

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

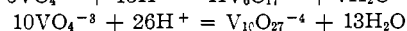
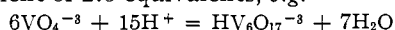
**A Spectrophotometric Investigation of Vanadium(V) Species in Acidic Solutions<sup>1</sup>**BY LEONARD NEWMAN<sup>2</sup> AND KENNETH P. QUINLAN

RECEIVED JULY 23, 1958

By utilizing a spectrophotometric approach, the hydrolysis reaction for the pervanadyl ion  $10\text{VO}_2^+ + 8\text{H}_2\text{O} = \text{H}_2\text{V}_{10}\text{O}_{28}^{-4} + 14\text{H}^+$  postulated in the literature has been examined. At 25° and at an ionic strength of 3.0, the logarithm of the hydrolysis constant was found to be  $-5.8 \pm 0.18$ . This constant is in good agreement with that reported by Rossotti and Rossotti. The extension in the range of the vanadium concentration over which this reaction has been studied further supports this mechanism.

**Introduction**

The species of vanadium(V) postulated to exist in acid solutions have been based largely on the stoichiometry of the titration of orthovanadate ion. From such measurements, a hexavanadate ion is reported by workers observing an acid requirement of 2.5 equivalents per vanadium, while a decavanadate ion is reported by workers observing an acid requirement of 2.6 equivalents, *e.g.*



The first work on the species formed during the third break in the titration of orthovanadate was carried out by Dullberg<sup>3</sup> and indicated that the  $\text{HV}_6\text{O}_{17}^{-3}$  ion was being formed. This conclusion has been supported by several other investigators.<sup>4-7</sup> The existence of  $\text{HV}_6\text{O}_{17}^{-3}$  anionic polymer is suggested by the work of Parks and Prebluda<sup>8</sup> who prepared a solid whose composition best could be described by the formula  $[\text{Co}(\text{N}-\text{H}_3)_6]_4(\text{V}_6\text{O}_{17})_3$ .

However, a recent careful investigation of the hydrolysis of the pervanadyl ion by Rossotti and Rossotti<sup>9</sup> gives substantial evidence for the formation of anionic polymers of composition  $\text{V}_{10}\text{O}_{28}^{-6}$ ,  $\text{HV}_{10}\text{O}_{28}^{-5}$  and  $\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}$ . These workers were able to show by utilizing the method of Sillén<sup>10</sup> that their potentiometric data can be explained on the basis of decavanadates. They further show that it is not possible to explain their data on the basis of hexavanadates. These results are in agreement with earlier postulates of Britton<sup>11-13</sup> and Hazel<sup>14</sup> and their co-workers. It is

interesting to note in respect to the  $\text{V}_{10}\text{O}_{28}^{-6}$  ion that recent crystallographic studies of several polyvanadates reveal the presence of ten, or multiples of ten, vanadium atoms per unit cell.<sup>15,16</sup>

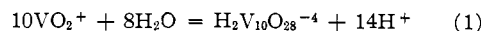
In order to ascertain the validity of a postulated polymeric reaction, it must be tested over a wide range in metal ion concentrations. Although Rossotti and Rossotti are the first to consider this matter, still, the main reservation that one might have to the conclusiveness of their results is that they could not measure the hydrolysis constant of the pervanadyl ion over a wide enough range of vanadium concentrations. In their method, the stoichiometry of the pervanadyl ion hydrolysis reaction is determined *solely* by very accurate hydrogen ion measurements. The low solubility of vanadium pentoxide restricts the maximum vanadium concentration that may be studied while the method that they employed limits the minimum vanadium concentration. It is possible to lower this limit by a spectrophotometric approach.

While the spectrophotometric method cannot be utilized as rigorously as can the potentiometric method for selecting particular polymeric reactions, it does provide a desirable alternative means of testing the validity of postulated reactions. In addition, this method has the advantage of giving an *independent* measure of the required ion concentrations. A further advantage is that the minimum usable ion concentration is not limited by the accuracy of the hydrogen ion measurements but only by the magnitude of the various extinction coefficients.

