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THE THERMODYNAMICS OF THE SOLID OXIDES OF VANADIUM

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ABSTRACT

The available thermodynamic data have been critically reviewed and extended to provide values of S_{298} and ΔH_{298}, and analytical equations for $-(G-H_{298})/T$ as a function of temperature for 14 of the high-temperature solid phases of the V–O system.

INTRODUCTION

Professor O. Kubaschewski has made many important contributions. We wish to emphasize the importance of his critical evaluations of thermodynamic data. Information about previously unused combinations of the elements and about materials under unprecedented conditions of temperature, pressure, and environmental exposure is urgently needed for research and developmental activities to meet our energy and materials needs. Kubaschewski has pointed out how powerfully thermodynamic data can be brought to bear on these problems if the relevant data have been brought together and critically evaluated to provide a consistent picture of the interrelated data. He recognized that it was impractical for most scientists and engineers to retrieve, critically evaluate, and put into usable form any significant fraction of the information they need. It is not only the tedious and time-consuming work of gathering and digesting the raw data that stands in the way of utilizing the exponentially growing mass of information, but also unusually broad experience in the field is required to be able to critically evaluate the reliability of each measurement. Kubaschewski has saved millions of dollars through the availability of his compilations, as each user of the data need not take the time to search the literature independently. There is an even greater saving if the user is directed to the most reliable data and is not misled by the erroneous values. The wrong choice

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Dedicated to Professor Oswald Kubaschewski on honour of his contribution to thermochemistry.

between divergent values could make the difference between success and failure of a proposed process.

Our presentation in honor of Professor Kubaschewski is designed to emphasize another aspect of evaluations of data. Each of us has to critically evaluate data of interest to our particular subfield. It is important to make the results of our evaluations generally available to others who would not be as expert in our subfield, in order to arrive at a reliable evaluation. We have been using the oxides of vanadium to characterize the very strong generalized G.N. Lewis acid–base interactions [1–3] between a left-hand transition metal like vanadium that has empty 3d and 4p orbitals and platinum group metals that have non-bonding d-electron pairs. By equilibrating a pair of vanadium oxides, for which the vanadium activity is fixed, with a platinum group metal and analyzing the vanadium content of the equilibrated metal phase, one can calculate the activity coefficient or excess partial molal Gibbs energy of the vanadium. Vanadium is particularly useful because it has so many oxide phases. To use this procedure, we have had to accurately fix the thermodynamic properties of the oxide phases of interest. The results of our critical review of the literature are presented here so that others will be able to use them, and not have to try to duplicate our evaluations and extensions of the literature results.

RESULTS AND DISCUSSION

The Giauque functions, $-(G-H_{298})/RT$, for VO, $VO_{3/2}$, VO_2, and $VO_{5/2}$ are tabulated by several authors. The data were fit to 3rd or 4th order analytical equations using the Chebyshev polynomials [4]. For VO, $VO_{3/2}$ and VO_2, the data compiled by JANAF [5] and those compiled by Gurvich [6] are in significant disagreement. Since there was some question as to the purity of the samples used for the data reported in JANAF, the data from Gurvich are used here. For the ΔH_{298} values, the accepted values are by Mah and Kelley [7]. The data for $VO_{5/2}$ were obtained from more recent work by Ferrante and Mrazek [8]. These compilations all assume that each of these phases are well ordered at 0 K as many of the vanadium oxides undergo magnetic transitions at low temperatures, and it is assumed that these transitions result in complete order ($S(0)=0$).

