 2[V_2O_7^{-4}] \qquad (B3)$$

Once again when all the vanadium is in the form of orthovanadate, the absorbance (for one-centimeter cells) is

$$A_0 = \epsilon_{VO_4^{-3}}(V_T) \qquad (B4)$$

Solving B2, B3 and B4 for orthovanadate and pyrovanadate, we obtain

$$K_h = \frac{(A_0 - A)[OH^-]^2[2\epsilon_{VO_4^{-3}} - \epsilon_{V_2O_7^{-4}}]}{2\left[A - \epsilon_{V_2O_7^{-4}}\left(\frac{V_T}{2}\right)\right]^2} \qquad (B5)$$

Upon rearranging, we obtain for $A_0 > A$

$$A = \left[\frac{2\epsilon_{VO_4^{-3}} - \epsilon_{V_2O_7^{-4}}}{4K_h}\right]^{1/2}(A_0 - A)^{1/2}[OH^-] + \frac{\epsilon_{V_2O_7^{-4}}}{2}(V_T) \qquad (B6)$$

and for $A_0 < A$

$$A = -\left[\frac{\epsilon_{V_2O_7^{-4}} - 2\epsilon_{VO_4^{-3}}}{4K_h}\right]^{1/2}(A - A_0)^{1/2}[OH^-] + \frac{\epsilon_{V_2O_7^{-4}}}{2}(V_T) \qquad (B7)$$

A plot of A *versus* $(A_0 - A)^{1/2}$ $[OH^-]$ or *versus* $(A - A_0)^{1/2}$ $[OH^-]$ permits the calculation of $\epsilon_{V_2O_7}{}^{-4}$ from the intercept and K_h from the slope. $\epsilon_{VO_4}{}^{-3}$ is obtained from B4.

C. Dimerization of Monohydrogen Orthovanadate to Pyrovanadate.—If we consider that monohydrogen orthovandate can dimerize

$$2HVO_4^{-2} = V_2O_7^{-4} + H_2O$$

and the dimerization constant to be

$$K_d = \frac{[V_2O_7^{-4}]}{[HVO_4^{-2}]^2} \qquad (C1)$$

the analytical concentration of vanadium becomes

$$V_T = [VO_4^{-3}] + [HVO_4^{-2}] + 2[V_2O_7^{-4}] \qquad (C2)$$

and the absorbance of the solution becomes

$$A = \epsilon_{VO_4^{-3}}[VO_4^{-3}] + \epsilon_{HVO_4^{-2}}[HVO_4^{-2}] + \epsilon_{V_2O_7^{-4}}[V_2O_7^{-4}] \qquad (C3)$$

Substituting for orthovanadate from equation A1 into equations C2 and C3, we find

$$V_T = b[HVO_4^{-2}] + 2[V_2O_7^{-4}] \qquad (C4)$$

and

$$A = a[HVO_4^{-2}] + \epsilon_{V_2O_7^{-4}}[V_2O_7^{-4}] \qquad (C5)$$

where

$$a = \frac{\epsilon_{VO_4^{-3}}[OH^-] + \epsilon_{HVO_4^{-2}}(K_h)}{K_h}$$

and

$$b = \frac{[OH^-] + K_h}{K_h}$$

Solving equations C4 and C5 for monohydrogen orthovanadate and pyrovanadate and substituting into equation C1, we obtain

$$K_d = \frac{(aV_T - bA)\left(a - \frac{b}{2}\epsilon_{V_2O_7^{-4}}\right)}{2\left(A - \frac{V_T}{2}\epsilon_{V_2O_7^{-4}}\right)^2} \qquad (C6)$$

From the measure of the absorbance of two solutions containing different vanadium concentrations but the same hydroxide concentrations, two simultaneous expressions can be obtained from C_6. With a knowledge of K_h, $\epsilon_{VO_4^{-3}}$ and $\epsilon_{HVO_4^{-2}}$, two simultaneous expressions can be solved for K_d and $\epsilon_{V_2O_7}{}^{-4}$. If desired, C6 can be rearranged to

$$\frac{A}{V_T} = \left(\frac{2a - b\epsilon_{V_2O_7^{-4}}}{4K_d}\right)^{1/2}\frac{(aV_T - bA)^{1/2}}{V_T} + \frac{\epsilon_{V_2O_7^{-4}}}{2} \qquad (C7)$$

whereby at constant hydroxide concentration, a plot of A/V_T *versus* $(aV_T - bA)^{1/2}/V_T$ permits the calculation of $\epsilon_{V_2O_7^{-4}}$ from the intercept and K_d from the slope.