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Thermodynamics of the thermal decomposition and formation of ytterbium(III) oxide selenide

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Abstract

The thermal decomposition of $(YbO)_2Se(s)$ was studied over the temperature range 1753-1997 K by the Knudsen effusion weight loss technique. The decomposition leads to a gas phase containing ytterbium and selenium with a molar ratio of 2:3 and to a residue of $Yb_2O_3(s)$. Using literature and estimated enthalpy and entropy data for the gaseous species Yb, Se, YbSe and Se_2, it could be established from the rates of effusion that the principal decomposition reaction is

$$(YbO)_2Se(s) \rightarrow \tfrac{2}{3}Yb_2O_3(s) + \tfrac{2}{3}Yb(g) + Se(g)$$

The following second-law (index II) and third-law (index III) enthalpies and entropies are found for this reaction:

$$\Delta H^\circ_{298}(\mathrm{II}) = 720.8 \pm 33.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(\mathrm{II}) = 230.6 \pm 18.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H^\circ_{298}(\mathrm{III}) = 711.4 \pm 28.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(\mathrm{III}) = 225.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

A value of -1594 ± 33 kJ mol^{-1} is derived for ΔH°_{f298} ($(YbO)_2Se(s)$). The feasibility of this value is discussed in view of the significant decrease of the formula volume accompanying the formation of $(YbO)_2Se$ from Yb_2O_3 and Yb_2Se_3.

1. Introduction

In the course of an investigation of the thermodynamics of sublimation of ytterbium(II) selenide, we occasionally observed the undesirable formation of the compound $(YbO)_2Se$ if oxidation and/or hydrolysis of the monoselenide could not be effectively avoided. While the structural, spectroscopic and magnetic properties of $(YbO)_2Se$ have already been studied in detail [1, 2], its thermochemical properties seem to be completely unknown, a situation which probably holds true for the lanthanoid oxide selenides of this formula type in general.

On account of our interest in the thermochemical systematics of certain lanthanoid chalcogenides and related compounds [3-5], we have now performed a

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vaporization study of $(YbO)_2Se$ by the Knudsen effusion method, the results of which are reported in this paper.

2. Experimental details

2.1. Preparation and characterization of $(YbO)_2Se$

$(YbO)_2Se$ was synthesized by reaction of Yb_2O_3 with H_2Se gas [6]. Yb_2O_3 (99.99% purity, Auer-Remy KG.) was annealed for 12 h at 1200 K to decompose small amounts of carbonate and hydroxide, and was then treated with a mixture of hydrogen and selenium (99.995% purity, Fluka) at 1350 K for 5 h to yield $(YbO)_2Se$. After cooling under hydrogen, the yellow reaction product was annealed in a high vacuum at approximately 950 K for 5 h to remove any excess selenium. X-ray powder patterns obtained by the Guinier technique with Cu $K\alpha_1$ radiation and with silicon (NBS 640 A) as internal calibration standard could be indexed hexagonally with lattice parameters $a = 376.31 \pm 0.03$ pm and $c = 669.92 \pm 0.05$ pm, in very good agreement with the data from ref. 6, $a = 376.1 \pm 2.0$ pm and $c = 669.7 \pm 2.0$ pm. The X-ray patterns did not indicate the presence of other crystalline phases.

The metal content of the compound was determined chemically as described in ref. 5. The result 76.6% ± 1% Yb by mass was found, in fair agreement with the value for the stoichiometric composition, 75.7%.

In order to confirm the existence of a phase transition at about 1030 K [7], $(YbO)_2Se$ was investigated by quantitative differential thermal analysis (DTA) within the temperature range 300–1250 K. The measurements were carried out in an apparatus for simultaneous DTA and thermogravimetric analysis (TGA), type Netzsch STA 429. The samples were contained in small gas-tight molybdenum autoclaves. Molybdenum was chosen as crucible material because it does not interact chemically and physically with $(YbO)_2Se$ in the said temperature range (see Section 2.2). The DTA experiment was carried out at heating and cooling rates of 5 K min^{-1} in a standing atmosphere of highly purified argon. The experiment did not give any hint of a phase transition between room temperature and 1250 K.

