THERMOCHEMISTRY AND OXIDATION POTENTIALS OF VANADIUM, NIOBIUM, AND TANTALUM

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Contents

I. Introduction

In this review we are primarily concerned with the chemical thermodynamics of compounds and aqueous ions of vanadium, niobium, and tantalum. The resulting thermodynamic data have long been known to be useful in electrochemistry, analytical chemistry, and many applications of chemical principles to other disciplines.

We have been critical in our tabulations of data and have recalculated many of the published results cited here. When data from different sources are not in good agreement, we have attempted to justify our choices. We have been explicit about the sources of data and also our treatment of data from the literature so that interested readers can check the steps leading to tabulated values of thermodynamic properties and form their own opinions about reliability and accuracy. When we have not read the original papers cited, we have listed the *Chemical Abstracts* reference or the name of the journal in which the article has been translated.

In several cases we have combined experimental data from a cited source with our estimate of some thermodynamic property. *Numerical values of our estimates are given in parentheses.*

Whenever possible we have used auxiliary thermodynamic data from the National Bureau of Standards Technical Note 270-3.[1] Other auxiliary data have been taken from sources such as NBS Circular 500[2] and Latimer's "Oxidation Potentials"[3] that are explicitly cited at appropriate places in the discussion.

Uncertainties in many thermodynamic quantities of interest are difficult to assess. For example, the uncertainty in a heat of formation calculated from a particular heat of reaction depends on the cumulative uncertainties of all the heats of formation used in the calculation as well as on the uncertainty in the reported heat of reaction. Further, many errors in thermochemical or electrochemical investigations are due to difficulties in the compounds or processes being studied (*i.e.*, unidentified hydrolysis phenomena, nonhomogeneous phases, impurities, etc.) which may be more difficult to assess than are uncertainties in the measurements. Our treatment of uncertainties has been simply to list results to a "reasonable" number of significant figures. In some cases we have indicated that an uncertainty is larger than usual by placing an approximate sign (~) in front of the cited quantity.

In spite of considerable discussion in recent years, general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic. *All potentials tabulated in this review are oxidation half-reaction potentials with algebraic signs.* This choice, which has been discussed previously,[4] permits straightforward use of $\Delta G° = RT \ln K = -nFE^0$.

We have reserved the symbols E^0 and K for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental data. Similarly, we use $\Delta G°$, $\Delta H°$, and $\Delta S°$ to indicate data that refer to the usual standard states.[1,2,5] Other useful investigations have been carried out in solutions maintained at some constant ionic strength by means of some "inert" supporting electrolyte. These investigations lead to equilibrium quotients represented by Q rather than to traditional equilibrium constants represented by K, and similarly lead to potentials that are not the same as the standard potentials (E^0) mentioned above. We have used such symbols as $Q_{0.5}$ and $\Delta H_{0.5}$ to indicate that the equilibrium quotient or heat of reaction was determined in solutions having ionic strength 0.5.

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Except where explicitly stated otherwise, all thermodynamic values cited in this review refer to 298°K.

II. Vanadium

A. DESCRIPTIVE CHEMISTRY

Of the known compounds and ionic species containing vanadium in oxidation states ranging from -1 to $+5$, we shall be concerned only with the common oxidation states from $+2$ to $+5$ for which we have relevant data. The coordination number of vanadium in most of its compounds and ions is six, although coordination numbers four, five, and eight have been reported.

Possibly the two most common compounds of vanadium in the $+5$ oxidation state are the pentoxide, V_2O_5, and the so-called ammonium metavanadate, NH_4VO_3. The pentoxide is often prepared by heating NH_4VO_3 to drive off ammonia and water. Taniguchi and Ingraham[6] have presented evidence that $(NH_4)_2O(V_2O_5)_3$ is a moderately stable intermediate formed in the decomposition of NH_4VO_3 and quote thermodynamic data for formation of this intermediate from NH_4VO_3.

Orange V_2O_5 dissolves in water to the extent of a few thousandths of a mole per liter to give light yellow solutions that are acidic. As expected, V_2O_5 is more acidic than lower oxidation state oxides of vanadium, but V_2O_5 may also be regarded as exhibiting basic properties in its reaction with and thence solution in aqueous acid. The vanadium species so formed are able to oxidize Cl^- to Cl_2 in moderately concentrated hydrochloric acid solutions.

Although identification and description of the aqueous ions of V(V) is an old and much investigated problem, we are still faced with uncertainties. In this connection we emphasize the often-made but sometimes ignored statement that there is no required relation between stoichiometries of solids and the aqueous ions they give in solution. It should be emphasized once again that equilibrium and other thermodynamic data alone give no information about the extent of hydration of aqueous species.

Many investigations designed to identify V(V) species in aqueous solutions or to provide equilibrium constants for interconversion of various species have been cited by Sillen,[7] while three useful reviews[8-10] of polyions of vanadium and other elements have been published.

Although there is nothing like complete agreement on values of equilibrium constants relating important species in various solutions, we qualitatively summarize the results of many investigations as follows. Below pH $\cong$ 2 the principal V(V) species is the pervanadyl ion of formula VO_2^+(aq). In acidic solutions with pH greater than about 2, there are various decanuclear species that have been represented as $H_2V_{10}O_{28}^{4-}$(aq), $HV_{10}O_{28}^{5-}$(aq), and $V_{10}O_{28}^{6-}$(aq). In the past various hexavanadates have been thought to be the principal species in weakly acidic solutions, but the best evidence now available[7-11] points toward the decavanadates as being considerably more important.

Above pH $\cong$ 6.5 decavanadate species are increasingly depolymerized and so-called metavanadate ions become prevalent in solutions with pH $\cong$ 7. There is disagreement as to whether the aqueous metavanadate ion is best represented by $V_4O_{12}^{4-}$(aq) or by $V_3O_9^{3-}$(aq). In weakly acidic or neutral solutions with total concentration of V(V) less than about 10^{-4} *M*, the principal species appears to be the monomeric $H_2VO_4^-$(aq), which might also be represented by VO_3^-(aq). Above pH $\cong$ 8.5 pyrovanadate ion represented by $V_2O_7^{4-}$(aq) and the monomeric HVO_4^{2-}(aq) become important. There is also some evidence for other monomeric and dimeric ions having charges of -1, -2, and -3. The orthovanadate ion represented by VO_4^{3-}(aq) is the only species that appears to be important in solutions more alkaline than pH $\cong$ 13.

As already mentioned, the various equilibrium investigations on which most of the preceding two paragraphs are based give no information on the extent of hydration of the various aqueous species. The "true" formulas of the species cited might well include various numbers of H_2O units.

Recent spectroscopic investigations by Griffith and Lesniak[11a] provide more detailed information in support of the general picture described above.

Under many conditions the $+4$ oxidation state is the most stable state for compounds and ions of vanadium. The blue dioxide VO_2 is amphoteric, being about equally soluble in acidic or basic solutions. Acidic solutions of VO_2 contain the blue vanadyl ion of simplest formula VO^{2+}(aq), while strongly alkaline solutions evidently contain ions that may be represented by VO_4^{4-}(aq). More nearly neutral solutions in general contain more complicated species that are poorly characterized. Various compounds having such formulas as $K_2V_4O_9 \cdot 7H_2O$(c), often called either vanadites or hypovanadates, have been crystallized from alkaline solutions of V(IV). Addition of H_2S to solutions of VO^{2+}(aq) causes precipitation of VS_2(c), which is sufficiently acidic that it dissolves in excess sulfide.

The basic black oxide V_2O_3(c) dissolves readily in acids to give green solutions of V^{3+}(aq) or complexes of this ion. Green hydrous V_2O_3, sometimes represented as $V(OH)_3$, is precipitated on addition of hydroxide to solutions of V^{3+}(aq).

Vanadium(II) is the least stable of the oxidation states of vanadium considered in this review. The black basic oxide of ideal stoichiometric formula VO (nonstoichiometric samples with deficiency of either V or O are known) dissolves in nonoxidizing acids to yield violet solutions containing V^{2+}(aq) ions.

B. THERMOCHEMISTRY

Low-temperature heat capacity data for V(c) have been reviewed by Kelley and King,[12] who give $S^\circ_{298} = 7.02 \pm 0.10$ cal deg^{-1} mol^{-1}. A later review[13] gives $S^\circ_{298} = 6.79 \pm 0.10$ cal deg^{-1} mol^{-1}, which is the value we adopt for Table I. Vapor pressure data have led[13] to $\Delta H_f^\circ = 123$ kcal mol^{-1} for V(g), which is combined with the entropy[12,13] to give our tabulated ΔG_f°. We take ΔH_f° values for gaseous ions from NBS Circular 500[2] after adjustment for the newer ΔH_f° for V(g).

