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## A Determination of $V_2O_5$ Activity in Corrosive Molten Vanadate-Sulfate Phases

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### ABSTRACT

Although aggressive hot corrosion by molten vanadate-sulfate deposits in boilers and engines burning low-quality fuel has been known for 75 years or more, there is surprisingly little data in the literature on the thermochemistry of vanadate-sulfate melts, especially as to the activity of the corrosive  $V_2O_5$  component. We have recently devised a thermogravimetric (TGA)/ $SO_3$  equilibrium technique that could potentially be used to "chart" the  $V_2O_5$  activity in vanadate-sulfate melts over a wide range of Na/V ratios,  $SO_3$  partial pressures and temperatures. The method is illustrated in a study of the reaction of  $CeO_2$  with a  $NaVO_3$ - $Na_2SO_4$ - $V_2O_5$ - $SO_3$  melt system ( $Na/V = 1$ ) at  $800^\circ C$ . Results from the study define the conditions under which  $CeO_2$  will be chemically nonreactive with the melt, and also show the  $V_2O_5$  activity coefficient to be, for the given experimental conditions, of the order of  $1 \times 10^{-2}$ .

### INTRODUCTION

Hot corrosion by molten vanadate-sulfate deposits resulting from vanadium and sulfur fuel impurities has been a recognized problem in boilers and engines for many years. One may wonder, however, why study vanadate-sulfate hot corrosion when the U.S. military, along with the civilian sector, is presently being pushed to burn only clean fuels because of environmental concerns. The primary answer, of course, is that in war there can be no guarantee of always

having clean fuel for our ship, tank and truck engines. It is important therefore that, even though "clean fuel" use is planned, we have engine materials and coatings that can tolerate low quality fuel if the wartime need arises.

A knowledge of the chemistry of vanadate-sulfate hot corrosion also has "dual usage" since many hot corrosion reactions are related to the reactions that can be used to clean up fuel. The removal of  $\text{SO}_3$  from smoke stack gases by  $\text{CaO}$  or  $\text{MgO}$  additives, for example, involves the same type of chemical reactions as molten sulfate-induced hot corrosion. Similarly, the reaction between yttria ( $\text{Y}_2\text{O}_3$ ) and  $\text{V}_2\text{O}_5$  to form highly stable  $\text{YVO}_4$ , which causes degradation of  $\text{Y}_2\text{O}_3$ -stabilized zirconia thermal barrier coatings in engines burning vanadium-contaminated fuel, has been recently "turned around" and used as the basis for a yttrium-based fuel additive for the prevention of hot corrosion by vanadium-containing fuels (1).

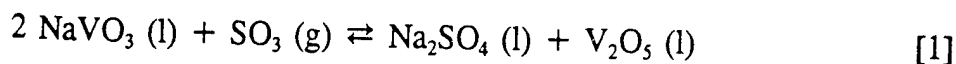
Attempts in the past to apply thermodynamics to predict and/or prevent hot corrosion have had limited success, perhaps partly because the difference in fuel impurity levels between "corrosive" and "noncorrosive" fuels is often small. Hot corrosion does not simply increase monotonically with fuel level, but frequently shows strongly accelerated attack for only small increases in fuel contaminants. For example, little hot corrosion is seen with aviation-quality ( $< 0.05\% \text{ S}$ ) gas turbine fuel, whereas extensive hot corrosion has been encountered with marine-quality fuel ( $< 1\% \text{ S}$ ), although the actual difference in sulfur content may be only 10-20X. In "low temperature" hot corrosion, even very small changes in the combustion gas  $\text{SO}_3$  partial pressure can determine whether engine deposits of eutectic  $\text{CoSO}_4\text{-Na}_2\text{SO}_4$  will be molten or not (2), which in turn can drastically effect the severity of hot corrosion (3,4). Vanadate hot corrosion has a similar short range of criticality, with vanadate-accelerated corrosion being generally negligible for V levels in fuel below 0.1 ppm, but often aggressive at V concentrations of only 1-10 ppm.

