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Thermochimica Acta 302 (1997) 63–68

thermochimica
acta

Thermal decomposition of niobium tetrachloride

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Received 22 November 1996; received in revised form 26 February 1997; accepted 5 March 1997

Abstract

The thermal decomposition process of solid $NbCl_4$ was studied by a tensimetric method using an ordinary and a two-zone membrane manometer. It was shown that the solid $NbCl_4$ decomposed to the upper limit of a solid solution on the basis of a niobium trichloride crystal lattice and gaseous $NbCl_5$. The homogeneity region of this solid solution is $NbCl_{3.13-2.67}$ and it decomposes from an upper to a lower border with formation of the same gaseous product. After complete decomposition of the solid solution to its lower limit in the closed system the $NbCl_{2.67}$ (cluster Nb_3Cl_8) form reacts with gaseous $NbCl_5$ with formation of gaseous $NbCl_4$. The thermodynamic characteristics of solid $NbCl_{3.13}$ and $NbCl_{2.67}$ and gaseous $NbCl_4$ were calculated on the basis of experimental data:$\Delta_f H^\circ(NbCl_{3.13}, s, 298.15\,K) = -599 \pm 10\,kJ\,mol^{-1}$. $\Delta_f H^\circ(NbCl_{2.67}, s, 298.15\,K) = -536.4 \pm 10.2\,kJ\,mol^{-1}$ $\Delta_f H^\circ(NbCl_4, g, 298.15\,K) = -577.1 \pm 8.5\,kJ\,mol^{-1}$. $\Delta_s H^\circ(NbCl_4, 298.15\,K) = 128.4 \pm 7.1\,kJ\,mol^{-1}$. © 1997 Elsevier Science B.V.

Keywords: Lower niobium chlorides; Thermal decomposition; Thermodynamics

1. Introduction

The detailed study of a niobium tetrachloride thermal decomposition process is important because different niobium clusters with metal–metal bonds are formed as intermediate products. The study of their step-by-step thermal decomposition reactions makes it possible, not only to receive data on their mechanism and quantitative characteristics, but also to obtain thermodynamic characteristics of these compounds. However at present this process has been studied insufficiently, although there are some papers dedicated to this problem [1–6]. There are discrepancies in determinations of intermediate solid and gaseous products of the decomposition and in the temperature intervals for intermediate reactions.

The goal of the present paper was to study the thermal decomposition process of niobium tetrachloride with determination of the intermediate products. An additional goal was to obtain the thermodynamic characteristics for these products and the reactions associated with their formation.

Niobium tetrachloride was synthesized from niobium metal powder, previously dried in vacuum (10^{-6} mm Hg) at 200°C, and niobium pentachloride sublimed in an evacuated quartz ampoule with a temperature drop from 800 to 200°C. The product obtained was analyzed for niobium gravimetrically (weighted as Nb_2O_5) and for chlorine by potentio-

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PII S0040-6031(97)00117-2

metric titration. It was found that (in parenthesis is the value calculated for $NbCl_4$):

$$\mathrm{Nb} - 39.58 \pm 0.01\ \mathrm{At.\%}(39.58);$$
$$\mathrm{Cl} - 60.41 \pm 0.03\ \mathrm{At.\%}(60.42)$$

The thermal decomposition process for $NbCl_4$ was studied by the tensimetric method using two types of quartz membrane null-manometers. One was the ordinary, described for example in [7]. The other was a two-zone manometer with a working chamber separated from the membrane by a capillary tube 12 cm long having an interior diameter of 2 mm. The membrane chamber was placed in the two-zone furnace section and its temperature was maintained by a separate temperature controller. Schematics of the two-zone manometer and the experimental apparatus are shown in Figs. 1 and 2

The equilibrium vapor pressure of the $NbCl_4$ thermal disproportionation reaction was measured by a Hg-manometer with an accuracy of ±0.5 mm. The temperature in each furnace zone was kept at the given point within ±0.5°C using a VRT-3 temperature controller. The weight of compound placed in the manometer was calculated so that after $NbCl_4$ completely decomposed to $NbCl_{2.67}$ the pressure of $NbCl_5$ vapor would not exceed 1 atm at 800°C. For such calculations data for the thermal stability of $NbCl_4$ and the composition of the decomposition intermediate products were used [6].

