Thermochemistry of Vanadium(5+) in Aqueous Solutions

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^{51}V NMR studies on the chemical equilibria of vanadium(5+) species were made for aqueous solutions of low ionic strength and pH values ranging from 2.0 to 12.0. The average charge per V atom of these ionic species is from +1 to −2, and the measurements were made at temperatures of 0, 25, and 50 °C. Analysis of these results gave accurate thermochemical values for the following major constituent ions of these solutions: VO_2^+, $H_2VO_4^-$, HVO_4^{2-}, $H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$, $V_2O_7^{4-}$, $V_4O_{12}^{4-}$, and $HV_{10}O_{28}^{5-}$.

Introduction

The present study of the equilibrium properties of aqueous vanadium(5+) solutions fills a void left by the many previous studies. Older electrochemical studies and UV spectrophotometric studies (Sillen and Martell, 1964; Rieger, 1973; Cruywagen and Heyns, 1991) attempted to identify species on the basis of limited structural data and formula subscripts experimentally obtained from exponents in the equilibrium expressions. Although many of the species of aqueous vanadium(5+) solutions were correctly identified, a number of the "identified" species such as $V_3O_9^{3-}$, $H_3V_2O_7^-$, and others have proven to be incorrect. The resulting thermochemical tabulations of data (Wagman et al., 1982) on vanadium contain some species that do not exist and do not contain other species such as $V_4O_{12}^{4-}$ and $H_2V_2O_7^{2-}$ that dominate the chemistry of aqueous vanadium(5+) over a wide pH range.

Modern NMR studies (Heath and Howarth, 1981; Rehder, 1991; Gesser and Tracey, 1985; Gesser and Tracey, 1986) give higher quality structural data that have revealed the correct structures and formulas of the major species present. The NMR studies have, however, been done at high ionic strengths, and no reconciliation of NMR results with older data has been attempted. Thermochemical data on the vanadium species in their standard states at infinite dilution cannot therefore be extracted from these data.

The present study focused on measurements from which reliable thermochemical data could be calculated. Analysis of NMR spectra obtained at low ionic strengths (less than 0.02 mol·kg^{-1}), in a wide pH range, and at 0, 25, and 50 °C yielded values of the equilibrium constants $\Delta_rG°$, $\Delta_rH°$, and $\Delta_rS°$ of the important aqueous reactions. The data obtained in this work have been critically analyzed to differentiate between those equilibria that are well defined and those that are approximate or speculative.

Experimental Section

The $NaVO_3$ (A. D. MacKay, Inc.) was analyzed for water by heating to 300 °C and found to contain 1.5%. Hydrochloric acid and sodium hydroxide solutions used to adjust the pH were analyzed by standard acidimetric titration methods. Vanadate solutions were made up by mass, and all solution concentrations reported in this work are in molalities.

Vanadium magnetic resonance spectra were obtained using a Varian XL-200 spectrometer. Typically 1000−10000 transients were obtained with acquisition times of 0.2 s. Longer acquisition times were periodically used to check that the spectra's intensities obtained were quantitative. Temperatures were controlled to ±0.3 °C and calibrated from the chemical shifts of the proton spectra of ethylene glycol. Chemical shifts are reported relative to $VOCl_3$ by setting the $V_4O_{12}^{4-}$ reference peak to −577.6 ppm (Heath and Howarth, 1981). This peak was selected because of its high intensity and its pH independence over the entire pH range in which it is present. The uncertainties in the chemical shifts relative to this peak are ±0.2 ppm.

The determination of pH was made after equilibration with a Fisher combination glass body electrode and a Corning Model 12 pH meter. The instrument was calibrated with commercial buffers at pH 4, 7, 9, and 10 at each temperature. Uncertainties in the pH are estimated to be ±0.03 unit between pH 2 and pH 10 and increasing to ±0.1 unit above pH = 11.

Solutions at 0 °C come to equilibrium slowly and all solutions at this temperature were held at 0 °C in an ice bath for 3 days prior to the initial measurements. Identical results were obtained after an additional 3 days of equilibration, confirming that equilibrium had been reached.

