[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Absorption Spectra of Vanadium(III) and Vanadium(IV) Ions in Complexing and Non-complexing Media

BY SYDNEY C. FURMAN AND CLIFFORD S. GARNER

The absorption spectra of vanadium(III) compounds in aqueous solutions have been reported by several investigators,[1,2,3] and in each case the spectrum has been obtained under conditions where complex ion formation was probable. We have observed in the studies of vanadium(III) compounds in this Laboratory that vanadium(III) perchlorate solutions do not exhibit the green color characteristic of vanadium(III) sulfate or chloride solutions, but rather show a green-tinged blue color.

The present study was undertaken with a view of obtaining the absorption spectra of the hydrated tripositive vanadium ion (written herein as V^{+++}), and of vanadium(III) complexes in hydrochloric acid solutions. Rabinowitch and Stockmayer[4] have shown in their very thorough work on iron(III) that absorption spectra must be analyzed critically in order to detect the true spectra of the non-complexed metal ions, and although complex formation in perchloric acid solutions is not expected, it is often necessary to consider hydrolysis products for complete resolution.

In a review of some early electromotive force studies involving vanadium(III) solutions Gerke[5] assumed the hydrolysis product of V^{+++} to be VO^+ (hydrated). Furman and Denison[6] have concluded from the data of Jones and Ray[7] that this hydrolysis was not complete but rather was stepwise, proceeding through the formation of VOH^{++} (hydrated). The VOH^{++} ion has been called upon by Lingane and Meites[8] in the interpretation of the effect of *p*H on their polarographic results and by Ramsey, Sugimoto and De Vorkin[9] in their kinetic study of the oxidation of vanadium(III) by oxygen. Accordingly, the present study was also designed to attempt to find spectrophotometric evidence for the formation of VOH^{++}.

Because of the presence of approximately 5% of vanadium(IV) in the solutions of vanadium(III), the absorption spectra of vanadium(IV) in perchloric acid and hydrochloric acid solutions were determined in order to permit suitable correction of the data.

Experimental

Absorption Measurements.—The spectra were determined by means of two Beckmann Model DU quartz spectrophotometers over a range of 250–1000 mμ. One of the instruments was equipped with a jacket thermostatically controlled to ±1° for the study of spectra at various temperatures. Glass-stoppered Pyrex cells of 1.00-cm. optical length were used for the region of 400–1000 mμ, and silica-stoppered silica cells of the same optical length were used for the ultraviolet region; in order to exclude oxygen, the cells were filled with oxygen-free nitrogen prior to being filled with the solutions to be measured. Samples that had been studied at higher temperatures were cooled to the initial temperature and the optical densities were found to reproduce the original values to within ±0.002, showing that appreciable decomposition of the solutions did not occur during the experiments.

Materials.—Vanadium(V) oxide was prepared from C. P. ammonium metavanadate (recrystallized from conductivity water) by controlled ignition to constant weight.

C. P. hydrochloric acid was used for the preparation of all chloride solutions. The perchloric acid solutions were made up with C. P. perchloric acid, distilled at 5 mm.

Saturated sodium perchlorate solution, used to attain constant ionic strength, was prepared by neutralizing "Reagent Grade" solid sodium hydroxide with perchloric acid. The solubility data of Cornec and Dickeley[10] were employed to calculate the concentration. All solutions were prepared in calibrated glass volumetric flasks at 25°, using conductivity water with a specific conductance of 1×10^{-6} ohm^{-1} cm.$^{-1}$.

Preparation and Analysis of Vanadium(III) and Vanadium(IV) Solutions.—Solutions of vanadium(III) perchlorate were prepared by electrolyzing, for a period of forty-eight hours, vanadium(V) oxide suspensions in perchloric acid solutions under an atmosphere of nitrogen freed from oxygen by passage through fresh chromium(II) chloride solutions. Platinized platinum electrodes were used at a current density of 0.1 amp./sq. cm.; the anode compartment consisted of a porous cup suspended in the cathode section. Vanadium(IV) solutions were prepared similarly by terminating the reduction at a time when no vanadium(III) or vanadium(V) could be detected chemically. Chloride ion could not be detected in these solutions by the addition of silver nitrate until at least twenty-four hours after termination of the electrolysis; all spectrophotometric measurements were completed within this time interval.