The importance of such small, but critical, changes in the fuel contaminant level is difficult to distinguish in the thermodynamic treatment of molten salt systems, since their energy effect is often hardly more than the probable error associated with much of our available thermodynamic data. For example, as shown below, a 10X change in the  $\text{V}_2\text{O}_5$  concentration (or equivalently, the  $\text{V}_2\text{O}_5$  activity coefficient) in a simulated vanadate-sulfate engine deposit typically corresponds to a difference of only about -10 kJ amidst calculations involving Gibbs energies of -1000 to -1500 kJ/mol, where each Gibbs energy may have a probable error of  $\pm 2$  kJ/mol or more. There is a strong need therefore for more accurate thermodynamic data, especially standard Gibbs energies of formation and activity

coefficients in melts, if thermodynamics are to be used with maximum effectiveness in predicting and/or preventing vanadate-sulfate hot corrosion.

The problem is compounded also by the uncertainty that still exists as to which "solution model" should be used for melts involving strong acid-base species such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{SO}_3$ ,  $\text{SiO}_2$ ,  $\text{V}_2\text{O}_5$ , etc. The solution model represents the framework by which the thermodynamicist seeks to describe how the activities of the various melt components change with concentration. In some cases, no solution model has been invoked, and the melts are simply assumed to be ideal (i.e., where the activity coefficient,  $\gamma$ , is unity, and the activity is equal to the mole fraction of the species). For example, Hwang and Rapp (5) assume that the Na-V-S-O systems at  $900^\circ\text{C}$  give ideal solution behavior, and that the activities of the component species can be equated to their molar concentrations. On the other hand, Bonnell and Hastie (6) believe that strong acid-base systems can be highly nonideal, with the activity of such species as  $\text{Na}_2\text{O}$  changing by many orders of magnitude over a narrow concentration range in some cases. Bonnell and Hastie have developed a solution model, the Ideal Mixing of Complex Components (IMCC) model, which they advocate as giving the best description of the solution behavior in strong acid-base melts. Numerous other possible solution models for melts have been proposed, however, as discussed, e.g., in the Proceedings of the Sixth International Conference on High Temperatures--Chemistry of Inorganic Materials (7).

In our own experience, we have found nonideal behavior for reaction [1],



which is, according to the thermodynamic calculations of Luthra and Spacil (8), the probable predominant reaction in blade deposits in gas turbine engines burning V- and S-containing fuels under normal marine operating conditions. Using a thermogravimetric analysis (TGA)/ $\text{SO}_3$  equilibrium technique (9), we equilibrated  $\text{NaVO}_3$  at  $700^\circ\text{C}$  and  $800^\circ\text{C}$  with fixed partial pressures of  $\text{SO}_3$  ranging from  $1 \times 10^{-7}$  to  $1 \times 10^{-3}$  atm, and determined the equilibrium weight gain resulting from the uptake of  $\text{SO}_3$ . From this data, we were able to calculate the mole fraction of  $\text{V}_2\text{O}_5$  experimentally formed by reaction [1], which we then subsequently compared with the "ideal behavior" expected for reaction [1], as explained below.

The activity,  $a_i$ , of a given species is described by

$$a_i = \gamma_i \cdot X_i \quad [2]$$

where  $\gamma_i$  is the activity coefficient, and  $X_i$  is the mole fraction. If the species gives ideal solution behavior, then the activity coefficient is equal to 1, and the activity is simply the mole fraction of the species.

For reaction [1], we have

$$\Delta G_T^\circ = -RT \ln K \quad [3]$$

where  $R$  is 8.3144 joules/degree-mole and  $T$  is 1073° K (i.e., for 800° C conditions), while

$$K = (a_{V_2O_5})(a_{Na_2SO_4})/(a_{NaVO_3})^2(P_{SO_3}) \quad [4]$$

and  $\Delta G_T^\circ$  is determined by

$$\Delta G_T^\circ = \sum \Delta_f G_{T, \text{Products}}^\circ - \sum \Delta_f G_{T, \text{Reagents}}^\circ \quad [5]$$

If reaction [1] follows ideal solution behavior, then using the standard Gibbs energies of formation for  $NaVO_3$  (l),  $SO_3$  (g),  $Na_2SO_4$  (l) and  $V_2O_5$  (l) provided by Luthra and Spacil (8), we can reduce equation [3] to

$$K \cdot P_{SO_3} = (MF_{V_2O_5})(MF_{Na_2SO_4})/(MF_{NaVO_3})^2 \quad [6a]$$

or, as a quadratic equation,

$$91.61166 \cdot P_{SO_3} = x^2/(1-2x)^2 \quad [6b]$$

Solving equation [6b] by numerical approximation on the computer then yields the ideal mole fraction of  $V_2O_5$  that should be formed at each given  $SO_3$  partial pressure.

