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Thermochimica Acta 303 (1997) 183–186

thermochimica acta

Note on the enthalpies of formation of $SrWO_4$ and $BaWO_4$ determined by high-temperature direct synthesis calorimetry from $SrCO_3 + WO_3$ and $BaCO_3 + WO_3$

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Received 25 April 1997; received in revised form 17 June 1997; accepted 29 June 1997

Abstract

A comparison has been made between the experimentally measured value of enthalpy change of the reaction

$$CaO(s,\ 298\ K) + WO_3(s,\ 298\ K) = CaWO_4(s,\ 1473\ K),$$

and the value for the same reaction derived from the measured enthalpy change of the reaction

$$CaCO_3(s,\ 298\ K) + WO_3(s,\ 298\ K) = CaWO_4(s,\ 1473\ K) + CO_2(g,\ 1473\ K).$$

The two values of ΔH, namely 13.97 ± 2.45 and 9.34 ± 3.55 kJ mol^{-1}, are roughly comparable when experimental uncertainties are taken into consideration. This suggests that the error induced in the value of the enthalpy of formation, from the component oxides, of $CaWO_4$ by using $CaCO_3$ instead of CaO as one of the reactants in direct synthesis experiments would not be very great. The lower value of ΔH, 9.34 ± 3.55 kJ mol^{-1}, indicates that the CO_2 formed in the reaction between $CaCO_3$ and WO_3 is released at a temperature somewhat lower than the calorimeter temperature.

For all partial pressures of CO_2, $SrCO_3$ and $BaCO_3$ decompose at much higher temperatures than $CaCO_3$. Hence, it can be inferred that the agreement between the two values of ΔH would be significantly better for SrO–$SrCO_3$ and BaO–$BaCO_3$, than for CaO–$CaCO_3$.

In a recent communication (Q. Guo and O.J. Kleppa, Thermochim. Acta, 288 (1996) 53–61), we assumed that the CO_2 formed from $SrCO_3 + WO_3$ and $BaCO_3 + WO_3$ in the high-temperature calorimeter is released at or very near the calorimeter temperature. Under this assumption, which we believe is valid, the enthalpies of formation for $SrWO_4$ and $BaWO_4$, from the component oxides, reported by these authors should be reliable. © 1997 Elsevier Science B.V.

Keywords: Alkaline-earth tungstates; Enthalpy of formation; High-temperature direct synthesis calorimetry

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In a recent communication [1], the present authors reported new values for the enthalpies of formation, from the component oxides, of $MeWO_4$ (Me = Mg, Ca, Sr, Ba); all values were determined by direct synthesis calorimetry in a high-temperature reaction calorimeter maintained at 1473 ± 2 K.

For Me = Mg and Ca, the synthesis reactions were all based on the equation

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PII S0040-6031(97)00259-1

$$\mathrm{MeO(s,\ 298\ K) + WO_3(s,\ 298\ K) = MeWO_4(s,\ 1473\ K)} \quad (1)$$

for which the measured heat effects were $\Delta H(1)$.

In a subsequent experiment, the heat contents of the reaction products at 1473 K were measured:

$$\mathrm{MeWO_4(s,\ 298\ K) = MeWO_4(s,\ 1473\ K)} \quad (2)$$

and

$$\Delta H(2) = H^0_{1473} - H^0_{298}$$

Taking $\Delta H(1) - \Delta H(2)$, we obtained the enthalpy change for the formation reaction from the two oxides at 298 K, ΔH_f as follows:

$$\mathrm{MeO(s,\ 298\ K) + WO_3(s,\ 298\ K) = MeWO_4(s,\ 298\ K)} \quad (3)$$

and

$$\Delta H_f = \Delta H(1) - \Delta H(2)$$

This method worked without any complications for Me = Mg and Ca. However, for Me = Sr and Ba, the extreme instability of the pure oxides SrO and BaO with respect to reactions with water vapor and with carbon dioxide in the air make this direct approach impractical. For this reason, the basic calorimetric reaction adopted for Me = Sr and Ba was:

$$\mathrm{MeCO_3(s,\ 298\ K) + WO_3(s,\ 298\ K) = MeWO_4(s,\ 1473\ K) + CO_2(g,\ 1473\ K)} \quad (4)$$