Solutions to be studied were prepared from the electrolyzed solutions by diluting in a purified nitrogen system with air-free reagents, consisting of conductivity water, saturated sodium perchlorate solution, and perchloric or hydrochloric acid. Solutions were allowed to stand for at least two hours under nitrogen, and the analyses for vanadium(III) and vanadium(IV) were conducted just prior to the spectrophotometric measurements.

The vanadium(III) solutions were analyzed by the method of Ramsey, Sugimoto and De Vorkin.[9] The procedure consisted of adding a measured excess of potassium iodate solution, of known titer, to an aliquot of the vanadium(III) solution and titrating with sodium thiosulfate the iodine liberated upon addition of potassium iodide. The concentration of vanadium(III) was calculated on the

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(1) M. S. Karim and R. Samuel, *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **3**, 157 (1934).

(2) Y. Uzumasa, H. Okuno and K. Doi, *J. Chem. Soc. Japan*, **59**, 655 (1938).

(3) Th. Dreisch and O. Kallscheuer, *Z. physik. Chem.*, **B45**, 19 (1939).

(4) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(5) R. H. Gerke, *Chem. Revs.*, **1**, 390 (1925).

(6) S. C. Furman and J. T. Denison, private communications.

(7) G. Jones and W. A. Ray, THIS JOURNAL, **66**, 1571 (1944).

(8) J. J. Lingane and L. Meites, *ibid.*, **70**, 2525 (1948).

(9) J. B. Ramsey, R. Sugimoto and H. De Vorkin, *ibid.*, **63**, 3480 (1941).

(10) E. Cornec and J. Dickeley, *Bull. soc. chim. France*, **41**, 1017 (1927).

basis of 5 equivalents/mole for potassium iodate in its reaction with vanadium(III). Solutions containing both vanadium(III) and vanadium(IV), as well as solutions containing only vanadium(IV), were titrated for total vanadium with potassium permanganate solution by the method of Willard and Young.[11]

The perchloric acid concentration of the electrolyzed solutions was determined by adding to an aliquot of the vanadium(III) solution such a measured volume of dilute air-free sodium hydroxide solution, standardized against potassium acid phthalate, that all the vanadium(III) would be precipitated as the insoluble hydroxide. After removing the hydroxide by centrifugation and adding the washings (made with air-free distilled water) to the centrifugate, the excess alkali in the centrifugate was titrated with dilute perchloric acid to a phenolphthalein end-point. The concentration of perchloric acid in the solution was calculated from the known concentration of vanadium(III).

Discussion

Spectrum of the Hydrated Tripositive Ion V^{+++}.—The blue color of vanadium(III) perchlorate in perchloric acid solutions can be attributed to a single maximum in the visible region at 580 mμ. The wing of another maximum at 400 mμ extends into the visible, and if the solution contains, in addition to V^{+++} ions, other species of ions absorbing in the region 400–500 mμ the color may be changed to a green as long as the absorption in the red is unchanged.

The curves in Fig. 1 show the effect of perchloric acid concentration on the spectrum; the increase in absorption with decreasing acidity, at constant ionic strength, may be attributed to absorption by a hydrolysis product.