The experimental mole fraction of  $V_2O_5$  was determined by converting the weight of  $SO_3$  taken up in reaction [1] to reflect the millimoles of  $Na_2SO_4$  and  $V_2O_5$  formed, as well as the millimoles of  $NaVO_3$  consumed, and calculating the resultant mole fraction of  $V_2O_5$ . (Note that the amount of free  $SO_3$  contained in the melt is so small that it can be ignored in this calculation.) The ideal vs. experimental mole fractions of  $V_2O_5$  formed at the different  $SO_3$  partial pressures are compared in Table 1, which also shows that division of the ideal  $V_2O_5$  mole

TABLE 1

Experimental vs. Ideal Solution Mole Fractions of  $V_2O_5$   
Formed at  $800^\circ\text{C}$  at the  $\text{SO}_3$  Partial Pressures Indicated

$P_{\text{SO}_3}$ (atm)	Wgt. Gain (mg/50mg $\text{NaVO}_3$ )	Ideal $M-F_{V_2O_5}$	Exptl. $M-F_{V_2O_5}$	"Activity Coeff.", $\gamma$
$1 \times 10^{-7}$	2.0	0.003	0.06	0.05
$1 \times 10^{-6}$	2.8	0.009	0.08	0.11
$1 \times 10^{-5}$	4.0	0.028	0.12	0.23
$1 \times 10^{-4}$	8.0	0.078	0.24	0.33
$1 \times 10^{-3}$	11.0	0.18	0.34	0.53

fraction by the experimental  $V_2O_5$  mole fraction yields an "activity coefficient" that indicates the nonideality of the  $V_2O_5$  solution behavior. This "activity coefficient" is not quantitative, however, because the actual  $V_2O_5$  activity in the melt is not (since  $a_{V_2O_5} \neq a_{\text{Na}_2\text{SO}_4}$ ) the ideal  $V_2O_5$  activity calculated here.

In the present paper, we describe a means, derived in a study of the reaction of  $\text{CeO}_2$  with the  $\text{NaVO}_3$ - $\text{SO}_3$  system at  $800^\circ\text{C}$  (10), by which it in fact appears possible to obtain quantitative values for the  $V_2O_5$  activity coefficient in vanadate-sulfate melts.

## EXPERIMENTAL

Our experiments were conducted using a Cahn 1000 thermobalance (Fig. 1) fitted with a system for controlling, and analyzing, the  $\text{SO}_2$  concentration in the furnace input air stream. The  $\text{SO}_3$  concentration was then established by equilibrating the  $\text{SO}_2$ -air mixture over a Pt catalyst at

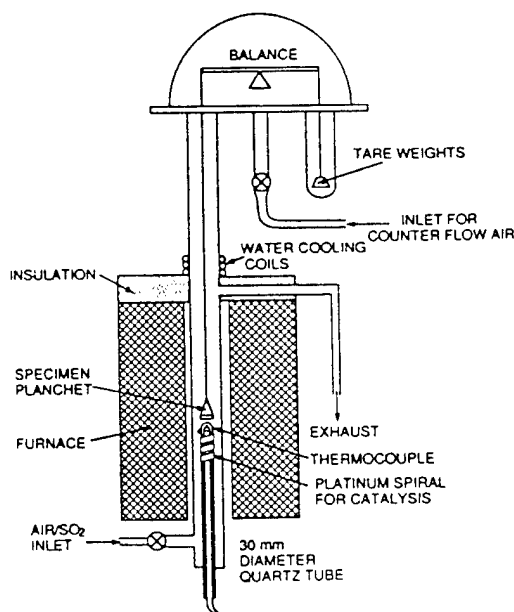


Fig. 1 Thermobalance/Furnace System

temperature in the furnace. Details of the experimental apparatus and procedure were published previously (9).

