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THE CHEMISTRY AND THERMODYNAMICS OF VANADIUM (V)

Mary Joan LaSalle

(Thesis - M. S.)

September 22, 1954

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Mary Joan LaSalle
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

September 22, 1954

ABSTRACT

The thermodynamic functions for the pervanadyl ion in perchloric acid solution were determined at 25° and compared to those for other ions of the MO_2^+ type and their anionic counterparts. The free energy of solution was determined by extrapolation of the equilibrium solubility product constant to zero ionic strength and the heat of solution was obtained by solution calorimetric methods.

Thermodynamic functions were also calculated for the vanadyl ion by using the above and other supplementary values.

The absorption spectra and calculated extinction coefficients are presented for the pervanadyl and vanadyl ions and the x-ray diffraction pattern for the hydrate $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ which was identified is also reported.

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I. INTRODUCTION

One of the few elements of low atomic number for which oxygenated cationic species have been reported in solution is the pervanadyl ion, VO_2^+ . The only others listed by Latimer¹ for $Z < 50$ are TiO^{++} , ZrO^{++} , and Be_2O^{++} . The existence of an NO_2^+ ion has also been postulated by MacGillavry². Compounds such as VOCl , VOCl_2 , VOCl_3 and the corresponding bromides are well known, but it was Düllberg³ who first noted that the vanadium (V) migrates to the cathode in acid solution. Coryell and Yost⁴ in their potentiometric measurements of the cell couple $\text{VO}^{++} - \text{VO}_2^+$ in HCl solutions found that their data indicated oxygenated forms for the ions with the oxygen present in a ratio of 1:2 for the IV and V ions, respectively. Carpenter⁵ repeated these experiments in HClO_4 to avoid a complexing medium and essentially confirmed the work of Coryell and Yost. The latter had suggested $\text{VO}_2^+ \cdot 2\text{H}_2\text{O}$ or $\text{V}(\text{OH})_4^+$ as the form of the oxygenated pentavalent ion, but Carpenter favors VO_2^+ as the most probable form of the ion, as do Hart and Partington,⁶ who measured the same cell potential in H_2SO_4 and HCl .

Thermodynamically, there is no way in which these two alternatives (VO_2^+ and $\text{V}(\text{OH})_4^+$) can be distinguished. A reason used to support the choice of the form $\text{V}(\text{OH})_4^+$ is that it indicates a higher coordination for vanadium. The recent studies of actinide-element

ions such as UO_2^+ , NpO_2^+ , PuO_2^+ , and AmO_2^+ , however, indicate that a lesser degree of coordination is very plausible.

Since the proposals of Latimer and Powell⁷, Connick and Powell⁸, and Cobble⁹ have been successful in correlating the entropy and the structure of ions, it was of interest to determine the entropy of the pervanadyl ion and compare it to another ion of similar structure, NpO_2^+ , whose entropy can be obtained from entropy changes experimentally determined by Cohen and Hindman¹⁰ for reactions involving Np^{+++} , Np^{++++} , and NpO_2^+ .

The value obtained for the entropy from solubility and calorimetric measurements in this research suggests that the ion has a VO_2^+ structure. Thermodynamic properties for the ion have been calculated.

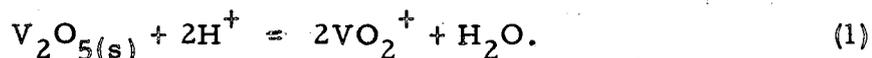
Raman spectra could conceivably be expected to uniquely determine the correct structure of the ion and some exploratory work has been done on this phase of the problem. Certain difficulties in the experimental procedure (the absorption band occurs at the main excitation line of mercury, 4358 Å), however, have delayed the completion of this phase of the research.

The entropy and thermodynamic functions for the VO^{++} ion were calculated using data obtained in this research, data from Carpenter⁵, and supplementary values from Latimer¹.

The X-ray powder pattern data for the hydrated vanadium pentoxide $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is also reported.

II. SOLUBILITY STUDIES

Since the entropy of V_2O_5 has been determined by low-temperature heat-capacity measurements¹¹ and since V_2O_5 has only a limited solubility in acid solutions, it is possible to obtain the entropy change for the reaction



The solubility of the pentoxide in various strong acids has been previously reported by Coryell and Yost⁴ in HCl; Britton and Welford¹² in HCl, H_2SO_4 , and $HClO_4$; Meyer and Aulich¹³ in H_2SO_4 ; and Ducret¹⁴ in HCl, H_2SO_4 , and $HClO_4$.

Values for the $(VO_2^+)/[H^+]$ relation determined from the solubilities reported by Coryell and Yost at 25° in HCl are in general higher than those obtained by the other authors in $HClO_4$. Complex ion formation may therefore be suspected as one possible reason. Colloid formation may have been more extensive than Coryell and Yost suspected (they state that colloid formation was evident at low acid concentrations, and it may be pointed out that vanadic gels and sols are commonly made in HCl solution), since the solubility they reported in approximately 0.5 N acid is more than that which would be calculated by Eq. (1) for total reaction of all hydrogen ion present. No explicit information is given as to how these equilibrium values were obtained or how it was determined that equilibrium had ever been reached. Further, no supporting evidence from the cell potential data can be found for any extensive chloride complex ion formation since variation in the vanadium concentration at a given ionic strength and HCl concentration causes no variation in the cell potential.