2.2. Knudsen effusion measurements

The vaporization behaviour of $(YbO)_2Se$ was investigated by the Knudsen effusion method using two molybdenum Knudsen cells with effective orifice areas of 4.548×10^{-3} cm^2 (cell A) and 2.700×10^{-3} cm^2 (cell B). The experimental details of these measurements have been described elsewhere [5].

Prior to the quantitative effusion measurements we had to find out in which way the compound vaporizes or decomposes incongruently. For this purpose pure $(YbO)_2Se$ was submitted to temperatures at which noticeable vaporization occurred. X-ray powder patterns of the residues displayed the presence of Yb_2O_3 besides the starting material. We therefore concluded tentatively that the compound decomposes incongruently into solid, involatile Yb_2O_3 and a gas phase containing ytterbium and selenium with a molar ratio 2:3, provided that the vapour does not include any oxygen-containing molecular species. This conclusion could be verified by an experiment, in which 91.9 mg of $(YbO)_2Se$ were decomposed at 2000 K until the rate of effusion dropped to zero. The residue consisted of 52.0 mg of pure Yb_2O_3, an amount in good agreement with the calculated amount for complete decomposition, 52.8 mg. Since the vapour pressure of pure Yb_2O_3 is less than 10^{-8} bar at 2000 K [8], our conclusion concerning the general composition of the equilibrium gas phase seemed to be quite reasonable. When a sample of $(YbO)_2Se$ was decomposed in several subsequent steps at the same temperature, the rates of effusion were found to be equal within the accuracy limits of such experiments. This result was an especially fortunate one, since thermal decompositions of this reaction type often lead to the formation of a layer of the decomposition product, which covers the decomposing crystals and can thus diminish the rate of effusion. In the case of $(YbO)_2Se$ the decomposition product was found to be extremely porous, and chemical equilibrium could apparently be easily approached.

The powder diffraction pattern obtained after the Knudsen measurements did not show any evidence of a variation of the lattice parameters of $(YbO)_2Se$ and Yb_2O_3.

Rates of effusion were measured in three series with a total of 30 data points in the temperature range 1753–1997 K. The experimental results are collected in Table 1.

3. Thermodynamic evaluation of effusion results

The amount m_i(g) of a gaseous species i of molar mass M_i (g mol^{-1}) effused in time t (s) at temperature T (K) from a Knudsen cell with an orifice of effective area a (cm^2) is related to the partial pressure p_i (bar) of species i by the Knudsen equation

$$p_i = \frac{m_i}{at}\left(\frac{2\pi RT}{M_i}\right)^{1/2} = \frac{m_i}{43.7519at}\left(\frac{T}{M_i}\right)^{1/2} \tag{1}$$

Earlier investigations of the vaporization behaviour of YbSe and other lanthanoid monoselenides [5, 9] have shown that only four gaseous species are of importance under the experimental conditions chosen here, namely Yb, Se, YbSe and Se_2. Hence in the incongruent decomposition of $(YbO)_2Se$ the following vaporization reactions have to be considered simultaneously for the thermodynamic evaluation of the effusion data:

$$(YbO)_2Se(s) \rightarrow \tfrac{2}{3}Yb_2O_3(s) + \tfrac{2}{3}Yb(g) + Se(g) \tag{2}$$

$$(YbO)_2Se(s) \rightarrow \tfrac{2}{3}Yb_2O_3(s) + \tfrac{2}{3}Yb(g) + \tfrac{1}{2}Se_2(g) \tag{3}$$

$$(YbO)_2Se(s) \rightarrow \tfrac{2}{3}Yb_2O_3(s) + \tfrac{2}{3}YbSe(g) + \tfrac{1}{3}Se(g) \tag{4}$$

