

THERMOCHEMISTRY AND OXIDATION POTENTIALS OF VANADIUM, NIOBIUM, AND TANTALUM

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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 500² 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 (\sim) 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 $\Delta G^\circ = RT \ln K = -nFE^\circ$.

We have reserved the symbols E° 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 ΔG° , ΔH° , and ΔS° 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°) 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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(1) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(2) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(3) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(4) R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, **68**, 229 (1968).

(5) G. N. Lewis and M. Randall (revised by K. S. Pitzer and L. Brewer), "Thermodynamics," McGraw-Hill, New York, N. Y., 1961.

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 Ingraham⁶ 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 reviews⁸⁻¹⁰ 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 available⁷⁻¹¹ points toward the decavanadates as being considerably more important.

(6) M. Taniguchi and T. R. Ingraham, *Can. J. Chem.*, **42**, 2467 (1964).

(7) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(8) P. Souchay, *Pure Appl. Chem.*, **6**, 61 (1963).

(9) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 280 (1964).

(10) M. T. Pope and B. W. Dale, *Quart. Rev., Chem. Soc.*, **22**, 527 (1968).

(11) A. W. Naumann and C. J. Hallada, *Inorg. Chem.*, **3**, 70 (1964).

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 non-oxidizing 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 $S_{298}^\circ = 7.02 \pm 0.10$ cal deg⁻¹ mol⁻¹. A later review¹³ gives $S_{298}^\circ = 6.79 \pm 0.10$ cal deg⁻¹ mol⁻¹, which is the value we adopt for Table I. Vapor pressure data have led¹³ 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 500² after adjustment for the newer ΔH_f° for V(g).

(11a) W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc. A*, 1066 (1969).

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

(13) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," Wiley, New York, N. Y., 1963.

Our tabulated ΔH_f° values for VO(c), V₂O₃(c), VO₂(c), and V₂O₅(c) are based on results of combustion measurements by Mah and Kelley.¹⁴ We adopt S°_{298} values for these oxides from Kelley and King¹² and combine with ΔH_f° values to obtain our tabulated ΔG_f° values. Other ΔH_f° values that appear to have larger uncertainties have been reported.¹⁵⁻¹⁹

The ΔH_f° data from the work of Mah and Kelley¹⁴ are in satisfactory agreement with ΔH°_{298} for

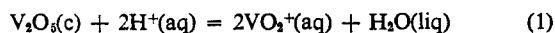


that was derived by Spencer and Justice²⁰ from results of high-temperature equilibrium measurements.

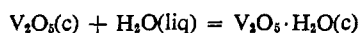
The thermodynamic properties we tabulate for V₆O₁₃(c) were estimated by Mah.²¹

Yannopoulos²² has carried out high-temperature investigations of reaction of V₂O₅ with H₂O and reports evidence and thermodynamic data for VO(OH)₃(g). He also questions earlier reports of more complex species, such as V₂O₅(OH)₄(g).

Solubility measurements by LaSalle and Cobble²³ lead to $\Delta G^\circ = 1.87 \text{ kcal mol}^{-1}$ for



We use this value with ΔG_f° for V₂O₅(c) from Table I to calculate $\Delta G_f^\circ = -140.4 \text{ kcal mol}^{-1}$ for pervanadyl ion represented by VO₂⁺(aq). LaSalle and Cobble²³ also observed that solubilities of V₂O₅(c) and V₂O₅·H₂O(c) are approximately the same and concluded that $\Delta G^\circ \cong 0$ for



We have used $\Delta G^\circ = 0$ for this reaction with our estimated entropy for V₂O₅·H₂O(c) in calculating ΔG_f° and ΔH_f° for this latter compound.

LaSalle and Cobble²³ have also reported $\Delta H^\circ = -5.78 \text{ kcal mol}^{-1}$ for the solution reaction represented by eq 1, but we adopt $\Delta H^\circ = -8.4 \text{ kcal mol}^{-1}$ from more recent calorimetric measurements.²⁴ This latter ΔH° leads to $\Delta H_f^\circ = -155.3 \text{ kcal mol}^{-1}$ and $S^\circ = -9.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for VO₂⁺(aq).

Although free energies of various other V(V) aqueous species can be calculated from the above ΔG_f° of VO₂⁺(aq) and appropriate equilibrium constants, we have not tabulated such ΔG_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 Hepler²⁵ have led to $\Delta H_f^\circ = -251.7 \text{ kcal mol}^{-1}$ for NH₄VO₃(c), often named ammonium metavanadate, and to $\Delta H_f^\circ = -274.2 \text{ kcal mol}^{-1}$ for NaVO₃(c). Earlier calorimetric measurements by Koehler²⁶ led her to report $\Delta H_f^\circ = -274.9 \text{ kcal mol}^{-1}$ for NaVO₃(c). Recalculation of her results with the most recent ΔH_f° for V₂O₅(c) from Table I leads to $\Delta H_f^\circ = -273.7 \text{ kcal mol}^{-1}$. We adopt the average ΔH_f° for NaVO₃(c) and combine with the entropy²⁷ to obtain the ΔG_f° we also list in Table I.

Koehler²⁶ has also made calorimetric measurements on Na₃VO₄(c) and Na₄V₂O₇(c), often called sodium orthovanadate and sodium pyrovanadate. We recalculate her results in terms of the new ΔH_f° for V₂O₅(c) to obtain the ΔH_f° values given in Table I. These ΔH_f° values have been combined with entropies from King and Weller²⁷ to yield the ΔG_f° values in Table I.

Measurements carried out in the Bureau of Mines Laboratories have provided ΔH_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 ΔH_f° values for CaV₂O₆(c), Ca₂V₂O₇(c), and Ca₃V₂O₈(c) from work of King, Koehler, and Adami,²⁸ while entropies for these compounds are from King and Weller.²⁹ The ΔH_f° and S°_{298} values lead to the tabulated ΔG_f° values for these compounds. King, Koehler, and Adami²⁸ have also reported ΔH_f° values for Mg₂V₂O₆(c) and Mg₃V₂O₇(c), which are combined with the entropies of these compounds from Weller and King³⁰ to give the ΔG_f° values listed in Table I.

Calorimetric measurements by Barany³¹ lead to $\Delta H_f^\circ = -453.8 \text{ kcal mol}^{-1}$ for ferrous vanadate, FeV₂O₆(c). We know of no experimental entropy for this compound, but note that Mah²¹ has cited a ΔG_f° value along with the ΔH_f° above. These values correspond to $S^\circ = (47) \text{ cal deg}^{-1} \text{ mol}^{-1}$, which we also adopt.

We take ΔH_f° values for Pb₂V₂O₇(c), Pb₃V₂O₈(c), and MnV₂O₆(c) from the calorimetric measurements of Kelley, Adami, and King.³² We also adopt their estimated entropies for these compounds and combine with the ΔH_f° values to obtain the approximate ΔG_f° values in Table I. Yokokawa and Kleppa^{32a} have also reported data for lead vanadates.

For VOF₃(c) Trevorrow³³ 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.

(14) A. D. Mah and K. K. Kelley, U. S. Bureau of Mines Report of Investigations No. 5858, U. S. Government Printing Office, Washington, D. C., 1961.

(15) L. Brewer, *Chem. Rev.*, **52**, 1 (1953).

(16) N. P. Allen, O. Kubaschewski, and O. von Goldbeck, *J. Electrochem. Soc.*, **98**, 417 (1951).

(17) E. Vol'f and S. M. Ariya, *Zh. Obshch. Khim.*, **29**, 2470 (1959).

(18) Yu. M. Golutin and T. M. Kozlovskaya, *Zh. Fiz. Khim.*, **34**, 2350 (1960).

(19) M. P. Morozova and G. Eger, *Zh. Obshch. Khim.*, **30**, 3514 (1960).

(20) H. M. Spencer and J. L. Justice, *J. Amer. Chem. Soc.*, **56**, 2306 (1934).

(21) A. D. Mah, U. S. Bureau of Mines Report of Investigations No. 6727, U. S. Government Printing Office, Washington, D. C., 1966.

