

as BaSO₄. A typical result of the elemental analysis is: N, 12.00, 12.20, 12.10; Ba, 88.5, 87.0, 87.5%. Calculated values for Ba₃N₄ are: N, 11.95; Ba, 88.05%.

When barium pernitride (5.1 g) was slowly heated up to 250° under nitrogen atmosphere, 260 ml (at 24°) of nitrogen gas (identified by means of a mass spectrometer) was eliminated. Theoretical amount of nitrogen expected according to eq 2 is 270 ml.

The nitrogen content in a barium nitride sample produced according to eq 2 was analyzed by the Kjeldahl method and found to be 6.45 wt % (calculated value of nitrogen in Ba₃N₂ is 6.35%). The barium in Ba₃N₂ was found to be 92.9 wt % (calculated value is 93.6%).

The nitrogen contents in Sr₃N₄ and Ca₃N₄ were determined in a manner exactly analogous to that of Ba₃N₄.

Decomposition of Alkaline Earth Pernitride by Aqueous Acid.—The alkaline earth pernitrides (Ba₃N₄, Ca₃N₄, and Sr₃N₄) were found to react vigorously with aqueous acids and to form metal salts, nitrogen gas, and ammonium salts (eq 3).

A typical experiment can be described as follows. Barium pernitride (7.7 g) was placed in a 50-ml three-neck flask under a dried nitrogen atmosphere and cooled with ice. A large excess of 5% aqueous HCl solution was added slowly dropwise to the flask with stirring. The decomposition of pernitride started immediately, and 385 ml of nitrogen gas was evolved at 27°. The calculated value according to eq 3 is 370 ml. After the decomposition, the ammonia content of the solution was determined by the Kjeldahl method and found to be 0.027 mole (calculated value using eq 3 is 0.030 mole).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PENNSYLVANIA

Thermochemistry of Aqueous Pervanadyl and Vanadyl Ions

BY GARY L. BERTRAND, GEORGE W. STAPLETON,¹
CLAUS A. WULFF, AND LOREN G. HEPLER

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In 1952 Latimer² was able to list only free energies of formation for the species of V(IV and V) in aqueous acid. These values were based on a free energy calculated from the solubility of V₂O₅ and the oxidation potential for the V(IV) = V(V) + e⁻ half-reaction. Subsequent measurements by LaSalle and Cobble³ have provided data for the heat of solution of V₂O₅ and more data for its solubility. Mah and Kelley⁴ have reported a new Δ*H*_f^o and derived Δ*G*_f^o for V₂O₅ (c).

We have remeasured the heat of solution of V₂O₅ in aqueous acid and have also measured the heat of reduction of V(V) to V(IV), with results being used in several thermodynamic calculations.

(1) National Science Foundation Research Participation for High School Teachers.

(2) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

(3) M. J. LaSalle and J. W. Cobble, *J. Phys. Chem.*, **59**, 519 (1955).

(4) A. D. Mah and K. K. Kelley, U. S. Department of the Interior, Bureau of Mines, Report of Investigations, No. 5858, Mines Bureau, Pittsburgh, Pa., 1961.

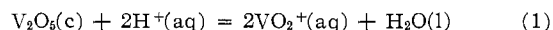
Experimental Section

The calorimeter used was patterned after one previously described,⁵ except that a Leeds and Northrup Mueller G-2 bridge and H.S. galvanometer were used with a nickel resistance thermometer. Also, the thermometer and calibration heater were contained in a glass spiral filled with mineral oil. All of the work reported here was carried out with 950 ml of solution in the calorimeter at 25.0 ± 0.2°.

Fisher Certified reagent V₂O₅ (100.0%) was leached with 1 *M* HClO₄ for periods from 1 hr to 1 month. After filtering and washing, the products were dried at 450° and stored in a vacuum desiccator with P₂O₅. Other samples were prepared by leaching with nitric acid and by thermal decomposition at 450° of ammonium metavanadate from Fisher and Mackay. Direct titration with standard KMnO₄ solution showed that these samples had less than 0.1% vanadium in lower oxidation states. Similar titration after reduction of V(V) to V(IV) with HSO₃⁻ led to calculated compositions in the range 100.1 ± 0.3% for all samples. Our heat measurements disclosed no thermochemical differences between any of these samples.