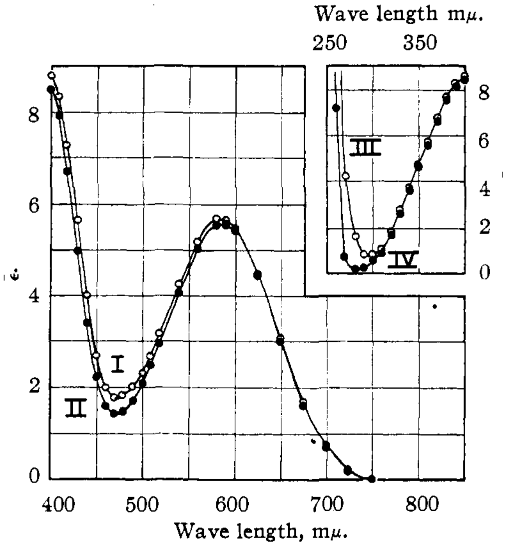

Fig. 1.—Average extinction coefficient of (V^{+++} + VOH^{++} + VO^{++}):

	Volume formal concentrations				
	$V(ClO_4)_3$	$VO(ClO_4)_2$	$NaClO_4$	$HClO_4$	μ
I	0.0725	0.004	0.56	0.38	1.4
II	.0725	.004	.15	.79	1.4
III	.0472	.004	.61	.33	1.2
IV	.0472	.004	.00	.94	1.2

We have followed the procedure suggested by Rabinowitch and Stockmayer[4] for the analysis of the spectra; the same symbols will be given here for convenience.

The average extinction coefficients, plotted in Fig. 1, are defined by the equation

$$\bar{\epsilon} = \frac{1}{d(V^{+3})_0} \log_{10} \frac{I_0}{I} \qquad (1)$$

where d is the optical length of the cell and $(V^{+3})_0$ is the total formal concentration of vanadium(III). The sum of the optical densities of the absorbing species, V^{+++} and VOH^{++}, may be written as

$$\bar{\epsilon}(V^{+3})_0 = \epsilon_{V^{+++}}(V^{+++}) + \epsilon_{VOH^{++}}(VOH^{++}) \qquad (2)$$

where VOH^{++} arises from the reaction

$$V^{+++} + H_2O \rightleftharpoons VOH^{++} + H^+ \qquad (3)$$

for which an equilibrium constant may be defined as

$$K_1 = (VOH^{++})(H^+)/(V^{+++}) \qquad (4)$$

where parentheses refer to molar concentrations. Although activity effects are not considered in the above equilibrium, the work was conducted in such a way that K_1 should be essentially constant between solutions used for the evaluation of the spectra of V^{+++} and VOH^{++}. Therefore, K_1 is not the thermodynamic equilibrium constant but only a "constant" for the solutions to be discussed here.

Under our experimental conditions $(V^{+++}) >> (VOH^{++})$ and $(H^+) >> (VOH^{++})$, whence equation (2) may be transformed into

$$\bar{\epsilon}(V^{+3})_0 = \epsilon_{V^{+++}}(V^{+3})_0 + K_1\epsilon_{VOH^{++}}(V^{+3})_0/(H^+) \qquad (5)$$

or

$$\bar{\epsilon} = \epsilon_{V^{+++}} + K_1\epsilon_{VOH^{++}}/(H^+) \qquad (6)$$

The extinction coefficient, $\epsilon_{V^{+++}}$, can be obtained from the spectra of two solutions of

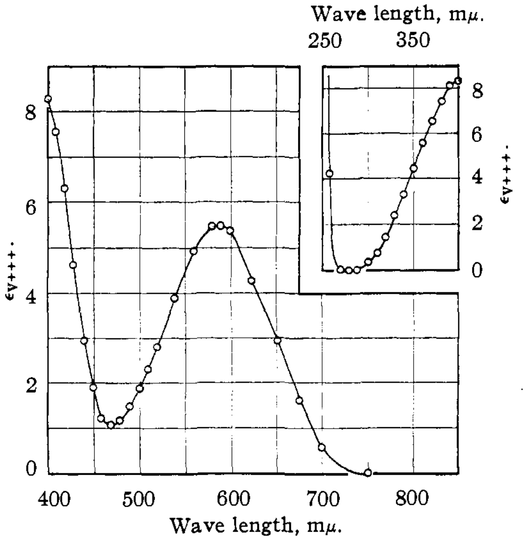

Fig. 2.—Absorption spectrum of V^{+++} (hydrated). The compositions of the solutions were the same as given under Fig. 1.