**Method**

The basis of the spectrophotometric method is similar to that employed previously.<sup>17,18</sup> First, a sufficient excess of the hydrogen ion is added to completely suppress the hydrolysis of the pervanadyl ion. Measuring the absorbance of this solution gives the extinction coefficient of this ion. Then by decreasing the hydrogen ion concentration and measuring the change in absorbance, one obtains a *direct* function of the amount of pervanadyl hydrolyzed. The derivation leading to the equation relating the change in absorbance of pervanadyl solutions to hydrogen ion concentration follows.

If we consider the first hydrolysis reaction given by Rossotti and Rossotti



$$K = \frac{[\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}][\text{H}^+]^{14}}{[\text{VO}_2^+]^{10}}$$

(15) H. T. Evans, M. E. Mrose and R. Marvin, *Am. Mineralogist*, **40**, 314 (1955).

(16) I. Lindquist, private communication to Rossotti and Rossotti, ref. 9.

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

(18) L. Newman, W. J. LaFleur, F. J. Broussides and A. M. Ross, *ibid.*, **80**, 4491 (1958).

(1) This work was done under U. S. Atomic Energy Commission Contract No. AT(49-6)-924.

(2) Address all correspondence to Leonard Newman, Brookhaven National Laboratories, Associated Universities, Inc., Upton, New York.

(3) P. Dullberg, *Z. physik. Chem.*, **45**, 129 (1903).

(4) W. C. Bray and V. J. Tihenko, quoted by W. M. Latimer, "Oxidation Potentials," 1st Ed., Prentice-Hall, Inc., New York, N. Y., 1938, p. 258.

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(6) R. Trujillo and J. Martinez, *Anales real soc. espan. fis. y quim.*, **45B**, 719 (1949); *C. A.*, **44**, 5751 (1950); *ibid.*, **46B**, 639 (1950), *C. A.*, **45**, 4596 (1951); *ibid.*, **47B**, 619 (1951), *C. A.*, **46**, 2949 (1952).

(7) P. Souchay and F. Chauveau, *Compt. rend.*, **244**, 1923 (1957).

(8) W. G. Parks and H. J. Prebluda, *THIS JOURNAL*, **57**, 1676 (1935).

(9) F. J. C. Rossotti and H. Rossotti, *J. Inorg. Chem.*, **2**, 201 (1956); *Acta Chem. Scand.*, **10**, 957 (1956).

(10) L. G. Sillén, *ibid.*, **8**, 299, 318 (1954).

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

(12) H. T. S. Britton, *ibid.*, 1842 (1932).

(13) H. T. S. Britton and G. Welford, *ibid.*, 764 (1940).

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

then the absorbance of a solution containing both  $\text{VO}_2^+$  and  $\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}$  is

$$A = \epsilon_1[\text{VO}_2^+] + \epsilon_2[\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}] \quad (2)$$

where  $\epsilon_1$  and  $\epsilon_2$  are the molar extinction coefficients for one cm. cells. The total vanadium concentration is

$$V_T = [\text{VO}_2^+] + 10[\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}] \quad (3)$$

and the absorbance when all the vanadium is in the form of  $\text{VO}_2^+$  becomes

$$A_0 = \epsilon_1 V_T \quad (4)$$

Solving (2), (3), and (4) for  $\text{VO}_2^+$  and  $\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}$  and substituting into (1), we obtain

$$K = \frac{(A - A_0)(\text{H}^+)^{14}(\epsilon_2 - 10\epsilon_1)^9}{(\epsilon_2 V_T - 10A)^{10}} \quad (5)$$

Upon rearranging (5), we obtain

$$A = -\frac{(\epsilon_2 - 10\epsilon_1)^{9/10}(A - A_0)^{1/10}(\text{H}^+)^{14/10}}{10(K)^{1/10}} + \frac{\epsilon_2 V_T}{10}$$

A plot of  $A$  versus  $(A - A_0)^{1/10}(\text{H}^+)^{14/10}$  should be a straight line. From the slope and intercept, values of  $K$  and  $\epsilon_2$  may be found.