(22) L. N. Yannopoulos, *J. Phys. Chem.*, **72**, 3293 (1968).

(23) M. J. LaSalle and J. W. Cobble, *ibid.*, **59**, 519 (1955).

(24) G. L. Bertrand, G. W. Stapleton, C. A. Wulff, and L. G. Hepler, *Inorg. Chem.*, **5**, 1283 (1966).

(25) G. L. Bertrand and L. G. Hepler, *J. Chem. Eng. Data*, **12**, 412 (1967).

(26) M. F. Koehler, U. S. Bureau of Mines Report of Investigations No. 5700, U. S. Government Printing Office, Washington, D. C., 1960.

(27) E. G. King and W. W. Weller, U. S. Bureau of Mines Report of Investigations No. 5715, U. S. Government Printing Office, Washington, D. C., 1961.

(28) E. G. King, M. F. Koehler, and L. H. Adami, U. S. Bureau of Mines Report of Investigations No. 6049, U. S. Government Printing Office, Washington, D. C., 1962.

(29) E. G. King and W. W. Weller, U. S. Bureau of Mines Report of Investigations No. 5954, U. S. Government Printing Office, Washington, D. C., 1961.

(30) W. W. Weller and E. G. King, U. S. Bureau of Mines Report of Investigations No. 6130, U. S. Government Printing Office, Washington, D. C., 1962.

(31) R. Barany, U. S. Bureau of Mines Report of Investigations No. 6618, U. S. Government Printing Office, Washington, D. C., 1965.

(32) K. K. Kelley, L. H. Adami, and E. G. King, U. S. Bureau of Mines Report of Investigations No. 6197, U. S. Government Printing Office, Washington, D. C., 1963.

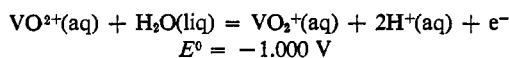
(32a) T. Yokokawa and O. J. Kleppa, *Inorg. Chem.*, **3**, 954 (1964).

(33) L. E. Trevorrow, *J. Phys. Chem.*, **62**, 362 (1958).

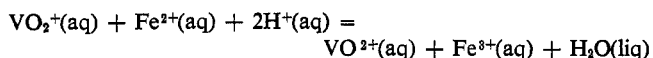
Heat of solution measurements³⁴ have led to a reported $\Delta H_f^\circ = -177.2 \text{ kcal mol}^{-1}$ for $\text{VOCl}_3(\text{liq})$. Mah²¹ has adjusted this value to conform to the same ΔH_f° for $\text{V}_2\text{O}_5(\text{c})$ we have adopted and has thereby obtained $\Delta H_f^\circ = -176.0 \text{ kcal mol}^{-1}$ for $\text{VOCl}_3(\text{liq})$. We adopt this value rather than the value cited earlier in NBS Circular 500.² Vapor pressure data³⁵ for $\text{VOCl}_3(\text{liq})$ lead to $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ values in fair agreement with older values.² Combination of these data with S°_{298} for $\text{VOCl}_3(\text{g})$ calculated^{12,36} from molecular constants leads to the values listed in Table I.

Cavell and Clark³⁷ have measured the heat of hydrolysis and reported $\Delta H_f^\circ = -352 \pm 4 \text{ kcal mol}^{-1}$ for $\text{VF}_5(\text{liq})$. Because the calorimetric reaction was ill-defined and auxiliary thermodynamic data for V(V) in alkaline solution² are uncertain, the derived ΔH_f° value is quite uncertain. Results of two investigations³⁸ of vapor pressure at several temperatures are in reasonable agreement on $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ of $\text{VF}_5(\text{liq})$. These values and the approximate ΔH_f° cited above for $\text{VF}_5(\text{liq})$ are combined with the S°_{298} for $\text{VF}_5(\text{g})$ calculated³⁹ from molecular constants to yield the thermodynamic properties of $\text{VF}_5(\text{liq})$ and $\text{VF}_5(\text{g})$ listed in Table I. The high entropy of vaporization suggests that VF_5 is an associated liquid.

Electrochemical measurements by Carpenter⁴⁰ and Coryell and Yost⁴¹ led Latimer³ to adopt the following potential for the vanadyl|pervanadyl couple.



We combine this potential with the ΔG_f° for $\text{VO}_2^+(\text{aq})$ to obtain $\Delta G_f^\circ = -106.8 \text{ kcal mol}^{-1}$ for $\text{VO}^{2+}(\text{aq})$. Results of three investigations⁴²⁻⁴⁴ of the equilibrium constant for the reaction



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

A calorimetric determination²⁴ of the heat of reduction of aqueous pervanadyl to vanadyl leads to $\Delta H^\circ = -166.4 \text{ kcal mol}^{-1}$ for $\text{VO}^{2+}(\text{aq})$. For this calculation we have taken $\Delta H_f^\circ(\text{Fe}^{3+}) - \Delta H_f^\circ(\text{Fe}^{2+}) = 9.7 \text{ kcal mol}^{-1}$ from the recent NBS Technical Note 270-4.⁴⁵ The ΔH° derived from the temperature coefficient of the $\text{VO}^{2+}|\text{VO}_2^+$ potential^{40,41} also leads to $\Delta H_f^\circ = -116.4 \text{ kcal mol}^{-1}$ for $\text{VO}^{2+}(\text{aq})$, 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 $-119 \text{ kcal mol}^{-1}$,

(34) I. L. Perfilova, I. V. Kozlova, S. A. Shchukarev, and I. V. Vasil'kova, *Vestn. Leningrad Univ., Fiz. Khim.*, No. 3, 130 (1961); *Chem. Abstr.*, **56**, 1010d (1962).

(35) A. V. Komandin and M. L. Vlodayets, *Zh. Fiz. Khim.*, **26**, 1291 (1952); *Chem. Abstr.*, **47**, 5751i (1953).

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(37) R. G. Cavell and H. C. Clark, *Trans. Faraday Soc.*, **59**, 2706 (1963).

(38) L. E. Trevorrow, J. Fischer, and R. K. Steuenberg, *J. Amer. Chem. Soc.*, **79**, 5167 (1957); H. C. Clark and H. J. Emeleus, *J. Chem. Soc.*, 2119 (1957).

(39) B. Vizi and J. Brunvoll, *Acta Chem. Scand.*, **22**, 1279 (1968).

(40) J. E. Carpenter, *J. Amer. Chem. Soc.*, **56**, 1847 (1934).

(41) C. D. Coryell and D. M. Yost, *ibid.*, **55**, 1909 (1933).

(42) J. Kentamaa, *Suomen Kemistilehti*, **31B**, 273 (1958).

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

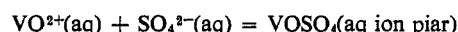
(44) D. R. Rosseinsky and M. J. Nicol, *Electrochim. Acta*, **11**, 1069 (1966).

(45) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-4, U. S. Government Printing Office, Washington, D. C., 1969.

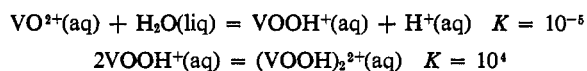
while a heat of hydrolysis of $\text{VCl}_4(\text{liq})$ leads to a reported⁴⁶ $\Delta H_f^\circ = -113 \text{ kcal mol}^{-1}$ for $\text{VO}^{2+}(\text{aq})$.

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

Several investigations^{7,47-49} provide strong evidence that the hydrolysis of $\text{VO}^{2+}(\text{aq})$ occurs in stepwise fashion with $\text{VOOH}^+(\text{aq})$ 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 Rossotti⁴⁷ 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. Meites⁴⁸ and more recently Khan and Martell⁴⁹ have reported equilibrium constants based on measurements on dilute solutions of vanadyl sulfate. In addition to assumptions that Meites⁴⁸ has correctly stated are involved in calculating K values from experimental data, both investigators implicitly assumed that association of $\text{VO}^{2+}(\text{aq})$ with $\text{SO}_4^{2-}(\text{aq})$ is negligible. Since Strehlow and Wendt⁵⁰ have reported $K = 3.0 \times 10^2$ for



it is clear that further measurements and calculations are desirable. In spite of some uncertainties, we largely follow Khan and Martell⁴⁹ in adopting the following equilibrium constants and the approximate ΔG_f° values cited in Table I.