In the present form, this equation assumes that the carbon dioxide liberated in the solid-state reaction between the carbonates and WO_3 is released at the operating temperature of the calorimeter. If this assumption is valid, the enthalpy change of reaction (1), namely $\Delta H(1)$, may readily be obtained from the measured enthalpy change of reaction (4), namely $\Delta H(4)$, through a simple calculation which involves only the known enthalpy changes associated with the following two equations:

$$\mathrm{MeCO_3(s,\ 298\ K) = MeO(s,\ 298\ K) + CO_2(g,\ 298\ K)} \quad (5)$$

and

$$\mathrm{CO_2(g,\ 298\ K) = CO_2(g,\ 1473\ K)} \quad (6)$$

Clearly, we have

$$\Delta H(1) = \Delta H(4) - \Delta H(5) - \Delta H(6) \quad (7)$$

However, questions may be raised regarding the assumption that the carbon dioxide gas is actually released at the temperature of the calorimeter. Is it possible that the carbon dioxide gas generated in Eq. (4) is, in fact, released at some temperature which is significantly lower than the calorimeter temperature of 1473 K? If this is the case, the observed value of $\Delta H(4)$ will be somewhat less endothermic and the value of $\Delta H(1)$ derived from Eq. (7) will also be less endothermic. If so, the calculated value of the enthalpy of formation at 298 K from the component oxides will be somewhat too exothermic.

We readily admit that when our assumption regarding Eq. (4) was originally made, we had no rigid proof for its correctness; clearly, we did not know for sure the exact temperature at which the carbon dioxide was released. The basis of this assumption was simply 'commonsense':

1. We know that the heat content of our calorimeter system was huge compared to the relatively small samples (0.5–0.7 mmol) used in reaction (4). Hence, we assumed that the calorimeter system would work like a buffer: a small sample dropped from room temperature into the calorimeter at 1473 K will not change its temperature very significantly. At the same time, the sample itself will be heated up very rapidly to the temperature of the calorimeter.
2. Even if it is true that the decomposition of $SrCO_3$ and $BaCO_3$ actually may be initiated at temperatures somewhat lower than 1473 K, their reactions with WO_3 will also release some heat. Hence, the temperature of the CO_2 gas formed should not be significantly lower than 1473 K.

Perhaps the best way to prove that our assumption is acceptable would be to carry out two series of experiments: In one series pure SrO and BaO are used, while in the other series $SrCO_3$ and $BaCO_3$ are used. If $\Delta H(1)$, measured directly according to Eq. (1), agrees with $\Delta H(1)$ derived from Eq. (7), it would indicate that Eq. (4) is valid for $SrCO_3$ and $BaCO_3$.

Unfortunately, this experimental comparison cannot be carried out in our laboratory due mainly to the extreme instability of SrO and BaO in air. For this reason, we instead decided to carry out a comparison based on CaO and $CaCO_3$ (calcite).

According to information provided by Professor Müller of Achen, Germany (personal communication, 1996), the following situation exists: when the partial pressure of CO_2 is ca. $10^{-3.5}$ bar (the partial pressure of CO_2 in air), solid $CaCO_3$, $SrCO_3$ and $BaCO_3$ will start decomposing at ca. 794, 1027 and 1171 K, respectively. On the other hand, if the partial pressure of CO_2 is raised to 1 bar, $CaCO_3$ and $SrCO_3$ will decompose at ca. 1163 and 1503 K. However, $BaCO_3$ will first melt at ca. 1686 K, and then decompose at ca. 1835 K.

In our calorimeter, the partial pressure of CO_2 in air will be changing significantly during the chemical reactions. It may start changing at ca. $10^{-3.5}$ bar, but will then rise gradually. However, it will never exceed 1 atm (1.013 bar). At this pressure, solid $CaCO_3$ will decompose at ca. 1172 K [2]. Hence, a sample of pure $CaCO_3$ in the calorimeter will decompose at temperatures between 794 K and 1172 K.

Of course, $CaCO_3$ decomposes at much lower temperatures than $SrCO_3$ and $BaCO_3$. For this reason, the carbon dioxide gas formed during the reaction between $CaCO_3$ and WO_3 will be released at lower temperatures than when this gas is formed in reactions between $SrCO_3$ or $BaCO_3$ and WO_3.

If a comparison between the values of $\Delta H(1)$ for $CaWO_4$, obtained directly from Eq. (1) and indirectly from Eq. (7), are in reasonable agreement, it will imply that our earlier assumptions for $SrCO_3$ and $BaCO_3$ are valid; i.e. the carbon dioxide gas is released essentially at the temperature of the calorimeter. On the other hand, if there is a significant difference between the two values of $\Delta H(1)$, we will be unable to draw any definite conclusions regarding our previously published values for the enthalpies of formation from the two oxides for $SrWO_4$ and $BaWO_4$.