Results and Calculations

Although there is poor agreement on values of equilibrium constants relating important species of V(V) and V(IV) in acidic solutions, it does appear that below pH ≅ 2 the principal species are the pervanadyl and vanadyl ions represented by VO₂⁺(aq) and VO²⁺(aq). The reaction equation for our measurements of the heats of solution of V₂O₅(c) in HClO₄ is written as



All measurements were made with approximately 1-g samples of V₂O₅ being dissolved in 950 ml of HClO₄ to yield solutions about 0.01 *M* in VO₂⁺(aq). Solution times varied from 10 to 20 min, depending on concentration of acid and method of preparation of V₂O₅. Most of the estimated uncertainties (~0.1 kcal/mole of V₂O₅) in results given in Table I stem from rather long extrapolations associated with these long reaction times.

TABLE I
HEATS OF SOLUTION OF V₂O₅(c) IN AQUEOUS HClO₄

[H ⁺], <i>M</i>	-Δ <i>H</i> , kcal/mole of V ₂ O ₅	[H ⁺], <i>M</i>	-Δ <i>H</i> , kcal/mole of V ₂ O ₅
0.25	8.25	0.60	7.90, 7.85, 7.88
0.35	8.09	0.70	7.94
0.40	7.98, 8.09	0.80	7.79
0.50	7.90, 8.15	1.00	7.67, 7.51

Extrapolation to infinite dilution of the data in Table I leads to Δ*H*^o = -8.4 kcal/mole of V₂O₅ for reaction 1. Because of uncertainties associated with this extrapolation to the reference state, the uncertainty in Δ*H*^o is several times that derived from purely experimental uncertainties, possibly being ~±0.3 kcal/mole of V₂O₅.

LaSalle and Cobble³ have also determined heats of solution of V₂O₅ (about the same total vanadium concentrations as in our measurements) in HClO₄ from 0.16 to 0.63 *M*. They reported an extrapolated Δ*H*^o = -5.78 ± 0.09 kcal for reaction 1. Their Δ*H*^o differs from ours by 2.6 kcal. Also, their measured heats became less exothermic with increasing dilution of acid while ours became more exothermic. We are

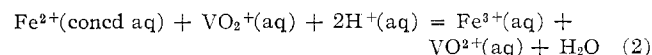
(5) W. F. O'Hara, C. H. Wu, and L. G. Hepler, *J. Chem. Educ.*, **38**, 512 (1961).

unable to account for the considerable difference in results, but, because our measurements were made with several samples prepared in different ways, we adopt our $\Delta H^\circ = -8.4$ kcal for calculations involving (1).

Combination of our ΔH° for reaction 1 with $\Delta H_f^\circ = -370.6$ kcal/mole for V_2O_5 from Mah and Kelley⁴ and ΔH_f° for H_2O from NBS Circular 500 gives $\Delta H_f^\circ = -155.3$ kcal/mole for $VO_2^+(aq)$.

Latimer estimated $\Delta G^\circ \cong 2.5$ kcal for reaction 1 from solubility data. More recently, LaSalle and Cobble³ have reviewed previous solubility measurements and made their own measurements. It now appears that the best ΔG° for (1) is 1.9 kcal from the data of LaSalle and Cobble. Combination of this ΔG° with our ΔH° leads to $\Delta S^\circ = -34.5$ cal/(deg mole of V_2O_5) for (1). Further combination with appropriate entropies⁶ leads to $\bar{S}_2^\circ = -9.9$ cal/deg mole and $\Delta G_f^\circ = -140.3$ kcal/mole for $VO_2^+(aq)$.

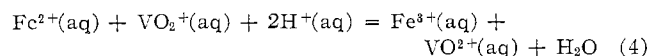
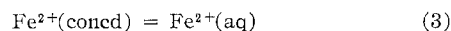
We have measured the heat of reaction of $VO_2^+(aq)$ with an excess of aqueous ferrous perchlorate solution. The calorimetric reaction equation is



All measurements were made with carefully weighed samples (~ 0.2 g) of V_2O_5 dissolved in 950 ml of $HClO_4$ of concentrations indicated in Table II. Reactions were carried out with 10–25-ml portions of standardized Fe^{2+} solutions (~ 0.7 M) so that final concentrations of $Fe^{3+}(aq)$ were in the range 0.005–0.015 M, while V(IV and V) concentrations were about 0.002 M. Separate determination of the heat of dilution of the concentrated Fe^{2+} solution as in eq 3 below permitted calculation of the desired ΔH for reaction 4 below, with results given in Table II.