Although equilibrium constants were also reported⁴⁹ 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° values for $\text{VOOH}^+(\text{aq})$ and $(\text{VOOH})_2^{2+}(\text{aq})$.

For $\text{VF}_4(\text{c})$ we have only $\Delta H_f^\circ = -321 \text{ kcal mol}^{-1}$ from Cavell and Clark.³⁷ Mah²¹ has estimated other thermodynamic properties for this compound.

Gross and Hayman⁵¹ have reported $\Delta H_f^\circ = -136.2 \text{ kcal mol}^{-1}$ for $\text{VCl}_4(\text{liq})$, based on their calorimetric measurements. Nagarajan⁵² has used molecular constants in calculating $S_{298}^\circ = 94.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for $\text{VCl}_4(\text{g})$, while Mah²¹ has obtained $S_{298}^\circ = 86.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ by a similar calculation. We adopt the latter value. On the basis of several investigations of vapor pressures of $\text{VCl}_4(\text{liq})$ that are cited in NBS Circular 500² and by Mah,²¹ we adopt $\Delta H^\circ_{\text{vap}} = 10 \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{\text{vap}} = 23 \text{ cal deg}^{-1} \text{ mol}^{-1}$. Values cited in this paragraph lead to the other thermodynamic properties for $\text{VCl}_4(\text{liq})$ and $\text{VCl}_4(\text{g})$ listed in Table I.

Mah²¹ has derived $\Delta H_f^\circ = -100 \pm 2 \text{ kcal mol}^{-1}$ for $\text{VBr}_4(\text{g})$, based on $\Delta H_f^\circ = 0$ for $\text{Br}_2(\text{g})$, from earlier equilibrium investigations and properties of $\text{VBr}_3(\text{c})$ and $\text{VBr}_2(\text{c})$ discussed later in this paper. We adopt $\Delta H_f^\circ \cong -85 \text{ kcal mol}^{-1}$ for $\text{VBr}_4(\text{g})$, based on the usual¹⁻⁸ choice of $\Delta H_f^\circ = 0$ for $\text{Br}_2(\text{liq})$. It should be noted that Mah's choice²¹ of $\text{Br}_2(\text{g})$, and also $\text{I}_2(\text{g})$, as standard state is often the most convenient choice for purposes of high-temperature work relevant to vanadium metallurgy.

(46) R. G. Cavell and H. C. Clark, *J. Chem. Soc.*, 3890 (1963).

(47) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(48) L. Meites, *J. Amer. Chem. Soc.*, **75**, 6059 (1953).

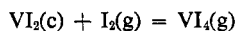
(49) M. M. T. Khan and A. E. Martell, *ibid.*, **90**, 6011 (1968).

(50) H. Strehlow and H. Wendt, *Inorg. Chem.*, **2**, 6 (1963).

(51) P. Gross and C. Hayman, *Trans. Faraday Soc.*, **60**, 45 (1964).

(52) G. Nagarajan, *Bull. Soc. Chim. Belg.*, **72**, 346 (1963).

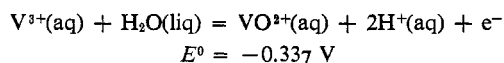
Berry, Smardzewski, and McCarley⁵³ have carried out high-temperature equilibrium investigations of the reaction



and derived $\log K$, ΔH° , and ΔS° 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 ΔH° with crude estimates and the ΔH_f° for $\text{VI}_2(\text{c})$ cited later to obtain $\Delta H_f^\circ \cong -31 \text{ kcal mol}^{-1}$ for $\text{VI}_4(\text{g})$, based on $\Delta H_f^\circ = 0$ for $\text{I}_2(\text{c})$.

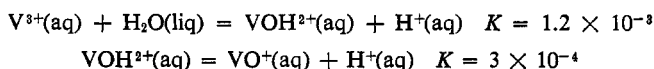
High-temperature equilibrium investigations by Flood and Kleppa⁵⁴ provide data that permit us to calculate our tabulated ΔG_f° , ΔH_f° , and S°_{298} values for $\text{VO}_2(\text{c})$. For these calculations we have used the properties of $\text{VO}_2(\text{c})$ from Table I, although Flood and Kleppa⁵⁴ were apparently working with a different crystal form having unknown thermodynamic properties. Their data also provide support for the properties of $\text{V}_2\text{O}_5(\text{c})$ and $\text{VO}_2(\text{c})$ in Table I, along with information relevant to the contact process for sulfuric acid.

Jones and Colvin⁵⁵ have determined the following potential.



We combine this potential with our ΔG_f° for $\text{VO}^{2+}(\text{aq})$ to obtain $\Delta G_f^\circ = -57.9 \text{ kcal mol}^{-1}$ for $\text{V}^{3+}(\text{aq})$. Since Jones and Colvin⁵⁵ also determined the potential for the above couple at 0°, we are able to calculate the approximate ΔH_f° and \bar{S}_2° values listed for $\text{V}^{3+}(\text{aq})$ in Table I. These latter values must be accepted with some reservations for two reasons. First, all uncertainties in the data for $\text{VO}^{2+}(\text{aq})$ are carried directly into the tabulated values for $\text{V}^{3+}(\text{aq})$. Second, heats and entropies calculated from temperature derivatives based on data at only two temperatures are notoriously and deservedly suspect.

Meites⁴⁸ has calculated the following equilibrium constants for hydrolysis of $\text{V}^{3+}(\text{aq})$.



In spite of uncertainties in these values due to association of $\text{V}^{3+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ and approximations already cited,⁴⁸ these values permit calculation of approximate ΔG_f° values for $\text{VOH}^+(\text{aq})$ and $\text{VO}^+(\text{aq})$. Here it should be emphasized that $\text{VO}^+(\text{aq})$ is only the simplest formula for this ion. A more realistic formula might well contain one or more H_2O units, with ΔG_f° correspondingly adjusted. It is also relevant to note that Newton and Baker⁵⁶ have reported kinetic evidence for a hydrolytic dimer of $\text{V}(\text{III})$ that may be similar to the more familiar dimer of $\text{Fe}(\text{III})$.

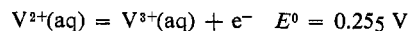
Other investigators^{57,58} have reported hydrolysis constants in reasonable agreement with values given above. Constants at different temperatures⁵⁷ permit estimates of ΔH and ΔS of hydrolysis in solutions with 1.0 *M* ionic strength but are not adequate for calculation of standard thermodynamic properties of the hydrolysis products.

Mrazek, Richardson, Poppleton, and Block⁵⁹ have employed solution calorimetry in determining $\Delta H_f^\circ = -138.9 \text{ kcal mol}^{-1}$ for $\text{VCl}_3(\text{c})$ and have also reviewed earlier values ranging from -134 to $-187 \text{ kcal mol}^{-1}$. We combine S°_{298} from Kelley and King¹² with the above ΔH_f° to obtain the ΔG_f° in Table I.

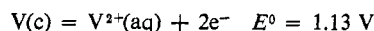
Mah²¹ has calculated $\Delta H_f^\circ = -117 \text{ kcal mol}^{-1}$ for $\text{VBr}_3(\text{c})$ from results of an earlier calorimetric investigation. This value is based on $\Delta H_f^\circ = 0$ for $\text{Br}_2(\text{g})$, so we use the heat of vaporization of bromine¹ to calculate $\Delta H_f^\circ = -106 \text{ kcal mol}^{-1}$ for $\text{VBr}_3(\text{c})$, based on $\text{Br}_2(\text{liq})$ standard state. We estimate S°_{298} and combine with this latter ΔH_f° to obtain the ΔG_f° for $\text{VBr}_3(\text{c})$ listed in Table I.