All the points for the solid $NbCl_4$ thermal decomposition process were obtained upon heating of specimens, since upon cooling the equilibrium was established extremely slowly. It was assumed that equilibrium was achieved if the pressure did not change more than 0.5 mm Hg in 2 h (usually after 36 h). All loading operations for manometers with niobium tetrachloride were carried out in a glove box filled with flowing dry argon.

2. Results and discussion

The experimental results for the dependence of the pressure of the decomposition's gaseous products on temperature are shown in Fig. 3. The curve ABCDE presents the results obtained with the ordinary membrane manometer, and the curve ABG′GH′HL′LMN presents the results obtained with two-zone membrane manometer.

2.1. Ordinary membrane manometer

A noted change in the rate of pressure increase occurred at about 557 K. The pressure dependence on temperature for the process of the $NbCl_4$ thermal decomposition is shown in Fig. 3 (curve ABC). The composition of the solid product at the end of this process (point ‘C’ on the curve, Fig. 3) was determined on the basis of the ideal gas law, the initial specimen weight, and the volume of the manometer's working chamber. It was $NbCl_{3.13\pm0.02}$. The same result was obtained in [6] on the basis of thermoanalytical data. Thus, the chemical reaction of $NbCl_4$ thermal decomposition is expressed as

$$2.15\,\mathrm{NbCl_4(s)}, = 1.15\,\mathrm{NbCl_{3.13}(s)} + \mathrm{NbCl_5(g)} \tag{1}$$

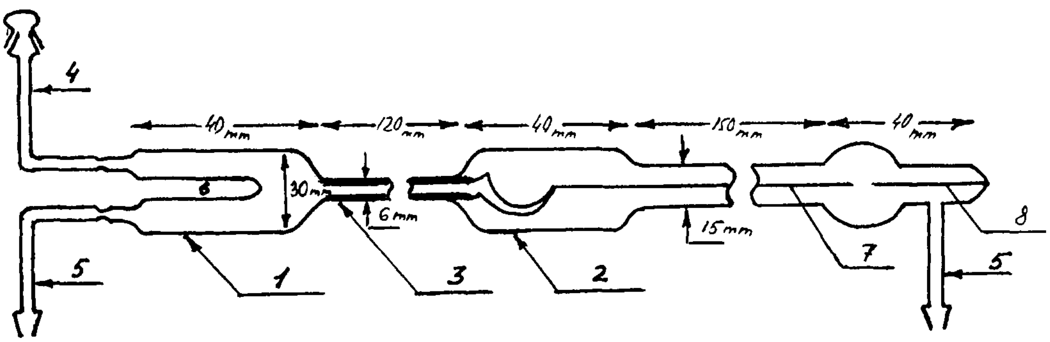

Fig. 1. Schematic drawing of the two-zone quartz membrane manometer: (1) working chamber; (2) membrane chamber; (3) tube connecting chambers; (4) inlet for loading; (5) outlet for vacuuming; (6) ‘pocket’ for thermocouple; (7) moving indicator; (8) fixed indicator.