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Our tabulated $\Delta H_f°$ values for VO(c), V_2O_3(c), VO_2(c), and V_2O_5(c) are based on results of combustion measurements by Mah and Kelley.[14] We adopt $S°_{298}$ values for these oxides from Kelley and King[12] and combine with $\Delta H_f°$ values to obtain our tabulated $\Delta G_f°$ values. Other $\Delta H_f°$ values that appear to have larger uncertainties have been reported.[15–19]

The $\Delta H_f°$ data from the work of Mah and Kelley[14] are in satisfactory agreement with $\Delta H°_{298}$ for

$$V_2O_3(c) + {}^1/_2O_2(g) = 2VO(c)$$

that was derived by Spencer and Justice[20] from results of high-temperature equilibrium measurements.

The thermodynamic properties we tabulate for V_6O_{13}(c) were estimated by Mah.[21]

Yannopoulos[22] has carried out high-temperature investigations of reaction of V_2O_5 with H_2O and reports evidence and thermodynamic data for $VO(OH)_3$(g). He also questions earlier reports of more complex species, such as $V_2O_3(OH)_4$(g).

Solubility measurements by LaSalle and Cobble[23] lead to $\Delta G° = 1.87$ kcal mol^{-1} for

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

We use this value with $\Delta G_f°$ for V_2O_5(c) from Table I to calculate $\Delta G_f° = -140.4$ kcal mol^{-1} for pervanadyl ion represented by VO_2^+(aq). LaSalle and Cobble[23] also observed that solubilities of V_2O_5(c) and $V_2O_5 \cdot H_2O$(c) are approximately the same and concluded that $\Delta G° \cong 0$ for

$$V_2O_5(c) + H_2O(liq) = V_2O_5 \cdot H_2O(c)$$

We have used $\Delta G° = 0$ for this reaction with our estimated entropy for $V_2O_5 \cdot H_2O$(c) in calculating $\Delta G_f°$ and $\Delta H_f°$ for this latter compound.

LaSalle and Cobble[23] have also reported $\Delta H° = -5.78$ kcal mol^{-1} for the solution reaction represented by eq 1, but we adopt $\Delta H° = -8.4$ kcal mol^{-1} from more recent calorimetric measurements.[24] This latter $\Delta H°$ leads to $\Delta H_f° = -155.3$ kcal mol^{-1} and $\bar{S}° = -9.8$ cal deg^{-1} mol^{-1} for VO_2^+(aq).

Although free energies of various other V(V) aqueous species can be calculated from the above $\Delta G_f°$ of VO_2^+(aq) and appropriate equilibrium constants, we have not tabulated such $\Delta G_f°$ values for several reasons. First, we cannot yet be certain as to stoichiometric formulas of some important ions in solution. Further, most of the "equilibrium constants" that would have to be used in such calculations are more properly designated "equilibrium quotients" that refer to solutions of fairly high ionic strength for which we have no relevant activity data.

Calorimetric measurements by Bertrand and Hepler[25] have led to $\Delta H_f° = -251.7$ kcal mol^{-1} for NH_4VO_3(c), often named ammonium metavanadate, and to $\Delta H_f° = -274.2$ kcal mol^{-1} for $NaVO_3$(c). Earlier calorimetric measurements by Koehler[26] led her to report $\Delta H_f° = -274.9$ kcal mol^{-1} for $NaVO_3$(c). Recalculation of her results with the most recent $\Delta H_f°$ for V_2O_5(c) from Table I leads to $\Delta H_f° = -273.7$ kcal mol^{-1}. We adopt the average $\Delta H_f°$ for $NaVO_3$(c) and combine with the entropy[27] to obtain the $\Delta G_f°$ we also list in Table I.

Koehler[26] has also made calorimetric measurements on Na_3VO_4(c) and $Na_4V_2O_7$(c), often called sodium orthovanadate and sodium pyrovanadate. We recalculate her results in terms of the new $\Delta H_f°$ for V_2O_5(c) to obtain the $\Delta H_f°$ values given in Table I. These $\Delta H_f°$ values have been combined with entropies from King and Weller[27] to yield the $\Delta G_f°$ values in Table I.

Measurements carried out in the Bureau of Mines Laboratories have provided $\Delta H_f°$ values from solution calorimetry and $S°_{298}$ values from heat capacities for several more compounds of vanadium in the +5 oxidation state (vanadates). We take $\Delta H_f°$ values for CaV_2O_6(c), $Ca_2V_2O_7$(c), and $Ca_3V_2O_8$(c) from work of King, Koehler, and Adami,[28] while entropies for these compounds are from King and Weller.[29] The $\Delta H_f°$ and $S°_{298}$ values lead to the tabulated $\Delta G_f°$ values for these compounds. King, Koehler, and Adami[28] have also reported $\Delta H_f°$ values for $Mg_2V_2O_6$(c) and $Mg_2V_2O_7$(c), which are combined with the entropies of these compounds from Weller and King[30] to give the $\Delta G_f°$ values listed in Table I.

Calorimetric measurements by Barany[31] lead to $\Delta H_f° = -453.8$ kcal mol^{-1} for ferrous vanadate, FeV_2O_6(c). We know of no experimental entropy for this compound, but note that Mah[21] has cited a $\Delta G_f°$ value along with the $\Delta H_f°$ above. These values correspond to $S° = (47)$ cal deg^{-1} mol^{-1}, which we also adopt.

We take $\Delta H_f°$ values for $Pb_2V_2O_7$(c), $Pb_3V_2O_8$(c), and MnV_2O_6(c) from the calorimetric measurements of Kelley, Adami, and King.[32] We also adopt their estimated entropies for these compounds and combine with the $\Delta H_f°$ values to obtain the approximate $\Delta G_f°$ values in Table I. Yokokawa and Kleppa[32a] have also reported data for lead vanadates.

For VOF_3(c) Trevorrow[33] has reported vapor pressure data which we find yield a moderately straight line plot of log p *vs.* $1/T$ and thence approximate values for ΔH and ΔS of sublimation. No other thermochemical data are available for this compound.

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Heat of solution measurements[34] have led to a reported $\Delta H_f^\circ = -177.2$ kcal mol^{-1} for $VOCl_3$(liq). Mah[21] has adjusted this value to conform to the same ΔH_f° for V_2O_5(c) we have adopted and has thereby obtained $\Delta H_f^\circ = -176.0$ kcal mol^{-1} for $VOCl_3$(liq). We adopt this value rather than the value cited earlier in NBS Circular 500.[2] Vapor pressure data[35] for $VOCl_3$(liq) lead to ΔH°_{vap} and ΔS°_{vap} values in fair agreement with older values.[2] Combination of these data with S°_{298} for $VOCl_3$(g) calculated[12,36] from molecular constants leads to the values listed in Table I.

Cavell and Clark[37] have measured the heat of hydrolysis and reported $\Delta H_f^\circ = -352 \pm 4$ kcal mol^{-1} for VF_5(liq). Because the calorimetric reaction was ill-defined and auxiliary thermodynamic data for V(V) in alkaline solution[2] are uncertain, the derived ΔH_f° value is quite uncertain. Results of two investigations[38] of vapor pressure at several temperatures are in reasonable agreement on ΔH°_{vap} and ΔS°_{vap} of VF_5(liq). These values and the approximate ΔH_f° cited above for VF_5(liq) are combined with the S°_{298} for VF_5(g) calculated[39] from molecular constants to yield the thermodynamic properties of VF_5(liq) and VF_5(g) listed in Table I. The high entropy of vaporization suggests that VF_5 is an associated liquid.

Electrochemical measurements by Carpenter[40] and Coryell and Yost[41] led Latimer[8] to adopt the following potential for the vanadyl|pervanadyl couple.

$$VO^{2+}(aq) + H_2O(liq) = VO_2^+(aq) + 2H^+(aq) + e^-$$
$$E^0 = -1.000 \text{ V}$$

We combine this potential with the ΔG_f° for VO_2^+(aq) to obtain $\Delta G_f^\circ = -106.8$ kcal mol^{-1} for VO^{2+}(aq). Results of three investigations[42-44] of the equilibrium constant for the reaction

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

are in satisfactory agreement with the potential above and the derived free energy.