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[11] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

different acidity through the application of equation (6), assuming K_1 does not change between the solutions. Since K_1 is expected to be dependent on the composition of the solution, the spectrum of V^{+++}, as shown in Fig. 2, was evaluated from the solutions (Fig. 1) in which $(V^{+3})_0$ was constant and only the concentrations of perchloric acid and sodium perchlorate were varied with the ionic strength held constant. The spectrum of V^{+++} has been determined from data that were corrected for the absorption of VO^{++}; this was accomplished, as discussed later, by studying vanadium(IV) solutions under comparable conditions.

The molar extinction coefficients of V^{+++} in the spectral region from 400–1000 mμ are presented in column 2 of Table I. Extinction coefficients in the ultraviolet have not been included in the table because of the large corrections arising from the strong absorption in the ultraviolet of the VO^{++} in the V^{+3} solutions.

TABLE I

MOLAR EXTINCTION COEFFICIENTS

λ, mμ	$\epsilon_{V^{+++}}$	$K_1\epsilon_{VOH^{++}}$	$\epsilon_{VOH^{++}}$	$\epsilon_{VO^{++}}$
400	8.3[a]	0.23	120	
410	7.6	.31	160	
420	6.2	.40	200	
430	4.5	.43[a]	220[a]	
440	2.9	.42	210	
450	1.9	.33	170	0.00
460	1.2	.30	150	.10
470	1.1[b]	.26	130	...
480	1.2	.23	120	.21
490	1.5	.22	110	...
500	1.8	.19	95	.42
510	2.3	.15	75	...
520	2.8	.15	75	.77
540	3.9	.13	65	1.48
560	4.9	.11	55	2.66
570	..	..	...	3.47
580	5.5[a]	.08	40	4.30
590	5.5[a]	.07	35	5.20
600	5.4			6.13
610	..			6.94
620	..			7.73
625	4.3			...
630	..			8.29
640	..			8.88
650	2.9			9.46
660	..			10.1
670	..			10.9
675	1.6			..
680	..			11.6
700	0.59			13.4
725	0.10			15.8
750	0.00			17.0[a]
775				16.6
800				14.7
850				7.90
900				2.83
950				0.62
1000				0.00

[a] Absorption maximum. [b] Absorption minimum.

Spectrum of VOH^{++}.—Although we were able to analyze the spectra for $\epsilon_{V^{+++}}$, the conditions of this study did not allow us to find $\epsilon_{VOH^{++}}$ directly, but only the product $K_1\epsilon_{VOH^{++}}$. Calculated values of $K_1\epsilon_{VOH^{++}}$ are presented in column 3 of Table I and graphically in Fig. 3 as a function of wave length. The location of the maximum at 430 mμ, as well as the absence of increased absorption in the red region, are in agreement with the observation that as the *p*H of the solution is increased, the color becomes green and remains so, terminating with the precipitation of the green hydroxide. In order to determine the molar extinction coefficient of VOH^{++} some independent means must be used to find K_1. A value of this hydrolysis constant has been calculated by Furman and Denison[6] to be approximately 2×10^{-3}. This same value may be taken for an approximate calculation of $\epsilon_{VOH^{++}}$ from the values of $K_1\epsilon_{VOH^{++}}$, giving the values shown in column 4 of Table I.