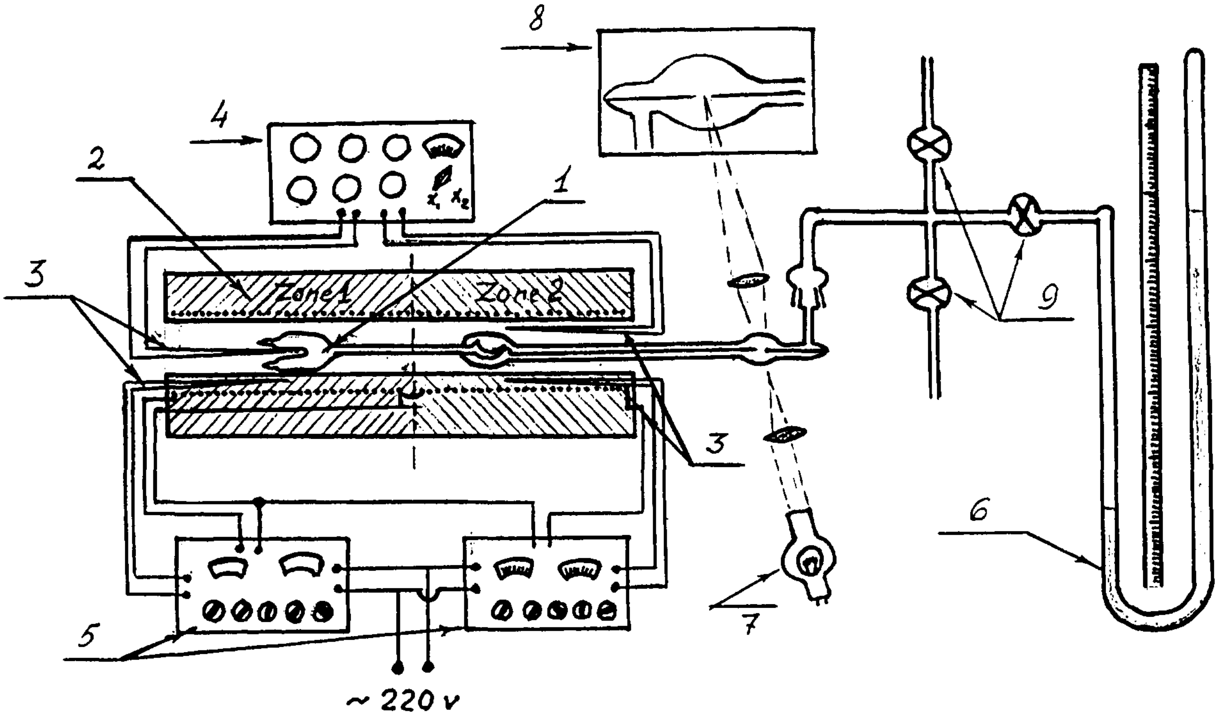

Fig. 2. Schematic drawing of the apparatus for the tensimetric study of the thermal decomposition of $NbCl_4$: (1) two-zone membrane manometer; (2) two-zone tube electrical furnace; (3) thermocouples; (4) PPTN-1 potentiometer with two inlets; (5) temperature controllers VRT-1; (6) mercury manometer; (7) optical system; (8) screen; (9) valves.

The gaseous $NbCl_5$ pressure dependence on temperature for this reaction is expressed by the equation:

$$\log P_{\mathrm{mm\,HG}} = -(6155 \pm 300).T^{-1} + (10.02 \pm 0.88\ (557 - 610\,\mathrm{K})$$

The enthalpy and entropy for this reaction of the first stage of the thermal decomposition process of $NbCl_4$ was calculated on the basis of this equation:

$$\Delta_r H^\circ(600\,\mathrm{K}) = 117.8 \pm 5.6\,\mathrm{kJ\,mol^{-1}\,NbCl_5}$$

$$\Delta_r S^\circ(600\,\mathrm{K}) = 191.8 \pm 16.9\,\mathrm{J\,K^{-1}\,mol^{-1}\,NbCl_5}$$

In this calculation it was assumed that $NbCl_4$ saturated vapor pressure in the given temperature range is less than 1 mm Hg, and it does not affect the final result.

After recalculating to standard conditions using data obtained earlier [8,9] and literature data [10], we determined the enthalpy for this reaction:

$$\Delta_r H^\circ(298.15\,\mathrm{K}) = 125.2 \pm 10.6\,\mathrm{kJ\,mol^{-1}NbCl_5}$$

One can calculate the enthalpy of formation for the solid product formed during the first stage thermal decomposition of $NbCl_4$ using refs. [8–10]:

$$\Delta_f H^\circ(\mathrm{NbCl_{3.13}}, 298.15\,\mathrm{K}) = -599 \pm 10\,\mathrm{kJ\,mol^{-1}}$$

This value is a little less than literature data (-605.4 kJ $\mathrm{mol^{-1}}$) [10], although it agrees reasonably well within the limits of adopted errors.

Point ‘D’ is the second break point on the 1st curve. The composition of the solid product at this point is $NbCl_{2.67}$. That is in a fair agreement with thermoanalytical data [6]. According to these tensimetric data the equilibrium in the region $NbCl_{3.13}$ – $NbCl_{2.67}$ is bivariant, and the solid phase is a solid solution based on the crystal lattice of $NbCl_{2.67}$. After point ‘D’ the equilibrium pressure dependence on temperature is expressed by the line (DE) which has a positive deviation from the ideal gas expansion line (DF). This deviation indicates an additional process with the formation of additional amounts of gaseous molecules. It cannot be attributed to thermal dissociation

