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High-Temperature Thermodynamics of the Vanadium–Oxygen System for $0 \leq O/V \leq 1.5$

II. Direct Measurements of $\Delta H(O_2)$ at 1323 K

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The Tian–Calvet microcalorimetric method has been used at 1323 K in order to determine $\Delta H(O_2)$, the partial molar enthalpy of mixing of oxygen, for the vanadium–oxygen system with O/V ratios from 0 to 1.5. Comparison is made with earlier independent determinations from electromotive force measurements.

I. Introduction

This work is the second part of a thermodynamic study of the vanadium–oxygen system up to $O/V = 1.5$. A phase diagram of this region can be found in the first part (*1*) in which $\Delta G(O_2)$, the partial Gibbs free energy of mixing of oxygen, has been determined by an electromotive (emf) method. Here, we present direct measurements of $\Delta H(O_2)$, the partial enthalpy of mixing of oxygen, by a high-temperature microcalorimetric technique. Accurate values of $\Delta H(O_2)$ concerning α and $\alpha + \beta$ fields, already obtained in our laboratory (*2*), have allowed a direct calibration of our measurements.

II. Experimental

The measurements were made with a Tian–Calvet type of microcalorimeter at 1323 K. A description of the method (*3*) and a discussion of the meaning of the heat effect can be found elsewhere (*4, 5*). Adaptation of the method to particular problems in the study of dilute solutions of oxygen in metals and of oxides with low P_{O_2} has already been described (*6–9*). A direct calibration of our measurements has been made by using the previous measurements on the α field by Boureau and Gerdanian (*2*).

Two types of experiments have been performed, starting with either pure vanadium samples supplied by Goodfellow (99.9+% purity) or sintered $VO_{0.6}$ samples. The metal samples were disks of 12.8 mm in diameter and 0.125 mm thick. The $VO_{0.6}$ sintered samples were about 0.2-mm-thick disks cut from a 10.6-mm-diameter cylinder prepared in the same way as the electrodes used for the emf measurements (*1*). Every sample was chemically polished in a fluoronitric solution and rinsed with alcohol and distilled water.

Three runs have been performed with a vanadium sample, each with a different starting oxygen quantities δn_{O_2}, respectively, 2.578×10^{-6} mol, 1.72×10^{-6} mol,

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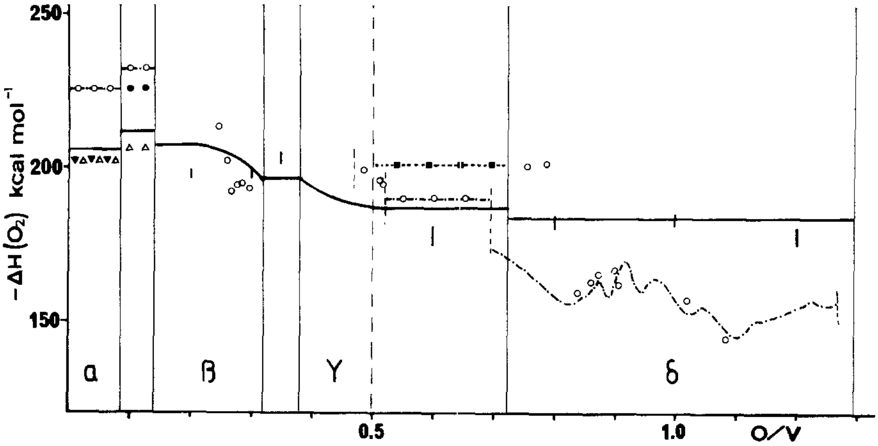

FIG. 1. $\Delta H(O_2)$ vs composition (O/V) at 1323 K: ——, present study; Derived values from emf measurements: |, our own values (*1*); △, Ref. (*10*); ▼, Ref. (*11*); ●, Ref. (*12*); ------ and ○, Refs. (*13–17*); ■——■, Alcock from (*10*).

and 1.27×10^{-6} mol, in order to decrease the oxygen flow. The oxygen flow, defined as the ratio $\delta n_{O_2}/S$ ($S \equiv$ sample surface), is an important parameter for calorimetric measurements. Its role in the process of reaching equilibrium has been described by Tetot *et al.* (*6*). No change has been found when this ratio has been modified. So a value of 10^{-8} mol/mm^2 (run 1), which is similar to the one used for the study of a Ti–O system, is low enough to allow the thermodynamic equilibrium to be reached at the end of the heat release for each elementary oxidation.