For the Magnelli phases, $VO_{13/6}$ and $VO_{7/3}$, there are insufficient data to provide a complete compilation. The Giauque functions for these phases were interpolated by taking a linear fit of the polynomial coefficients as a function of oxygen composition (VO_x). Paukov et al. [9] showed that the S_{350} values for the phases VO to $VO_{5/2}$ vary linearly, in contrast to the S_{298} values which vary similarly, except for VO_2 which is shifted because it has a phase transition at 339 K [9]. The S_{298} value presented here for VO_2 is that of the high temperature phase extrapolated to 298 K by using the S_{350} value

TABLE 1

$VO_{2/3} + 1/12\ O_2 \rightarrow VO_{5/3}$

T (K)	Calculated $\Delta H_{f298}/R$ (kK)
1173	−77.768 [a]
1273	−77.746 [a]
1323	−77.725 [a]
1373	−77.722 [a]
1423	−77.710 [a]
1307	−77.730 [b]
1400	−77.719 [c]
1500	−77.728 [c]
1600	−77.725 [c]
1700	−77.710 [c]
Best value $\Delta H_{f298}/R = -77.728$	

[a] Values calculated from ref. 13. [b] Values calculated from ref. 12. [c] Values calculated from ref. 11.

and heat capacity data. This makes the linearity of the S_{298} values also excellent. Consequently, linear fits over the ranges $VO_{3/2}$ to VO_2 and VO_2 to $VO_{5/2}$ should be accurate. The $VO_{5/3}$ phase also undergoes a phase transition at 430 K [10]. The S_{298} value of the high temperature phase is given by linear interpolation. Note also that for $VO_{5/3}$ and VO_2 the ΔH_{298} values, as well as the S_{298} values presented here, correspond to the high temperature phases. A linear fit is not expected for the ΔH_{298} values. Consequently, the ΔH_{298} values were obtained from a knowledge of the partial pressure of oxygen in equilibrium with these phases. Several authors have made these measurements using both e.m.f. [11,12] and gas equilibration techniques [13], and their data are in good agreement. For each temperature that they obtained a ΔG, the corresponding ΔH_{298} value was calculated using the proposed Giauque functions. The results for the equilibria between $VO_{3/2}$ and $VO_{5/3}$ are given in Table 1. Since the variation is small, it appears that the assumption that $C_p(T)$ and S_{298} are linear in oxygen composition is accurate. Similarly, the calculated ΔH_{298} for the other Magnelli phases deviated little. For the phases $VO_{13/6}$ and $VO_{7/3}$ the same technique was tried, however, with less success. Most recently, Dziembaj [14] has reviewed and done some measurements on the $VO_{13/6}$–$VO_{5/2}$ phases. The values he presents scatter widely. As a result, the thermodynamics of these phases cannot yet be fixed accurately, but the linear fit of S_{298} and $C_p(T)$ selected is within the uncertainty. Equations for Giaque functions are also given for O_2(g) [5,6] and for V(s, l) [27].

For the lower oxides $VO_{1/9}$, $VO_{1/4}$ and $VO_{1/2}$ accurate thermodynamic functions cannot be presented either. Nevertheless, equations for ΔG_f are

TABLE 2

$\Delta G_f/R = A + BT$ (kK)

$VO_{1/9}(s)$	$-7.10+2.65(T/1000)\pm0.1$ [a]	750–1050 K
$VO_{1/4}(s)$	$-14.60+2.83(T/1000)\pm0.1$ [b]	1120–1380 K
$VO_{1/2}(s)$	$-27.23\pm5.56(T/1000)\pm0.1$ [b]	1120–1380 K

[a] Values calculated from ref. 15.

[b] Values calculated from refs. 16–18.

TABLE 3

Thermodynamics of vanadium oxides: $-(G-H_{298})/RT = A + BT + CT^2 + DT^3 + ET^4$