The values calculated for the $(VO_2^+)/ (H^+)$ ratio from the data of Britton and Welford at 18° in HCl show a variation with increase in (H^+) just opposite to that of the values from Coryell and Yost's measurements. Their values for H_2SO_4 are an order of magnitude greater than those reported for H_2SO_4 by Aulich and Meyer and about one-third of the values Britton and Welford list for HCl. It is, therefore, very likely that neither Britton and Welford's nor Aulich and Meyer's values represent a true equilibrium concentration.

Since Britton and Welford and Aulich and Meyer also report determinations of the solubility in these acids at 100° C, one can observe in these data a tendency for vanadium pentoxide to become less soluble at higher temperatures and low acid concentration. For example, the solubility determined by Britton and Welford for V_2O_5 in $HClO_4$ at 18° is higher than the values to be reported from this research at 25° . If an equilibrium concentration at 18° is calculated from the reaction

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \quad (2)$$

using the experimentally determined ΔH for the reaction of Eq. (1) (see Section IV), however, a pronounced discrepancy is noted between the calculated values and those reported in the literature.

Since a variation in heat capacity over a seven-degree temperature interval adequate to account for such an increase in solubility is very unlikely, these values reported by Britton and Welford are considered evidence that small traces of the fairly soluble oxide V_2O_4 were present in their V_2O_5 samples.

Table I
Equilibrium Concentrations of (VO_2^+) at 18° and 25°

Final (H^+)	Equilibrium (VO_2^+) this research, 25°	Equilibrium (VO_2^+) calculated for 18°	Equilibrium (VO_2^+) Britton-Welford, 18°
0.264	0.0625	0.0791	0.111
0.063	0.0128	0.0162	0.0314

Ducret's experimental work was done at 100° in $HClO_4$, HCl , and H_2SO_4 with a constant value for the $(VO_2^+)/ (H^+)$ ratio as his criterion for equilibrium. He had noted in the work of Britton and Welford that the ratio of the solubility of V_2O_5 in HCl at 100° and at 18° was fairly constant and equal to approximately 1.2 for any hydrogen ion concentration. He employs this approximate ratio to calculate an equilibrium value for the solubility of V_2O_5 in these acids at 25° from his work at 100° .

This procedure is subject to obvious criticism because (1) the constant, while perhaps approximately true for HCl , is not true for H_2SO_4 where its value is approximately 5.7, and cannot be calculated at all for $HClO_4$ because no data are given at 100° ; (2) the absolute values for the solubilities at 100° reported in the two papers do not agree for any acid (those reported by Britton and Welford are always greater than those reported by Ducret--approximately 1.5 times in HCl , approximately 2 times in H_2SO_4 , and approximately 3.5 times in $HClO_4$), and (3) it is also doubtful that Ducret had really reached equilibrium.

Table II presents data taken from solubility-vs-time curves determined in this research at 25° for 0.230 N and 0.470 N HClO₄. Since the (VO₂⁺)/(H⁺) ratio here is as constant at any given time as Ducret's value after refluxing for four hours at 100° (0.136 ± 0.014 m/l--10 percent), one might conclude that merely obtaining a constant K₁ is not a proper criterion for equilibrium.

It is also interesting to note that in another section of the paper, Ducret calculates a $K_{(1)25^{\circ}} \approx 0.8$ from data on experiments in which he neutralized an acid solution of vanadate with a strong base and analyzed for vanadium content and pH when precipitation of the pentoxide began. This is about five times as great as the $K_{(1)25^{\circ}} = 0.15$ which he obtains by extrapolating the experimental value $K_{(1)100^{\circ}} = 0.13$ from 100° to 25°.

Finally, preliminary studies made in HClO₄ indicated that equilibrium was approached at some HClO₄ concentrations so slowly that it is doubtful if even approximate values of the solubility can ever be obtained by approaching equilibrium from only one direction (usually undersaturation).

Because of the obvious confusion in the solubility data as well as the results of preliminary studies, it was decided that only if an equilibrium concentration were approached from both directions (in a saturated and a supersaturated solution) could a significant value for the free energy of solution of V₂O₅ be obtained.

The solubilities of V₂O₅ in solutions of HClO₄ and NH₄ClO₄ were determined at 25.10° C in a thermostating device consisting of a galvanized sheet-iron tank of 15-gallon capacity equipped with a

Table II
Calculation of $(VO_2^+)/ (H^+)$ as a Function of Time

Time (min)	60		120		180		240	
Initial (H^+)	0.230	0.470	0.230	0.470	0.230	0.470	0.230	0.470
Final (H^+) (m/l)	0.193	0.387	0.182	0.384	0.182	0.378	0.169	0.374
Final (VO_2^+) (m/l)	0.0366	0.0832	0.0478	0.0864	0.0478	0.0906	0.0506	0.0960
$(VO_2^+)/ (H^+)$	0.190	0.215	0.263	0.225	0.263	0.239	0.299	0.257
Percent deviation from average	5.91%		7.78%		4.78%		7.55%	

stirring motor, cooling coil, and a thyatron-controlled knife-edge heater and Philadelphia Micro-Set thermo regulator.