In the investigation, we first established a "baseline" curve of equilibrium weight gain vs.  $\text{SO}_3$  partial pressure at  $800^\circ\text{C}$  for 50 mg (0.41 mmols) of pure  $\text{NaVO}_3$ . We then ran duplicate experiments using just the same conditions except that 17 mg (0.1 mmols) of  $\text{CeO}_2$  was now mixed with the 50 mg of  $\text{NaVO}_3$ . The weight gain curve (Fig. 2) for  $\text{CeO}_2\text{-NaVO}_3$  was just the same as for  $\text{NaVO}_3$  alone (100%  $\text{NaVO}_3$ ) up to the  $\text{SO}_3$  partial pressure at which the  $\text{V}_2\text{O}_5$  activity of the melt was increased sufficiently, by reaction [1], that reaction [7] could commence:



X-ray diffraction was used to confirm that only  $\text{CeO}_2$  exists in the melts at  $\text{SO}_3$  partial pressures below the critical  $P_{\text{SO}_3}$  for reaction [7], and that  $\text{CeVO}_4$  is formed above this  $\text{SO}_3$  partial pressure.

## RESULTS AND DISCUSSION

Our experimental data are summarized in Fig. 2. The weight gain for  $\text{CeO}_2\text{-NaVO}_3$  as a function of  $\text{SO}_3$  partial pressure is the same as for  $\text{NaVO}_3$  alone up to an  $\text{SO}_3$  pressure of  $2\text{-}3 \times 10^{-6}$  atm. The absence of any extra increment of weight gain at the lower  $\text{SO}_3$  partial pressures shows that  $\text{CeO}_2$  is chemically inert (just as the Pt weighing planchet is) to the  $\text{NaVO}_3\text{-SO}_3$  system over this lower  $P_{\text{SO}_3}$  range.

However, an additional increment of weight gain begins to occur at  $2\text{-}3 \times 10^{-6}$  atm of  $\text{SO}_3$ , which marks the onset of reaction [7] where  $\text{CeO}_2 \rightarrow \text{CeVO}_4$ . The extra weight gain arises by the following mechanism. The  $\text{Na}_2\text{O}$ ,  $\text{V}_2\text{O}_5$  and  $\text{SO}_3$  components of the melt are interrelated through two dissociation reactions,

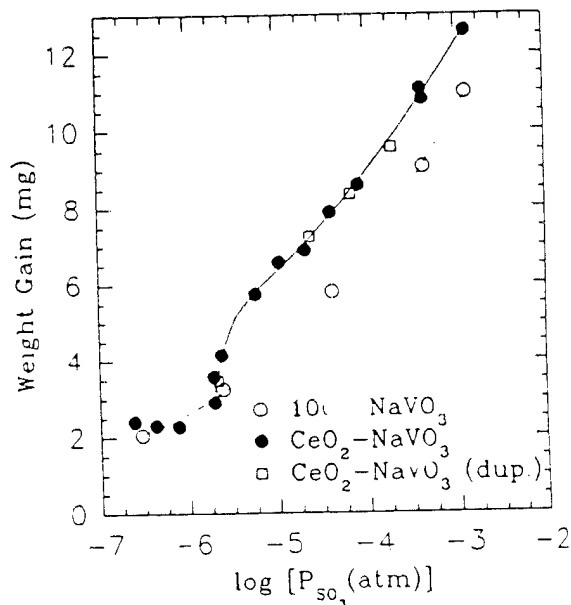
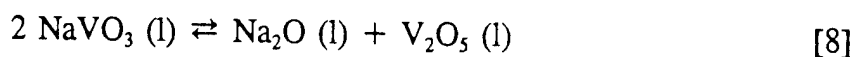


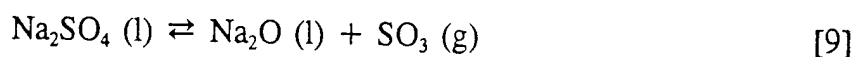
Fig. 2 Wgt. gain vs  $P_{\text{SO}_3}$  for  $\text{NaVO}_3$  and  $\text{CeO}_2\text{-NaVO}_3$  at  $800^\circ\text{C}$ .



one involving  $\text{NaVO}_3$ ,



and the other,  $\text{Na}_2\text{SO}_4$ ,



(Note that reversing reaction [9], and then adding reactions [8] and [9] to "cancel out"  $\text{Na}_2\text{O} (\text{l})$  yields reaction [1].) When  $\text{V}_2\text{O}_5$  begins to be consumed from the melt via reaction [7], this increases the  $\text{Na}_2\text{O}$  activity in the melt through reaction [8]. The increased  $\text{Na}_2\text{O}$  activity, in turn, allows more  $\text{SO}_3$  to enter the melt to form additional  $\text{Na}_2\text{SO}_4$  by reaction [9]. The combined reactions thus result in a "weight gain step" just at the  $P_{\text{SO}_3}$  at which reaction [7] commences.