A calorimetric determination[24] of the heat of reduction of aqueous pervanadyl to vanadyl leads to $\Delta H^\circ = -166.4$ kcal mol^{-1} for VO^{2+}(aq). For this calculation we have taken $\Delta H_f^\circ(Fe^{3+}) - \Delta H_f^\circ(Fe^{2+}) = 9.7$ kcal mol^{-1} from the recent NBS Technical Note 270-4.[45] The ΔH° derived from the temperature coefficient of the $VO^{2+}|VO_2^+$ potential[40,41] also leads to $\Delta H_f^\circ = -116.4$ kcal mol^{-1} for VO^{2+}(aq), which is the value we adopt for Table I. Three other values for this ΔH_f° may also be calculated. Equilibrium constants at different temperatures[43,44] lead to $\Delta H_f^\circ \cong -115$ and -119 kcal mol^{-1}, while a heat of hydrolysis of VCl_4(liq) leads to a reported[46] $\Delta H_f^\circ = -113$ kcal mol^{-1} for VO^{2+}(aq).

Combination of the ΔG_f° and ΔH_f° values leads to $\bar{S}_2^\circ = -32$ cal deg^{-1} mol^{-1} for VO^{2+}(aq).

Several investigations[7,47-49] provide strong evidence that the hydrolysis of VO^{2+}(aq) occurs in stepwise fashion with $VOOH^+$(aq) as the first product and with more complicated species as products of further hydrolysis, but there is considerable uncertainty to be associated with reported equilibrium constants. Rossotti and Rossotti[47] have reported equilibrium quotients for hydrolysis of VO^{2+} in 3 M ClO_4^- solutions, but we have no activity coefficients to use to convert to our standard state based on pure water as solvent. Meites[48] and more recently Khan and Martell[49] have reported equilibrium constants based on measurements on dilute solutions of vanadyl sulfate. In addition to assumptions that Meites[48] has correctly stated are involved in calculating K values from experimental data, both investigators implicitly assumed that association of VO^{2+}(aq) with SO_4^{2-}(aq) is negligible. Since Strehlow and Wendt[50] have reported $K = 3.0 \times 10^2$ for

$$VO^{2+}(aq) + SO_4^{2-}(aq) = VOSO_4(\text{aq ion piar})$$

it is clear that further measurements and calculations are desirable. In spite of some uncertainties, we largely follow Khan and Martell[49] in adopting the following equilibrium constants and the approximate ΔG_f° values cited in Table I.

$$VO^{2+}(aq) + H_2O(liq) = VOOH^+(aq) + H^+(aq) \quad K = 10^{-5}$$
$$2VOOH^+(aq) = (VOOH)_2^{2+}(aq) \quad K = 10^4$$

Although equilibrium constants were also reported[49] at 0.4°, we do not believe the derived ΔH° and ΔS° values are reliable enough to justify tabulation of ΔH_f° and $\bar{S}_2^\circ$ values for $VOOH^+$(aq) and $(VOOH)_2^{2+}$(aq).

For VF_4(c) we have only $\Delta H_f^\circ = -321$ kcal mol^{-1} from Cavell and Clark.[37] Mah[21] has estimated other thermodynamic properties for this compound.

Gross and Hayman[51] have reported $\Delta H_f^\circ = -136.2$ kcal mol^{-1} for VCl_4(liq), based on their calorimetric measurements. Nagarajan[52] has used molecular constants in calculating $S_{298}^\circ = 94.0$ cal deg^{-1} mol^{-1} for VCl_4(g), while Mah[21] has obtained $S_{298}^\circ = 86.9$ cal deg^{-1} mol^{-1} by a similar calculation. We adopt the latter value. On the basis of several investigations of vapor pressures of VCl_4(liq) that are cited in NBS Circular 500[2] and by Mah,[21] we adopt $\Delta H^\circ_{vap} = 10$ kcal mol^{-1} and $\Delta S^\circ_{vap} = 23$ cal deg^{-1} mol^{-1}. Values cited in this paragraph lead to the other thermodynamic properties for VCl_4(liq) and VCl_4(g) listed in Table I.

Mah[21] has derived $\Delta H_f^\circ = -100 \pm 2$ kcal mol^{-1} for VBr_4(g), based on $\Delta H_f^\circ = 0$ for Br_2(g), from earlier equilibrium investigations and properties of VBr_3(c) and VBr_2(c) discussed later in this paper. We adopt $\Delta H_f^\circ \cong -85$ kcal mol^{-1} for VBr_4(g), based on the usual[1-8] choice of $\Delta H_f^\circ = 0$ for Br_2(liq). It should be noted that Mah's choice[21] of Br_2(g), and also I_2(g), as standard state is often the most convenient choice for purposes of high-temperature work relevant to vanadium metallurgy.

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Berry, Smardzewski, and McCarley[53] have carried out high-temperature equilibrium investigations of the reaction

$$VI_2(c) + I_2(g) = VI_4(g)$$

and derived log K, $\Delta H°$, and $\Delta S°$ values for this reaction in the range 495–722°K. Because there are no high-temperature heat content data for any vanadium iodides, the best we can do is combine their $\Delta H°$ with crude estimates and the $\Delta H_f°$ for $VI_2(c)$ cited later to obtain $\Delta H_f° \cong -31$ kcal mol^{-1} for $VI_4(g)$, based on $\Delta H_f° = 0$ for $I_2(c)$.

High-temperature equilibrium investigations by Flood and Kleppa[54] provide data that permit us to calculate our tabulated $\Delta G_f°$, $\Delta H_f°$, and $S°_{298}$ values for $VOSO_4(c)$. For these calculations we have used the properties of $VO_2(c)$ from Table I, although Flood and Kleppa[54] were apparently working with a different crystal form having unknown thermodynamic properties. Their data also provide support for the properties of $V_2O_5(c)$ and $VO_2(c)$ in Table I, along with information relevant to the contact process for sulfuric acid.

Jones and Colvin[55] have determined the following potential.

$$V^{3+}(aq) + H_2O(liq) = VO^{2+}(aq) + 2H^+(aq) + e^- \quad E^0 = -0.337 \text{ V}$$

We combine this potential with our $\Delta G_f°$ for $VO^{2+}(aq)$ to obtain $\Delta G_f° = -57.9$ kcal mol^{-1} for $V^{3+}(aq)$. Since Jones and Colvin[55] also determined the potential for the above couple at 0°, we are able to calculate the approximate $\Delta H_f°$ and $\bar{S}_2°$ values listed for $V^{3+}(aq)$ in Table I. These latter values must be accepted with some reservations for two reasons. First, all uncertainties in the data for $VO^{2+}(aq)$ are carried directly into the tabulated values for $V^{3+}(aq)$. Second, heats and entropies calculated from temperature derivatives based on data at only two temperatures are notoriously and deservedly suspect.

Meites[48] has calculated the following equilibrium constants for hydrolysis of $V^{3+}(aq)$.

$$V^{3+}(aq) + H_2O(liq) = VOH^{2+}(aq) + H^+(aq) \quad K = 1.2 \times 10^{-3}$$

$$VOH^{2+}(aq) = VO^+(aq) + H^+(aq) \quad K = 3 \times 10^{-4}$$

In spite of uncertainties in these values due to association of $V^{3+}(aq)$ and $SO_4^{2-}(aq)$ and approximations already cited,[48] these values permit calculation of approximate $\Delta G_f°$ values for $VOH^+(aq)$ and $VO^+(aq)$. Here it should be emphasized that $VO^+(aq)$ is only the simplest formula for this ion. A more realistic formula might well contain one or more H_2O units, with $\Delta G_f°$ correspondingly adjusted. It is also relevant to note that Newton and Baker[56] have reported kinetic evidence for a hydrolytic dimer of V(III) that may be similar to the more familiar dimer of Fe(III).

Other investigators[57,58] have reported hydrolysis constants in reasonable agreement with values given above. Constants at different temperatures[57] permit estimates of ΔH and ΔS of hydrolysis in solutions with 1.0 M ionic strength but are not adequate for calculation of standard thermodynamic properties of the hydrolysis products.

Mrazek, Richardson, Poppleton, and Block[59] have employed solution calorimetry in determining $\Delta H_f° = -138.9$ kcal mol^{-1} for $VCl_3(c)$ and have also reviewed earlier values ranging from -134 to -187 kcal mol^{-1}. We combine $S°_{298}$ from Kelley and King[12] with the above $\Delta H_f°$ to obtain the $\Delta G_f°$ in Table I.

Mah[21] has calculated $\Delta H_f° = -117$ kcal mol^{-1} for $VBr_3(c)$ from results of an earlier calorimetric investigation. This value is based on $\Delta H_f° = 0$ for $Br_2(g)$, so we use the heat of vaporization of bromine[1] to calculate $\Delta H_f° = -106$ kcal mol^{-1} for $VBr_3(c)$, based on Br_2(liq) standard state. We estimate $S°_{298}$ and combine with this latter $\Delta H_f°$ to obtain the $\Delta G_f°$ for $VBr_3(c)$ listed in Table I.