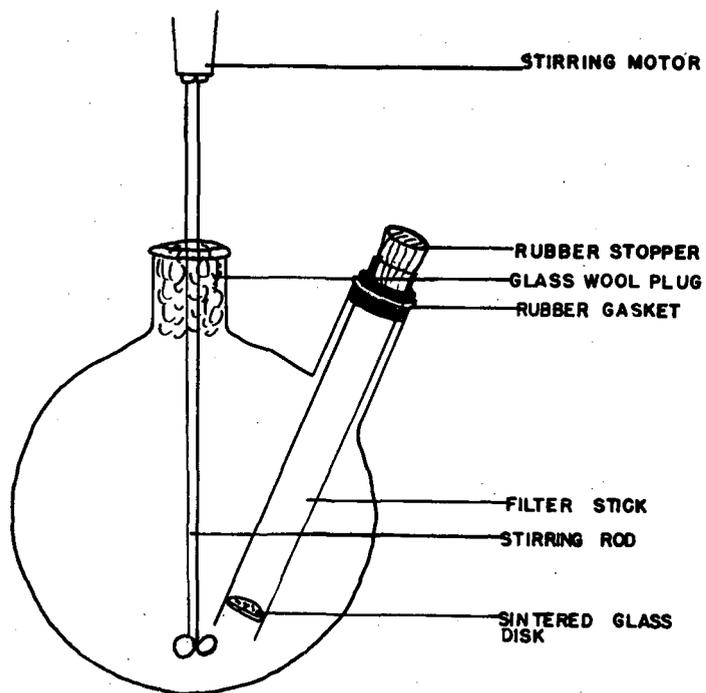
The runs were carried out in apparatus which consists essentially of a series of double-necked 250-ml flasks, each containing a filtering stick (F grade), a glass wool plug to prevent a change in concentration of the solution by evaporation during the run, a rubber gasket and stopper, and a glass stirring rod driven by a stirring motor (see Fig. 1).

Vanadium pentoxide was obtained from the A. D. Mackay Co. and leached for several hours with hot approximately 1.0 N HClO_4 , washed repeatedly with distilled water, dried in a vacuum desiccator containing P_2O_5 , and sealed in small vials. Just prior to the addition of the V_2O_5 to the HClO_4 - NH_4ClO_4 solution, a portion was tested for the presence of lower oxides with 0.1 N KMnO_4 solution. Spectrographic analyses were also performed, the contaminants present in greatest abundance being barium and zinc (<0.1 and 0.05 ppm respectively).

Stock solutions of HClO_4 were prepared with 72 percent double vacuum-distilled HClO_4 and standardized against 1.000 N NaOH with phenolphthalein as indicator. The NH_4ClO_4 stock solutions were prepared from C.P. grade dried NH_4ClO_4 and distilled water.

The flasks, containing 200 ml of solution, were clamped into the thermostating tank in pairs, each pair at a given ionic strength but at different hydrogen ion concentration. Then a previously determined amount of V_2O_5 (in excess of the equilibrium value) from a sealed vial was added and this time recorded as T_0 .

Sampling was carried out as follows: At intervals solution from the



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Fig. 1. Apparatus used in the solubility studies.

flask was drawn up into the filter stick by applying suction. Micro-pipets (500 λ) which had previously been coated with Dri-Film (dimethyldichlorosilane) and calibrated with mercury were used to withdraw aliquots. The excess solution was forced back into the flask by applying pressure.

The aliquots were placed on weighed platinum plates (pressed into the shape of a hat), evaporated to dryness under a heat lamp, and the residue, after ignition, was weighed as V_2O_5 . The balance used in these weighings had a sensitivity of 0.02 mg; duplicate samples showed a total weighing and volumetric error of the order of ± 0.05 mg.

To determine if there had been any appreciable oxidation of the platinum hats some of them were cleaned of their vanadium residue in a solution of 30 percent H_2O_2 and concentrated NH_4OH . The plates were then washed thoroughly in distilled water, dried, and reweighed. Within the instrumental uncertainty of the balance, the original weights of the plates were reproduced.

At a time when the solubility-versus-time curve began to flatten out, an amount of standardized concentrated NH_4OH (approximately 12 M) was added to the flask of each pair with the higher (H^+) to bring it to the lower (H^+), creating a solution supersaturated in vanadium. This amount of water in the NH_4OH (never greater than approximately 1.4 ml) had a negligible effect on the ionic strength.

During the first run, it was noted that the solid material in some of the flasks was changing color (usually from the typical

yellow of the anhydrous material to some shade of orange, red, rust, or brown). No matter what color the residue became, the filtered solution always showed a characteristic clear pale-gold color. Portions of the residues in some of the flasks were washed with absolute alcohol, air dried, and ignited on weighed platinum plates. Calculation showed that the formula of all but the yellow residues was $V_2O_5 \cdot H_2O$. There was no color change in the samples while the material was being washed with absolute alcohol, but all passed through the typical yellow color of the anhydrous V_2O_5 prior to melting, or returned to it if desiccated over P_2O_5 .

The addition of the NH_4OH in small amounts over the space of an hour was found somewhat effective in retarding this color change of the residue.

It was most fortunate that some of the flasks reached equilibrium with the solid material in the anhydrous state, since the entropy of the hydrated species has not been determined. Inspection of the data in Table III indicates that within the limits of experimental error there is no difference in the solubility of the two forms. This also implies a ΔF^0 of essentially zero for the conversion of one species to the other.

Some preliminary Raman work on the solutions above the residue (considering it as a very sensitive Tyndall test) shows no indication of any colloid formation, nor do the studies of the absorption spectra (see Section III).

From an analysis of these solubility curves it becomes apparent that the time to reach an equilibrium value in the saturated solution is

proportional to some power of the acid concentration greater than one. Extrapolation to one-molar perchloric acid shows that about six months are needed to reach equilibrium when this experimental method is used.