The theoretical weight gain, by way of reactions [7]-[9], for the conversion of 0.1 mmols of  $\text{CeO}_2$  totally to  $\text{CeVO}_4$  is 3.2 mg. In an ideal, infinite system, one would thus expect a "vertical step" additional weight gain increment of 3.2 mg just at the critical  $P_{\text{SO}_3}$  at which reaction [7] becomes possible. In contrast, the maximum observed weight gain increment in Fig. 2 is only slightly more than 2 mg. However, subsequent work (10) since these initial experiments has confirmed that the experimental weight gain does in fact approach the theoretical value when higher dilutions (i.e., more  $\text{NaVO}_3$  to  $\text{CeO}_2$ ) are used. The failure to obtain full theoretical weight in Fig. 2 for  $\text{CeO}_2 \rightarrow \text{CeVO}_4$  is therefore probably only the result of the experimental conditions.

In earlier work (11), we determined the solubility of  $\text{CeO}_2$  in molten  $\text{NaVO}_3$  at  $800^\circ \text{C}$  to be approximately 0.2 mole percent, and showed also that  $\text{CeVO}_4$  crystals were precipitated at temperature from molten deposits produced by equilibrating  $\text{NaVO}_3$  on ceria-stabilized zirconia at  $700^\circ \text{C}$  with  $\text{SO}_3$ . In the latter case, the residual molten deposits were so depleted of vanadium (being strongly converted to sulfates) that no V could be detected by energy dispersive x-ray analysis. Only minimal solubility of the initial  $\text{CeO}_2$  in  $800^\circ \text{C}$   $\text{NaVO}_3$  (less than 1/125 of the total  $\text{CeO}_2$  present), or of the  $\text{CeVO}_4$  product in the reaction melt, is expected therefore in the present experiments.

If ideal behavior is assumed, then the Gibbs energy for reaction [7], and an "ideal" Gibbs energy of formation for  $\text{CeVO}_4$ , can be calculated as follows. As shown in Fig. 2, the amount of weight gain of the melt before reaction [7] begins is  $3.0 \pm 0.2$  mg. This weight gain represents the uptake of 0.0375 mmols of  $\text{SO}_3$  which, by reaction [1], corresponds to the formation of 0.0375 mmols

each of  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$ , and the consumption of 0.075 mmols of the 0.41 mmols of  $\text{NaVO}_3$  originally present. The resultant mole fraction of  $\text{V}_2\text{O}_5$  is 0.091 which, for ideal behavior, equates to a  $\text{V}_2\text{O}_5$  activity in the melt of 0.091. This is the  $\text{V}_2\text{O}_5$  activity at which reaction [7] just begins, and for reaction [7] we therefore have the thermodynamic relationship,

$$\Delta G^\circ_{1073\text{K}} = -RT \ln \frac{(a_{\text{CeVO}_4})^2 (P_{\text{O}_2})^{0.5}}{(a_{\text{CeO}_2})^2 (a_{\text{V}_2\text{O}_5})} \quad [10]$$

where, as pure solids,  $\text{CeVO}_4$  and  $\text{CeO}_2$  have activities of 1, and the activities of  $\text{O}_2$  in the air and  $\text{V}_2\text{O}_5$  are 0.21 and 0.091, respectively. This yields a calculated  $\Delta G^\circ_{1073\text{K}}$  for reaction [7] of -14.422 kJ, where the experimental uncertainty is  $\pm 0.4$  kJ assuming the melt weight gain to be  $3.0 \pm 0.2$  mg, the weight of the initial  $\text{NaVO}_3$  to be  $50.0 \pm 0.5$  mg, and the temperature to be  $1073 \pm 5^\circ \text{K}$ . Taking the Gibbs energies of formation for  $\text{CeO}_2$  (s) and  $\text{V}_2\text{O}_5$  (l) at  $800^\circ \text{C}$  as -865.890 kJ/mol and -1098.211 kJ/mol (12), we can then derive, as indicated by equation [5], an "ideal" standard Gibbs energy of formation of  $\text{CeVO}_4$  (s) at  $800^\circ \text{C}$  of -1422.207 kJ/mol.