Mah²¹ has calculated $\Delta H_f^\circ = -88 \pm 2 \text{ kcal mol}^{-1}$ for $\text{VI}_3(\text{c})$ from results of earlier calorimetric data. We have concluded from reconsideration of these data and also more recent high-temperature equilibrium data⁵⁵ that $\Delta H_f^\circ = -87 \text{ kcal mol}^{-1}$ (based on $\text{I}_2(\text{g})$ standard state) best satisfies all the available data. We combine this value with the heat of sublimation of iodine¹ to obtain $\Delta H_f^\circ = -65 \text{ kcal mol}^{-1}$ for $\text{VI}_3(\text{c})$, based on $\Delta H_f^\circ = 0$ for $\text{I}_2(\text{c})$. We combine this ΔH_f° with our estimated S°_{298} to obtain the tabulated ΔG_f° .

Jones and Colvin⁶⁰ have reported the following potential.



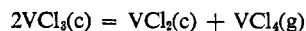
We use this potential with the ΔG_f° of $\text{V}^{3+}(\text{aq})$ to obtain $\Delta G_f^\circ = -52.0 \text{ kcal mol}^{-1}$ for $\text{V}^{2+}(\text{aq})$ and thence calculate the new potential.



Jones and Colvin⁶⁰ have also reported E^0 for the $\text{V}^{2+}|\text{V}^{3+}$ couple at 0°, which permits us to calculate the approximate ΔH_f° and \bar{S}_2° values for $\text{V}^{2+}(\text{aq})$ given in Table I.

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

Mah²¹ has described calculations with high-temperature equilibrium data for reduction of $\text{VCl}_2(\text{c})$ with $\text{H}_2(\text{g})$ and from two different calculations has obtained $\Delta H_f^\circ = -110$ and $-101 \text{ kcal mol}^{-1}$ for $\text{VCl}_2(\text{c})$, without any clear evidence as to which is the "best" value. Mah²¹ has also derived $\Delta H^\circ_{298} = 43 \text{ kcal mol}^{-1}$ of VCl_2 for



from results of high-temperature vapor pressure measurements. We use this ΔH°_{298} with ΔH_f° values from Table I to obtain $\Delta H_f^\circ = -109 \text{ kcal mol}^{-1}$ for $\text{VCl}_2(\text{c})$. On the basis of earlier calorimetric data, NBS Circular 500² adopted $\Delta H_f^\circ = -108 \text{ kcal mol}^{-1}$. Although the uncertainty is presently rather large, we adopt $\Delta H_f^\circ = -109 \text{ kcal mol}^{-1}$ for $\text{VCl}_2(\text{c})$ and combine with its S°_{298} from Kelley and King¹² to obtain the ΔG_f° in Table I.

Mah²¹ has obtained $\Delta H_f^\circ = -93 \pm 2 \text{ kcal mol}^{-1}$ for $\text{VBr}(\text{c})$ from the ΔH_f° of $\text{VBr}(\text{c})$ and high-temperature equilibrium data. We use this value, based on $\text{Br}_2(\text{g})$ standard state, to obtain $\Delta H_f^\circ = -86 \text{ kcal mol}^{-1}$ for $\text{VBr}_2(\text{c})$, based

(53) K. O. Berry, R. R. Smardzewski, and R. E. McCarley, *Inorg. Chem.*, **8**, 1994 (1969).

(54) H. Flood and O. J. Kleppa, *J. Amer. Chem. Soc.*, **69**, 998 (1947).

(55) G. Jones and J. H. Colvin, *ibid.*, **66**, 1563 (1944).

(56) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

(57) S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, **72**, 1785 (1950).

(58) J. Gandeboeuf and P. Souchay, *J. Chim. Phys.*, **56**, 358 (1959).

(59) R. V. Mrazek, D. W. Richardson, H. O. Poppleton, and F. E. Block, U. S. Bureau of Mines Report of Investigations No. 7096, U. S. Government Printing Office, Washington, D. C., 1968.

(60) G. Jones and J. H. Colvin, *J. Amer. Chem. Soc.*, **66**, 1573 (1944).

(61) F. H. Guzzetta and W. B. Hadley, *Inorg. Chem.*, **3**, 259 (1964).

Table I
Thermodynamic Data for Vanadium at 298°K

Substance	ΔH_f° , kcal mol ⁻¹	ΔG_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)	~-54 ⁶⁰	-52.0 ⁶⁰	~-31 ⁶⁰
V ³⁺ (aq)	~-62 ⁶⁵	-57.9 ⁶⁵	~-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 ⁶⁰	
VO ₂ ⁺ (aq)	-155.3 ²⁴	-140.4 ²³	-9.8
VO(c)	-103.2 ¹⁴	-96.6	9.3 ¹³
V ₂ O ₅ (c)	-291.3 ¹⁴	-272.3	23.5 ¹²
VO ₂ (c)	-170.6 ¹⁴	-157.6	12.3 ¹²
V ₆ O ₁₁ (c)	(-1065) ²¹	(-982) ³¹	(80) ²¹
V ₂ O ₅ (c)	-370.6 ¹⁴	-339.4	31.3 ¹²
V ₂ O ₅ ·H ₂ O(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 ₃ (c)	-321 ³⁷	(-299) ³¹	(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)	~-31 ⁵³		
VF ₅ (liq)	~-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 ¹³
V ₂ C(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 ₄ VO ₃ (c)	-251.7 ²⁵	-212.3	33.6 ¹³
NaVO ₃ (c)	-273.9 ^{25,26}	-254.4	27.2 ²⁷
Na ₃ VO ₄ (c)	-419.8 ²⁶	-391.2	45.3 ²⁷
Na ₄ V ₂ O ₇ (c)	-697.2 ²⁶	-650.1	76.1 ²⁷
MgV ₂ O ₆ (c)	-526.2 ²⁸	-487.4	38.4 ³⁰
Mg ₂ V ₂ O ₇ (c)	-677.7 ²⁸	-632.1	47.9 ³⁰
CaV ₂ O ₆ (c)	-556.7 ²⁸	-518.6	42.8 ²⁹
Ca ₂ V ₂ O ₇ (c)	-736.9 ²⁸	-691.5	52.7 ²⁹
Ca ₃ V ₂ O ₈ (c)	-903.0 ²⁸	-851.2	65.7 ²⁹
MnV ₂ O ₆ (c)	-477.9 ²⁹	-441.9	(47.5) ³²
FeV ₂ O ₆ (c)	-453.8 ³¹	-418.1	(47) ²¹
Pb ₂ V ₂ O ₇ (c)	-509.9 ³²	-465.0	(65.5) ³²
Pb ₃ V ₂ O ₈ (c)	-567.7 ³²	-516.5	(84.5) ³²

on Br₂(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 ΔH_f° to yield the tabulated ΔG_f° for VBr₂(c).

(62) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964).

On the basis of data cited by Mah²¹ and more recent measurements by Berry, Smardzewski, and McCarley,⁶³ we adopt the thermodynamic properties listed for VI₂(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^{58,63,64} 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 Chipman⁶⁵ have estimated ΔH_f° and ΔS_f° for VC_{0.73}(c) and V₂C(c) from their high-temperature equilibrium data and phase diagrams for the vanadium-carbon system. These values also lead to the ΔG_f° and S°_{298} values in Table I.

We take ΔH_f° for VN(c) from Mah⁶⁶ and S°_{298} from Kelley and King¹² to obtain the ΔG_f° listed in Table I.

Veleckis and Edwards⁶⁷ 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 Jones⁶⁸ 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 Walker⁶⁹ have led to ΔH values for reaction of a number of nitrogen and oxygen donors with vanadyl acetylacetonate in nitrobenzene. Bradley and Hillyer⁷⁰ have determined calorimetrically the ΔH_f° of vanadium tetra-*tert*-butoxide. Popp, Nelson, and Ragsdale⁷¹ 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

(63) R. E. McCarley, J. W. Roddy, and K. O. Berry, *ibid.*, **3**, 50 (1964).

(64) R. E. McCarley and J. W. Roddy, *ibid.*, **3**, 60 (1964).

(65) W. L. Worrell and J. Chipman, *J. Phys. Chem.*, **68**, 860 (1964).