To approach equilibrium in a different manner, a flask was set up containing NH_4ClO_4 and NH_4VO_3 so that when a calculated amount of HClO_4 was added to it, a solution would result equal in (H^+) and μ to 0.0472 m/l and 0.1220 respectively with enough VO_2^+ released to be in excess of the equilibrium value of runs 9a and 10a. This excess formed a precipitate which is probably the hydrated species. (The solid material became reddish-brown almost immediately). The solution was sampled periodically and, while it has not yet reached equilibrium, the concentration is continuing to increase.

Typical solubility curves are given in Fig. 2, curves A and A' constituting one pair and B and B' another. A and B represent the supersaturated solutions, and the sharp break at C in the curves is the point where the base was added. A' and B' in the same way indicate the saturated solution. Table III is a summary of the equilibrium values so obtained. A plot of the $(\text{VO}_2^+)/(\text{H}^+)$ ratios against ionic strength indicates a value of 0.207 ± 0.011 for zero ionic strength, giving ΔF° for equation 1 as 1870 ± 63 cal.

Portions of all the residues were washed with absolute alcohol, air dried, and sent for x-ray crystallographic analysis. The results showed that the samples either had the diffraction pattern of the anhydrous oxide or a new pattern which was assigned to the hydrated species on the basis of chemical analyses described above. The x-ray powder-diffraction pattern for $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is given in Table IV.

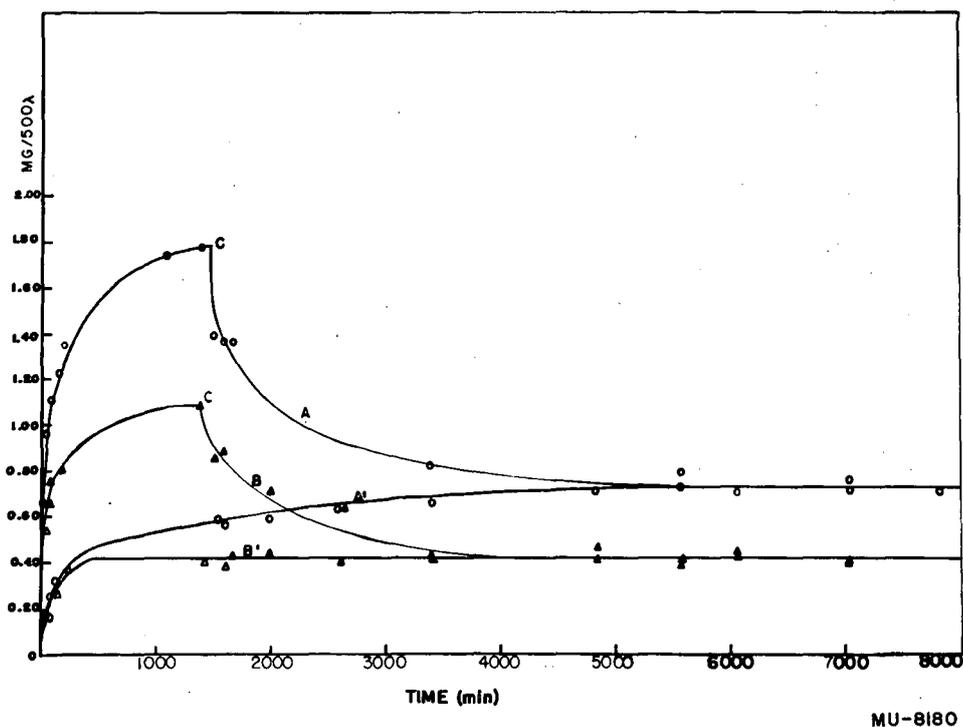


Fig. 2. Typical solubility curves of V_2O_5 in $HClO_4-NH_4ClO_4$ solutions. A and B are supersaturated after point C. A' and B' are saturated solutions.

Table III

Results of the Solubility Studies

Solid phase ^a	Initial (H ⁺)	Final (H ⁺)	μ	Equilibrium solubility in m/l VO ₂ ⁺				(VO ₂ ⁺)/(H ⁺)
				Supersat. approach	Undersat. approach	Average	Final average	
^b Hyxc	0.0970		0.122	0.0092		0.0090	0.0090	0.236 ± 0.029
^o Hyx	0.0472	0.0382	0.122		0.0088			
^{ru} Hyxc	0.0970	0.0798	0.219		0.0172	0.0172		
^o Hyx	0.194		0.219	0.0158		0.0158	0.0165	0.205 ± 0.014
^o Hyx	0.0970	0.0812	0.219		0.0158			
^y Anhx	0.194	0.160	0.343		0.0340	0.0340		
^{re} Hyxc	0.194	0.159	0.343		0.0350	0.0350	0.0334	0.207 ± 0.007
^{ru} Hyc	0.292		0.343	0.00318		0.0312		
^{ru} Hyc	0.194	0.163	0.343		0.0306			
^y Anhx	0.292	0.233	0.443		0.0594	0.0594	0.0590	0.253 ± 0.005
^{re} Hyxc	0.292	0.234	0.443		0.0584	0.0584		
^y Anhx	0.394	0.318	0.543		0.0756	0.0756		
^{re} Hyx	0.394	0.315	0.543		0.0794	0.0794	0.0790	0.251 ± 0.03
^{ru} Hyc	0.394	0.312	0.543		0.0818	0.0818		

^aSymbols as follows: Hy-hydrated form V₂O₅·H₂O; Anh-anhydrous form V₂O₅; x-x-ray evidence; c-chemical evidence; b-brown; o-orange; ru-rust; y-yellow; re-red.