There are no experimental  $\Delta_f G^\circ$ 's for  $\text{CeVO}_4$  in the literature to compare with this "ideal" value, but Yokokawa *et al* (12) have estimated the Gibbs energy of formation of  $\text{CeVO}_4$  (s) at  $800^\circ \text{C}$  as -1444.785 kJ/mol. This gives agreement to within about 20 kJ/mol. However, we know from our earlier study (9) that the  $\text{NaVO}_3$ - $\text{V}_2\text{O}_5$ - $\text{Na}_2\text{SO}_4$  melt system is clearly nonideal, with the  $\text{V}_2\text{O}_5$  activity coefficients being of the order of 0.1 to 0.01 at the lower  $\text{V}_2\text{O}_5$  concentrations (Table 1). If  $\text{V}_2\text{O}_5$  activity coefficients of 0.1, 0.01, etc. are introduced into equation [10], the resultant  $\Delta_f G^\circ_{\text{CeVO}_4}$  becomes about 10 kJ/mol more negative for each 10X reduction in the activity coefficient, and equals -1442.749 kJ/mol for a  $\text{V}_2\text{O}_5$  activity coefficient of 0.01. This last value agrees very well with the  $\Delta_f G^\circ_{\text{CeVO}_4}$  of -1444.785 kJ/mol estimated by Yokokawa *et al*, and we take the agreement therefore as indicating that a  $\Delta_f G^\circ$  for  $\text{CeVO}_4$  at  $800^\circ \text{C}$  of about -1445 kJ/mol, and a  $\text{V}_2\text{O}_5$  (l) activity coefficient in the melt of about 0.01, are both essentially correct.

Our TGA/ $\text{SO}_3$  equilibrium technique can be expanded to include different temperatures, vanadate-sulfate melt compositions (i.e., by using different Na/V ratios in the initial vanadate deposit), and "indicator" reaction pairs (i.e.,  $\text{CeO}_2 \rightarrow \text{CeVO}_4$ ). We have shown earlier (9), for example, that  $\text{Sc}_2\text{O}_3 \rightarrow \text{ScVO}_4$  at  $\sim 5 \times 10^{-6}$  atm of  $\text{SO}_3$ , and  $\text{In}_2\text{O}_3 \rightarrow \text{InVO}_4$  at  $\sim 5 \times 10^{-4}$  atm of  $\text{SO}_3$ , in the  $\text{NaVO}_3$ - $\text{SO}_3$  system by reactions analogous to  $\text{CeO}_2 \rightarrow \text{CeVO}_4$ . The TGA/ $\text{SO}_3$  equilibrium

technique therefore has the potential to provide, by a series of studies of the various oxide  $\rightarrow$  vanadate reactions over an array of different sulfate-vanadate melt compositions and temperatures, the high accuracy thermodynamic data (including Gibbs energies of formation, activity coefficients, solution models, etc.) that are needed to understand and predict the reaction behavior of high temperature oxides with vanadate-sulfate melts.

## CONCLUSIONS

A thermogravimetric analysis (TGA)/SO<sub>3</sub> equilibrium study of the reaction of CeO<sub>2</sub> with the NaVO<sub>3</sub>-SO<sub>3</sub> system at 800° C shows CeO<sub>2</sub> to be inert to chemical reaction with the NaVO<sub>3</sub>-SO<sub>3</sub> melt at SO<sub>3</sub> partial pressures up to  $2-3 \times 10^{-6}$  atm, with CeVO<sub>4</sub> being formed above this SO<sub>3</sub> partial pressure.

Thermodynamic analysis of the reaction data indicates the  $\Delta_f G^\circ$  for CeVO<sub>4</sub> (s) at 800° C as being -1445 kJ/mol, and the V<sub>2</sub>O<sub>5</sub> activity coefficient of the melt at the point of CeVO<sub>4</sub> formation as being approximately  $1 \times 10^{-2}$ .

The TGA/SO<sub>3</sub> equilibrium technique has the potential to significantly increase our knowledge of the thermochemistry and melt solution chemistry involved in the reactions of high temperature oxides with molten vanadate-sulfate melts.

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