Mah[21] has calculated $\Delta H_f° = -88 \pm 2$ kcal mol^{-1} for $VI_3(c)$ from results of earlier calorimetric data. We have concluded from reconsideration of these data and also more recent high-temperature equilibrium data[53] that $\Delta H_f° = -87$ kcal mol^{-1} (based on $I_2(g)$ standard state) best satisfies all the available data. We combine this value with the heat of sublimation of iodine[1] to obtain $\Delta H_f° = -65$ kcal mol^{-1} for $VI_3(c)$, based on $\Delta H_f° = 0$ for $I_2(c)$. We combine this $\Delta H_f°$ with our estimated $S°_{298}$ to obtain the tabulated $\Delta G_f°$.

Jones and Colvin[60] have reported the following potential.

$$V^{2+}(aq) = V^{3+}(aq) + e^- \quad E^0 = 0.255 \text{ V}$$

We use this potential with the $\Delta G_f°$ of $V^{3+}(aq)$ to obtain $\Delta G_f° = -52.0$ kcal mol^{-1} for $V^{2+}(aq)$ and thence calculate the new potential.

$$V(c) = V^{2+}(aq) + 2e^- \quad E^0 = 1.13 \text{ V}$$

Jones and Colvin[60] have also reported E^0 for the $V^{2+}|V^{3+}$ couple at 0°, which permits us to calculate the approximate $\Delta H_f°$ and $\bar{S}_2°$ values for $V^{2+}(aq)$ given in Table I.

Calorimetric data for the the heat of association of V^{2+}(aq) with excess $CN^-(aq)$ to form $V(CN)_6^{4-}(aq)$ have been reported,[61] but uncertainties are too large to justify calculation and tabulation of thermodynamic properties for the latter ion.

Mah[21] has described calculations with high-temperature equilibrium data for reduction of $VCl_2(c)$ with $H_2(g)$ and from two different calculations has obtained $\Delta H_f° = -110$ and -101 kcal mol^{-1} for $VCl_2(c)$, without any clear evidence as to which is the "best" value. Mah[21] has also derived $\Delta H°_{298} = 43$ kcal mol^{-1} of VCl_2 for

$$2VCl_3(c) = VCl_2(c) + VCl_4(g)$$

from results of high-temperature vapor pressure measurements. We use this $\Delta H°_{298}$ with $\Delta H_f°$ values from Table I to obtain $\Delta H_f° = -109$ kcal mol^{-1} for $VCl_2(c)$. On the basis of earlier calorimetric data, NBS Circular 500[2] adopted $\Delta H_f° = -108$ kcal mol^{-1}. Although the uncertainty is presently rather large, we adopt $\Delta H_f° = -109$ kcal mol^{-1} for $VCl_2(c)$ and combine with its $S°_{298}$ from Kelley and King[12] to obtain the $\Delta G_f°$ in Table I.

Mah[21] has obtained $\Delta H_f° = -93 \pm 2$ kcal mol^{-1} for VBr(c) from the $\Delta H_f°$ of VBr(c) and high-temperature equilibrium data. We use this value, based on $Br_2(g)$ standard state, to obtain $\Delta H_f° = -86$ kcal mol^{-1} for $VBr_2(c)$, based

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Table I

Thermodynamic Data for Vanadium at 298°K

Substance	$\Delta H_f°$, *kcal mol*$^{-1}$	$\Delta G_f°$, *kcal mol*$^{-1}$	$S°$, cal *deg*$^{-1}$ *mol*$^{-1}$
V(c)	0	0	6.8^{13}
V(g)	123^{13}	112	$43.55^{12,13}$
V^+(g)	279		
V^{2+}(g)	608		
V^{3+}(g)	1221		
V^{4+}(g)	2340		
V^{5+}(g)	3828		
V^{2+}(aq)	$\sim -54^{60}$	-52.0^{60}	$\sim -31^{60}$
V^{3+}(aq)	$\sim -62^{55}$	-57.9^{55}	~ -55
VOH^+(aq)		-101^{48}	
VO^+(aq)		-96^{48}	
VO^{2+}(aq)	-116.4^{24}	$-106.8^{40,41}$	-32
$VOOH^+$(aq)		-157^{49}	
$(VOOH)_2{}^{2+}$(aq)		-318^{49}	
$VOSO_4$(aq ion pair)		-288^{50}	
$VO_2{}^+$(aq)	-155.3^{24}	-140.4^{23}	-9.8
VO(c)	-103.2^{14}	-96.6	9.3^{12}
V_2O_3(c)	-291.3^{14}	-272.3	23.5^{12}
VO_2(c)	-170.6^{14}	-157.6	12.3^{12}
V_6O_{13}(c)	$(-1065)^{21}$	$(-982)^{21}$	$(80)^{21}$
V_2O_5(c)	-370.6^{14}	-339.4	31.3^{12}
$V_2O_5 \cdot H_2O$(c)	~ -441	~ -396	(41)
VCl_2(c)	-109	-98	23.2^{12}
VBr_2(c)	-86	-81	(27)
VI_2(c)	-60	-59	(32)
VCl_3(c)	-138.9^{59}	-122.4	31.3^{12}
VBr_3(c)	-106	-100	(40)
VI_3(c)	-65	-64	(44)
VF_4(c)	-321^{37}	$(-299)^{21}$	$(30)^{21}$
VCl_4(liq)	-136.2^{51}	-121	63
VCl_4(g)	$-126^{2,21}$	$-118^{2,21}$	86.9^{21}
VBr_4(g)	~ -85		
VI_4(g)	$\sim -31^{53}$		
VF_5(liq)	$\sim -352^{37}$	~ -327	45
VF_5(g)	~ -341	~ -326	77.9^{39}
$VOCl_3$(liq)	$-176.0^{21,34}$	-161	61
$VOCl_3$(g)	-167	-158	$82.1^{12,36}$
$VOSO_4$(c)	-312.1^{54}	-279.4^{54}	27.1^{54}
VN(c)	-51.9^{66}	-45.7	8.91^{12}
V_2C(c)	$(-35)^{65}$	$(-35)^{65}$	$(14)^{65}$
$VC_{0.73}$(c)	$(-22)^{65}$	$(-22)^{65}$	$(6)^{65}$
$VC_{0.88}$(c)	-24.4^{21}	-24.0^{21}	6.61^{21}
NH_4VO_3(c)	-251.7^{25}	-212.3	33.6^{12}
$NaVO_3$(c)	$-273.9^{25,26}$	-254.4	27.2^{27}
Na_3VO_4(c)	-419.8^{26}	-391.2	45.3^{27}
$Na_4V_2O_7$(c)	-697.2^{26}	-650.1	76.1^{27}
MgV_2O_6(c)	-526.2^{28}	-487.4	38.4^{30}
$Mg_2V_2O_7$(c)	-677.7^{28}	-632.1	47.9^{30}
CaV_2O_6(c)	-556.7^{28}	-518.6	42.8^{29}
$Ca_2V_2O_7$(c)	-736.9^{28}	-691.5	52.7^{29}
$Ca_3V_2O_8$(c)	-903.0^{28}	-851.2	65.7^{29}
MnV_2O_6(c)	-477.9^{32}	-441.9	$(47.5)^{32}$
FeV_2O_6(c)	-453.8^{31}	-418.1	$(47)^{21}$
$Pb_2V_2O_7$(c)	-509.9^{32}	-465.0	$(65.5)^{32}$
$Pb_3V_2O_8$(c)	-567.7^{32}	-516.5	$(84.5)^{32}$

on Br_2(liq) standard state. The estimated entropy, which must fall within certain limits to be consistent with Mah's calculations and the equilibrium data of McCarley and Roddy,[62] is combined with our $\Delta H_f°$ to yield the tabulated $\Delta G_f°$ for VBr_2(c).

On the basis of data cited by Mah[21] and more recent measurements by Berry, Smardzewski, and McCarley,[53] we adopt the thermodynamic properties listed for VI_2(c) in Table I.

Although we do not use their data for further calculations of standard thermodynamic properties of vanadium halides, it should be noted that McCarley and others[53,63,64] have carried out a variety of high-temperature equilibrium investigations that provide thermodynamic data for gaseous halides of vanadium, for solid solutions of vanadium halides, and for mixed halides of vanadium, all at temperatures above 360°.

