as $BaSO_4$. 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 Ba_3N_4 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 Ba_3N_2 is 6.35%). The barium in Ba_3N_2 was found to be 92.9 wt % (calculated value is 93.6%).

The nitrogen contents in Sr_3N_4 and Ca_3N_4 were determined in a manner exactly analogous to that of Ba_3N_4.

Decomposition of Alkaline Earth Pernitride by Aqueous Acid.—The alkaline earth pernitrides (Ba_3N_4, Ca_3N_4, and Sr_3N_4) 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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Thermochemistry of Aqueous Pervanadyl and Vanadyl Ions

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In 1952 Latimer[2] 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 V_2O_5 and the oxidation potential for the $V(IV) = V(V) + e^-$ half-reaction. Subsequent measurements by LaSalle and Cobble[3] have provided data for the heat of solution of V_2O_5 and more data for its solubility. Mah and Kelley[4] have reported a new $\Delta H_f°$ and derived $\Delta G_f°$ for V_2O_5 (c).

We have remeasured the heat of solution of V_2O_5 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.

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 V_2O_5 (100.0%) was leached with 1 *M* $HClO_4$ 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 P_2O_5. 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 $KMnO_4$ 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 HSO_3^- 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 $\cong 2$ the principal species are the pervanadyl and vanadyl ions represented by $VO_2^+(aq)$ and $VO^{2+}(aq)$. The reaction equation for our measurements of the heats of solution of $V_2O_5(c)$ in $HClO_4$ is written as

$$V_2O_5(c) + 2H^+(aq) = 2VO_2^+(aq) + H_2O(l) \qquad (1)$$

All measurements were made with approximately 1-g samples of V_2O_5 being dissolved in 950 ml of $HClO_4$ to yield solutions about 0.01 *M* in $VO_2^+(aq)$. Solution times varied from 10 to 20 min, depending on concentration of acid and method of preparation of V_2O_5. Most of the estimated uncertainties (~0.1 kcal/mole of V_2O_5) in results given in Table I stem from rather long extrapolations associated with these long reaction times.

TABLE I
HEATS OF SOLUTION OF $V_2O_5(c)$ IN AQUEOUS $HClO_4$

$[H^+]$, *M*	$-\Delta H$, kcal/mole of V_2O_5	$[H^+]$, *M*	$-\Delta H$, kcal/mole of V_2O_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 $\Delta H° = -8.4$ kcal/mole of V_2O_5 for reaction 1. Because of uncertainties associated with this extrapolation to the reference state, the uncertainty in $\Delta H°$ is several times that derived from purely experimental uncertainties, possibly being ~±0.3 kcal/mole of V_2O_5.

LaSalle and Cobble[3] have also determined heats of solution of V_2O_5 (about the same total vanadium concentrations as in our measurements) in $HClO_4$ from 0.16 to 0.63 *M*. They reported an extrapolated $\Delta H° = -5.78 \pm 0.09$ kcal for reaction 1. Their $\Delta H°$ 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

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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 $\Delta H° = -8.4$ kcal for calculations involving (1).

Combination of our $\Delta H°$ for reaction 1 with $\Delta H_f° = -370.6$ kcal/mole for V_2O_5 from Mah and Kelley[4] and $\Delta H_f°$ for H_2O from NBS Circular 500 gives $\Delta H_f° = -155.3$ kcal/mole for VO_2^+(aq).

Latimer estimated $\Delta G° \cong 2.5$ kcal for reaction 1 from solubility data. More recently, LaSalle and Cobble[3] have reviewed previous solubility measurements and made their own measurements. It now appears that the best $\Delta G°$ for (1) is 1.9 kcal from the data of LaSalle and Cobble. Combination of this $\Delta G°$ with our $\Delta H°$ leads to $\Delta S° = -34.5$ cal/(deg mole of V_2O_5) for (1). Further combination with appropriate entropies[6] leads to $\bar{S}_2° = -9.9$ cal/deg mole and $\Delta G_f° = -140.3$ 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

$$Fe^{2+}(\text{concd aq}) + VO_2^+(aq) + 2H^+(aq) = Fe^{3+}(aq) + VO^{2+}(aq) + H_2O \quad (2)$$

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	$-\Delta H_4$, 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

$$Fe^{2+}(\text{concd}) = Fe^{2+}(aq) \quad (3)$$

$$Fe^{2+}(aq) + VO_2^+(aq) + 2H^+(aq) = Fe^{3+}(aq) + VO^{2+}(aq) + H_2O \quad (4)$$

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 $\Delta H° = -19.7$ kcal/mole for (4). Combination of this $\Delta H°$ with our $\Delta H_f°$ for VO_2^+(aq) and other $\Delta H_f°$ values from NBS Circular 500 leads to $\Delta H_f° = -116.3$ kcal/mole for VO^{2+}(aq).

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

$$V_2O_5(c) + 2Fe^{2+}(aq) + 6H^+(aq) = 2VO^{2+}(aq) + 2Fe^{3+}(aq) + 3H_2O \quad (5)$$

Because of the slowness of the reaction, the best we can report is that $\Delta H_5° = -47 \pm 1$ 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 $\Delta G_f°$ for VO_2^+(aq) with the standard potential[2] for the VO^{2+}–VO_2^+ half-reaction leads to $\Delta G_f° = -106.7$ kcal/mole for VO^{2+}(aq). Combination of this $\Delta G_f°$ with $\Delta H_f° = -116.3$ kcal/mole and entropy data[6] leads to $\bar{S}_2° = -32$ cal/deg mole for VO^{2+}(aq).

The VO^{2+}–VO_2^+ potential has been determined at two temperatures,[2] which permits calculation of $\Delta H_f°$ 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

	$\Delta G_f°$, kcal/mole	$\Delta H_f°$, 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

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CONTRIBUTION FROM REACTION MOTORS DIVISION,
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The Chemistry of Alane. XII.[1] The Lithium Tetrahydroalanate–Triethylamine Complex

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

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