(66) A. D. Mah, U. S. Bureau of Mines Report of Investigations No. 6177, U. S. Government Printing Office, Washington, D. C., 1963.

(67) E. Veleckis and R. K. Edwards, *J. Phys. Chem.*, **73**, 683 (1969).

(68) R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Amer. Chem. Soc.*, **83**, 1073 (1961).

(69) R. L. Carlin and F. A. Walker, *ibid.*, **87**, 2128 (1965).

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

(71) C. J. Popp, J. H. Nelson, and R. O. Ragsdale, *J. Amer. Chem. Soc.*, **91**, 610 (1969).

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 Dale¹⁰ have reviewed most investigations of isopolyniobates and cite extensive evidence for hexameric $\text{Nb}_6\text{O}_{19}^{8-}$ (aq) as the principal anionic species in alkaline solution. Equilibrium quotients referring to 3 M KCl solutions have been reported¹⁰ for protonation of $\text{Nb}_6\text{O}_{19}^{8-}$ (aq) to $\text{HNb}_6\text{O}_{19}^{7-}$ (aq) and $\text{H}_2\text{Nb}_6\text{O}_{19}^{6-}$ (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 $S^\circ_{298} = 8.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for Nb(c) based on heat capacity data from Clusius, Franzosini, and Piesbergen.⁷² High-temperature vapor pressure data led Speiser, Blackburn, and Johnston⁷³ to report $\Delta H^\circ_{298} = 172.5 \text{ kcal mol}^{-1}$ for sublimation of Nb(c). Although it has been noted⁷⁴ that a different treatment of the data leads to a considerably larger value for this heat of sublimation, we adopt $\Delta H^\circ_f = 172.5 \text{ kcal mol}^{-1}$ for Nb(g) and combine with its $S^\circ_{298} = 44.49 \text{ cal deg}^{-1} \text{ mol}^{-1}$ from Kelley and King¹² to obtain the ΔG°_f given in Table II.

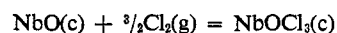
Subsequent to early determinations of relatively low accuracy, we have the following calorimetric ΔH°_f values (kcal mol^{-1}) for Nb_2O_5 (c): -455.2 from Humphrey,⁷⁵ -454.4 from Huber, Head, Holley, Storms, and Krikorian,⁷⁶ -455.1 from Kusenko and Geld,⁷⁷ -454.8 from Morozova and Stolyarova,⁷⁸ and -453.5 from Kornilov, Leonidov, and Skuratov.⁷⁹ We adopt $\Delta H^\circ_f = -454.4 \text{ kcal mol}^{-1}$ for Nb_2O_5 (c) and combine with its $S^\circ_{298} = 32.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$ from Kelley and King¹² to obtain the ΔG°_f given in Table II.

Table II
Thermodynamic Data for Niobium at 298°K

Substance	ΔH°_f , kcal mol ⁻¹	ΔG°_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 ₂ O ₅ (c)	-454.5 ⁷⁵⁻⁷⁹	-422.6	32.8 ¹²
Nb ₂ O ₅ (hyd ppt)	-479 ^{89a}		
NbF ₅ (c)	-433.5 ⁸⁵	-406.1	38 ⁸⁶
NbF ₃ (g)	~-414	~-400	84 ⁸⁷
NbCl _{2.38} (c)	-114 ⁹⁷	-102	(31) ⁹⁷
NbCl _{2.67} (c)	-129 ⁹⁷	-115	(33) ⁹⁷
"NbCl ₃ "(c)	-140 ⁹⁷	-124	(35)
NbCl _{2.13} (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 ₃ (c)	-190.5 ^{92,93}	-163.2	50.4 ⁹⁶
NbCl ₃ (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 ⁸²		
NbOCl ₂ (g)	-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 ₂ N(c)	-60.4 ⁸⁰		
NbN(c)	-56.4 ¹⁰⁸	-49.7	(9) ¹²
Nb ₂ C(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 Mah⁸⁰ and from Morozova and Getskina⁸¹ with our adopted ΔH°_f of Nb_2O_5 (c) to obtain $\Delta H^\circ_f = -190.6$ and $-190.2 \text{ kcal mol}^{-1}$ for NbO_2 (c). High-temperature equilibrium data from Worrell⁸² lead us to $\Delta H^\circ_f = -190.4 \text{ kcal mol}^{-1}$ 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 $\Delta H^\circ_f = -190.4 \text{ kcal mol}^{-1}$ and combine with $S^\circ = 13.03 \text{ cal deg}^{-1} \text{ mol}^{-1}$ from Kelley and King¹² to obtain its ΔG°_f .

We calculate $\Delta H^\circ_f = -99.8 \text{ kcal mol}^{-1}$ for NbO(c) from its heat of combustion reported by Morozova and Getskina⁸¹ and our adopted ΔH°_f for Nb_2O_5 (c). We also have $\Delta H^\circ = -113.2 \text{ kcal mol}^{-1}$ of NbO(c) for the reaction



from Schäfer and Liedmeier.⁸⁸ Combination of this ΔH° with ΔH°_f values for NbOCl_3 (c) cited later leads to $\Delta H^\circ_f = -97.0$ and $-98.2 \text{ kcal mol}^{-1}$ for NbO(c). On the basis of these results, we adopt $\Delta H^\circ_f = -98 \text{ kcal mol}^{-1}$ for NbO(c) and combine this value with our estimated S°_{298} to obtain

(72) K. Clusius, P. Franzosini, and U. Piesbergen, *Z. Naturforsch. A*, **15**, 728 (1960).

(73) R. Speiser, P. Blackburn, and H. L. Johnston, *J. Electrochem. Soc.*, **106**, 52 (1959).

(74) P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, *Trans. Faraday Soc.*, **58**, 890 (1962).

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(76) E. J. Huber, E. L. Head, C. E. Holley, E. K. Storms, and N. H. Krikorian, *J. Phys. Chem.*, **65**, 1846 (1961).

(77) F. G. Kusenko and P. V. Geld, *Zh. Obshch. Khim.*, **30**, 3847 (1960); *J. Gen. Chem. USSR*, **30**, 3806 (1960).

(78) M. P. Morozova and T. A. Stolyarova, *Zh. Obshch. Khim.*, **30**, 3848 (1960); *J. Gen. Chem. USSR*, **30**, 3808 (1960).

(79) A. N. Kornilov, V. Y. Leonidov, and S. M. Skuratov, *Dokl. Akad. Nauk SSSR*, **144**, 355 (1962); *Proc. Acad. Sci. USSR*, **144**, 427 (1962).

(80) A. D. Mah, *J. Amer. Chem. Soc.*, **80**, 3872 (1958).

(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).

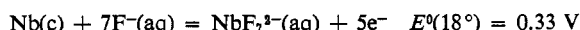
(83) H. Schäfer and F. Liedmeier, *Z. Anorg. Allg. Chem.*, **329**, 225 (1964).

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 Davies⁸⁴ and from earlier workers they cite.

For NbF₅(c) we have $\Delta H_f^\circ = -433.5$ kcal mol⁻¹ from fluorine combustion calorimetry⁸⁵ and $S^\circ_{298} = 38.3$ cal deg⁻¹ mol⁻¹ from heat capacity data.⁸⁶ Statistical mechanical calculations by Nagarajan⁸⁷ have led to $S^\circ_{298} = 84.4$ cal deg⁻¹ mol⁻¹ for NbF₅(g). We calculate $\Delta S^\circ_{298} = 46.1$ cal deg⁻¹ mol⁻¹ for sublimation of NbF₅(c). Fairbrother and Frith⁸⁸ and Junkins, Farrar, Barber, and Bernhardt⁸⁹ have reported vapor pressures, mostly for NbF₅(liq), over a wide range of temperatures. The latter workers⁸⁹ reported $\Delta H = 8.6$ kcal mol⁻¹ for melting of NbF₅(c), while Brady, Myers, and Clauss⁸⁶ 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 NbF₅(liq) with these heats of melting and estimated ΔC_p values leads to $\Delta H = 17$ and 23 kcal mol⁻¹ for sublimation of NbF₅(c). Another calculation in which we combine the third-law ΔS°_{298} cited above with an extrapolated vapor pressure for NbF₅(c) at 298°K leads to $\Delta H = 19$ kcal mol⁻¹ for sublimation of NbF₅(c). The tentative ΔG_f° and ΔH_f° values for NbF₅(g) in Table II are based on this last calculation.