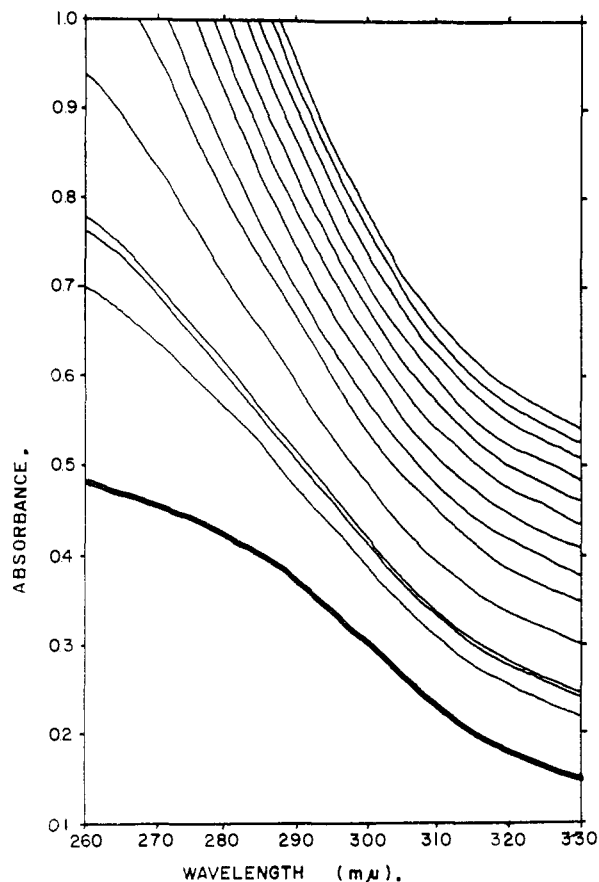


Fig. 1.—Absorbance data for  $5.25 \times 10^{-4} M$  vanadium. Ionic strength = 3.0, temperature =  $25^\circ$ . The hydrogen ion concentrations  $\times 10^3$  from the uppermost curve proceeding downwards are 0.31, 0.59, 0.88, 1.11, 1.40, 1.69, 1.90, 2.15, 2.38, 2.85, 3.25, 3.30, 3.59, and finally the heavy curve represents five solutions covering the range 8.20 to 20.0.

### Experimental

**Reagents and Instruments.**—Fisher Scientific Co. purified sodium metavanadate was used as a source of vanadium and the sodium perchlorate monohydrate as a source of perchlorate. Baker and Adamson Co. reagent grade perchloric acid 70–72% was used. For the  $pH$  measurements, a Beckman Model G  $pH$  meter was used equipped with a gen-

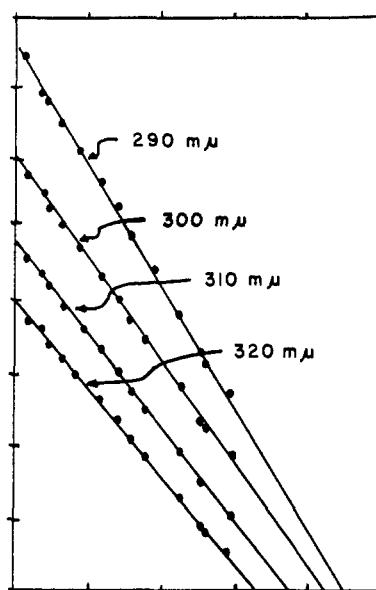


Fig. 2.—Straight line plots illustrating the hydrolysis of the pervanadyl ion to the decavanadate ion. Vanadium =  $5.25 \times 10^{-4} M$ ; ionic strength = 3.0, temperature =  $25^\circ$ .