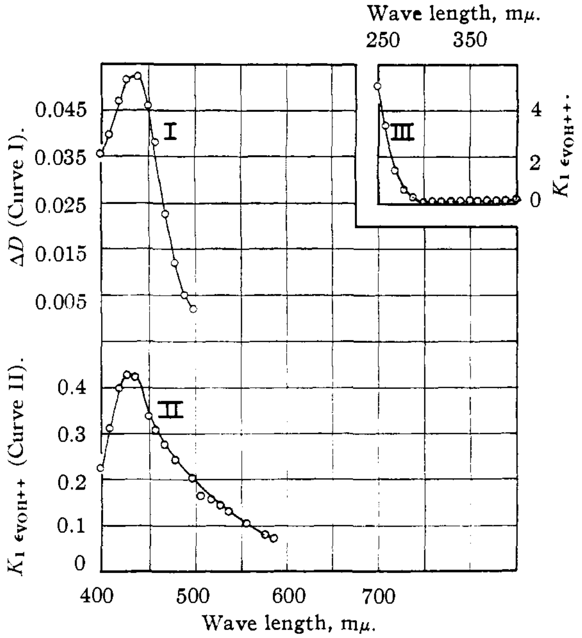

Fig. 3.—Absorption spectrum of VOH^{++} and relative absorption of chloride complexes of V^{+3}. Curves II and III were calculated using the data given in Fig. 1. Curve I was calculated from the optical densities of the following two solutions:

Volume formal concentrations				
$V(ClO_4)_3$	$VO(ClO_4)_2$	HCl	$HClO_4$	μ
0.0466	0.005	1.90	0.0	2.2
.0466	.005	0.0	1.9	2.2

It remains to be shown that VOH^{++} is the species responsible for this increased absorption. It is apparent that the average extinction coefficient will be proportional to the reciprocal of (H^+) if reaction (3) correctly represents the major hydrolysis step. On the other hand, if the hydrolysis were represented by

$$V^{+++} + H_2O \rightleftharpoons VO^+ + 2H^+ \qquad (7)$$

the average extinction coefficient would be proportional to the square of the reciprocal of (H^+). In Fig. 4 the average extinction coefficient has been plotted against $1/(H^+)$ (curve I) and against $1/(H^+)^2$ (curve II). The dashed extension of curve II indicates the expected shape if reaction (7) predominated. The linearity of curve I confirms that the absorption may be attributed to VOH^{++} in the region of concentrations studied.

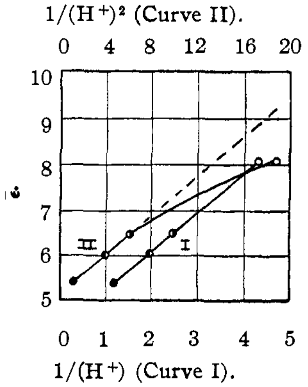

Fig. 4.—Effect of H^+ on the average extinction coefficient of V^{+3}; data taken at 40° and 430 mμ:

	Volume formal concentrations				
	$V(ClO_4)_3$	$VO(ClO_4)_2$	$HClO_4$	$NaClO_4$	μ
○	0.0483	0.004	0.23	0.37	0.90
◑	.0725	.004	.38	.56	1.4
◐	.0483	.004	.50	.10	0.90
●	.0725	.004	.79	.15	1.4

A vanadium(III) perchlorate solution visibly changes color from blue to green upon being heated to approximately 70° and returns to blue upon cooling to room temperature. This indicates a larger degree of hydrolysis at higher temperatures, corresponding to reaction (3) being endothermic. Figure 5 shows the effect of temperature on the average extinction coefficient at two wave lengths, the effect being more pronounced at 430 mμ than at 580 mμ because of the larger absorption of VOH^{++} at the shorter wave length.