TABLE 1

Knudsen vaporization data of $(YbO)_2Se(s)$

T (K)	Cell	Rate ($mg\,h^{-1}$)	p_{Yb} (bar)	p_{Se} (bar)	p_{Se_2} (bar)	p_{YbSe} (bar)	K[a] reaction (2)	ΔH°_{298}(III) ($kJ\,mol^{-1}$)
1753	B	0.469	2.69×10^{-6}	1.19×10^{-6}	1.56×10^{-8}	2.89×10^{-11}	2.25×10^{-10}	706.6
1774	A	0.708	2.43×10^{-6}	1.08×10^{-6}	9.82×10^{-9}	2.03×10^{-11}	1.91×10^{-10}	717.2
1786	B	0.760	4.40×10^{-6}	1.94×10^{-6}	2.75×10^{-8}	6.06×10^{-11}	5.10×10^{-10}	707.2
1797	A	1.050	3.62×10^{-6}	1.61×10^{-6}	1.63×10^{-8}	3.81×10^{-11}	3.71×10^{-10}	716.4
1806	B	1.063	6.19×10^{-6}	2.73×10^{-6}	4.20×10^{-8}	1.04×10^{-10}	8.99×10^{-10}	706.6
1816	B	1.017	5.94×10^{-6}	2.63×10^{-6}	3.42×10^{-8}	8.83×10^{-11}	8.42×10^{-10}	711.7
1822	A	1.525	5.30×10^{-6}	2.35×10^{-6}	2.56×10^{-8}	6.80×10^{-11}	6.98×10^{-10}	716.5
1828	A	1.500	5.22×10^{-6}	2.32×10^{-6}	2.31×10^{-8}	6.29×10^{-11}	6.82×10^{-10}	719.4
1832	B	1.586	9.30×10^{-6}	4.09×10^{-6}	6.90×10^{-8}	1.93×10^{-10}	1.80×10^{-9}	706.2
1840	B	1.613	9.48×10^{-6}	4.18×10^{-6}	6.51×10^{-8}	1.89×10^{-10}	1.83×10^{-9}	708.9
1852	B	2.460	1.45×10^{-5}	6.35×10^{-6}	1.31×10^{-7}	4.05×10^{-10}	3.69×10^{-9}	702.6
1859	A	2.400	8.42×10^{-6}	3.73×10^{-6}	4.18×10^{-8}	1.33×10^{-10}	1.51×10^{-9}	718.7
1867	B	1.900	1.13×10^{-5}	4.97×10^{-6}	6.72×10^{-8}	2.22×10^{-10}	2.44×10^{-9}	714.6
1883	B	3.150	1.87×10^{-5}	8.22×10^{-6}	1.54×10^{-7}	5.50×10^{-10}	5.67×10^{-9}	707.2
1888	A	3.575	1.26×10^{-5}	5.60×10^{-6}	6.72×10^{-8}	2.45×10^{-10}	2.97×10^{-9}	719.2
1889	A	3.575	1.26×10^{-5}	5.60×10^{-6}	6.66×10^{-8}	2.45×10^{-10}	2.97×10^{-9}	719.5
1899	B	3.850	2.30×10^{-5}	1.01×10^{-5}	1.93×10^{-7}	7.43×10^{-10}	7.97×10^{-9}	707.7
1906	B	4.950	2.96×10^{-5}	1.29×10^{-5}	2.93×10^{-7}	1.17×10^{-9}	1.21×10^{-8}	703.7
1912	A	5.500	1.96×10^{-5}	8.64×10^{-6}	1.23×10^{-7}	5.00×10^{-10}	6.14×10^{-9}	716.6
1921	B	4.750	2.85×10^{-5}	1.25×10^{-5}	2.32×10^{-7}	9.86×10^{-10}	1.14×10^{-8}	710.2
1928	B	5.550	3.34×10^{-5}	1.46×10^{-5}	2.94×10^{-7}	1.30×10^{-9}	1.48×10^{-8}	708.5
1928	B	4.925	2.96×10^{-5}	1.30×10^{-5}	2.33×10^{-7}	1.03×10^{-9}	1.22×10^{-8}	711.6
1937	B	7.967	4.80×10^{-5}	2.09×10^{-5}	5.44×10^{-7}	2.52×10^{-9}	2.70×10^{-8}	702.0
1939	A	7.775	2.79×10^{-5}	1.23×10^{-5}	1.85×10^{-7}	8.51×10^{-10}	1.10×10^{-8}	716.9
1943	A	8.133	2.92×10^{-5}	1.29×10^{-5}	1.94×10^{-7}	9.08×10^{-10}	1.19×10^{-8}	717.4
1945	B	6.433	3.89×10^{-5}	1.70×10^{-5}	3.32×10^{-7}	1.58×10^{-9}	1.91×10^{-8}	710.5
1954	B	8.000	4.85×10^{-5}	2.12×10^{-5}	4.66×10^{-7}	2.30×10^{-9}	2.75×10^{-8}	707.8
1957	A	9.043	3.26×10^{-5}	1.44×10^{-5}	2.08×10^{-7}	1.04×10^{-9}	1.43×10^{-8}	719.5
1969	B	10.12	6.15×10^{-5}	2.68×10^{-5}	6.43×10^{-7}	3.40×10^{-9}	4.09×10^{-8}	706.3
1997	A	24.72	8.99×10^{-5}	3.90×10^{-5}	1.02×10^{-6}	6.10×10^{-9}	7.66×10^{-8}	705.7

