The Standard Enthalpy and Entropy of Formation of Rh_2O_3 – A Third-Law Optimization

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ABSTRACT

The standard Gibbs energy of formation of Rh_2O_3 at high temperature has been determined recently with high precision. The new data are significantly different from those given in thermodynamic compilations. Accurate values for enthalpy and entropy of formation at 298.15 K could not be evaluated from the new data, because reliable values for heat capacity of Rh_2O_3 were not available. In this article, a new measurement of the high temperature heat capacity of Rh_2O_3 using differential scanning calorimetry (DSC) is presented. The new values for heat capacity also differ significantly from those given in compilations. The information on heat capacity is coupled with standard Gibbs energy of formation to evaluate values for standard enthalpy and entropy of formation at 289.15 K using a multivariate analysis. The results suggest a major revision in thermodynamic data for Rh_2O_3. For example, it is recommended that the standard entropy of Rh_2O_3 at 298.15 K be changed from 106.27 J mol^{-1} K^{-1} given in the compilations of Barin and Knacke *et al.* to 75.69 J mol^{-1} K^{-1}. The recommended revision in the standard enthalpy of formation is from –355.64 kJ mol^{-1} to -405.53 kJ mol^{-1}.

1. INTRODUCTION

Thermodynamic information on oxides and sulfides of metals of the Pt-group are important for optimizing the condition for their recovery during both primary and secondary processing. Although it is often thought that good data exist at least for the binary compounds in current thermodynamic compilations, a closer examination reveals many instances of major uncertainty. As part of a larger program of research aimed at filling the major gaps in essential data, measurements have been conducted on several binary and ternary oxides involving Pt-group metals /1-6/.

Recent measurements /7,8/ on the Gibbs energy of formation of Rh_2O_3 at high temperatures indicate that values given in current thermodynamic compilations /9,10/ may involve serious error, especially at lower temperatures. Since cryogenic heat capacity of Rh_2O_3 has not been determined, there is no accurate assessment of its standard entropy at 298.15 K. Direct calorimetric measurement of enthalpy of formation of Rh_2O_3 has not been performed. Available high-temperature heat capacity data /8-11/ are also not in good agreement. Therefore, a rigorous analysis of the Gibbs energy of formation data for Rh_2O_3 to obtain accurate enthalpy and entropy of formation was not possible /7/. Reported in this article is a new

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measurement of the heat capacity of rhodium sesquioxide at high temperature using a differential scanning calorimeter (DSC). This information is then coupled with information on the Gibbs energy of formation, to derive the standard enthalpy and entropy using a multivariate analysis. A comparative discussion of the various results is then presented.

2. HIGH-TEMPERATURE HEAT CAPACITY

A differential scanning calorimeter (DSC) was used to measure the heat capacity of Rh_2O_3 under pure dry oxygen gas from 350 to 1075 K. A sample of 99.99 % purity was heat treated at 1250 K under dry oxygen gas for ~ 200 ks. X-ray diffraction analysis of the sample after annealing, using Si powder as an internal standard, indicated that Rh_2O_3 had an orthorhombic structure, space group Pbca (61), with $a = 0.5148$, $b = 0.5438$ and $c = 1.4693$ nm. The DSC was operated in the step heating mode to increase accuracy with α-Al_2O_3 as the reference material. The alumina powder was dehydrated by vacuum treatment at 1200 K before use. The difference in the heat flux into the sample and the reference material was integrated during heating at a constant rate (0.0333 K s^{-1}) over small temperature steps (25 K) with isothermal dwell time of 0.9 ks. Analysis of Rh_2O_3 by XRD after the DSC experiment indicated no detectable change in its structure or lattice parameter.

The measured heat capacity is displayed as a function of temperature in Figure 1 in comparison with values reported in the literature /8, 9-11/. The accuracy of the measured heat capacity is estimated to vary from ± 0.3 J mol^{-1} K^{-1} at 350 K to ± 0.6 J mol^{-1} K^{-1} at 1075 K. The heat capacity measured in this study can be represented by the equation,

$$C_P^o / \mathrm{J\ mol^{-1}\ K^{-1}} = 114.1 + 1.896\times10^{-2}\,T - 2.723\times10^{6}\,T^{-2} \qquad (1)$$

The results of this study are slightly higher than the recent values of Nell and O'Neill /8/ also obtained using a DSC. The difference is considered to be within the combined uncertainty of the two measurements. The overall agreement is reasonable. The old data of Wöhler and Jochum /11/ are significantly different. Since details regarding the quality of the sample used and accuracy of measurement are not known, it is difficult to speculate on the reason for the difference. There is a large discrepancy between the Dulong-Petit approximation for C_V ($3nR$, where n is the number of atoms per formula unit) and the data of Wöhler and Jochum. The data given in current thermodynamic compilations /9,10/ are better than that reported by Wöhler and Jochum. However, they require further revision in the light of the results obtained in this study and by Nell and O'Neill /8/.