Results and Calculations

Twenty-five 0.0067 *m* vanadate solutions were made up at pH values between 2 and 12 with measured quantities of HCl and NaOH and were allowed to equilibrate for several days, after which their ^{51}V NMR spectra were recorded. The peaks present in vanadium spectra have been the subject of several recent papers (Heath and Howarth, 1981; Rehder, 1991; Gesser and Tracey, 1985; Gesser and Tracey, 1986). The four major peaks that are kinetically separated on the NMR time scale from 0 to 50 °C correspond to V species of formulas $H_xVO_y^q$, $H_xV_2O_7^q$, $V_4O_{12}^{4-}$, and $H_xV_{10}O_{28}^q$. Two additional minor peaks appear at higher concentrations of 0.1 *m* and at lower temperatures. Identification of these peaks is still uncertain, and these species have not been included in the present analysis except for accounting for their presence in the analysis of the major peaks. In addition to the chemical shifts of the V species and their fractions, the average charge per V atom in the vanadium species can be calculated from the charge balance equation

$$q_V = (m_{Cl} + m_{OH} - m_{Na} - m_H)/m_V$$

Examples of the data obtained are given in Figures 1−3 for 25 °C. Data were also obtained at 0 and 50 °C for this

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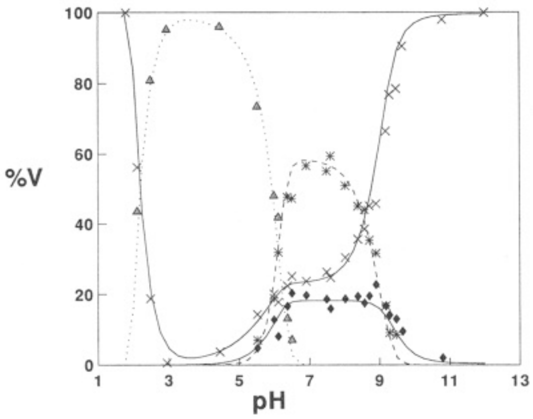


Figure 1. Mole percent of monovanadate species (×), divandate species (♦), tetravanadate (*), and decavanadate species (△) as a function of pH at a total vanadium molality of 0.0067 and at 25 °C. Lines are calculated from values given in Figure 4.

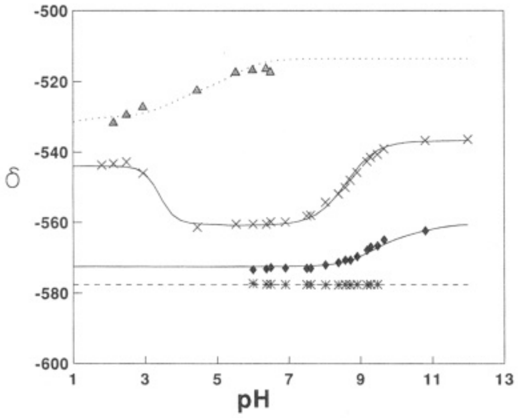


Figure 2. Chemical shifts of monovanadate species (×), divandate species (♦), tetravanadate (*), and decavanadate species (△) as a function of pH at 25 °C. Lines are calculated by values given in Figure 4.

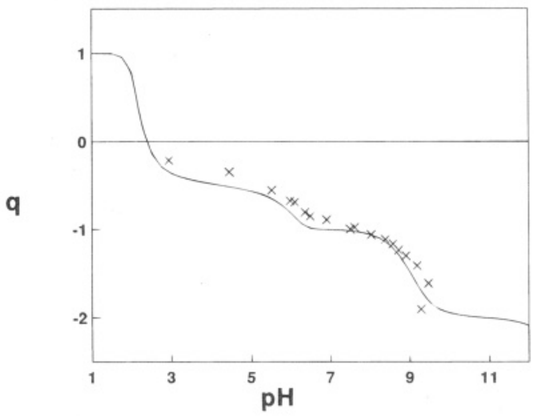
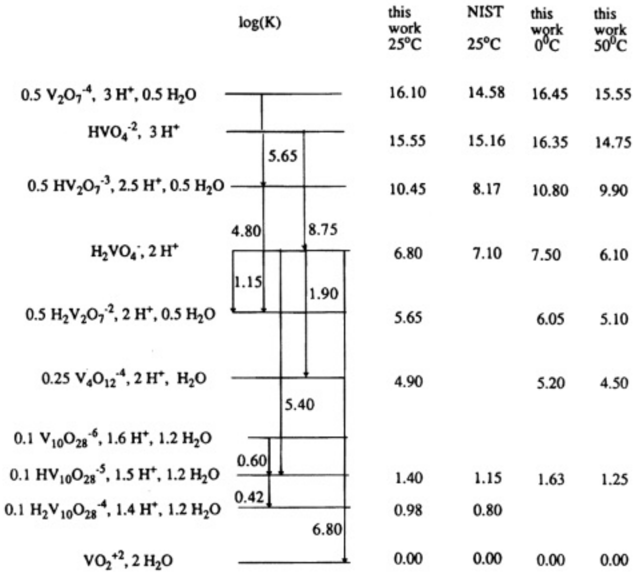