[a] Standard state pressure is $p^{\circ} = 0.1013$ MPa.

Reactions (2)–(4) are interrelated by

$$YbSe(g) \rightarrow Yb(g) + Se(g) \tag{5}$$

$$Se_2(g) \rightarrow 2Se(g) \tag{6}$$

The individual partial pressures of the various species depend on the stoichiometry of the evaporation process, the equilibrium constants for reactions (5) and (6) and the temperature. Taking advantage of the Knudsen effusion data, it is possible to set up a cubic equation for the determination of the individual partial pressures.

The individual partial pressures, which together with K for reaction (2) are listed in Table 1, were calculated by using the following experimental or estimated data: The free energy function of gaseous YbSe [10], Yb [11], Se and Se_2 [10]; the standard enthalpies of dissociation of YbSe(g), 184.2 ± 50.2 kJ mol^{-1}, and of $Se_2(g)$, 289.9 ± 4 kJ mol^{-1} [10].

Obviously, the partial pressures of the molecular species YbSe and Se_2 are at most 1% of the total pressure. Therefore reaction (2) can be considered as the major mode of vaporization of $(YbO)_2Se$. A plot of log K *vs.* T^{-1} for reaction (2) is shown in Fig. 1.

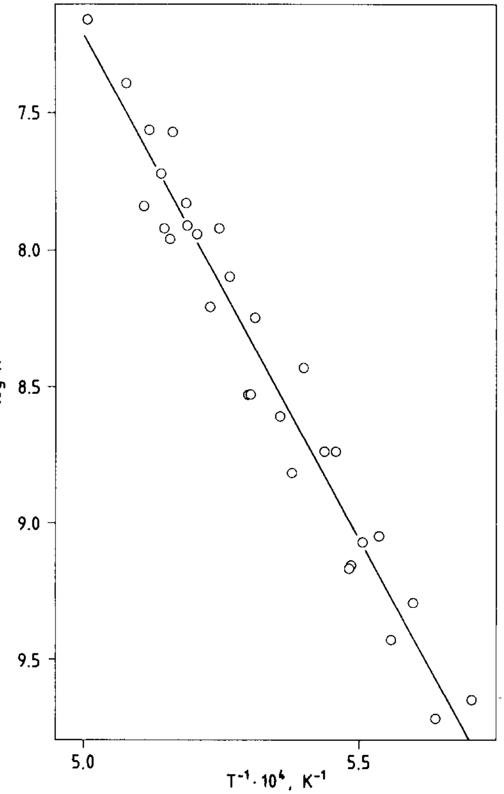

Fig. 1. Plot of log K *vs.* T^{-1} for the vaporization of $(YbO)_2Se(s)$ with $K = a_{Yb}^{2/3} a_{Se}$.