For vanadium carbide represented by $VC_{0.88}$(c) we adopt the thermodynamic properties cited by Mah.[21] Worrell and Chipman[65] have estimated $\Delta H_f°$ and $\Delta S_f°$ for $VC_{0.73}$(c) and V_2C(c) from their high-temperature equilibrium data and phase diagrams for the vanadium–carbon system. These values also lead to the $\Delta G_f°$ and $S°_{298}$ values in Table I.

We take $\Delta H_f°$ for VN(c) from Mah[66] and $S°_{298}$ from Kelley and King[12] to obtain the $\Delta G_f°$ listed in Table I.

Veleckis and Edwards[67] have reviewed earlier work and reported results of their equilibrium measurements on the vanadium–hydrogen system at several temperatures in the range 246–554°. The resulting data have permitted calculation of thermodynamic properties for compositions up to 0.34 mole fraction of H.

Although this review has been limited to detailed consideration of the inorganic thermochemistry of vanadium, it is appropriate to call attention to some investigations of organic compounds of vanadium. Claunch, Martin, and Jones[68] have used vapor pressure data to evaluate free energies, enthalpies, and entropies of coordination of ammonia and some amines to the sixth "unsolvated" position in bis(2,4-pentanediono)oxovanadium(IV). Calorimetric measurements by Carlin and Walker[69] have led to ΔH values for reaction of a number of nitrogen and oxygen donors with vanadyl acetylacetonate in nitrobenzene. Bradley and Hillyer[70] have determined calorimetrically the $\Delta H_f°$ of vanadium tetra-*tert*-butoxide. Popp, Nelson, and Ragsdale[71] have made calorimetric measurements of heats of reaction of tertiary amine oxides with bis(2,4-pentanedionato)oxovanadium(IV) in chloroform and dichloromethane.

III. Niobium

A. DESCRIPTIVE CHEMISTRY

The chemical properties of niobium (formerly called columbium) are typical in many respects of second-row transition elements as compared to the properties of corresponding first-row transition elements. For example, higher oxidation state compounds of niobium are more stable and lower

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[70] D. C. Bradley and M. J. Hillyer, *Trans. Faraday Soc.*, 62, 2382 (1966).

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oxidation state compounds are less stable than many corresponding compounds of vanadium.

There are similarities between niobium and the nonmetallic phosphorus and arsenic in that they form a considerable number of similar anionic species but few cationic species. The halides and oxyhalides of these elements are also similar in that bonding is largely covalent and the compounds are readily hydrolyzed.

The aqueous chemistry of niobium is rather limited because so many compounds are nearly insoluble or react with water to form very slightly soluble compounds. Among the most common compounds of niobium is the pentoxide Nb_2O_5, which is usually brought into solution after fusion with an alkali hydrogen sulfate or hydroxide or by treatment with concentrated HF solution. White gelatinous precipitates of the hydrous pentoxide (sometimes called "niobic acid") are formed when halides of Nb(V) are treated with water or when alkaline solutions of niobates are neutralized.

Pope and Dale[10] have reviewed most investigations of isopolyniobates and cite extensive evidence for hexameric $Nb_6O_{19}^{8-}$(aq) as the principal anionic species in alkaline solution. Equilibrium quotients referring to 3 *M* KCl solutions have been reported[10] for protonation of $Nb_6O_{19}^{8-}$(aq) to $HNb_6O_{19}^{7-}$(aq) and $H_2Nb_6O_{19}^{6-}$(aq). Products of reactions of Nb(V) with H_2O_2 have been described by Connor and Ebsworth,[9] but we have no quantitative stability or thermochemical data.

B. THERMOCHEMISTRY

We adopt $S°_{298}$ = 8.6 cal deg^{-1} mol^{-1} for Nb(c) based on heat capacity data from Clusius, Franzosini, and Piesbergen.[72] High-temperature vapor pressure data led Speiser, Blackburn, and Johnston[73] to report $\Delta H°_{298}$ = 172.5 kcal mol^{-1} for sublimation of Nb(c). Although it has been noted[74] that a different treatment of the data leads to a considerably larger value for this heat of sublimation, we adopt $\Delta H_f°$ = 172.5 kcal mol^{-1} for Nb(g) and combine with its $S°_{298}$ = 44.49 cal deg^{-1} mol^{-1} from Kelley and King[12] to obtain the $\Delta G_f°$ given in Table II.

Subsequent to early determinations of relatively low accuracy, we have the following calorimetric $\Delta H_f°$ values (kcal mol^{-1}) for Nb_2O_5(c): −455.2 from Humphrey,[75] −454.4 from Huber, Head, Holley, Storms, and Krikorian,[76] −455.1 from Kusenko and Geld,[77] −454.8 from Morozova and Stolyarova,[78] and −453.5 from Kornilov, Leonidov, and Skuratov.[79] We adopt $\Delta H_f°$ = −454.4 kcal mol^{-1} for Nb_2O_5(c) and combine with its $S°_{298}$ = 32.8 cal deg^{-1} mol^{-1} from Kelley and King[12] to obtain the $\Delta G_f°$ given in Table II.

Table II

Thermodynamic Data for Niobium at 298°K

Substance	$\Delta H_f°$, *kcal mol*$^{-1}$	$\Delta G_f°$, *kcal mol*$^{-1}$	$S°$, *cal deg*$^{-1}$ *mol*$^{-1}$
Nb(c)	0	0	8.6^{72}
Nb(g)	172.5^{73}	162.0	44.49^{12}
NbO(c)	$-98^{81,83}$	−91	(11)
NbO_2(c)	-190.4^{80-82}	−177.1	13.03^{12}
Nb_2O_5(c)	-454.5^{75-79}	−422.6	32.8^{12}
Nb_2O_5 (hyd ppt)	-479^{89a}		
NbF_5(c)	-433.5^{85}	−406.1	38^{86}
NbF_5(g)	∼−414	∼−400	84^{87}
$NbCl_{2.33}$(c)	-114^{97}	−102	$(31)^{97}$
$NbCl_{2.67}$(c)	-129^{97}	−115	$(33)^{97}$
"$NbCl_3$"(c)	-140^{97}	−124	(35)
$NbCl_{3.13}$(c)	-144^{97}	−127	$(36)^{97}$
$NbCl_4$(c)	-166.0^{92}	−145	$(44)^{92}$
$NbCl_4$(g)	-136.6^{92}	−128	$(85)^{92}$
$NbCl_5$(c)	$-190.5^{92,93}$	−163.2	50.4^{96}
$NbCl_5$(g)	$-168.1^{92,93,96}$	−154.4	95.8^{96}
$NbBr_5$(c)	-132.8^{74}	−122	(62)
$NbBr_5$(g)	$-105.2^{74,101}$	−108	(109)
NbI_5(c)	-64.6^{100}		
$NbOCl_2$(c)	-186^{83}		
$NbOCl_3$(c)	$-211^{102,103}$	−189	$(38)^{102}$
$NbOCl_3$(g)	$-185^{92,102}$	−176	$(82)^{102}$
$NbOBr_3$(c)	-179.1^{99}		
$NaNbCl_6$(c)	-291^{107}		
$KNbCl_6$(c)	-301^{107}		
$RbNbCl_6$(c)	-306^{107}		
$CsNbCl_6$(c)	-318^{107}		
Nb_2N(c)	-60.4^{80}		
NbN(c)	-56.4^{108}	−49.7	$(9)^{12}$
Nb_2C(c)	-47^{76}	−47	(18)
NbC(c)	$-33^{65,76,109}$	−33	8.5^{110}
"NbB_2"(c)	-61^{113}	−60	9.0^{114}

We have combined heats of combustion of NbO_2(c) from Mah[80] and from Morozova and Getskina[81] with our adopted $\Delta H_f°$ of Nb_2O_5(c) to obtain $\Delta H_f°$ = −190.6 and −190.2 kcal mol^{-1} for NbO_2(c). High-temperature equilibrium data from Worrell[82] lead us to $\Delta H_f°$ = −190.4 kcal mol^{-1} for NbO_2(c). On the basis of these three values, which appear to be more reliable than those derived from earlier high-temperature equilibrium studies cited by Brewer,[15] we adopt an average $\Delta H_f°$ = −190.4 kcal mol and combine with $S°$ = 13.03 cal deg^{-1} mol^{-1} from Kelley and King[12] to obtain its $\Delta G_f°$.