Myers and Brady^{89a} have reported ΔH values for reactions of NbF₅(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 NbF₅(c) is much less certain than the ΔH_f° value⁸⁵ 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 Nb₂O₅·nH₂O. In Table II we list $\Delta H_f^\circ = -479$ kcal mol⁻¹ for Nb₂O₅(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 studies⁹⁰ of solutions of K₂NbO₅·H₂O and K₂NbF₇ have provided evidence for NbOF₅²⁻(aq) and NbF₆⁻(aq), but not for NbF₇²⁻(aq). On the other hand, Haissinsky⁹¹ has interpreted his potentiometric data on similar systems in terms of NbF₇²⁻(aq) and the following half-reaction potential.



Heat of solution data for Nb(c) and NbCl₅(c) have led Schäfer and Kahlenberg⁹² to $\Delta H_f^\circ = -190.4$ kcal mol⁻¹

for NbCl₅(c). Gross, Hayman, Levi, and Wilson⁹³ have measured directly the heat of formation from the elements and have reported $\Delta H_f^\circ = -190.6$ kcal mol⁻¹ for NbCl₅(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 NbCl₅(c). Two other investigations^{94,96} have led to less certain ΔH_f° values that are slightly more negative than those cited above.

Keneshea, Cubicciotti, Withers, and Eding⁹⁶ have made calorimetric ($H_T - H_{298}$) measurements on NbCl₅(c) and NbCl₅(liq) up to 600°K. They have used these data and results of statistical thermodynamic calculations for NbCl₅(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 NbCl₅(c). Their statistical calculations have yielded $S^\circ_{298} = 95.8$ cal deg⁻¹ mol⁻¹ for NbCl₅(g), and thence they have obtained $S^\circ_{298} = 50.4$ cal deg⁻¹ mol⁻¹ for NbCl₅(c). It should be mentioned that this paper⁹⁶ 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 NbCl₅(c) to obtain its ΔG_f° and also both ΔH_f° and ΔG_f° for NbCl₅(g).

Heats of solution of Nb(c) and NbCl₄(c) led Schäfer and Kahlenberg⁹² to $\Delta H_f^\circ = -166.0$ kcal mol⁻¹ for NbCl₄(c). Their analysis of earlier vapor pressure data gave $\Delta H^\circ_{298} = 29.4$ kcal mol⁻¹ for sublimation of NbCl₄(c) and thence $\Delta H_f^\circ = -136.6$ kcal mol⁻¹ for NbCl₄(g). Their $\Delta S^\circ_{298} = 41$ cal deg⁻¹ mol⁻¹ for sublimation of NbCl₄(c) and estimated S°_{298} for NbCl₄(c) leads to S°_{298} for NbCl₄(g) and thence to ΔG_f° values for both NbCl₄(c) and NbCl₄(g).

Schäfer 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 Nb₆Cl₁₄ 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 Nb₆X₁₄·7H₂O (X = Cl or Br) are soluble in water and alcohol, and X-ray investigations⁹⁸ of solutions have shown that there are Nb₆X₁₂²⁺ 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 Wilson⁷⁴ led them to report $\Delta H_f^\circ = -132.85$ kcal mol⁻¹ for NbBr₅(c), which we adopt. This value is in fair agreement with results of two other investigations.^{99,100} Vapor pressure

(84) S. Ignatowicz and M. W. Davies, *J. Less Common Metals*, **15**, 100 (1968).

(85) E. Greenberg, C. A. Natke, and W. N. Hubbard, *J. Phys. Chem.*, **69**, 2089 (1965).

(86) A. P. Brady, O. E. Myers, and J. D. Clauss, *ibid.*, **64**, 588 (1960).

(87) G. Nagarajan, *Bull. Soc. Chim. Belg.*, **71**, 324 (1962); also see ref 92.

(88) F. Fairbrother and W. C. Frith, *J. Chem. Soc.*, 3051 (1951).

(89) J. H. Junkins, R. L. Farrar, E. J. Barber, and H. A. Bernhardt, *J. Amer. Chem. Soc.*, **74**, 3464 (1952).

(89a) O. E. Myers and A. P. Brady, *J. Phys. Chem.*, **64**, 591 (1960).

(90) O. L. Keller, *Inorg. Chem.*, **2**, 783 (1963).

(91) M. Haissinsky, *Com. Int. Thermodyn. Cinet. Electrochim. C. R. Reunion*, **222** (1951); *Chem. Abstr.*, **48**, 1858e (1954).

(92) H. Schäfer and F. Kahlenberg, *Z. Anorg. Allg. Chem.*, **305**, 291 (1960).

(93) P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, *Trans. Faraday Soc.*, **56**, 318 (1960).

(94) L. A. Reznitskii, *Zh. Fiz. Khim.*, **41**, 1482 (1967); *Russ. J. Phys. Chem.*, **41**, 787 (1967).

(95) S. A. Shchukarev, M. A. Oranskaya, and T. S. Shemyakina, *Zh. Neorg. Khim.*, **5**, 2135 (1960); *Russ. J. Inorg. Chem.*, **5**, 1036 (1960).

(96) F. J. Keneshea, D. Cubicciotti, G. Withers, and H. Eding, *J. Phys. Chem.*, **72**, 1272 (1968).

(97) H. Schäfer, *Angew. Chem.*, **67**, 748 (1955); H. Schäfer and K. D. Dohmann, *Z. Anorg. Allg. Chem.*, **300**, 1 (1965); H. Schäfer and F. Liedmeier, *J. Less Common Metals*, **6**, 307 (1964); A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **339**, 155 (1965).

(98) P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *J. Amer. Chem. Soc.*, **72**, 5477 (1950).

(99) S. A. Shchukarev, E. K. Smirnova, I. V. Vasil'kova, and N. I. Borovkova, *Zh. Neorg. Khim.*, **7**, 1213 (1962); *Russ. J. Inorg. Chem.*, **7**, 625 (1962).

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

data¹⁰¹ lead us to $\Delta H_{298}^{\circ} = 27.6$ kcal mol⁻¹ for sublimation of NbBr₃(c) and thence to ΔH_f° for NbBr₃(g). Our estimated S_{298}° values are chosen to be consistent with $\Delta S_{298}^{\circ} = 47$ 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 NbBr₃(c) and NbBr₃(g).

For NbI₃(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 Kahlenberg¹⁰² to report $\Delta H_f^{\circ} = -210.2$ kcal mol⁻¹ for NbOCl₃(c), while other calorimetric measurements by Shchukarev, Smirnova, Shemyakina, and Ryabov¹⁰³ led them to $\Delta H_f^{\circ} = -212.2$ kcal mol⁻¹. Recalculation of the latter result with our adopted ΔH_f° for Nb₂O₅(c) leads us to $\Delta H_f^{\circ} = -211.4$ kcal mol⁻¹ for NbOCl₃(c). On the basis of the values cited here, our estimates of uncertainties, and the relation of NbOCl₃(c) to NbO(c) cited earlier, we adopt $\Delta H_f^{\circ} = -211$ kcal mol⁻¹ for NbOCl₃(c) and combine with its estimated¹⁰² S_{298}° to obtain the ΔG_f° in Table II. Vapor pressure data from Schäfer and Kahlenberg^{92,102} lead to $\Delta H_{298}^{\circ} = 26.2$ kcal mol⁻¹ for sublimation and thence to ΔH_f° for NbOCl₃(g). Estimated entropies¹⁰² for NbOCl₃(c) and NbOCl₃(g) are consistent with $\Delta S_{298}^{\circ} = 44$ cal deg⁻¹ mol⁻¹ for sublimation, as calculated from the vapor pressure data.