Species	T_{min}	T_{max}	A	$B\times10^3$	$C\times10^6$	$D\times10^9$	$E\times10^{12}$
V(s)	298	1000	4.53	−8.45	23.216	−20.97	6.854
V(s)	1000	2300	2.023	3.942	−1.141	0.2465	−0.0224
V(l)	2000	3800	0.037	5.164	−1.119	0.1542	−0.00923
VO(s)	298	1000	5.878	−15.730	41.837	−36.550	11.678
VO(s)	1000	2100	1.316	7.004	−1.359	0.1476	
VO(l)	2000	4100	−3.758	10.5840	−1.8925	0.14318	
$VO_{3/2}(s)$	298	1000	7.933	−19.456	52.560	−46.835	15.13
$VO_{3/2}(s)$	1000	2300	2.516	8.576	−1.999	0.2372	
$VO_{3/2}(l)$	2200	3800	−3.430	11.9097	−2.1329	0.1631	
$VO_{5/3}(s)$	400	1000	8.531	−20.320	54.946	−48.941	15.81
$VO_{5/3}(s)$	1000	2100	2.843	9.013	−2.075	0.2461	
$VO_{7/4}(s)$	298	1000	8.830	−20.753	56.139	−49.995	16.16
$VO_{7/4}(s)$	1000	2100	3.006	9.321	−2.113	0.2506	
$VO_{9/5}(s)$	298	1000	9.009	−21.021	56.854	−50.626	16.36
$VO_{9/5}(s)$	1000	2100	3.104	9.362	−2.135	0.2533	
$VO_{11/6}(s)$	298	1000	9.129	−21.185	57.331	−51.048	16.50
$VO_{11/6}(s)$	1000	2100	3.169	9.449	−2.150	0.2551	
$VO_{13/7}(s)$	298	1000	9.214	−21.308	57.672	−51.349	16.59
$VO_{13/7}(s)$	1000	2100	3.216	9.512	−2.161	0.2563	
$VO_{15/8}(s)$	298	1000	9.279	−21.401	57.928	−51.574	16.67
$VO_{15/8}(s)$	1000	2100	3.251	9.559	−2.169	0.2573	
$VO_{17/9}(s)$	298	1000	9.328	−21.473	58.127	−51.750	16.72
$VO_{17/9}(s)$	1000	2000	3.278	9.595	−2.176	0.2580	
$VO_{19/10}(s)$	298	1000	9.368	−21.530	58.286	−51.890	16.77
$VO_{19/10}(s)$	1000	2000	3.300	9.624	−2.181	0.2586	
$VO_2(s)$	300	1000	9.727	−22.049	59.717	−53.154	17.18
$VO_2(s)$	1000	1900	3.496	9.886	−2.226	0.2640	
$VO_2(l)$	1800	3300	−2.763	14.860	−3.0879	0.2760	
$VO_{13/6}(s)$	298	1000	10.000	−22.496	60.983	−54.252	17.54
$VO_{7/3}(s)$	298	1000	10.273	−22.942	62.294	−55.350	17.90
$VO_{5/2}(s)$	298	1000	10.546	−23.389	63.515	−56.448	18.26
$VO_{5/2}(l)$	900	1500	−5.170	26.904	−11.094	2.0387	
$O_2(9)$	298	1000	25.757	−9.743	26.812	−24.157	7.8845
$O_2(9)$	1000	3000	22.987	4.5769	−1.2107	0.2154	−0.01686

TABLE 4

Thermodynamics of vanadium oxides

Species	$\Delta H_{f298}/R$ (kK)	S_{298}/R
VO(s)	−51.927 [b] ±0.11	4.030 [e] ±0.048
$VO_{3/2}$(s)	−73.291±0.10	5.691 [f] ±0.02
$VO_{5/3}$(s) [a]	−77.728(±0.02)	6.164±0.02
$VO_{7/4}$(s)	−79.884(±0.02)	6.414±0.02
$VO_{9/5}$(s)	−81.107(±0.02)	6.564±0.02
$VO_{11/6}$(s)	−81.915(±0.02)	6.664±0.02
$VO_{13/7}$(s)	−82.402(±0.03)	6.735±0.02
$VO_{15/8}$(s)	−82.868(±0.03)	6.789±0.02
$VO_{17/9}$(s)	−83.139(±0.03)	6.830±0.02
$VO_{19/10}$(s)	−83.357(±0.03)	6.863±0.02
VO_2(s) [a]	−85.311 [b] ±0.10	7.189 [e] ±0.015
$VO_{13/6}$(s)	−88.725 [c] ±0.20	7.415±0.05
$VO_{7/3}$(s)	−91.31 [d] ±0.50	7.64±0.05
$VO_{5/2}$(s)	−93.256 [b] ±0.10	7.867 [f] ±0.015