III. Results and Discussion

Figure 1 and Table I show our results as well as values of $\Delta H(O_2)$ derived from our own $\Delta G(O_2)$ determinations (*1*). One notes the good agreement between our two independent determinations of $\Delta H(O_2)$ by direct measurements and by derivation from $\Delta G(O_2)$ which shows the coherence between our results. Nevertheless, the method of derivation of $\Delta G(O_2)$ is not reliable enough and does not allow one account for the composition variations of $\Delta H(O_2)$. All the other results plotted in Fig. 1 are also obtained by derivation from emf measurements.

Generally, disagreements between our results and published data are observed. Moreover, we have already noticed (*1*) that, in spite of the large discrepancies observed between the various emf results, the various derived values of $\Delta H(O_2)$ are not very different. It is particularly striking for the results of Fromm and Kirchheim (*10*) and Steckel and Altstetter (*11*) in α phase.

An interesting by-product of the present study is the determination of the phase boundaries at 1323 K. The results are reported in Table II and are compared with other proposed values at different temperatures. The agreement is generally satisfactory. The boundaries of the α and β phases as well as the lower boundaries of the γ and δ phases are represented by well-marked discontinuities or angular points on $\Delta H(O_2)$ (see Fig. 1). Such discontinuities suggest that the thermodynamic equilibrium is reached at the end of the heat release (*21*). Therefore, the compositions of these boundaries are well determined. For

TABLE I

COMPARISON BETWEEN OUR $\Delta H(O_2)$ DETERMINATIONS AND RESULTS OF EARLIER STUDIES (IN kcal mol^{-1})

Range	Present study	From our emf measurements *(1)*	Fromm and Kirchheim *(10)*	Steckel and Altstetter *(11)*	Vasil'eva and co-workers *(13–17)*	Vecher and Savitskii *(12)*
α	−205.8 ± 0.8*		−201.9	−202	−225.3	
α + β	−211.1 ± 3.3		−206		−232	−226 ± 7
β	−207.3 ± 2.9 ↘ −196	−198			−213 ↘ 194.8	
β + γ	−196.6 ± 2.8	−203.3 ± 1.2			−200.75	
γ	−196.6 ↘ −186.9				−198.8 ↘ −195.1	
γ + δ	−186.9 ± 2.2	−177.8 ± 1.8	−200.8 (from Alcock)		−189.9	
δ	−183.7 ± 1.9	(0.8) −182.3 ± 1.8 (1.0) −182.8 ± 1.8 (1.2) −177.8 ± 1.8			(see Fig. 1)	

Note. * from (*2*), this value is used for calibration.

$\Delta H(O_2)$ in the α phase, the dilute solution of oxygen in vanadium, a complete discussion can be found elsewhere (*2*).

The characteristic shape of $\Delta H(O_2)$ in the β phase, constant $\Delta H(O_2)$ in the first half of the field and then a strongly increasing of $\Delta H(O_2)$, is similar to the one obtained for α Ti (*6*), α Zr, and α Hf phases (*22*). This implies the occurrence of O–O repulsive interactions for concentrated solutions. Nevertheless, two features make the β V phase different from the α Ti, α Zr, and α Hf phases:

(i) It has been noticed by Boureau *et al.* (*22*) that the enthalpies at infinite dilution of α oxygen solutions in Ti, Zr, and Hf are all almost identical to about −285 kcal mol^{-1}. The enthalpy of β V, −200 kcal mol^{-1}, is very different from this last value.