Figure 3. Average charge per vanadium atom as a function of pH at 25 °C. The line is calculated by values given in Figure 4.



log(K)	this work 25°C	NIST 25°C	this work 0°C	this work 50°C
0.5 $V_2O_7^{-4}$, 3 H^+, 0.5 H_2O	16.10	14.58	16.45	15.55
HVO_4^{-2}, 3 H^+	15.55	15.16	16.35	14.75
0.5 $HV_2O_7^{-3}$, 2.5 H^+, 0.5 H_2O	10.45	8.17	10.80	9.90
$H_2VO_4^-$, 2 H^+	6.80	7.10	7.50	6.10
0.5 $H_2V_2O_7^{-2}$, 2 H^+, 0.5 H_2O	5.65		6.05	5.10
0.25 $V_4O_{12}^{-4}$, 2 H^+, H_2O	4.90		5.20	4.50
0.1 $V_{10}O_{28}^{-6}$, 1.6 H^+, 1.2 H_2O				
0.1 $HV_{10}O_{28}^{-5}$, 1.5 H^+, 1.2 H_2O	1.40	1.15	1.63	1.25
0.1 $H_2V_{10}O_{28}^{-4}$, 1.4 H^+, 1.2 H_2O	0.98	0.80		
VO_2^{+2}, 2 H_2O	0.00	0.00	0.00	0.00

Figure 4. Measured values of the equilibrium constants between species at 25 °C and the potential diagram for vanadium(5+) species. log(K_1) values are at 0, 25, and 50 °C.

solution. Two additional vanadium concentrations of 0.067 and 0.02 *m* were run throughout the pH range at 25 °C.

Analysis of the data was done by considering the ten vanadium species indicated in the left column of Figure 4 and the three condensation reactions and six protonation reactions as indicated by the arrows in the potential diagram of Figure 4. The values on the right side of Figure 4 are log(*K*) for reaction 1.

$$\frac{1}{y}\,H_xV_yO_z^{\,q}(aq) + 0.5\left(3 + \left(\frac{q-x}{y}\right)\right)H_2O(l) + \left(1 - \frac{q}{y}\right)H^+(aq) \rightarrow VO_2^{\,+}(aq) + 2H_2O(l) \quad (1)$$

Figure 4 is a convenient way of reporting the present results because of the following: (i) The values of log(K_1) reported in this figure in this way have approximately the same uncertainty of ±0.1 unit associated with them and (ii) There are 90 different equilibrium constants that can relate the 10 major aqueous species. The nine constants selected in this work are not unique, and a method is needed whereby values of the equilibrium constants between any two species can be quickly calculated. This can be done by reference to Figure 4 as simply *y* times the difference in log(K_1) for the two species. For example, the common divanadate equilibrium reported by previous researchers is for equilibrium reaction 2.

$$2HVO_4^{\,2-}(aq) \rightleftarrows V_2O_7^{\,4-}(aq) + H_2O(l) \qquad (2)$$

Our value of log(K_2) at 25 °C can be calculated as 2 × (15.55−16.10) = −1.10. (iii) The values obtained in this work can be readily compared to other reference data in this format as indicated by the values of log(K_1) calculated from the most recent NIST tabulation (Wagman et al., 1982).