Combination of the heat of chlorination⁸³ of NbOCl₂(c) to NbOCl₃(c) with our adopted ΔH_f° of the latter compound leads to $\Delta H_f^{\circ} = -186$ kcal mol⁻¹ for NbOCl₂(c).

Using calorimetric data from Shchukarev, Smirnova, Vasil'kova, and Borovkova⁹⁹ with our adopted ΔH_f° for Nb₂O₅(c), we calculate $\Delta H_f^{\circ} = -179.1$ kcal mol⁻¹ for NbOBr₃(c). We have no other thermodynamic data for this compound.

Vapor pressures of NbOCl₃(g) over compounds of types M₂NbOCl₅ and MNbOCl₄ have been measured¹⁰⁴⁻¹⁰⁶ 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 Kudryashova¹⁰⁷ for reactions of type



have been used with our adopted ΔH_f° for NbCl₃(c) and ΔH_f° values for the alkali chlorides from NBS Circular 500² to yield ΔH_f° values given in Table II for MNbCl₆(c) compounds.

We have combined heat of combustion data from Mah⁸⁰ and from Mah and Gellert¹⁰⁸ with our adopted ΔH_f° for Nb₂O₅(c) to obtain $\Delta H_f^{\circ} = -60.4$ kcal mol⁻¹ for Nb₂N(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.

(101) S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, *Zh. Neorg. Khim.*, **10**, 322 (1965); *Russ. J. Inorg. Chem.*, **10**, 173 (1965).

(102) H. Schäfer and F. Kahlenberg, *Z. Anorg. Allg. Chem.*, **305**, 327 (1960).

(103) S. A. Shchukarev, E. K. Smirnova, T. S. Shemyakina, and E. N. Ryabov, *Zh. Neorg. Khim.*, **7**, 1216 (1962); *Russ. J. Inorg. Chem.*, **7**, 626 (1962).

(104) I. Zvara and L. K. Tarasov, *Zh. Neorg. Khim.*, **7**, 2665 (1962); *Russ. J. Inorg. Chem.*, **7**, 1388 (1962).

(105) I. S. Morozov and V. A. Krokhin, *Zh. Neorg. Khim.*, **8**, 2376 (1963); *Russ. J. Inorg. Chem.*, **8**, 1430 (1963).

(106) S. A. Shchukarev, T. S. Shemyakina, and E. K. Smirnova, *Zh. Neorg. Khim.*, **9**, 547 (1964); *Russ. J. Inorg. Chem.*, **9**, 304 (1964).

(107) E. K. Smirnova, I. V. Vasil'kova, and N. F. Kudryashova, *Zh. Neorg. Khim.*, **9**, 489 (1964); *Russ. J. Inorg. Chem.*, **9**, 268 (1964).

(108) A. D. Mah and N. L. Gellert, *J. Amer. Chem. Soc.*, **78**, 3261 (1956).

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 Nb₂C and NbC. For example, Mah and Boyle¹⁰⁹ 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 Nb₂O₅(c) leads us to $\Delta H_f^{\circ} = -33.2$ kcal mol⁻¹ for NbC(c). Other calorimetric measurements⁷⁸ on samples represented by NbC_x (x from 0.489 to 0.984) in combination with our ΔH_f° for Nb₂O₅(c) also lead to $\Delta H_f^{\circ} = -33.2$ kcal mol⁻¹ for NbC(c). High-temperature equilibrium measurements by Worrell and Chipman⁶⁵ 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 Kelley¹¹⁰ to obtain the ΔG_f° listed for NbC(c) in Table II. Combustion data⁷⁶ also lead us to $\Delta H_f^{\circ} = -47$ kcal mol⁻¹ for Nb₂C(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 equilibria¹¹¹ 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 measurements¹¹⁴ have led to $S_{298}^{\circ} = 8.91$ cal deg⁻¹ mol⁻¹ for NbB_{1.968}(c). On the basis of these values, we cite thermodynamic properties of "NbB₂"(c) in Table II.

Valeckis and Edwards⁶⁷ have reviewed earlier work and measured equilibrium pressures of H₂ 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 HNO₃ and HF. Similarly, Ta₂O₅ is generally less reactive than Nb₂O₅.

Pope and Dale¹⁰ have reviewed investigations of isopoly-tantalates. 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, Na₃TaF₈(c) has been found¹¹⁵

(109) A. D. Mah and B. J. Boyle, *ibid.*, **77**, 6512 (1955).

(110) L. B. Pankratz, W. W. Weller, and K. K. Kelley, U. S. Bureau of Mines Report of Investigations No. 6446, U. S. Government Printing Office, Washington, D. C., 1964.

(111) L. Brewer and H. Haraldsen, *J. Electrochem. Soc.*, **102**, 399 (1955).

(112) G. V. Samsonov, *Zh. Fiz. Khim.*, **30**, 2057 (1956).

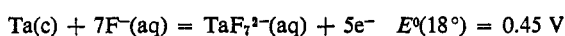
(113) G. K. Johnson, E. Greenberg, J. L. Margrave, and W. N. Hubbard, *J. Chem. Eng. Data*, **12**, 597 (1967).

(114) E. F. Westrum, Jr., and G. A. Clay, *J. Phys. Chem.*, **67**, 2385 (1963).

(114a) J. A. Pryde and C. G. Titcomb, *Trans. Faraday Soc.*, **65**, 2758 (1969).

(115) J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *J. Amer. Chem. Soc.*, **76**, 3820 (1954).

to contain eight-coordinated tantalum in TaF_8^{3-} ions. The results of potentiometric and ion-exchange measurements by Varga and Freund¹¹⁶ suggest that a variety of species of type $\text{TaF}_n^{(6-n)+}$ ($n = 4-9$) are present in various aqueous solutions. Reported¹¹⁶ potentials for $\text{Ta}/\text{TaF}_n^{(6-n)+}(\text{aq})$ range from 0.2 to 0.4 V. Haissinsky^{91,117} has interpreted his potentiometric data on similar systems in terms of $\text{TaF}_7^{2-}(\text{aq})$ and the following.



The potential data^{91,116,117} and the ΔG_f° of $\text{Ta}_2\text{O}_5(\text{c})$ cited later are consistent with the observed hydrolysis of K_2TaF_7 in water and the slight solubility of $\text{Ta}_2\text{O}_5(\text{c})$ in cold $\text{HF}(\text{aq})$. 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 King¹² have reviewed C_p data leading to $S^\circ_{298} = 9.92 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for $\text{Ta}(\text{c})$. They have also calculated $S^\circ_{298} = 44.24 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for $\text{Ta}(\text{g})$. Using the high-temperature vapor pressure data of Edwards, Johnston, and Blackburn,¹¹⁸ we have calculated $\Delta H_f^\circ = 187 \text{ kcal mol}^{-1}$ for $\text{Ta}(\text{g})$, and combined this value with entropy data to obtain the ΔG_f° given in Table III.

Table III
Thermodynamic Data for Tantalum at 298°K

Substance	$\Delta H_f^\circ, \text{kcal mol}^{-1}$	$\Delta G_f^\circ, \text{kcal mol}^{-1}$	$S^\circ, \text{cal deg}^{-1} \text{ mol}^{-1}$
Ta(c)	0	0	9.92 ¹²
Ta(g)	187 ¹¹⁸	177	44.29 ¹²
Ta ₂ O 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 ₅ (c)	-139 ¹²¹	-123	(37)
TaCl ₄ (c)	-170 ^{121,122}	-149	(46) ¹²³
TaCl ₄ (g)	-139 ^{121,122}	-131	(89)
TaCl ₃ (c)	-205.5 ⁹⁰	-179	(55)
TaCl ₃ (g)	-182.3 ¹²⁰⁻¹²²	-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 ₂ N(c)	~ -65 ⁸⁰		
TaN(c)	-60 ¹⁰⁸	-53	(10) ¹⁰⁸
Ta ₂ C(c)	~ -47 ¹¹⁹	~ -46	(19)
TaC(c)	-35.5 ^{85,119,127}	-35.0	9.7 ⁸⁵
"TaB ₂ "(c)	-44 ¹¹³	-43 ¹¹³	10.6 ¹¹³

Of the several reported heats of combustion leading to ΔH_f° for $\text{Ta}_2\text{O}_5(\text{c})$, only three need be considered here.