(ii) Second, the magnitude of the increasing $\Delta H(O_2)$, which is 30 kcal mol^{-1} for α Zr and 40 kcal mol^{-1} for α Ti, is only 12 kcal mol^{-1} for β V in comparable composition ranges. The case of α Hf is special owing to the smaller homogeneity range of this phase.

TABLE II

PHASE BOUNDARIES OF THE V–O SYSTEM: COMPARISON WITH EARLIER STUDIES

Field	Alexander and Carlson *(18)* (1323 K)	Steckel and Altstetter *(11)* (1253 K)	Fromm and Kirchheim *(10)* (1273 K)	Vasil'eva and co-workers *(13–17)* (1323 K)	Boureau and Gerdanian *(22)* (1323 K)	Henry *et al.* *(19)* (1273 K)	Yakovkva and Krasilavo *(20)*	Our results	
								1323 K	Galv. cell *(1)*
α upper	0.093	0.092	0.087		0.08	0.0917		0.0865	
β lower	0.130				0.14	0.143		0.140	
β upper	0.373			0.33		0.354		0.32	
γ lower	0.466			0.47				0.385	
γ upper	0.526			0.525				0.5 ?	
δ lower	0.754 (1458 K)			0.695				0.723	0.8 (1213 K)
δ upper							1.27 (728–1321 K)	1.285 – 1.305	

TABLE III

SOME THERMODYNAMIC PROPERTIES OF THE V–O SYSTEM AT 1323 K

x	Field	$\log_{10}P_{O_2}$	$\Delta G(O_2)$ kcal mol^{-1}	$\Delta H(O_2)$ kcal mol^{-1}	$\Delta S(O_2)$ cal K^{-1} mol^{-1}	ΔH_f° VO$_x$ kcal mol^{-1}
0.2	β	−23.80 ± 0.1	−144.0 ± 0.6	−207.3 ± 2.9	−47.6 ± 2.6	−20.77 ± 0.26
0.3	β	−23.57 ± 0.1	−142.7 ± 0.6	−198 ± 3	−41.8 ± 2.7	−30.90 ± 0.39
0.35	$\beta + \gamma$	−23.44 ± 0.1	−141.9 ± 0.6	−196.6 ± 2.8	−41.6 ± 2.6	−35.84 ± 0.45
0.4	γ	−23.40 ± 0.2*	−141.6 ± 1.2	−195 ± 3	−40.4 ± 3.2	−40.76 ± 0.51
0.5	γ	−23.11 ± 0.2*	−139.9 ± 1.2	−186.9 ± 2.2	−35.6 ± 2.6	−50.31 ± 0.63
0.6	$\gamma + \delta$	−23.11 ± 0.1	−139.9 ± 0.6	−186.9 ± 2.2	−35.6 ± 2.1	−59.66 ± 0.75
0.7	$\gamma + \delta$	−23.11 ± 0.1	−139.9 ± 0.6	−186.9 ± 2.2	−35.6 ± 2.1	−68.95 ± 0.86
0.8	δ	−23.05 ± 0.1	−139.5 ± 0.6	−183.7 ± 1.9	−33.3 ± 1.9	−78.16 ± 0.98
0.9	δ	−23.0 ± 0.2*	−139.2 ± 1.2	−183.7 ± 1.9	−33.6 ± 2.4	−87.34 ± 1.09
1.0	δ	−22.88 ± 0.1	−138.5 ± 0.6	−183.7 ± 1.9	−34.1 ± 1.9	−96.52 ± 1.20
1.1	δ	−22.76 ± 0.2*	−137.8 ± 1.2	−183.7 ± 1.9	−34.6 ± 2.4	−105.70 ± 1.32
1.2	δ	−22.51 ± 0.1	−136.3 ± 0.6	−183.7 ± 1.9	−35.8 ± 1.9	−114.88 ± 1.44
1.3	$\delta + V_2O_3$	−22.06 ± 0.1	−133.5 ± 0.6			

Note. *, interpolated values.