Table IV

Powder-Diffraction Pattern for $V_2O_5 \cdot H_2O^a$ (CuK α radiation $\lambda = 1.5418 \text{ \AA}$)

$\text{Sin}^2 \theta$	Intensity ^b	$\text{Sin}^2 \theta$	Intensity	$\text{Sin}^2 \theta$	Intensity
0.01781	S	0.12173	S	0.26975	M
0.02367	M	0.12983	W	0.27815	W
0.02992	W ⁻	0.13397	VW	0.29265	M ⁺
0.03240	W ^{-c}	0.14534	S	0.30127	M
0.04098	M ^{-c}	0.15621	W	0.31157	M
0.04685	M ⁺	0.16388	M	0.33277	VW ^c
0.05714	VS	0.17343	W ^c	0.33854	VW ^c
0.06465	W	0.18277	W ⁺	0.35231	VW ^c
0.07106	S	0.19011	W ^c	0.35749	VW ^c
0.07774	W	0.19756	W	0.37633	W
0.08441	W	0.20385	M	0.38498	W
0.08943	W	0.22011	W	0.39519	W
0.09621	M	0.22432	W	0.40442	VW
0.09984	VW	0.23179	M	0.41542	W
0.10386	W	0.23890	M	0.42523	W
0.10967	W ⁻	0.24985	M ⁺	0.44288	W
0.11485	W	0.25318	W	0.45156	VW
				0.46704	W ^{+c}

^aPattern determined by Mrs. C. H. Dauben, Chemistry Dept., University of California.

^bSymbols: S, strong; M, medium; W, weak; V, very.

^cThese lines were found to be quite broad on the photographic film.

III. ABSORPTION SPECTRA

Although there had previously been no reason for doubt, it seemed desirable to investigate spectrophotometrically that the ionic species in final equilibrium with the solid V_2O_5 or $V_2O_5 \cdot H_2O$ -- what might be termed an "aged" pervanadyl solution--was identical with the ionic species formed immediately as V_2O_5 dissolved in acid solution. Therefore, the absorption spectra of all the solutions used in the solubility determinations and a solution simulating that resulting from the calorimetric experiments (see Section IV) were determined. So that the spectra of the vanadyl and pervanadyl ions might be compared, the absorption spectrum of a solution of V_2O_4 in approximately 0.1 N $HClO_4$ was also determined.

The instrument used was a Beckman Quartz Spectrophotometer, Model DU, adjusted to give maximum resolution. The light sources utilized were standard water-cooled hydrogen (220 to 320 $m\mu$ region) and tungsten (320 to 100 $m\mu$ region) lamps.

Portions of all the pervanadyl solutions used in the solubility studies were centrifuged and aliquots were removed with calibrated micropipets. The proper dilution was made with solutions of the same hydrogen ion concentration and ionic strength. The reference cell contained solutions identical in hydrogen ion concentration and ionic strength with those to be determined except for vanadium content.

Vanadium tetroxide was obtained for these experiments by neutralizing with concentrated ammonia a solution of vanadyl sulfate. The dark blue-grey precipitate was digested for several hours, filtered through a sintered glass funnel (F grade), and washed

repeatedly with distilled water. It was then placed in a vacuum desiccator containing P_2O_5 and subsequently in a nitrogen-filled dry box. A portion was then dissolved in 0.09440 N $HClO_4$, and this blue solution was analyzed for its vanadium content by placing duplicate 500 λ samples from calibrated micropipets in weighed platinum hats, evaporating the solution to dryness under a heat lamp, igniting them, and weighing the residue as V_2O_5 . Spectrographic analysis of this material showed barium and zinc to be the impurities present in greatest amount (<0.1 and <0.05 ppm) respectively.

Calorimetric experimental conditions in the heat-of-solution experiments were simulated by placing an arbitrary amount of V_2O_5 and approximately 0.1 N $HClO_4$ in a flask and magnetically stirring for 40 minutes. The absorption spectra for an aliquot was then determined immediately. The analysis of this solution for its vanadium content has already been described.

The absorption spectra of solutions containing the pervanadyl and vanadyl ions are given in Fig. 3, curves A and B. These confirm spectra reported previously for these ions by Tewes, Ramsey, and Garner¹⁵ and by Furman and Garner¹⁶.

A Beer's law plot of the pervanadyl solutions is given in Fig. 4 and the calculated extinction coefficient for the ion at the peak, $\lambda = 2250 \text{ \AA}$, is $2.24 \pm 0.41 \times 10^3$. There is no evidence of any deviation from normal ionic behavior except at very high optical density (see Fig. 4). The variation in this region is very likely due to instrumental difficulties. The extinction coefficient for the vanadyl ion is calculated to be 15.9 at 7500 \AA . Furman and Garner have calculated $\epsilon = 17.0$ at this wave length.

All the solutions used in the solubility determinations, regardless of the color or form of the solid phase in equilibrium with them, gave identical absorption spectra (see Fig. 3, curve A) and extinction coefficients, as did the solution simulating experimental conditions in the calorimeter. These comparisons are good evidence that the solubility studies and the heat-of-solution experiments involved the same ionic species regardless of hydrogen ion concentration, ionic strength, and "age" of the solution.

IV. CALORIMETRY

The other thermodynamic function, ΔH° , needed to calculate the entropy change for the reaction of equation (1) was determined by extrapolation to zero ionic strength of determinations at 25° C of the heat of solution of V_2O_5 in various concentrations of perchloric acid.