The equilibrium constants for the reactions reported here are thermodynamic equilibrium constants in which the activities of the solutes are given relative to a hypothetical 1 *m* solution. For reaction 3, the equilibrium expression is given as eq 4.

$$H_2VO_4^{\,-}(aq) = H^+(aq) + HVO_4^{\,2-}(aq) \qquad (3)$$

$$K_3 = \left(\frac{m_H m_{HVO_4}}{m_{H_2VO_4}}\right)\left(\frac{\gamma_1\gamma_2}{\gamma_1}\right) \qquad (4)$$

The extended Debye−Huckel equation (Robinson and Stokes), eq 5, was used to estimate the activity coefficients, where values of *A* are taken as 0.4918, 0.5115, and 0.5373 at 0, 25, and 50 °C, respectively.

$$\log \gamma_z = -Az^2\sqrt{I}/(1 + \sqrt{I}) \qquad (5)$$

Standard methods have been used to solve this multiple equilibria problem with the calculation of ionic strength, *I*, done reiteratively after an initial calculation of the speciation of ions in the solution. Most of the experiments done in this work were carried out at an ionic strength of about 0.015 *m* where eq 5 can be expected to provide an accurate estimate of the activity coefficient even for the highly charged species.

Each of the graphs in Figures 1–3 defines certain equilibria well, but not others. The chemical shift against pH is most useful in determining the protonation equilibrium constants, the fraction of V species present most clearly defines the condensation equilibrium constants, and the charge per V is most useful in defining the protonation of the major species present.

Speciation of the Monovanadium Ions. The three monovanadium ionic species needed to correlate the data of this work are VO_2^+, $H_2VO_4^-$, and HVO_4^{2-}. These species have well-defined V chemical shifts of −543, −561, and −537 ppm, respectively. If the H_3VO_4 species reported by some researchers exists, it is only a minor species over a very narrow pH range. This latter conclusion is the same as that of another recent study (Pettersson et al., 1985). VO^{3+} species and VO_4^{3-} have also been reported. The former species may exist but at a $pH < 1$ that is outside the pH range of this study; while the latter ion almost certainly exists, we are only able to establish a lower limit of its existence as $pK_a(HVO_4^{2-}) > 13.3$. Measurements that lead to a value of the second ionization constant of vanadic acid, eq 3, have been made many times previously (Sillen and Martell, 1964; Rieger, 1973; Gesser and Tracy, 1985; Heath and Howarth; Pettersson et al., 1985) and have lead to values from $pK_a = 7.7$ to $pK_a = 9.5$. The most frequently cited values (Wagman et al., 1982; Rehder, 1991; Clark, 1973) are around $pK_a = 8.1$. The value obtained in the present study, $pK_a(H_2VO_4^-) = (8.75 \pm 0.05)$, is considerably higher than these values, but is between the values of $pK_a = 8.95$ obtained from results that were apparently extrapolated to zero ionic strength and values of $pK_a = 8.0–8.8$ that were obtained from NMR studies at low ionic strengths (Sillen and Martell, 1964; Gresser and Tracey, 1985; Gresser and Tracey, 1986). Because the chemical shift change for this reaction is large, the ionic strength of this work is low, and this ionization is well separated from the third ionization. The value obtained here for the pK_a is relatively accurate, ±0.05 unit.

The enthalpy and entropy of ionization of $H_2VO_4^-$ are calculated from the temperature coefficient of pK_a as $\Delta_r H_3^\circ = (7 \pm 2)$ kJ mol^{-1} and $\Delta_r S_3^\circ = (-145 \pm 5)$ J mol^{-1} K^{-1}, respectively. No previous values have been reported.