We calculate $\Delta H_f°$ = −99.8 kcal mol^{-1} for NbO(c) from its heat of combustion reported by Morozova and Getskina[81] and our adopted $\Delta H_f°$ for Nb_2O_5(c). We also have $\Delta H°$ = −113.2 kcal mol^{-1} of NbO(c) for the reaction

$$NbO(c) + {}^3/_2Cl_2(g) = NbOCl_3(c)$$

from Schäfer and Liedmeier.[83] Combination of this $\Delta H°$ with $\Delta H_f°$ values for $NbOCl_3$(c) cited later leads to $\Delta H_f°$ = −97.0 and −98.2 kcal mol^{-1} for NbO(c). On the basis of these results, we adopt $\Delta H_f°$ = −98 kcal mol^{-1} for NbO(c) and combine this value with our estimated $S°_{298}$ to obtain

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(81) M. P. Morozova and L. I. Getskina, *Zh. Obshch. Khim.*, **29**, 1049 (1959); *J. Gen. Chem. USSR*, **29**, 1019 (1959).

(82) W. L. Worrell, *J. Phys. Chem.*, **68**, 952 (1964).

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its ΔG_f°. In the absence of thermal data that would permit accurate comparisons, all we can say is that the properties of NbO(c) given in Table II are reasonably consistent with high temperature data from Ignatowicz and Davies[84] and from earlier workers they cite.

For NbF_5(c) we have $\Delta H_f^\circ = -433.5$ kcal mol^{-1} from fluorine combustion calorimetry[85] and $S^\circ_{298} = 38.3$ cal deg^{-1} mol^{-1} from heat capacity data.[86] Statistical mechanical calculations by Nagarajan[87] have led to $S^\circ_{298} = 84.4$ cal deg^{-1} mol^{-1} for NbF_5(g). We calculate $\Delta S^\circ_{298} = 46.1$ cal deg^{-1} mol^{-1} for sublimation of NbF_5(c). Fairbrother and Frith[88] and Junkins, Farrar, Barber, and Bernhardt[89] have reported vapor pressures, mostly for NbF_5(liq), over a wide range of temperatures. The latter workers[89] reported $\Delta H = 8.6$ kcal mol^{-1} for melting of NbF_5(c), while Brady, Myers, and Clauss[86] have reported $\Delta H = 2.9$ kcal mol^{-1} for melting, along with an incorrectly calculated entropy of melting. Combination of the vapor pressure data for NbF_5(liq) with these heats of melting and estimated ΔC_p values leads to $\Delta H = 17$ and 23 kcal mol^{-1} for sublimation of NbF_5(c). Another calculation in which we combine the third-law ΔS°_{298} cited above with an extrapolated vapor pressure for NbF_5(c) at 298°K leads to $\Delta H = 19$ kcal mol^{-1} for sublimation of NbF_5(c). The tentative ΔG_f° and ΔH_f° values for NbF_5(g) in Table II are based on this last calculation.

Myers and Brady[89a] have reported ΔH values for reactions of NbF_5(c) with several aqueous solutions. Uncertainties in their calorimetric reactions and the auxiliary ΔH_f° values used in their calculations are so large that their derived ΔH_f° for NbF_5(c) is much less certain than the ΔH_f° value[85] we have adopted above. Uncertainties about the species formed in their reactions 6 and 8 prevent our making meaningful thermodynamic calculations with their reported ΔH values for these reactions. We can, however, use their ΔH for their reaction 7 for calculation of $\Delta H_f^\circ = -(479 + 68.3n)$ kcal mol^{-1} for hydrous precipitated $Nb_2O_5 \cdot nH_2O$. In Table II we list $\Delta H_f^\circ = -479$ kcal mol^{-1} for Nb_2O_5(hyd ppt) for which we have set $n = 0$.

A variety of complex fluorides of Nb(V) have been reported and investigated. For example, spectroscopic studies[90] of solutions of $K_2NbO_5 \cdot H_2O$ and K_2NbF_7 have provided evidence for $NbOF_5^{2-}$(aq) and NbF_6^-(aq), but not for NbF_7^{2-}(aq). On the other hand, Haissinsky[91] has interpreted his potentiometric data on similar systems in terms of NbF_7^{2-}(aq) and the following half-reaction potential.

$$Nb(c) + 7F^-(aq) = NbF_7^{2-}(aq) + 5e^- \quad E^0(18^\circ) = 0.33\ V$$

Heat of solution data for Nb(c) and $NbCl_5$(c) have led Schäfer and Kahlenberg[92] to $\Delta H_f^\circ = -190.4$ kcal mol^{-1} for $NbCl_5$(c). Gross, Hayman, Levi, and Wilson[93] have measured directly the heat of formation from the elements and have reported $\Delta H_f^\circ = -190.6$ kcal mol^{-1} for $NbCl_5$(c). On the basis of the impressive agreement of these two independent results, we confidently adopt $\Delta H_f^\circ = -190.5$ kcal mol^{-1} for $NbCl_5$(c). Two other investigations[94,95] have led to less certain ΔH_f° values that are slightly more negative than those cited above.

Keneshea, Cubicciotti, Withers, and Eding[96] have made calorimetric ($H_T - H_{298}$) measurements on $NbCl_5$(c) and $NbCl_5$(liq) up to 600°K. They have used these data and results of statistical thermodynamic calculations for $NbCl_5$(g) with vapor pressure data from the literature in deriving $\Delta H^\circ_{298} = 22.4$ kcal mol^{-1} and $\Delta S^\circ_{298} = 45.4$ cal deg^{-1} mol^{-1} for sublimation of $NbCl_5$(c). Their statistical calculations have yielded $S^\circ_{298} = 95.8$ cal deg^{-1} mol^{-1} for $NbCl_5$(g), and thence they have obtained $S^\circ_{298} = 50.4$ cal deg^{-1} mol^{-1} for $NbCl_5$(c). It should be mentioned that this paper[96] is an admirable example of thorough thermodynamic treatment of vapor pressure data. We combine all the results given in this paragraph with our adopted ΔH_f° for $NbCl_5$(c) to obtain its ΔG_f° and also both ΔH_f° and ΔG_f° for $NbCl_5$(g).

Heats of solution of Nb(c) and $NbCl_4$(c) led Schäfer and Kahlenberg[92] to $\Delta H_f^\circ = -166.0$ kcal mol^{-1} for $NbCl_4$(c). Their analysis of earlier vapor pressure data gave $\Delta H^\circ_{298} = 29.4$ kcal mol^{-1} for sublimation of $NbCl_4$(c) and thence $\Delta H_f^\circ = -136.6$ kcal mol^{-1} for $NbCl_4$(g). Their $\Delta S^\circ_{298} = 41$ cal deg^{-1} mol^{-1} for sublimation of $NbCl_4$(c) and estimated S°_{298} for $NbCl_4$(c) leads to S°_{298} for $NbCl_4$(g) and thence to ΔG_f° values for both $NbCl_4$(c) and $NbCl_4$(g).

Shäfer and others[92,97] have investigated $NbCl_n$ compounds and phases for which $n < 4$ with some results given in Table II. It is now known that the "dichloride" is Nb_6Cl_{14} or $NbCl_{2.33}$, for which we adopt $\Delta H_f^\circ = -114$ kcal mol^{-1} of $NbCl_{2.33}$ and combine with its estimated $S^\circ_{298} = (31)$ to obtain its ΔG_f°. Data are also available for solids in the homogeneity range from $NbCl_{2.67}$ to $NbCl_{3.13}$, leading to an interpolated $\Delta H_f^\circ = -140$ kcal mol^{-1} for the "trichloride."

Compounds of formula $Nb_6X_{14} \cdot 7H_2O$ (X = Cl or Br) are soluble in water and alcohol, and X-ray investigations[98] of solutions have shown that there are $Nb_6X_{12}^{2+}$ ions. This formulation is consistent with the observation that Ag^+(aq) rapidly precipitates only one-seventh of the total chloride.

Calorimetric measurements by Gross, Hayman, Levi, and Wilson[74] led them to report $\Delta H_f^\circ = -132.85$ kcal mol^{-1} for $NbBr_5$(c), which we adopt. This value is in fair agreement with results of two other investigations.[99,100] Vapor pressure

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(100) H. Schäfer and H. Heine, *Z. Anorg. Allg. Chem.*, **352**, 258 (1967).

data[101] lead us to $\Delta H^\circ_{298} = 27.6$ kcal mol^{-1} for sublimation of $NbBr_5$(c) and thence to ΔH_f° for $NbBr_5$(g). Our estimated S°_{298} values are chosen to be consistent with $\Delta S^\circ_{298} = 47$ cal deg^{-1} mol^{-1} for sublimation that we have calculated from the vapor pressure data.[101] We have combined ΔH_f° and S°_{298} values to obtain the ΔG_f° values given in Table II for $NbBr_5$(c) and $NbBr_5$(g).