These experiments were carried out in a calorimeter which has been described elsewhere^{17,18} with the V_2O_5 samples suspended at the central axis of the stirring apparatus in thin-walled glass bulbs. At the proper time, the V_2O_5 bulb was broken in the calorimeter solution. In some experiments the nature of the stirring, rate of solution, and amount of V_2O_5 placed in the bulb were such that not all of the oxide dissolved, even though the temperature-time measurements indicated that the reactions were complete. Since these values agree well with those in which the sample did completely dissolve, no difficulty was encountered in the interpretation of these former runs.

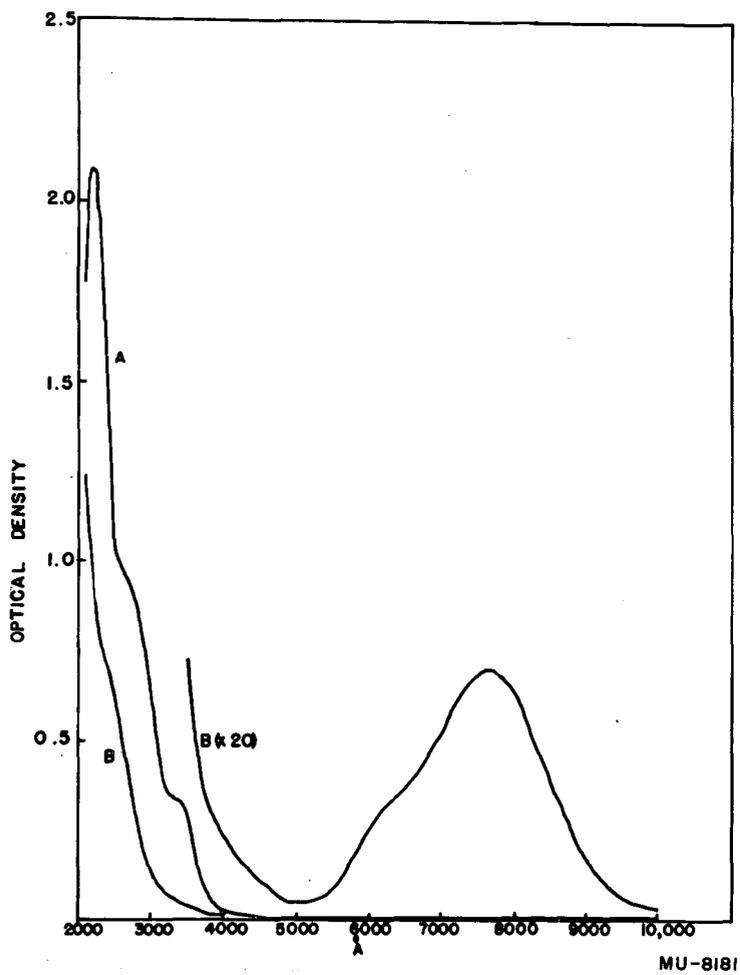


Fig. 3. Curve A: Typical absorption spectrum of the pervanadyl ion; Curve B: Absorption spectrum of a solution of V_2O_4 (0.0022 m/l in 0.09440 N $HClO_4$).

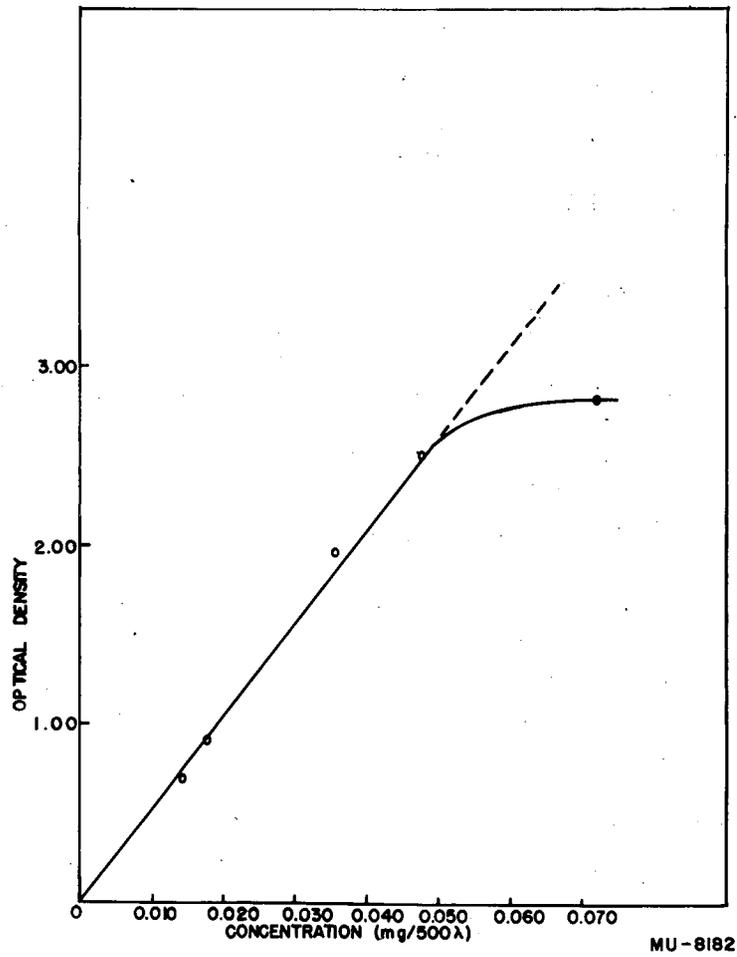


Fig. 4. Beer's Law plot for solutions of the pervanadyl ion.