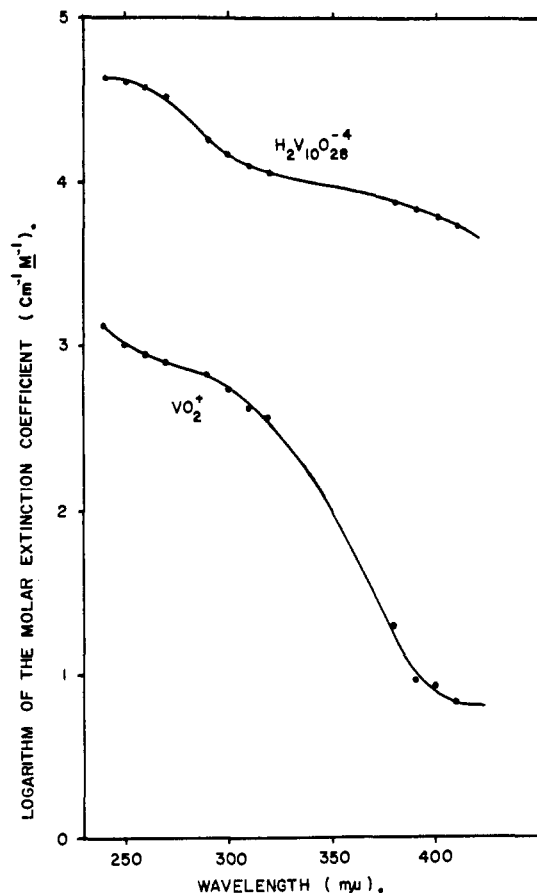


Fig. 3.—Resolved absorption spectra of the pervanadyl and decavanadate ions. Ionic strength = 3.0, temperature =  $25^\circ$ .

eral-purpose-glass electrode. The meter was standardized versus a Beckman  $pH$  4 buffer. For the spectrophotometric measurements, a Beckman Model DK-2 ratio recording spectrophotometer was used.

TABLE I  
THE HYDROLYSIS CONSTANT FOR THE PERVANADYL REACTION COVERING THE RANGE IN FREE HYDROGEN ION CONCENTRATION OF  $0.2 \times 10^{-3}$  TO  $20 \times 10^{-3}$  M AT AN IONIC STRENGTH OF 3.0 AND 25°

| Concn., M             | Wave length, m $\mu$ | Log K |
|-----------------------|----------------------|-------|
| $1.05 \times 10^{-3}$ | 410                  | -5.8  |
| $1.05 \times 10^{-3}$ | 400                  | -5.8  |
| $1.05 \times 10^{-3}$ | 390                  | -5.8  |
| $1.05 \times 10^{-3}$ | 380                  | -5.9  |
| $5.25 \times 10^{-4}$ | 320                  | -5.7  |
| $5.25 \times 10^{-4}$ | 310                  | -5.5  |
| $5.25 \times 10^{-4}$ | 300                  | -5.6  |
| $5.25 \times 10^{-4}$ | 290                  | -5.6  |
| $1.05 \times 10^{-4}$ | 270                  | -6.0  |
| $1.05 \times 10^{-4}$ | 260                  | -5.9  |
| $1.05 \times 10^{-4}$ | 250                  | -6.0  |
| $1.05 \times 10^{-4}$ | 240                  | -6.1  |

Av.  $-5.8 \pm 0.18$

**Procedure.**—Aliquots of a solution containing the vanadium concentration under investigation were mixed with aliquots of a 3.0 M perchloric acid solution containing the same vanadium concentration. To attain equilibrium the mixed solutions were brought to a quick boil and cooled to 25°. It was found that irreproducible results were obtained if the temperature of the solutions were only brought to 70–80°. The establishment of equilibrium was ascertained by observing that the absorbance and pH values measured on the day of mixing were identical with those measured after three days. The three vanadium concentrations investigated were  $1.05 \times 10^{-4}$  M,  $5.25 \times 10^{-4}$  M and  $1.05 \times 10^{-3}$  M. Typical results are presented in Fig. 1.

The free hydrogen ion concentration was determined from pH measurements utilizing a calibration procedure similar to that previously described.<sup>18</sup> In this case the electrodes were calibrated by obtaining pH values of acid solutions between  $0.2 \times 10^{-3}$  M to  $20 \times 10^{-3}$  M. As in the previous publication, the ionic strength was maintained at 3.0.