[a] Values are extrapolated values for the high temperature form. [b] Values from ref. 7. [c] Value from ref. 25. [d] Value from ref. 26. [e] Values from ref. 6. [f] Values from ref. 9.

shown for these phases in Table 2. The large uncertainties presented are necessary due to the sparse and conflicting data available for these phases. For $VO_{1/9}$ the only data available comes from Smith [15] who obtained ΔG_f from the oxygen concentration in sodium of various Na–V–$VO_{1/9}$ equilibria. Thermodynamic measurements on the $VO_{1/4}$ and $VO_{1/2}$ phases have been done by several authors [16–22]. Their results scatter widely and it is difficult to say which data are the most accurate. This is not surprising since most of the data were obtained from e.m.f. measurements involving a high temperature solid-state galvanic cell. Numerous errors can arise in such experiments, and Vasil'eva and Seregin [16–18] were the only experimenters who checked to see if their measurements were true equilibrium measurements by polarizing their electrodes, then observing to see if the e.m.f. returned to the same value. Consequently, their data are presented here.

Some investigators disagree on whether the Magnelli phases are stable up to $VO_{17/9}$ and $VO_{19/10}$ [23,24], but all investigators agree that they are stable to at least $VO_{15/8}$. With the selected enthalpies of formation, the calculated activity drops across these questionable phases will be zero. The Giauque functions for all the phases VO to $VO_{5/2}$ are given in Table 3. The ΔH_{298} values and the errors are given in Table 4, and a comparison with experimental ΔH_{298} values is given in Table 5. Note that there are some discrepancies between the values presented and the values given by Charlu and Kleppa [25], for whose measurements the oxide phases were ground and mixed with silica powder and burned to $VO_{5/2}$. They found that one burning was insufficient to completely oxidize their samples. Since they assumed that

TABLE 5

Comparison between calculated and experimental $\Delta H_{f298}/R$ values

Species	$\Delta H_{f298}/R$ (kK)	
	Calculated	Experimental
$VO_{2/3}$	-73.293 ± 0.10	-73.293 ± 0.10 [a]
$VO_{5/3}$	$-77.728(\pm 0.02)$	-79.357 ± 0.18 [b]
$VO_{7/4}$	$-79.884(\pm 0.02)$	-80.917 ± 0.23 [b]
$VO_{9/5}$	$-81.107(\pm 0.02)$	-81.632 ± 0.18 [b]
$VO_{11/6}$	$-81.915(\pm 0.02)$	-82.158 ± 0.16 [b]
$VO_{13/7}$	$-82.402(\pm 0.03)$	–
$VO_{15/8}$	$-82.868(\pm 0.03)$	-82.527 ± 0.18 [b]
$VO_{17/9}$	$-83.139(\pm 0.03)$	–
$VO_{19/10}$	$-83.357(\pm 0.03)$	–
VO_2	-85.311 ± 0.10	-85.311 ± 0.10 [c]

[a] Values calculated from ref. 7. [b] Values calculated from ref. 25. [c] Value extrapolated using data from refs. 6 and 7.

their samples were completely oxidized after the second burning, it is possible that they could have overestimated the magnitude of the ΔH_{298} values. For the $VO_{5/3}$ phase they reported a two-phase mixture, and hence, their value is not representative of the ΔH_{298} value for the pure phase. On the contrary, it is difficult to say with certainty that the ΔH_{298} values presented here are the correct ones. However, when using them with their respective Giauque functions, the free energy calculated will be accurate. The enthalpy errors shown for the Magnelli phases are relative to $VO_{3/2}$ and VO_2, and they are correct for any equilibria within this range. When considering equilibria with other phases such as VO and $VO_{5/2}$, add 0.1 to the error for each of the Magnelli phases. All tabulated thermodynamic values are divided by R, the gas constant, and are given for the standard states at 1 atm pressure.

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