The preparation of the V_2O_5 and the stock perchloric acid solutions, together with the standardization of the latter and the method of analyses of the calorimeter solutions, has been previously described in section II.

Table V summarizes the calorimetric data obtained in these experiments.

Since reaction 1 is found to be exothermic in nature, the solubility of V_2O_5 in perchloric acid must decrease with an increase in temperature. This is in qualitative agreement with the solubilities reported at 18° , 25° , and 100° C and discussed in section II.

V. THERMODYNAMIC CALCULATIONS AND GENERAL DISCUSSION

The calculation of the entropy change for equation (1) can be effected by the use of the relations

$$\Delta F_{298}^{\circ} = -RT \ln K = -RT \ln \left[\frac{(\text{VO}_2^+)}{(\text{H}^+)} \right]^2 \quad (3)$$

$$\text{and } \Delta F_{298}^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}. \quad (4)$$

Substitution of the values for ΔF_{298}° ($= 1870 \pm 63$ cal from the solubility studies of section II) and ΔH_{298}° ($= -5.78 \pm 0.09$ kcal from the calorimetric determinations of the heat of solution reported in section IV) gives $\Delta S_{298}^{\circ} = -25.7$ e. u. Using this value together with supplementary values from Latimer¹ in the relation

$$\Delta S_{298}^{\circ} = 2S_{\text{VO}_2^+}^{\circ} + S_{\text{H}_2\text{O}}^{\circ} - S_{\text{V}_2\text{O}_5}^{\circ}, \quad (5)$$

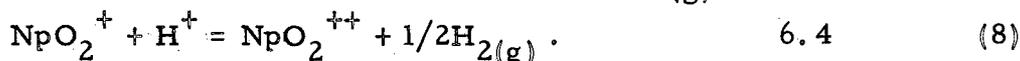
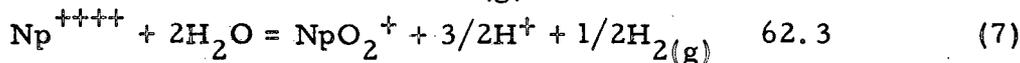
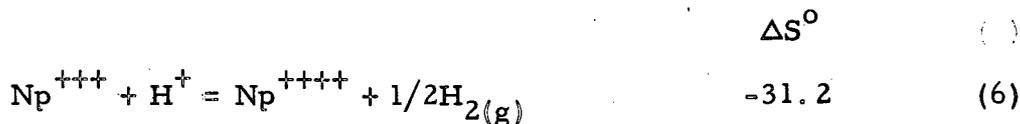
we find $S_{\text{VO}_2^+}^{\circ} = -5.5 \pm 0.4$ e. u.

Table V

Results of the Calorimetric Determinations

Run	Heat evolved (cal.)	V ₂ O ₅ dissolved (g)	Final (VO ₂ ⁺) (m/l)	Final (H ⁺) (m/l)	μ	-ΔH (kcal/mole V ₂ O ₅)	-ΔH (average) (kcal/mole V ₂ O ₅)
V-10	65.12	1.635	0.0171	0.627	0.644	7.24	7.24
V-1	106.642	2.792	0.0320	0.405	0.437	6.95	7.00 ± 0.04
V-2	61.815	1.597	0.0174	0.419	0.437	7.04	
V-11	43.11	1.118	0.0120	0.314	0.327	7.01	6.74 ± 0.28
V-12	41.916	1.181	0.0124	0.314	0.327	6.46	
V-3	70.724	2.092	0.0232	0.158	0.181	6.17	6.23 ± 0.05
V-4	74.03	2.144	0.0242	0.157	0.181	6.28	
						0 (Extrapolated)	5.78 ± 0.09

The following equations and entropy values from the work of Hindman and Cohen¹⁰ on neptunium ions in 1 M HClO₄ can be used to obtain a good estimate of the entropy of the NpO₂⁺ ion as follows.

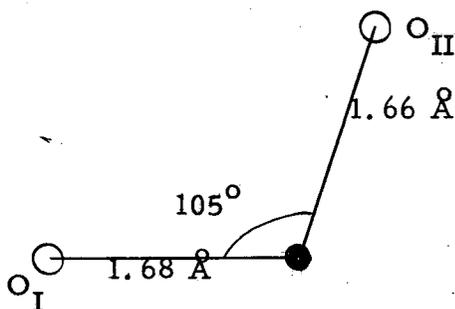


The equation of Latimer and Powell⁷ allows one to assign an entropy for the Np⁺⁺⁺ ion at zero ionic strength from which a value of -1 ± 2 e. u. is calculated for NpO₂⁺ using the ΔS° values from equations (6) and (7) above. The obvious error in such a calculation arises from the fact that the ΔS° values determined for equations (6) and (7) are in 1 M HClO₄, while the absolute entropy for Np⁺⁺⁺ was estimated for zero ionic strength. An alternate method is to assume that the entropy of NpO₂⁺⁺ in 1 M HClO₄ can be approximated by the experimentally determined entropy for uranyl ion, UO₂⁺⁺, of -17 ± 5 e. u., and the ΔS° value of equation (8) above. The value obtained for NpO₂⁺ from this calculation is -8 ± 5 e. u., which is within the quoted experimental error of the first estimate, -1 ± 2 e. u. A "best" average might be taken as -5 ± 4 e. u.