The thermodynamic equilibrium constant for the formation of the VO_2^+ ion from vanadate, eq 6, at 25 °C is

$$H_2VO_4^-(aq) + 2H^+(aq) \rightleftarrows VO_2^+(aq) + 2H_2O(l) \quad (6)$$

obtained as $\log(K_6) = (6.80 \pm 0.10)$ and can be compared with values of 7.00 (0.5 M $NaClO_4$), 6.97 (0.6 M NaCl), and 7.30 (dilute solutions at 19 °C) (Sillen and Martell, Pettersson et al., 1985). These values are all in reasonable agreement considering the differences in the conditions and uncertainties in the measurements. The values of $\Delta_r H_6^\circ = (-47 \pm 5)$ kJ mol^{-1} and $\Delta_r S_6^\circ = (-29 \pm 15)$ J mol^{-1} K^{-1} obtained from the temperature coefficient of the equilibrium constant are in excellent agreement with values of −48 kJ mol^{-1} and −24 J mol^{-1} K^{-1} from the most recent NIST tabulation (Wagman et al., 1982).

Protonation of the Divanadate Ion. The divanadate species $H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$, and $V_2O_7^{4-}$ have been used in fitting the data obtained in this work. The first of these species has a chemical shift of −572.5 ppm. Its peak overlaps that of the tetravanadate ion (−577.6 ppm), but clearly shows a separate maximum, especially at 0 °C, and is the major form of the divanadate ion from pH 8.0 down to pH less than 6 where the divanadate ion concentration becomes too small to measure. There is no indication of any change in chemical shift or any unexplained concentration change that would indicate formation of the $H_3V_2O_7^-$ species (Sillen and Martell, 1964; Wagman et al., 1982) included as a major species in earlier work. Using previously reported equilibrium constants attributed to the formation of this species results in much larger concentrations of the divanadate ion in the pH range of 5–8 than is experimentally observed, and we therefore conclude that the older work must be in error.

An appreciable change in the chemical shift of divanadate starts to occur at $pH \approx 8$ and continues to $pH \approx 11$ where it again levels off at about −560.5 ppm. At least one proton is lost in this pH range to form the $HV_2O_7^{3-}$ species (−564.0 ppm), and our data are best explained by the assumption that the second proton is also lost in this pH range to form $V_2O_7^{4-}$ (−560.5 ppm). The pK_a of $H_2V_2O_7^{2-}$ is found to be (9.6 ± 0.2) at 25 °C with a $\Delta_r H^\circ$ of ionization of (−3.5 ± 5) kJ mol^{-1} and $\Delta_r S^\circ = (-195 \pm 15)$ J mol^{-1} K^{-1}. The pK_a of $HV_2O_7^{3-}$ was found to be (11.3 ± 0.4) at 25 °C and assumed not to change with temperature in analyzing the data at 0 °C. The only previous measurements are values of 7.2 and 8.9 for these two ionization processes obtained at an ionic strength of 1.0 and at 0 °C (Heath and Howarth, 1981).

Protonation of the Decavanadate Ion. The decavanadate species $H_xV_{10}O_{28}^{6-}$ is the major vanadate species in aqueous solutions studied here between pH 2.5 and pH 6. At the midpoint of this range the experimentally obtained charge per vanadium atom is close to 0.50, indicating a formula of $HV_{10}O_{28}^{5-}$ for the major species in agreement with earlier work. The chemical shifts of the three broad peaks due to the decavanadate ion are relatively constant (−513.5, −508, −420 ppm) in the range of pH 6–12, and these chemical shifts are associated with the $x = 0$ species. At lower pH values, the chemical shift of decavanadate species drops. Two additional species with $x = 1$ (−522.5, −515, and −430 ppm) and $x = 2$ (−530.0, −514, and −437 ppm) with pK_a values of (4.2 ± 0.5) and (6.0 ± 0.5) are the minimum number of species needed to approximately fit the chemical shift data. Previous researchers (Sillen and Martell, 1964) have also included these species in their analysis. The uncertainties in the equilibrium constant quantities are too large to allow meaningful calculations of enthalpies and entropies of reaction from their temperature coefficients.