TABLE II
HEATS OF REDUCTION OF VO_2^+ WITH $Fe^{2+}(aq)$

[H ⁺], M	Moles of $VO_2^+ \times 10^3$	Moles of $Fe^{2+} \times 10^3$	-Q ₂ , cal	-Q ₃ , cal	- ΔH_4 , kcal/mole
0.1	1.921	6.75	39.5	1.9	19.6
0.1	1.974	16.88	44.1	5.3	19.7
0.3	1.877	6.23	37.0	1.0	19.2
0.3	2.201	6.23	43.5	1.1	19.3
0.3	2.134	6.75	46.2	4.1	19.7
0.6	2.396	7.58	48.8	2.0	19.5
0.6	2.193	6.75	49.4	6.7	19.5



In eq 2–4 we have used the abbreviation (aq) to indicate that the preceding species are present at low concentrations within the ranges given above. Since all reacting species except H^+ were present at concentrations less than 0.02 M, reasonably accurate estimates of heats of dilution lead to $\Delta H^\circ = -19.7$ kcal/mole for (4). Combination of this ΔH° with our ΔH_f° for $VO_2^+(aq)$ and other ΔH_f° values from NBS Circular 500 leads to $\Delta H_f^\circ = -116.3$ kcal/mole for $VO^{2+}(aq)$.

(6) K. K. Kelley and E. G. King, U. S. Department of the Interior, Bureau of Mines, Bulletin, No. 592, U. S. Government Printing Office, Washington, D. C., 1961.

We have also measured the heat of reaction of V_2O_5 (c) with an excess of $Fe^{2+}(aq)$ in $HClO_4$ as represented by $V_2O_5(c) + 2Fe^{2+}(aq) + 6H^+(aq) = 2VO^{2+}(aq) + 2Fe^{3+}(aq) + 3H_2O$ (5)

Because of the slowness of the reaction, the best we can report is that $\Delta H_5^\circ = -47 \pm 1$ kcal/mole of V_2O_5 . This value is consistent with our earlier results but is not precise enough to warrant further calculations.

Combination of the previously quoted ΔG_f° for $VO_2^+(aq)$ with the standard potential² for the $VO^{2+}-VO_2^+$ half-reaction leads to $\Delta G_f^\circ = -106.7$ kcal/mole for $VO^{2+}(aq)$. Combination of this ΔG_f° with $\Delta H_f^\circ = -116.3$ kcal/mole and entropy data⁶ leads to $\bar{S}_2^\circ = -32$ cal/deg mole for $VO^{2+}(aq)$.

The $VO^{2+}-VO_2^+$ potential has been determined at two temperatures,² which permits calculation of ΔH_f° and \bar{S}_2° for $VO^{2+}(aq)$ by combination with the corresponding values for $VO_2^+(aq)$. The results are in reasonable agreement with our values but are much less certain because of the notorious uncertainties associated with deriving slopes from lines based on only two points a few degrees apart. Another approximate approach to these values is by means of the temperature dependence of the equilibrium reduction of VO_2^+ to VO^{2+} by Fe^{2+} (ref 7). Although the relevant equilibrium quotients are for solutions of high ionic strength, we have estimated the corrections that permit calculation of heats and entropies in reasonable agreement with our results.

We judge the values summarized in Table III to be the best that are presently available for $VO_2^+(aq)$ and $VO^{2+}(aq)$.

TABLE III
SUMMARY OF THERMODYNAMIC DATA

	ΔG_f° , kcal/mole	ΔH_f° , kcal/mole	\bar{S}_2° , cal/deg mole
$VO_2^+(aq)$	-140.3	-155.3	-9.9
$VO^{2+}(aq)$	-106.7	-116.3	-32

Acknowledgment.—We thank the National Science Foundation for support of this research.

(7) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962).

CONTRIBUTION FROM REACTION MOTORS DIVISION,
THIOLKOL CHEMICAL CORPORATION, DENVER, NEW JERSEY

The Chemistry of Alane. XII.¹ The Lithium Tetrahydroalane-Triethylamine Complex

BY ROBERT EHRlich² AND GEORGE RICE

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In a recent publication by Peters,³ the reaction of lithium tetrahydroalane, $LiAlH_4$, with trimethyl-

(1) Paper XI: R. Ehrlich, A. R. Young, II, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Am. Chem. Soc.*, **88**, 858 (1966).

(2) Propellants Laboratory, Feltman Research Laboratories, Picatinny Arsenal, Dover, N. J. Requests for reprints should be sent to A. Marcellis, Reaction Motors Division, Thiokol Chemical Corp., Denville, N. J.

(3) F. M. Peters, *Can. J. Chem.*, **42**, 1755 (1964).