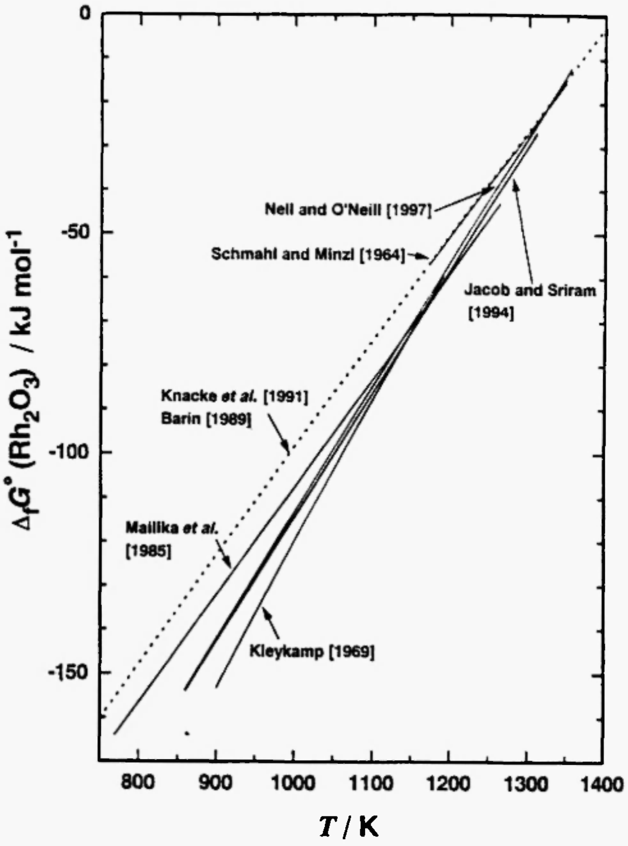

Fig. 1: Heat capacity of Rh_2O_3 at constant pressure as a function of temperature.

3. SELECTION OF GIBBS ENERGY OF FORMATION

All available information in the literature /7-10,12-14/ on the Gibbs energy of formation of Rh_2O_3 at high temperature is plotted in Figure 2 as a function of temperature. Despite the fact that solid oxide

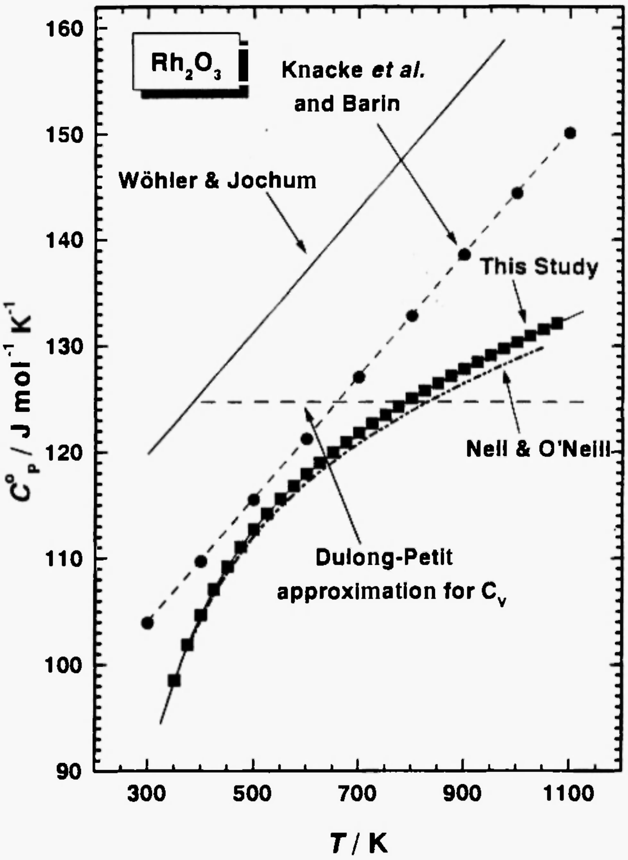

Fig. 2: Comparison of data on the standard Gibbs energy of formation of Rh_2O_3 reported in the literature.

galvanic cells were used in four experimental studies /7,8,12,13/, there are significant differences at the lower temperatures. The measurements of Jacob and Sriram /7/ were conducted relative to the primary reference standard for oxygen potential (pure O_2) using an advanced version of the solid state cell incorporating a buffer electrode to prevent polarization of the working electrode. The most recent study of Nell and O'Neill /8/ using air as the reference electrode is in reasonable agreement with the results of Jacob and Sriram; the slightly more positive value at high temperature may be attributed to either minor polarization of their measuring electrode caused by the small electrochemical flux of oxygen through the solid electrolyte, or the use of bielectrolyte cell with yttria-doped thoria (YDT) in contact with air reference. Because of significant hole conduction in YDT at high oxygen partial pressures, there would be a reduction in their cell emf if a gradient of oxygen potential existed across the YDT pellet. Moreover, air is not a good reference for precise measurements, because the partial pressure of oxygen varies with atmospheric parameters such as wind velocity and relative humidity.