Condensation to the Divanadate Ion. Part of the reason for the present study was an interest in knowing the equilibrium constant for the formation of the divanadate ion to compare to values for the formation of similar species such as the dichromate anion, $Cr_2O_7^{2-}$, and the small heteronuclear species $HPVO_7^{2-}$, and $HCrVO_7^{2-}$. In spite of the numerous studies previously made on this reaction, the uncertainties in the protonation assumed for the divanadate ion and the combined uncertainties in the pK_a's of both vanadate and divanadate species made the literature on these ions intractable. An indication of the problem associated with the divanadate species is given in Figure 4 in which all the other vanadium species have values of $\log(K_1)$ that agree to within 1 unit with the NIST tabulated values. The divanadate species differ by much more than 1 unit, and no value is listed for the species that dominates in neutral solutions, the species that would be of most interest to chemists involved in biochemical or geological chemistry. The most commonly reported value in previous work is for reaction 2 for which the present value is log(K_2) = (−1.10 ± 0.50) at 25 °C and 0 ionic strength. It may be compared to the previous values of +0.83 in 1 M NaCl, +0.82 in 2 M NaCl, +1.68 in 3.0 M $NaClO_4$, +1.54 in 2 M $NaClO_4$, +2.79 and +2.12 in 0.2 M $NaClO_4$, and +1.39 in 2 M $LiClO_4$ (Sillen and Martell, 1964; Heath and Howarth, 1981; Cruywagen and Heyns, 1991). The large discrepancy, in both sign and magnitude, between our value and those previously measured is apparently due primarily to the high ionic strength of most previous work. This is most clearly shown by comparing results in Figure 5 of Heath and Howarth's work, where the divanadate is the major vanadium species from pH 9 to pH 11.5, to our Figure 1 in which divanadate is never the major vanadium species.

The $\Delta_r H°$ determined in this work of −47 kJ also differs considerably from the value of −28 kJ determined calorimetrically in 1 M NaCl (Cruywagen and Heyns, 1991).

Another commonly reported value is for reaction 7. Our value of log(K_7) = (−3.80 ± 0.30) can be compared to values of −3.18 at 0.5 M NaCl and −3.25 at 3 M NaCl (Sillen and Martell, 1964). The reaction of most interest to us was the

$$2HVO_4^{2-}(aq) \rightleftharpoons HV_2O_7^{3-}(aq) + OH^-(aq) \qquad (7)$$

reaction that takes place in dilute solution from pH 6 to p H 8.5, eq 8. The value obtained at 25 °C and I = 0, log(K_8) = (2.30 ± 0.25), can be compared to a value of 3.29 obtained in 2 M $LiClO_4$ at 0 °C (Heath and Howarth, 1981). In

$$2H_2VO_4^-(aq) \rightleftharpoons H_2V_2O_7^{2-}(aq) + H_2O(l) \qquad (8)$$

addition, measurements have been made for the dimerization of monomeric vanadate species at pH close to 7 that can be associated with reaction 8. The values obtained for log(K_8) are 2.54 and 2.75 in 1 M KCl (Gresser and Tracy, 1985, 1986).

The enthalpy and entropy of reaction 8 obtained from this work are $\Delta_r H_8°$ = (−30 ± 8) kJ mol^{-1} and $\Delta_r S_8°$ = (−58 ± 25) J mol^{-1} K^{-1}, respectively. No previous values have been reported for these quantities.

Condensation to the Tetravanadate Ion. The thermochemical values for reaction 9 calculated from this work are log(K_9) = (7.6 ± 0.2), $\Delta_r H_9°$ = (−95 ± 10) kJ mol^{-1}, and $\Delta_r S_9°$ = (−170 ± 30) J mol^{-1} K^{-1}. The value of log(K_9)

$$4H_2VO_4^-(aq) \rightleftharpoons V_4O_{12}^{4-}(aq) + 4H_2O(l) \qquad (9)$$

can be compared to previous values of 8.7 measured in 1 M KCl (Gresser and Tracey, 1985) and 10.9 in 3 M $NaClO_4$ (Rieger, 1973). Most of the tetravanadate equilibria are reported as values for reaction 10 for which our value of

$$4HVO_4^{2-} + 4H^+ \rightleftharpoons V_4O_{12}^{4-} + 4H_2O(l) \qquad (10)$$

log(K) of 42.60 can be compared to values of 40.01 in 2 M $LiClO_4$, 40.6 in 2 M $NaClO_4$, and 41.16 in 0.2 M $NaClO_4$ (Sillen and Martell, 1964; Heath and Howarth, 1981).