(116) L. P. Varga and H. Freund, *J. Phys. Chem.*, **66**, 22, 187 (1962).

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Humphrey⁷⁶ reported $\Delta H_f^\circ = -488.8 \pm 0.5 \text{ kcal mol}^{-1}$ for $\text{Ta}_2\text{O}_5(\text{c})$, which is revised to $-489.0 \text{ kcal mol}^{-1}$ on the basis of the current atomic weight of tantalum. Kornilov, Leonidov, and Skuratov⁷⁹ have reported $\Delta H_f^\circ = -489.3 \pm 0.4 \text{ kcal mol}^{-1}$, while Huber, Head, Holley, and Bowman¹¹⁹ have reported $\Delta H_f^\circ = -487.7 \pm 0.9 \text{ kcal mol}^{-1}$. On the basis of the first two of these three careful investigations, we adopt $\Delta H_f^\circ = -489.2 \text{ kcal mol}^{-1}$ for $\text{Ta}_2\text{O}_5(\text{c})$ and combine with $S^\circ_{298} = 34.2$ from Kelley and King¹² to obtain the ΔG_f° given in Table III.

Greenberg, Natke, and Hubbard⁸⁵ have determined $\Delta H_f^\circ = -455.0 \text{ kcal mol}^{-1}$ for $\text{TaF}_5(\text{c})$ by means of fluorine bomb calorimetry. We follow these workers in taking $S^\circ_{298} = (41) \text{ cal deg}^{-1} \text{ mol}^{-1}$ for $\text{TaF}_5(\text{c})$ and thence obtain the ΔG_f° given in Table III. The vapor pressure data of Fairbrother and Frith⁸⁸ do not permit calculation of ΔH° and ΔS° of sublimation of $\text{TaF}_5(\text{c})$, but do suggest that $\text{TaF}_5(\text{c})$ is slightly more volatile than NbF_5 , thus permitting us to estimate the properties given in Table III for $\text{TaF}_5(\text{g})$.

For $\text{TaCl}_5(\text{c})$ we have $\Delta H_f^\circ = -205.5 \text{ kcal mol}^{-1}$ from the heat of combination of the elements⁹⁰ and $\Delta H_f^\circ = -205.0 \text{ kcal mol}^{-1}$ from solution calorimetry.¹²⁰ In their discussion of the thermodynamic properties of several tantalum chlorides, Kurbanov, Suvorov, Shchukarev, and Novikov¹²¹ cite $\Delta H_f^\circ = -206.0 \text{ kcal mol}^{-1}$ derived from the heat of reaction of $\text{TaCl}_5(\text{c})$ with water. The first of these values appears to be the most certain and we therefore adopt $\Delta H_f^\circ = -205.5 \text{ kcal mol}^{-1}$ for $\text{TaCl}_5(\text{c})$. Our tabulated properties of $\text{TaCl}_5(\text{g})$ are based on results of several investigations of vapor pressures and estimated entropies.^{2,120-122}

For $\text{TaCl}_4(\text{c})$ we have $\Delta H_f^\circ = -168.8 \text{ kcal mol}^{-1}$ from Schäfer and Kahlenberg.¹²² Another investigation¹²¹ has led to a reported $\Delta H_f^\circ = -172.6 \text{ kcal mol}^{-1}$. On the basis of these values and our recalculations using our adopted ΔH_f° for TaCl_5 , we adopt $\Delta H_f^\circ = -170 \text{ kcal mol}^{-1}$ for $\text{TaCl}_4(\text{c})$ and combine with an estimated¹²² $S^\circ_{298} = (46) \text{ cal deg}^{-1} \text{ mol}^{-1}$ to obtain our tabulated ΔG_f° . We combine these values for $\text{TaCl}_4(\text{c})$ with $\Delta H^\circ = 31 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 43 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for sublimation^{121,122} to obtain the thermodynamic properties of $\text{TaCl}_4(\text{g})$.

Calorimetric and equilibrium data^{97,121-123} for $\text{TaCl}_3(\text{c})$ 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 $\text{TaCl}_3(\text{c})$ shown in Table III.

Although some data have been reported^{97,121} for TaCl_2 and $\text{TaCl}_{2.5}$, we do not tabulate thermodynamic properties for these substances.

Schäfer and Sibbing¹²⁴ have reported $\Delta H^\circ_{298} = 101.3 \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = 98 \text{ cal deg}^{-1} \text{ mol}^{-1}$ of Ta_2O_5 for the reaction

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We use these values with our tabulated thermodynamic properties of $\text{Ta}_2\text{O}_5(\text{c})$ and $\text{TaCl}_5(\text{g})$ to obtain $\Delta H_f^\circ = -187$ kcal mol⁻¹ and $S^\circ_{298} = 87$ cal deg⁻¹ mol⁻¹ for $\text{TaOCl}_3(\text{g})$. No vapor pressure data are available to use in calculating the thermodynamic properties of $\text{TaOCl}_3(\text{c})$, so we estimate them on the basis of the thermodynamics of sublimation of $\text{NbOCl}_3(\text{c})$.

Calorimetric data from Smirnova, Vasil'kova, and Kudryashova¹⁰⁷ for reactions of type



have been used with our adopted ΔH_f° for $\text{TaCl}_5(\text{c})$ and ΔH_f° values for the alkali chlorides² to yield the ΔH_f° values given in Table III for $\text{MTaCl}_6(\text{c})$ compounds. The ΔH_f° so obtained for $\text{KTaCl}_6(\text{c})$ differs considerably from a less certain value that can be calculated from high-temperature decomposition pressure data.¹⁰⁴

We adopt $\Delta H_f^\circ = -143.0$ kcal mol⁻¹ for $\text{TaBr}_5(\text{c})$ 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 $\Delta H^\circ_{298} = 27$ kcal mol⁻¹ and $\Delta S^\circ_{298} = 47$ cal deg⁻¹ mol⁻¹ for sublimation of $\text{TaBr}_5(\text{c})$. We combined this ΔH°_{298} with the adopted ΔH_f° for $\text{TaBr}_5(\text{c})$ to obtain ΔH_f° for $\text{TaBr}_5(\text{c})$, and have also estimated entropies to be consistent with the ΔS°_{298} of sublimation. Free energies are calculated from the ΔH_f° and S°_{298} values.

For $\text{TaI}_5(\text{c})$ we have vapor pressure data from Alexander and Fairbrother,¹²⁶ but no other data with which to calculate thermodynamic properties for Table III.

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Heat of combustion measurements by Mah⁸⁰ lead to $\Delta H_f^\circ \cong -65$ kcal mol⁻¹ for $\text{Ta}_2\text{N}(\text{c})$, while similar measurements by Mah and Gellert¹⁰⁸ lead to $\Delta H_f^\circ = -60$ kcal mol⁻¹ for $\text{TaN}(\text{c})$. No free energy or entropy data are available, but an estimated¹⁰⁸ $S^\circ_{298} = (10)$ cal deg⁻¹ mol⁻¹ for $\text{TaN}(\text{c})$ permits calculation of its ΔG_f° .

Heats of combustion^{119,127} and high-temperature equilibrium data⁶⁵ are in good agreement with $\Delta H_f^\circ = -35.5$ kcal mol⁻¹ for $\text{TaC}(\text{c})$, for which we also have high-temperature heat content data.¹²⁸ The high-temperature equilibrium data⁶⁵ indicate that $S^\circ_{298} = 9.7$ cal deg⁻¹ mol⁻¹ for $\text{TaC}(\text{c})$ rather than 10.1 cal deg⁻¹ mol⁻¹ from low-temperature heat capacity data.¹² For $\text{Ta}_2\text{C}(\text{c})$ we have only $\Delta H_f^\circ \cong -47$ kcal mol⁻¹ from heats of combustion.¹¹⁹

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

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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