At the lower end of the temperature range of measurements, the recent results of Jacob and Sriram and Nell and O'Neill fall between those of Kleykamp /12/ and Mallika *et al.* /13/. Kleykamp used Fe+FeO as the reference electrode, while Mallika *et al.* used air as the reference. Thus, their emfs are smaller than what would be expected from the data of Jacob and Sriram, or Nell and O'Neill, suggesting sluggish reactions at the electrode at lower temperatures as a possible source of error.

Except for the data of Mallika *et al.*, results from the three other electrochemical measurements converge at high temperature with that of Schmahl and Minzl /14/ who used a manometric technique. Viewed both from a comparative standpoint of the results obtained and intrinsic superiority of the measurement technique, the reliability of the values suggested by Jacob and Sriram over the entire temperature range is recognized. Their results are summarized by the equation /7/:

$$\Delta_f G^\circ = -396{,}365 + 282.00T \quad (\pm 120) \ \text{J mol}^{-1} \qquad (2)$$

Values given in the current compilations of Knacke *et al.* /9/ and Barin /10/ are not consistent with recent measurements and clearly require revision.

4. EVALUATION OF STANDARD ENTHALPY AND ENTROPYOF FORMATION

The third-law analysis of the high-temperature data on Gibbs energy of formation of orthorhombic Rh_2O_3 is based on the equation,

$$\Delta_f G^\circ(T) = \Delta_f H^\circ_{298.15} + \int_{298.15}^{T} \Delta C^\circ_P dT - T\left(\Delta_f S^\circ_{298.15} + \int_{298.15}^{T} \frac{\Delta C^\circ_P}{T} dT\right) \qquad (3)$$

where the changes in the thermodynamic parameters are defined for the formation reaction;

$$2\,Rh + 3/2\,O_2 \rightarrow Rh_2O_3\ (\text{orthorhombic}) \qquad (4)$$

The conventional third-law analysis is based on knowledge of the absolute entropy of the reactants and products at 298.15 K. For solid materials, this requires measurement of low temperature heat capacity. Furthermore, high temperature heat capacity of reactants and products should be available. Then, the third-law analysis allows us to calculate the enthalpy change for the reaction at 298.15 K from each value of the Gibbs energy change at high temperature. When all the data are correct, the derived enthalpy change is independent of the temperature of measurement of the Gibbs energy change. A drift with temperature of the derived enthalpy change at 298.15 K indicates error in at least one set of input data.

When the absolute entropies of either reactants or products are not known, but the enthalpy change for the reaction is measured independently by a calorimetric method, equation 3, permits calculation of the standard entropy change for the reaction at 298.15 K from each measurement of the Gibbs energy of formation as a function of temperature. Again, if all the data are correct the derived entropy change should be independent of temperature corresponding to the Gibbs energy of formation.

When neither the standard enthalpy nor the standard entropy change at 298.15 K is known independently, equation (3) can still be used to derive reliable values for these unknown quantities. For this, the Gibbs energy change should be known accurately over a wide range of temperature and the heat capacities of reactants and products should be available form independent sources as a function of temperature from 298.15 K to the highest temperature of the Gibbs energy measurement. This situation prevails for the reaction corresponding to the formation of Rh_2O_3. Both the unknown quantities can be treated as constants in a set of simultaneous equations. At each temperature of measurement of the Gibbs energy change, all the other quantities in equation (3) are well defined. In principle, solution of any two simultaneous equations can yield values of the enthalpy and entropy change. In practice, the maximum sets of equations are solved and an average value of the enthalpy and entropy change is obtained. The problem of estimating the best values of two constants in a set of simultaneous equations can be addressed by an optimization procedure.

An analysis along the lines suggested above using Gibbs energy of formation reported by Jacob and Sriram /7/, heat capacities for Rh and O_2 from Knacke *et al.* /9/ and that for Rh_2O_3 from this study yields the following values: $\Delta H^{o}_{298.15} = -405.53\ (\pm 0.26)\ \text{kJ mol}^{-1}$, and $\Delta S^{o}_{298.15} = -295.04\ (\pm 0.24)\ \text{J mol}^{-1}\ \text{K}^{-1}$. Using values for standard entropies of Rh and O_2 at 298.15 K from Knacke et al. /9/, the standard entropy of Rh_2O_3 is obtained as $S^{o}_{298.15} = 75.69\ (\pm 0.5)\ \text{J mol}^{-1}\ \text{K}^{-1}$. The internal consistency of the procedure can be checked by using the derived value of standard entropy of Rh_2O_3 in the conventional third-law analysis of the high temperature data on the Gibbs energy of formation /7/. The results, demonstrated in Figure 3, provide validation of the optimization procedure. The values deduced in this study are for the orthorhombic form of Rh_2O_3. A corundum-type structure (space group $R\bar{3}c$) is probably more stable at low temperature. However, the transformation is sluggish and thermodynamic parameters characterizing the transition are not known. Therefore, thermodynamic properties of the