We think that these differences are correlated by the fact that the β V phase structure is body centered tetragonal whereas the α oxygen solutions in Ti, Zr, and Hf are all close packed hexagonal structure.

The results concerning the monoxide $VO_{1\pm x}$ are somewhat surprising owing to the complex defect structure of this phase. Two runs performed starting with sintered $VO_{0.6}$ samples have confirmed that $\Delta H(O_2)$ is a constant in the whole homogeneity range of monoxide. These results are very different from those obtained for the monoxide $TiO_{1\pm x}$ (*7*). For $TiO_{1\pm x}$, $\Delta H(O_2)$ strongly increases by 50 kcal mol^{-1} in the first third of the homogeneity range, remains constant up to $TiO_{1.22}$, and then decreases a little until the phase boundary. Large concentrations of both oxygen and metal vacancies are present in VO and TiO sublattices, 15% remaining at the stoichiometry (*23*). We think that the strong increasing $\Delta H(O_2)$ between $TiO_{0.98}$ and $TiO_{1.08}$ must be imputed to the progressive disappearance of the short range order of the vacancies remaining from the long range order present near to $TiO_{1.0}$ at $T < 1300$ K (*24, 25*).

Such an order $\rightleftarrows$ disorder transition does not appear in the case of VO which can therefore explain the lack of increasing of $\Delta H(O_2)$. Moreover, from X-ray diffraction (*26*), it has been shown that rather than an ordering of the vacancies there would be a clustering of the vacancies in $VO_{1\pm x}$ promoted by the presence of a significant content of metal interstitials (*27, 28*) not present in TiO.

This study also has determined a value of $\Delta H^\circ_{f\,1323\,\mathrm{K}}$ ($VO_{1.00}$) = −96.5 ± 1.2 kcal mol^{-1}, a little different from the value in the JANAF tables (*29*), −100.4 ± 1.5 kcal mol^{-1}.

IV. Thermodynamics of the V–O System

We report in Table III thermodynamic properties of the V–O system at 1323 K. The P_{O_2} values for the compositions O/V = 0.2, 0.3, 0.35, 0.6, 0.8, 1.0, 1.2, and 1.3 are from Ref. (*1*). From these values and considering the phase boundaries obtained in this study (Table II), we reasonably may interpolate to obtain the P_{O_2} values for the compositions 0.4, 0.5, 0.7, 0.9, and 1.1 with the same uncertainty (0.1) for biphasic ranges and with an estimated uncertainty of 0.2 for monophasic ranges.

$\Delta G(O_2)$ and $\Delta S(O_2)$ are calculated from the well-known relationships:

$$\Delta G(O_2) = RT\ln P_{O2}$$

$$\Delta G(O_2) = \Delta H(O_2) - T\Delta S(O_2)$$

$\Delta H_f^\circ(VO_x)_{1323\ K}$ is obtained by integrating our calorimetric measurements:

$$\Delta H_f^\circ(VO_x) = \tfrac{1}{2}\int_0^x \Delta H(O_2)dx.$$

The uncertainties depend on the calibration of the calorimeter, 0.4% on the $\Delta H(O_2)$ value for the α phase (*2*) and 0.45% due to the experimental fluctuations (16 measurements; 95% confidence interval) and the sum of the quantities of heat released from O/V = 0 to x estimated with an accuracy of 0.4%.

V. Conclusion

In this study, we have obtained accurate values of $\Delta H(O_2)$ for the vanadium–oxygen system with O/V ratios from 0 to 1.3 at 1323 K by direct microcalorimetric determinations.

Independent determinations of $\Delta H(O_2)$ have been obtained by analyzing our previous emf measurements. The satisfactory agreement observed between the two sets of results shows the consistency of our thermodynamic measurements. Moreover, accurate values of phase boundaries in the studied composition range have been determined.

Henceforth, accurate thermodynamic data are available for the two phases V_β and VO which present a particular theoretical interest as concentrated solution of oxygen in metal for the first and as representative of a particular family of nonstoichiometric phases with high defect content for the second.

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