In order to find ΔH_1, the heat effect attending reaction (3), $\log_{10}(\bar{\epsilon} - \epsilon_{V^{+++}})$ has been plotted against $1/T$ in Fig. 6. Since $\epsilon_{VOH^{++}}$ is not affected by a change in temperature, the slope of this curve allows us to find ΔH_1 from the relation $d \log_{10} K_1/d(1/T) = -\Delta H_1/2.3R$. The value of 11.1 kcal./mole at 440 mμ has been calculated in this way. ΔH_1 has been calculated similarly at five different wave lengths and in solutions of different compositions, and the average of ten values gives $\Delta H_1 = 10 \pm 1$ kcal./mole in the range from 25–50°. Very approximate values of the corresponding molar free energy increase and entropy increase of hydrolysis are $\Delta F_1 =$ 4 kcal./mole and $\Delta S_1 = 20$ cal./deg./mole, respectively, obtained from the rough value of Furman and Denison[6] for the hydrolysis equilibrium constant. It is interesting to note that the above thermodynamic constants for the hydrolysis of V^{+++} are similar to the corresponding constants for the hydrolysis of (hydrated) Fe^{+++}; namely, $\Delta H_1 = 12.3 \pm 1$ kcal./mole, $\Delta F_1 = 3.4$ kcal./mole, and $\Delta S_1 = 30$ cal./deg./mole.[4,12]

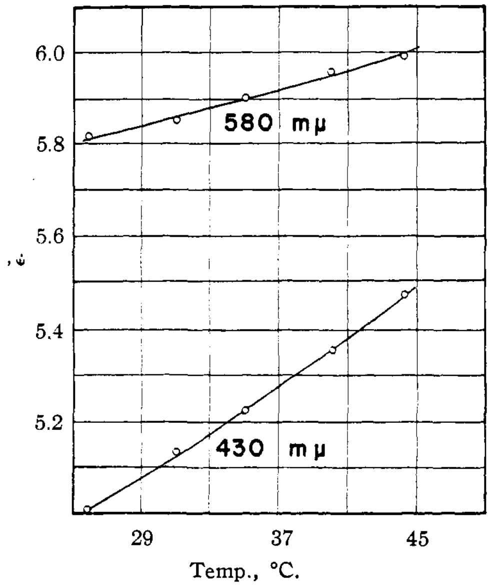

Fig. 5.—Increase in the average extinction coefficient of V^{+3} with temperature: 0.0725 *f* in $V(ClO_4)_3$, 0.004 *f* in $VO(ClO_4)_2$, 0.79 *f* in $HClO_4$, 0.15 *f* in $NaClO_4$, $\mu = 1.4$.

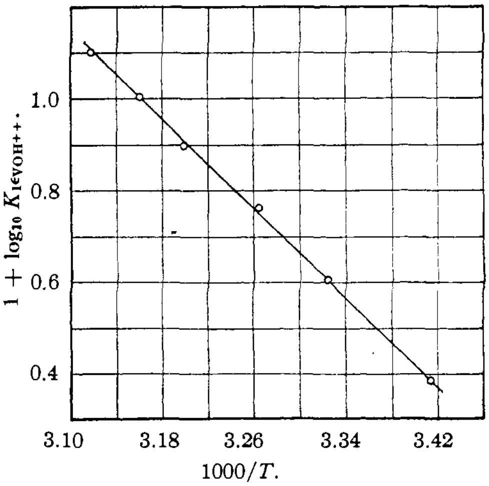

Fig. 6.—$\log_{10} K_1\epsilon_{VOH^{++}}$ as a function of $1/T$. Values of $K_1\epsilon_{VOH^{++}}$ have been calculated from the following solutions:

Volume formal concentrations				
$V(ClO_4)_3$	$VO(ClO_4)_2$	$HClO_4$	$NaClO_4$	μ
0.0483	0.004	0.23	0.37	0.90
.0483	.004	.50	.10	.90

Absorption of V^{+3} Chloride Complexes.—In an attempt to study the association of chloride ion

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[12] A. B. Lamb and A. G. Jacques, THIS JOURNAL, 60, 977, 1215 (1938).

with tripositive vanadium ion, it was found necessary to have the Cl^- concentration at least twenty times the total vanadium concentration before a measurable difference in the spectra could be detected spectrophotometrically.