An unweighted linear least-squares treatment of the data for reaction (2) yields the following vapour pressure equation with associated standard deviations:

$$\log K = (-36881 \pm 1615)T^{-1} + 11.225 \pm 0.860 \qquad (7)$$

From eqn. (7) the following enthalpy and entropy of vaporization for the median temperature $T = 1875$ K can be calculated:

$$\Delta H^\circ_T = 706.1 \pm 30.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_T = 214.9 \pm 16.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

For an extrapolation to 298 K by the second- and third-law methods we used the thermodynamic data for $Yb_2O_3(s)$ reported by Pankratz and King [12]. Since no thermodynamic data for $(YbO)_2Se$ are available, the increments $H^\circ_T - H^\circ_{298}$ and $S^\circ_T - S^\circ_{298}$ as well as the standard entropy were estimated as follows. It was assumed that the standard entropy of this predominantly ionic compound can be considered as being equal to the sum of the entropy contributions from its characteristic constituent parts Yb_2O_3 and Yb_2Se_3. Taking S°_{298} $(Yb_2O_3(s)) = 144.3$ J mol^{-1} K^{-1} [13] and S°_{298} $(Yb_2Se_3(s)) = 198.7 \pm 2.0$ J mol^{-1} K^{-1} [10], one finds 162.4 J mol^{-1} K^{-1} for the standard entropy of $(YbO)_2Se$. The enthalpy and free-energy functions of $(YbO)_2Se$ were estimated by assuming the c_p values of this compound to be equal to the sum of the values for $\frac{2}{3}Yb_2O_3$ [14] and $\frac{1}{3}La_2Se_3$ [10].

The following second-law (index II) and third-law (index III) enthalpies and entropies are found for the decomposition of solid $(YbO)_2Se$ according to reaction (2):

$$\Delta H^\circ_{298}(\text{II}) = 720.8 \pm 33.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(\text{II}) = 230.6 \pm 18.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H^\circ_{298}(\text{III}) = 711.4 \pm 28.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(\text{III}) = 225.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

The second- and third-law enthalpies are in good agreement and the third-law enthalpy data listed in Table 1 indicate that no obvious trend with T exists.

The uncertainties include the standard deviations of the experimental results, a 5% uncertainty in Δfef and a 15% uncertainty of the data necessary for the second-law reduction to 298 K.

Considering the standard enthalpies of formation of $Yb_2O_3(s)$, -1814.5 ± 2.2 kJ mol^{-1} [15], Yb(g), 152.1 ± 0.3 kJ mol^{-1} [16], and Se(g), 235.4 ± 3.1 kJ mol^{-1} [10], and considering the second-law enthalpy for reaction (2), a value of -1594 ± 33 kJ mol^{-1} is found for the standard enthalpy of formation of $(YbO)_2Se(s)$.

4. Discussion

Since no experimental data for the enthalpies of formation of the lanthanoid oxide selenides exist, the question arises whether the value for $(YbO)_2Se$ derived in this work can be considered as representative of all compounds of the formula type $(LnO)_2Se$. Assuming $\Delta H \approx 0$ for the formation of the predominantly ionic, ternary compound $(YbO)_2Se$ from the constituent binary compounds Yb_2O_3 and Yb_2Se_3, a hypothetical upper limit of the standard enthalpy of formation of -1531.6 ± 10.4 kJ mol^{-1} is calculated using the literature data for Yb_2O_3 and Yb_2Se_3, -1815.4 ± 2.2 [15] and -965.7 ± 31.0 kJ mol^{-1} [17] respectively. Our result, -1594 ± 33 kJ mol^{-1}, is more negative by 62 ± 34.6 kJ mol^{-1} and can hence be considered as a significant thermochemical quantity. For predominantly ionic, ordered compounds one would expect that a decrease of the enthalpy of formation as compared to the hypothetical situation should be accompanied by a decrease of the formula volume. This conclusion holds true for $(YbO)_2Se$, whose experimental formula volume $(8.2157 \pm 0.0004) \times 10^7$ pm^3 is distinctly smaller than the weighted mean of the formula volumes of Yb_2O_3 and of Yb_2Se_3, 9.2749×10^7 pm^3.

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