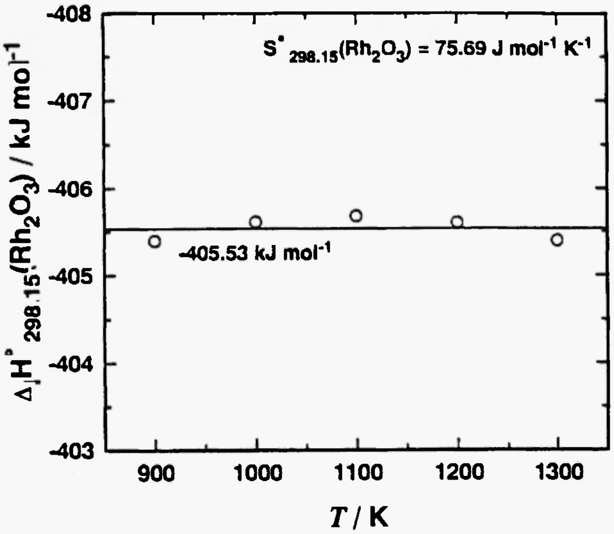

Fig. 3: Third-law analysis of the data on the Gibbs energy of formation of Rh_2O_3 reported by Jacob and Sriram /7/ using heat capacity and standard entropy of Rh_2O_3 from this study.

Table 1

Comparison of values for orthorhombic Rh_2O_3 optimized in this study with data in the literature

Source	$\Delta_f H^{\circ}_{298.15}$ kJ mol^{-1}	$S^{\circ}_{298.15}$ J mol^{-1} K^{-1}	Comments
Kleykamp/12/	-451.9 (±16.7)	40.2 (±16)	Second-law
Mallika *et al.* /13/	-360 (±3)	104.8 (±3.2)	Third-law for enthalpy; second-law for entropy
Nell and O'Neill /8/	-405.96 (±1.15)	71.50 (±1.5)	Third-law for enthalpy; method of successive approximation for entropy
Knacke *et al.* /9/	-355.64	106.27	Evaluation
Barin/10/	-355.64	106.27	Evaluation
This Study	-405.53 (±0.26)	75.69 (±0.5)	Multivariate analysis; third-law optimization

corundum-type Rh_2O_3 cannot be deduced now.

Values for enthalpy of formation and standard entropy of Rh_2O_3 at 298.15 K obtained in this study is compared in Table 1 with values suggested in the literature. The values of Kleykamp /12/ are based on second-law analysis of his emf measurement and heat capacity of Rh_2O_3 identical to that in Barin /10/. The enthalpy of formation suggested by Mallika *et al.* /13/ are based on third-law evaluation of their emf data using standard entropy and heat capacity of Rh_2O_3 from Barin /10/, while the standard entropy is derived by the second-law method using heat capacity from Barin. There is an inconsistency between their recommended entropy and the value used in their third-law evaluation. The results of this study are in fair agreement with values suggested by Nell and O'Neill /9/. Both sets of data are internally consistent. The present results, based on more accurate measurement of the Gibbs energy of formation using an advanced version of the solid state cell, refine the values suggested by Nell and O'Neill /9/. The data in the compilations of Knacke *et al.* /9/ and Barin /10/ need revision since they do not agree with recent studies on Gibbs energy of formation and high-temperature heat capacity of Rh_2O_3. The revision is major since the enthalpy correction is ~ 50 kJ mol^{-1} and the entropy correction is ~ 30 J mol^{-1} K^{-1}.

5. SUMMARY

Demonstrated in this article is a rigorous optimization procedure for deriving simultaneously values for standard enthalpy and entropy of formation at 298.15 K when accurate values for Gibbs energy of formation over a wide range of temperature and the high temperature heat capacities of reactants and products are known. DSC was used to measure the heat capacity of the orthorhombic form of Rh_2O_3. This data was coupled with recent measurement of the Gibbs energy of formation of Rh_2O_3 to derive values for the standard enthalpy of formation $\{\Delta H^{o}_{298.15} = -405.53\ (\pm 0.26)$ kJ mol$^{-1}\}$ and entropy $\{S^{o}_{298.15} = 75.69\ (\pm 0.5)$ J mol^{-1} K$^{-1}\}$. The values given in current thermodynamic tables /9,10/ require major revision.

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