For NbI_5(c) we have only $\Delta H_f^\circ = -64.6$ kcal mol^{-1} from calorimetric measurements by Schäfer and Heine.[100]

Calorimetric measurements have led Schäfer and Kahlenberg[102] to report $\Delta H_f^\circ = -210.2$ kcal mol^{-1} for $NbOCl_3$(c), while other calorimetric measurements by Shchukarev, Smirnova, Shemyakina, and Ryabov[103] led them to $\Delta H_f^\circ = -212.2$ kcal mol^{-1}. Recalculation of the latter result with our adopted ΔH_f° for Nb_2O_5(c) leads us to $\Delta H_f^\circ = -211.4$ kcal mol^{-1} for $NbOCl_3$(c). On the basis of the values cited here, our estimates of uncertainties, and the relation of $NbOCl_3$(c) to NbO(c) cited earlier, we adopt $\Delta H_f^\circ = -211$ kcal mol^{-1} for $NbOCl_3$(c) and combine with its estimated[102] S°_{298} to obtain the ΔG_f° in Table II. Vapor pressure data from Schäfer and Kahlenberg[92,102] lead to $\Delta H^\circ_{298} = 26.2$ kcal mol^{-1} for sublimation and thence to ΔH_f° for $NbOCl_3$(g). Estimated entropies[102] for $NbOCl_3$(c) and $NbOCl_3$(g) are consistent with $\Delta S^\circ_{298} = 44$ cal deg^{-1} mol^{-1} for sublimation, as calculated from the vapor pressure data.

Combination of the heat of chlorination[83] of $NbOCl_2$(c) to $NbOCl_3$(c) with our adopted ΔH_f° of the latter compound leads to $\Delta H_f^\circ = -186$ kcal mol^{-1} for $NbOCl_2$(c).

Using calorimetric data from Shchukarev, Smirnova, Vasil'kova, and Borovkova[99] with our adopted ΔH_f° for Nb_2O_5(c), we calculate $\Delta H_f^\circ = -179.1$ kcal mol^{-1} for $NbOBr_3$(c). We have no other thermodynamic data for this compound.

Vapor pressures of $NbOCl_3$(g) over compounds of types M_2NbOCl_5 and $MNbOCl_4$ have been measured[104-106] at high temperatures. We have no C_p or $(H_T - H_{298})$ data to use with the vapor pressures in evaluating the thermodynamic properties at 25°. Calorimetric data from Smirnova, Vasil'kova and Kudryashova[107] for reactions of type

$$NbCl_5(c) + MCl(c) = MNbCl_6(c)$$

have been used with our adopted ΔH_f° for $NbCl_5$(c) and ΔH_f° values for the alkali chlorides from NBS Circular 500[2] to yield ΔH_f° values given in Table II for $MNbCl_6$(c) compounds.

We have combined heat of combustion data from Mah[80] and from Mah and Gellert[108] with our adopted ΔH_f° for Nb_2O_5(c) to obtain $\Delta H_f^\circ = -60.4$ kcal mol^{-1} for Nb_2N(c) and $\Delta H_f^\circ = -56.4$ kcal mol^{-1} for NbN(c). We use an estimated S° for NbN(c) with the ΔH_f° to calculate ΔG_f° as in Table II.

Because of fairly wide homogeneity ranges in the Nb–C system, thermodynamic measurements have generally been made on samples that deviated from composition denoted by Nb_2C and NbC. For example, Mah and Boyle[109] carried out heat of combustion measurements on samples of composition $NbC_{0.9445}$. Combining their results and their correction to composition corresponding to NbC with our adopted ΔH_f° for Nb_2O_5(c) leads us to $\Delta H_f^\circ = -33.2$ kcal mol^{-1} for NbC(c). Other calorimetric measurements[76] on samples represented by NbC_x (x from 0.489 to 0.984) in combination with our ΔH_f° for Nb_2O_5(c) also lead to $\Delta H_f^\circ = -33.2$ kcal mol^{-1} for NbC(c). High-temperature equilibrium measurements by Worrell and Chipman[65] led to a reported $\Delta H_f^\circ = -31.8$ kcal mol^{-1} for NbC(c). We adopt $\Delta H_f^\circ = -33$ kcal mol^{-1} and combine with the third-law entropy from Pankratz, Weller, and Kelley[110] to obtain the ΔG_f° listed for NbC(c) in Table II. Combustion data[76] also lead us to $\Delta H_f^\circ = -47$ kcal mol^{-1} for Nb_2C(c), which we combine with an estimated S°_{298} to obtain its ΔG_f°.

For niobium diboride we have ΔH_f° values calculated from phase equilibria[111] and estimated from molar volumes.[112] The best value is $\Delta H_f^\circ = -58.6$ kcal mol^{-1} for $NbB_{1.875}$(c) from fluorine combustion calorimetry.[113] Thermal measurements[114] have led to $S^\circ_{298} = 8.91$ cal deg^{-1} mol^{-1} for $NbB_{1.963}$(c). On the basis of these values, we cite thermodynamic properties of "NbB_2"(c) in Table II.

Valeckis and Edwards[67] have reviewed earlier work and measured equilibrium pressures of H_2 in the Nb–H system from 352 to 671°. Their data have been used in calculating thermodynamic properties for compositions up to 0.39 mole fraction of H. Further data have been reported by Pryde and Titcomb.[114a]

IV. Tantalum

A. DESCRIPTIVE CHEMISTRY

The chemical properties of tantalum and its compounds are generally similar to those of niobium. Although metallic vanadium, niobium, and tantalum are similar in their reactions, the extreme sluggishness of tantalum with respect to oxidation accounts for several uses of this metal, which reacts readily near room temperature only with a mixture of HNO_3 and HF. Similarly, Ta_2O_5 is generally less reactive than Nb_2O_5.

Pope and Dale[10] have reviewed investigations of isopolytantalates. Most evidence suggests the existence of hexameric anionic species similar to the isopolyniobates. A few solid compounds of similar stoichiometry appear to be well characterized, but we have no relevant thermodynamic data.

A variety of complex halides, both solid and aqueous, have been reported. For example, Na_3TaF_8(c) has been found[115]

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to contain eight-coordinated tantalum in TaF_8^{3-} ions. The results of potentiometric and ion-exchange measurements by Varga and Freund[116] suggest that a variety of species of type $TaF_n^{(5-n)+}$ (n = 4-9) are present in various aqueous solutions. Reported[116] potentials for $Ta/TaF_n^{(5-n)+}(aq)$ range from 0.2 to 0.4 V. Haissinsky[91,117] has interpreted his potentiometric data on similar systems in terms of $TaF_7^{2-}(aq)$ and the following.

$$Ta(c) + 7F^-(aq) = TaF_7^{2-}(aq) + 5e^- \quad E^0(18°) = 0.45 \text{ V}$$

The potential data[91,116,117] and the $\Delta G_f°$ of $Ta_2O_5(c)$ cited later are consistent with the observed hydrolysis of K_2TaF_7 in water and the slight solubility of $Ta_2O_5(c)$ in cold HF(aq). We have thermodynamic data for some $MTaCl_6$ compounds.

Reactions of Ta(V) with H_2O_2 have been reviewed,[9] but we have no thermochemical data to cite for these reactions.

B. THERMOCHEMISTRY

Kelley and King[12] have reviewed C_p data leading to $S°_{298}$ = 9.92 cal deg^{-1} mol^{-1} for Ta(c). They have also calculated $S°_{298}$ = 44.24 cal deg^{-1} mol^{-1} for Ta(g). Using the high-temperature vapor pressure data of Edwards, Johnston, and Blackburn,[118] we have calculated $\Delta H_f°$ = 187 kcal mol^{-1} for Ta(g), and combined this value with entropy data to obtain the $\Delta G_f°$ given in Table III.