Condensation to the Decavanadate Ion. The values of the formation of the decavanadate ion from both $H_2VO_4^-$ and VO_2^+, eqs 11 and 12, respectively, can be calculated

$$10H_2VO_4^-(aq) + 5H^+(aq) \rightleftharpoons HV_{10}O_{28}^{5-} + 12H_2O(l) \qquad (11)$$

$$10VO_2^+(aq) + 8H_2O(l) \rightleftharpoons H_2V_{10}O_{28}^{4-}(aq) + 14H^+(aq) \qquad (12)$$

from Figure 4 as log(K_{11}) = (54.0 ± 0.8) and log(K_{12}) = (−9.8 ± 0.8). The latter value can be compared to previous values of −5.5 and −5.8 in 3 M $NaClO_4$, −6.75 and −6.24 in 1 M $NaClO_4$, and −7.5 in 0.2 M $NaClO_4$ (Sillen and Martell, 1964).

Table 1. Thermodynamics of Formation of Aqueous Vanadium(5+)

	$\Delta_f G°$ [a]/ (kJ mol^{-1})	$\Delta_f H°$ [b]/ (kJ mol^{-1})	$\Delta_f S°$ [c]/ (J mol^{-1} K^{-1})
$VO_2^+(aq)$	(−587)	(−649.8)	(−42.3)
$H_2VO_4^-(aq)$	−1022.5	−1174.2	126
$HVO_4^{2-}(aq)$	−972.5	−1167.4	−19
$H_2V_2O_7^{2-}(aq)$	−1820.9	−2092.9	124
$HV_2O_7^{3-}(aq)$	−1766.1	−2096.9	−71
$V_2O_7^{4-}(aq)$	−1701.7	−2096.3	−287
$V_4O_{12}^{4-}(aq)$	−3185	−3648	52
$H_2V_{10}O_{28}^{4-}(aq)$	−7711		
$HV_{10}O_{28}^{5-}(aq)$	−7687	−865	299

[a] Uncertainties of 0.5 kJ mol^{-1} for vanadium. [b] Uncertainties of 2.5 kJ mol^{-1} for vanadium. [c] Uncertainties of 8 J K^{-1} mol^{-1} for vanadium.

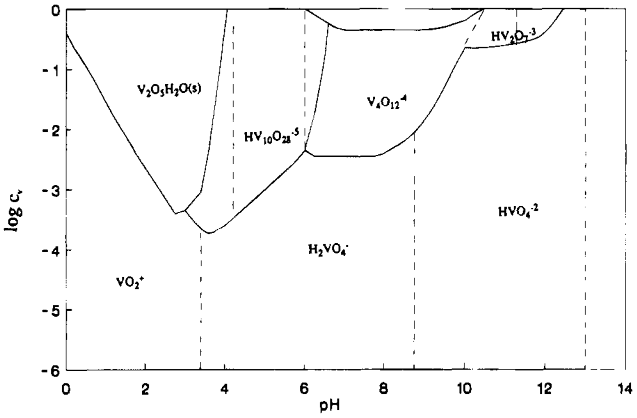


Figure 5. Phase diagram for vanadium(5+) species as a function of pH and vanadium concentration at 25 °C.

The value of $\Delta_r H_{11}°$ = (−342 ± 50) kJ mol^{-1} and $\Delta_r S_{11}°$ = (−121 ± 100) J mol^{-1} K^{-1} are obtained from the temperature dependence of these results. The former value can be compared to −385 kJ mol^{-1} obtained previously (Sillen and Martell, 1964). A summary of the data obtained in this work is given in Figure 4, where the results of this work are also compared to the latest NIST values. Note that the largest discrepancies between the NIST values and our values occur in the data for the dimer condensation reactions.

The atomic parameters that can be used to predict the free energy of the dimerization condensation reactions will be discussed further in future papers. The thermochemical values for the ions studied are calculated from the equilibrium constants and their temperature coefficients and are reported in Table 1. A phase diagram for major species of isopolyanions of vanadium has also been calculated on the basis of the measured equilibrium constants and is shown in Figure 5.

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