We carried out two new series of experiments on $CaCO_3 + WO_3$. In the first series, the adopted experimental conditions essentially duplicated the conditions used in our earlier work on $SrCO_3$ or $BaCO_3 + WO_3$. All relevant results are presented in Table 1. In the first row of this table, we restate our earlier results for $\Delta H(1)$, for $H^0_{1473} - H^0_{298}$ and for ΔH_f, all taken from [1]. In the second row of this table, we give our five experimental values for $\Delta H(4)$, the mean of these five values and the newly derived value of $\Delta H(1)$, calculated from Eq. (7). We see that the earlier direct value of $\Delta H(1)$ was 13.97 ± 2.45 kJ mol^{-1}, whereas the newly derived value is 9.34 ± 3.55 kJ mol^{-1}. These two values are roughly comparable when the considerable experi-

Table 1
A comparison between the enthalpies of formation of $CaWO_4$ from the component oxides determined, on the one hand, from $CaO + WO_3$ and, on the other, from $CaCO_3 + WO_3$. All values are based on high-temperature direct synthesis calorimetry at 1473 K

Starting materials	$\Delta H(4)$/(kJ mol^{-1})	$\Delta H(1)$/(kJ mol^{-1})	$H^0_{1473} - H^0_{298}$/(kJ mol^{-1})	ΔH_f/(kJ mol^{-1})
$CaO + WO_3$ [1]		13.97 ± 2.45	182.50 ± 2.09	−168.5 ± 3.3
$CaCO_3 + WO_3$ measured without Al_2O_3 spheres in the reaction crucible	246.21			
	243.86			
	254.27			
	248.34			
	248.49			
	248.23 ± 3.46	9.34 ± 3.55		−173.2 ± 4.1
$CaCO_3 + WO_3$ measured with Al_2O_3 spheres in the reaction crucible	252.93			
	248.10			
	256.72			
	247.03			
	249.80			
	250.92 ± 3.52	12.03 ± 3.61		−170.5 ± 4.2

mental uncertainties in the two results are taken into account. Though the agreement between the two values is far from perfect, the results indicate that the error induced in the value of ΔH_f by using $CaCO_3$ instead of CaO would not be very great. The lower value of $\Delta H(1)$, in the second row, suggests that although the CO_2 released in the reaction between WO_3 and $CaCO_3$ was not fully heated to the temperature of the calorimeter, it was released at a temperature not far below the calorimeter temperature. Since we know that for all partial pressures of CO_2, $SrCO_3$ and $BaCO_3$ decompose at much higher temperatures than $CaCO_3$, we infer that the agreement between the two values of $\Delta H(1)$ would be significantly better for SrO–$SrCO_3$ and BaO–$BaCO_3$ than we have found for CaO–$CaCO_3$. We concluded from this, that our assumption regarding the CO_2, formed from $SrCO_3 + WO_3$ and from $BaCO_3 + WO_3$, actually released at or near the calorimeter temperature is a very reasonable assumption. Hence, our reported values for the enthalpies of formation of $SrWO_4$ and $BaWO_4$ from the component oxides given in [1] should be reliable.

Because the agreement between the results of our two experiments with CaO and $CaCO_3$ was not perfect, we decided to carry out a second series of measurements on $CaCO_3 + WO_3$. In these experiments, we loaded a small amount of alumina spheres with diameters of ca. 1 mm into the bottom of the alumina crucible of the calorimeter. The amount of alumina spheres was large enough so that the sample capsule would be buried among the alumina spheres after the sample had been dropped into the crucible. We assumed that the presence of these spheres might possibly improve the heat transfer between the released CO_2 gas and the rest of the calorimeter. Hence, we hoped that the second series of experiments might improve the agreement between the CaO and $CaCO_3$ measurements. The experimental results of this second series are given in row 3, Table 1. Apparently, the presence of the alumina spheres did function in the way we had hoped; the new calculated value of $\Delta H(1)$ was 12.03 ± 3.61 kJ mol^{-1}. This result should be compared both with our earlier calculated value of 9.34 ± 3.55 kJ mol^{-1} and with our original value of $\Delta H(1)$, based on the use of pure CaO, which was 13.97 ± 2.45 kJ mol^{-1}.

In conclusion, we believe that our assumption, that the CO_2 gas formed in the reactions between $SrCO_3$ or $BaCO_3$ with WO_3 in our high-temperature calorimeter is released at or near the temperature of the calorimeter, is a very reasonable one. Hence, our reported values for the enthalpies of formation of $SrWO_4$ and $BaWO_4$ from the component oxides should be quite accurate.

On the other hand, if $CaCO_3$ is used instead of CaO in direct synthesis experiments at 1473 K, one should be very cautious. We have shown that loading the receiving crucible with small alumina spheres may improve the values somewhat.

Acknowledgements

This work has been supported by NSF under grant CHE-9313885, and has also made use of The University of Chicago Materials Research Science and Engineering Center Shared Facilities supported by the NSF under grant DMR-9400379. The authors also would like to extend their thanks to Professor Dr. F. Müller of Rhenisch-Westfalische Technische Hochschule, Aachen, Germany, for providing us with the quoted information regarding the dependence on temperature of the partial pressure of CO_2 in alkaline-earth oxide–carbonate equilibria.

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