Typical straight line plots obtained upon application of equation 6 are presented in Fig. 2. The calculated values of the logarithm of the hydrolysis constant for twelve wave lengths, a tenfold change in vanadium concentration and a hundred-fold change in hydrogen ion concentration are summarized in Table I. The logarithm of the molar extinction coefficients are plotted versus wave length in Fig. 3.

### Discussion

The value of  $-5.8 \pm 0.18$  obtained for the logarithm of the hydrolysis constant is in excellent agreement with the value of  $-5.5 \pm 0.15$  obtained by Rossotti and Rossotti at an ionic strength of 3.0. By utilizing the spectrophotometric method, the experimental data for this reaction have been extended from an eightfold change in vanadium concentration to a two hundred-fold change.

While our data fit the decavanadate mechanism very well, they are not sufficiently unique to distinguish between a decavanadate and hexavanadate mechanism. However, the data of Rossotti and Rossotti distinguish between these two mechanisms. This fact combined with the accompanying agreement of the hydrolysis constant over a wide range in vanadium concentration strongly supports the decavanadate mechanism for the hydrolysis of the pervanadyl ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## The Structures of Ammonium and Rubidium Ethylenediaminetetraacetatocobaltate(III)<sup>1</sup>

BY H. A. WEAKLIEM<sup>2</sup> AND J. L. HOARD

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Isomorphous crystals of  $\text{NH}_4\text{CoY} \cdot 2\text{H}_2\text{O}$  and  $\text{RbCoY} \cdot 2\text{H}_2\text{O}$  ( $\text{Y}^{4-} \equiv$  ethylenediaminetetraacetate) have a four-molecule orthorhombic cell of space group  $\text{P2}_12_12_1$ . The techniques of isomorphous replacement, Fourier and difference syntheses were applied to spectrometrically measured X-ray zonal data from single crystals to achieve determination of structure. The sexadentate octahedral complex  $\text{CoY}^-$  (Fig. 2), containing five chelate rings, shows effectively twofold symmetry about an axis bisecting the  $\text{NCoN}$  angle of the ethylenediamine (E) ring. The four glycinic rings are thus classified into pairs: the relatively flat and unstrained R rings lie in planes nearly at right angles to each other and to E; the strongly folded and quite strained G rings, together with E, form closing Co–O, Co–N bonds in a girdle around the central atom.

### Introduction

The capacity of ethylenediaminetetraacetic acid (abbreviated formula,  $\text{H}_4\text{Y}$ ) to complex with many different cations has been studied by many workers. Among crystalline complexes of the transition elements first prepared by Brintzinger, *et al.*,<sup>3</sup> was the diamagnetic<sup>4</sup>  $\text{NaCoY} \cdot 4\text{H}_2\text{O}$ . Since the complexing species contains six functional groups, a sexadentate complex  $\text{CoY}^-$  with five five-membered chelate rings is theoretically possible. The existence of the sexadentate  $\text{CoY}^-$  and also of the quinquedentate  $\text{CoYX}^-$ ,  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_2^-$ , receives strong support from the physico-

chemical studies of Schwarzenbach<sup>5</sup> and the infrared studies of Busch and Bailar<sup>6</sup> and Morris and Busch.<sup>7</sup> The X-ray study now reported was undertaken to determine directly the configuration and bond data for one of the stable complexes, namely,  $\text{CoY}^-$ . Orthorhombic crystals of  $\text{NH}_4\text{CoY} \cdot 2\text{H}_2\text{O}$  and  $\text{RbCoY} \cdot 2\text{H}_2\text{O}$  prove to be isomorphous and well suited to structure determination.

### Experimental

Crystals of  $\text{NaCoY} \cdot 4\text{H}_2\text{O}$ ,  $\text{NH}_4\text{CoY} \cdot 2\text{H}_2\text{O}$  and  $\text{RbCoY} \cdot 2\text{H}_2\text{O}$  were prepared by methods similar to those used by Burke.<sup>8</sup> A slurry containing newly precipitated  $\text{Co}(\text{OH})_2$

(1) Supported by National Science Foundation.  
(2) General Electric Company Fellow, 1956–1957.  
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