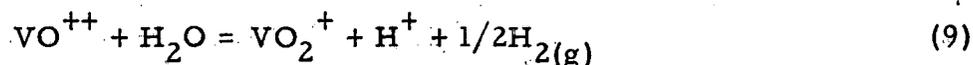
Although the latest evidence¹⁹ indicates that NpO₂⁺ probably has a linear structure and VO₂⁺ is believed to be bent (from x-ray diffraction evidence following), this should have only a minor effect in comparison of the two structures. Such a comparison of entropy and formula indicates that the form VO₂⁺ is consistent with its entropy: NpO₂⁺, -5 ± 4 e. u.; VO₂⁺, -5.5 ± 0.4 e. u.

Examination of the structure-entropy comparison of the other proposed form is also enlightening. If the structure of the pervanadyl ion were in reality $V(OH)_4^+$, its experimentally determined entropy would be $-5.5 + 2S_{H_2O}^{\circ} = 27.9$ e.u. While there is no experimentally determined entropy available for a similar ion, the method given by Cobble⁹ would indicate a value of approximately 65 ± 10 e.u. for such a structure. Thus this comparison also favors the structure VO_2^+ .

In a discussion of the crystal structure of $KVO_3 \cdot H_2O$, Christ, Clark, and Evans²⁰ report that there are two markedly short vanadium-oxygen bonds with an angle of 105° between them and bond lengths of $V-O_I = 1.68 \text{ \AA}$ and $V-O_{II} = 1.66 \text{ \AA}$. This, we propose, is evidence for the existence of a bent VO_2^+ ion in the solid state and is supplementary evidence for supporting the form VO_2^+ in aqueous solution.



For the reaction



in 1 N HCl, a $\Delta F_{298} = -23,600$ cal can be calculated from the corrected cell potential given in Carpenter's⁵ paper and a $\Delta H_{298} = 29,350$ cal for the reaction is found in Coryell and Yost's⁴ report. The ΔS_{298} for equation (9) is then 19.5 e.u. by relation 4, and substitution of this value for $S_{VO_2^+}^{\circ}$ in the relation

$$\Delta S_{298}^{\circ} = S_{VO_2^+}^{\circ} + 1/2 S_{H_2(g)}^{\circ} - S_{H_2O}^{\circ} - S_{VO^{++}}^{\circ} \quad (10)$$

(taking the other values from Latimer's compilation) results in

$$S_{VO^{++}}^{\circ} = -26.0 \text{ e. u.}$$

The entropy of VO^{++} is only approximate, since the calculation was made using values for ΔF° and ΔH° for HCl , $\mu = 1.0$ (where complexing is still in doubt), instead of $HClO_4$. However, if further calculations are made using the ΔH° and Carpenter's⁵ cell potential for $\mu = 0.5$, the $S_{VO^{++}}^{\circ}$ changes by only 0.3 e. u. There is, of course, the possibility that the extrapolations from these values to $\mu = 0$ will not be smooth and that the values will change more in low acid concentrations.

So that we may compare these cationic species with their anionic counterparts, an S° for a hypothetical MO^{--} ion can be calculated using the formula of Connick and Powell⁸

$$S_2^{\circ} = 43.5 - 46.5 (Z - 0.28n), \quad (11)$$

where Z is the charge on the ion and n is the number of oxygen atoms in the ion. This calculation gives $S_{MO^{--}}^{\circ} = -36.5 \text{ e. u.}$

As an anionic counterpart of the VO_2^+ ion, we can choose ions such as ClO_2^- ($S^{\circ} = 24.1 \text{ e. u.}$) or NO_2^- ($S^{\circ} = 29.9 \text{ e. u.}$).

The $S_{MO_2^+} - S_{MO_2^-}$ pair have the most striking dissimilarity--a change in sign and a difference of approximately 304 e. u.--while the $S_{MO^{++}} - S_{MO^{--}}$ pair are of the same sign and only of about 10 e. u. difference.

Using the above values and the value for the ΔH_f° for V_2O_5 from the National Bureau of Standards²¹ ($-373 \pm 3 \text{ kcal}$), it is possible to calculate the heats and free energies of formation of the pervanadyl

and vanadyl ions. The relations

$$\Delta H_{298}^{\circ} = 2\Delta H_{f,VO_2}^{\circ} + \Delta H_{f,H_2O}^{\circ} - \Delta H_{f,V_2O_5}^{\circ} \quad (12)$$

and

$$\Delta F_{298}^{\circ} = 2\Delta F_{f,VO_2}^{\circ} + \Delta F_{f,H_2O}^{\circ} - \Delta F_{f,V_2O_5}^{\circ} \quad (13)$$

hold for equation (1), and substitution of the appropriate values given in this section or taken from Latimer¹ result in values of -155 kcal for the heat of formation and -143 kcal for the free energy of formation of the pervanadyl ion.

Similar relations,

$$\Delta H_{298}^{\circ} = \Delta H_{f,VO_2}^{\circ} - \Delta H_{f,H_2O}^{\circ} - \Delta H_{f,VO^{++}}^{\circ} \quad (14)$$

and

$$\Delta F_{298}^{\circ} = \Delta F_{f,VO_2}^{\circ} - \Delta F_{f,H_2O}^{\circ} - \Delta F_{f,VO^{++}}^{\circ}, \quad (15)$$

can be written for equation (9). Again, the substitution of the proper values gives the heat of formation of the vanadyl ion as -116 kcal and the free energy of formation equal to -63 kcal.

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