A measure of the absorption of the chloride complexes may be found by subtracting from the optical density of a solution containing chloride ion the optical density of a solution having the same vanadium(III) content and *p*H, but with no chloride ion, both solutions having the same ionic strength. This difference, ΔD, calculated from our data corresponding to the largest ratio of $(\text{Cl}^-)/(\text{V}^{+3})_0$, is presented in Fig. 3 as a function of wave length. A maximum in this curve occurs at approximately 440 mμ.

That ΔD is so small unless the chloride ion concentration is many times that of the vanadium(III) requires either that the extinction coefficients of the complex ions are only slightly larger than those of V^{+++} or that a stable complex is not formed. Because of the possibility that a first association step may have resulted in a weakly colored ion and that higher complexes have become important in our solutions, this study was not pursued further. It was found in these preliminary experiments that ΔD increased with increasing temperature; therefore, if this increase in absorption can be attributed to only one complex species the formation of this species takes place by an endothermic reaction.

Spectrum of Hydrated VO^{++}.—It was concluded by Jones and Ray[7] that the hydrolysis of VO^{++} would be repressed almost completely in solutions 0.04 molar in acid. That hydrolysis is negligible in solutions 0.2 *m* or greater in H^+ is indicated by the fact that vanadium(IV) perchlorate solutions differing only in (H^+) in the range from 0.2 to 1.0 *m* at an ionic strength of 2.0 gave no detectable difference in spectra.

Vanadium(IV) perchlorate solutions, with added hydrochloric acid, were examined and the results indicated very little complexing in the range of concentrations studied: namely, the same as those involved in the V^{+3} studies. It was necessary to have the Cl^- concentration 100 times the VO^{++} concentration to obtain a 5% increase in absorption. The spectrum of VO^{++}, as shown in Fig. 7, exhibits one maximum in the visible at 750 mμ and a large absorption in the ultraviolet.

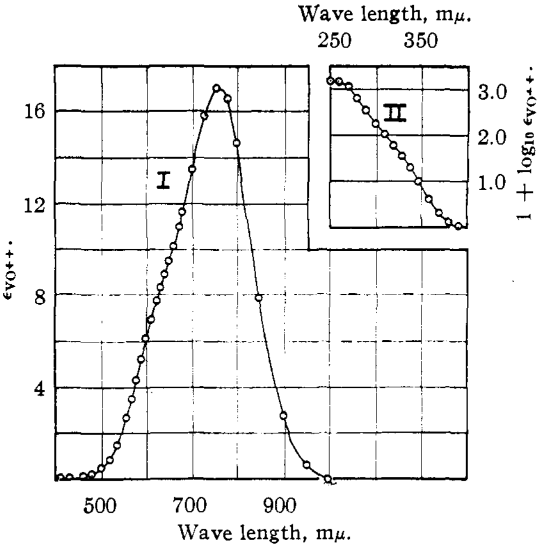

Fig. 7.—Absorption spectrum of VO^{++}:

	Volume formal concentrations		
	$\text{VO(ClO}_4)_2$	HClO_4	μ
I	0.0490	1.1	1.3
II	.0201	0.70	0.76

Acknowledgment.—The authors wish to thank Professor J. B. Ramsey for many helpful suggestions.

Summary

1. The absorption spectra of aqueous vanadium(III) perchlorate solutions have been determined and analyzed into the absorption curves for the free (hydrated) V^{+++} ion and its hydrolysis product (hydrated) VOH^{++}.

2. The heat of the hydrolysis of V^{+++} to form VOH^{++} has been found to be $\Delta H_1 = 10 \pm 1$ kcal./mole at room temperature from measurements made at different temperatures with solutions having an ionic strength of 1.0. ΔF_1 and ΔS_1 have been calculated from an approximate value of the hydrolysis equilibrium constant to be 4 kcal./mole and 20 cal./deg./mole, respectively.

3. The spectra of aqueous vanadium(III) chloride solutions indicate complex ion formation.

4. The absorption spectra of aqueous vanadium(IV) perchlorate solutions have been determined.

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