Table III

Thermodynamic Data for Tantalum at 298°K

Substance	$\Delta H_f°$, *kcal mol^{-1}*	$\Delta G_f°$, *kcal mol^{-1}*	$S°$, *cal deg^{-1} mol^{-1}*
Ta(c)	0	0	9.92[12]
Ta(g)	187[118]	177	44.29[12]
$Ta_2O_5(c)$	−489.2[75,79]	−457.0	34.2[12]
$TaF_5(c)$	−455.0[85]	−428	(41)[85]
$TaF_5(g)$	(−435)	(−422)	(88)
$TaCl_3(c)$	−139[121]	−123	(37)
$TaCl_4(c)$	−170[121,122]	−149	(46)[122]
$TaCl_4(g)$	−139[121,122]	−131	(89)
$TaCl_5(c)$	−205.5[90]	−179	(55)
$TaCl_5(g)$	−182[2,120–122]	−169	(101)
$TaBr_5(c)$	−143.0[74]	−132	(65)
$TaBr_5(g)$	−166[101,125]	−119	(112)
$TaOCl_3(c)$	(−213)	(−191)	(42)
$TaOCl_3(g)$	−187[124]	−179	87[124]
$NaTaCl_6(c)$	−308[107]		
$KTaCl_6(c)$	−320[107]		
$RbTaCl_6(c)$	−326[107]		
$CsTaCl_6(c)$	−337[107]		
$Ta_2N(c)$	∼−65[80]		
TaN(c)	−60[108]	−53	(10)[108]
$Ta_2C(c)$	∼−47[119]	∼−46	(19)
TaC(c)	−35.5[65,119,127]	−35.0	9.7[65]
"TaB_2"(c)	−44[113]	−43[113]	10.6[113]

Of the several reported heats of combustion leading to $\Delta H_f°$ for $Ta_2O_5(c)$, only three need be considered here. Humphrey[75] reported $\Delta H_f°$ = −488.8 ± 0.5 kcal mol^{-1} for $Ta_2O_5(c)$, which is revised to −489.0 kcal mol^{-1} on the basis of the current atomic weight of tantalum. Kornilov, Leonidov, and Skuratov[79] have reported $\Delta H_f°$ = −489.3 ± 0.4 kcal mol^{-1}, while Huber, Head, Holley, and Bowman[119] have reported $\Delta H_f°$ = −487.7 ± 0.9 kcal mol^{-1}. On the basis of the first two of these three careful investigations, we adopt $\Delta H_f°$ = −489.2 kcal mol^{-1} for $Ta_2O_5(c)$ and combine with $S°_{298}$ = 34.2 from Kelley and King[12] to obtain the $\Delta G_f°$ given in Table III.

Greenberg, Natke, and Hubbard[85] have determined $\Delta H_f°$ = −455.0 kcal mol^{-1} for $TaF_5(c)$ by means of fluorine bomb calorimetry. We follow these workers in taking $S°_{298}$ = (41) cal deg^{-1} mol^{-1} for $TaF_5(c)$ and thence obtain the $\Delta G_f°$ given in Table III. The vapor pressure data of Fairbrother and Frith[88] do not permit calculation of $\Delta H°$ and $\Delta S°$ of sublimation of $TaF_5(c)$, but do suggest that $TaF_5(c)$ is slightly more volatile than NbF_5, thus permitting us to estimate the properties given in Table III for $TaF_5(g)$.

For $TaCl_5(c)$ we have $\Delta H_f°$ = −205.5 kcal mol^{-1} from the heat of combination of the elements[90] and $\Delta H_f°$ = −205.0 kcal mol^{-1} from solution calorimetry.[120] In their discussion of the thermodynamic properties of several tantalum chlorides, Kurbanov, Suvorov, Shchukarev, and Novikov[121] cite $\Delta H_f°$ = −206.0 kcal mol^{-1} derived from the heat of reaction of $TaCl_5(c)$ with water. The first of these values appears to be the most certain and we therefore adopt $\Delta H_f°$ = −205.5 kcal mol^{-1} for $TaCl_5(c)$. Our tabulated properties of $TaCl_5(g)$ are based on results of several investigations of vapor pressures and estimated entropies.[2,120–122]

For $TaCl_4(c)$ we have $\Delta H_f°$ = −168.8 kcal mol^{-1} from Schäfer and Kahlenberg.[122] Another investigation[121] has led to a reported $\Delta H_f°$ = −172.6 kcal mol^{-1}. On the basis of these values and our recalculations using our adopted $\Delta H_f°$ for $TaCl_5$, we adopt $\Delta H_f°$ = −170 kcal mol^{-1} for $TaCl_4(c)$ and combine with an estimated[122] $S°_{298}$ = (46) cal deg^{-1} mol^{-1} to obtain our tabulated $\Delta G_f°$. We combine these values for $TaCl_4(c)$ with $\Delta H°$ = 31 kcal mol^{-1} and $\Delta S°$ = 43 cal deg^{-1} mol^{-1} for sublimation[121,122] to obtain the thermodynamic properties of $TaCl_4(g)$.

Calorimetric and equilibrium data[97,121–123] for $TaCl_3(c)$ are not entirely consistent with our adopted thermodynamic properties of $TaCl_5$ and $TaCl_4$. Because of uncertainties about homogeneity ranges and composition of solids, particularly in the high-temperature equilibrium work, we weigh the calorimetric results most heavily in tentatively adopting the properties of $TaCl_3(c)$ shown in Table III.

Although some data have been reported[97,121] for $TaCl_2$ and $TaCl_{2.5}$, we do not tabulate thermodynamic properties for these substances.

Schäfer and Sibbing[124] have reported $\Delta H°_{298}$ = 101.3 kcal mol^{-1} and $\Delta S°_{298}$ = 98 cal deg^{-1} mol^{-1} of Ta_2O_5 for the reaction

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$$Ta_2O_5(c) + 3TaCl_5(g) = 5TaOCl_3(g)$$

We use these values with our tabulated thermodynamic properties of $Ta_2O_5(c)$ and $TaCl_5(g)$ to obtain $\Delta H_f° = -187$ kcal mol^{-1} and $S°_{298} = 87$ cal deg^{-1} mol^{-1} for $TaOCl_3(g)$. No vapor pressure data are available to use in calculating the thermodynamic properties of $TaOCl_3(c)$, so we estimate them on the basis of the thermodynamics of sublimation of $NbOCl_3(c)$.

Calorimetric data from Smirnova, Vasil'kova, and Kudryashova[107] for reactions of type

$$TaCl_5(c) + MCl(c) = MTaCl_6(c)$$

have been used with our adopted $\Delta H_f°$ for $TaCl_5(c)$ and $\Delta H_f°$ values for the alkali chlorides[2] to yield the $\Delta H_f°$ values given in Table III for $MTaCl_6(c)$ compounds. The $\Delta H_f°$ so obtained for $KTaCl_6(c)$ differs considerably from a less certain value that can be calculated from high-temperature decomposition pressure data.[104]

We adopt $\Delta H_f° = -143.0$ kcal mol^{-1} for $TaBr_5(c)$ from the calorimetric measurements of Gross, Hayman, Levi, and Wilson,[74] who cite another investigation leading to a more negative value. Vapor pressure data[101,125] and our estimated ΔC_p lead to $\Delta H°_{298} = 27$ kcal mol^{-1} and $\Delta S°_{298} = 47$ cal deg^{-1} mol^{-1} for sublimation of $TaBr_5(c)$. We combined this $\Delta H°_{298}$ with the adopted $\Delta H_f°$ for $TaBr_5(c)$ to obtain $\Delta H_f°$ for $TaBr_5(c)$, and have also estimated entropies to be consistent with the $\Delta S°_{298}$ of sublimation. Free energies are calculated from the $\Delta H_f°$ and $S°_{298}$ values.

For $TaI_5(c)$ we have vapor pressure data from Alexander and Fairbrother,[126] but no other data with which to calculate thermodynamic properties for Table III.

Heat of combustion measurements by Mah[80] lead to $\Delta H_f° \cong -65$ kcal mol^{-1} for $Ta_2N(c)$, while similar measurements by Mah and Gellert[108] lead to $\Delta H_f° = -60$ kcal mol^{-1} for TaN(c). No free energy or entropy data are available, but an estimated[108] $S°_{298} = (10)$ cal deg^{-1} mol^{-1} for TaN(c) permits calculation of its $\Delta G_f°$.

Heats of combustion[119,127] and high-temperature equilibrium data[65] are in good agreement with $\Delta H_f° = -35.5$ kcal mol^{-1} for TaC(c), for which we also have high-temperature heat content data.[128] The high-temperature equilibrium data[65] indicate that $S°_{298} = 9.7$ cal deg^{-1} mol^{-1} for TaC(c) rather than 10.1 cal deg^{-1} mol^{-1} from low-temperature heat capacity data.[12] For $Ta_2C(c)$ we have only $\Delta H_f° \cong -47$ kcal mol^{-1} from heats of combustion.[119]

We have $\Delta H_f° = -43.9$ kcal mol^{-1} for $TaB_{1.919}(c)$ from fluorine combustion calorimetry by Johnson, Greenberg, Margrave, and Hubbard,[113] who also list $S°_{298} = 10.57$ cal deg^{-1} mol^{-1} for "TaB_2"(c) and $\Delta G_f° = -43$ kcal mol^{-1} for $TaB_{1.919}(c)$.

Data for the tantalum–hydrogen system have been reported in two recent papers,[67,129] in which earlier results are reviewed.

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