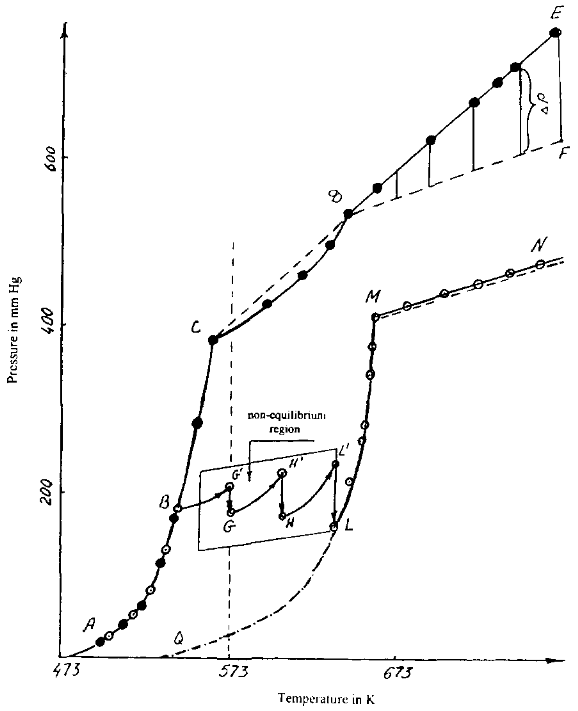

Fig. 3. Dependence of the vapor pressure on temperature during thermal decomposition of $NbCl_4$. ○ – experiment with the ordinary membrane manometer; ● – experiment with the two-zone membrane manometer.

Table 1
Values of the reaction $0.75\,NbCl_{2.67}(s) + NbCl_5(g) = 1.75\,NbCl_4(g)$ constants for some temperatures in the experimental range

		Pressure, mm Hg				
T in K	T^{-1} in K	Total	$NbCl_4$	$NbCl_5$	K_p	log K_p
673	1,486	596	42	554	1,25	0,097
698	1,433	640	84	556	4,19	0,622
723	1,383	688	133	555	9,38	0,972
748	1,337	732	175	557	15,10	1,179
773	1,294	766	210	566	22,03	1,319

of gaseous niobium pentachloride because it is thermodynamically stable to at least 1500 K. It is also not the thermal decomposition of $NbCl_{2.67}$, because it was shown to be stable up to 1100 K [6]. We can explain this phenomenon in terms of the interaction of solid phase $NbCl_{2.67}$ with gaseous $NbCl_5$. In this process 1.75 mol. of gaseous $NbCl_4$ are formed instead of 1 mol. of gaseous $NbCl_5$ according to an equation:

$$0.75\,NbCl_{2.67}(s) + NbCl_5(g) = 1.75\,NbCl_4(g) \tag{2}$$

One can calculate the reaction constants as a function of temperature from the curve (DE) assuming that the $1.75\Delta P$ (ΔP – difference between the experimental pressure value and the pressure for ideal gas expansion value) is the pressure of the gaseous $NbCl_4$ formed. The results of these calculations are presented in Table 1. From the dependence of these constants on temperature one can calculate the enthalpy of this reaction. The reaction enthalpy calculated on the basis of these data is

$$\Delta_r H^\circ(720\,K) = 123.8 \pm 6.7\,kJ$$

The $NbCl_{2.67}$ formation enthalpy at standard conditions was calculated using this value and literature data [8–10]

$$\Delta_f H^\circ(NbCl_{2.67}, 298.15\,K) = -536.4 \pm 10.2\,kJ\,mol^{-1}$$

The good agreement of this value with the literature [10] confirms the reliability of our assumption about the existence of the process described by reaction 2 in a closed system after the end of the thermal decomposition of $NbCl_4$ (reaction 1).

2.2. *Two-zone membrane manometer*

In the first part of this experiment the temperature of the membrane chamber was kept constant (573 K). This temperature was chosen because at this temperature the $NbCl_5$ vapor does not condense (boiling point of liquid $NbCl_5$ is 479 K [10]), and it is in the temperature range for existence of $NbCl_{3.13}$, according to the thermoanalitical experimental results [6]. The temperature of the working chamber with $NbCl_4$ was gradually increased from room temperature. At the beginning the points of equilibrium pressure fell exactly on the curve AB obtained in the experiment with the ordinary manometer. At point 'B', however, all the niobium tetrachloride had decomposed to $NbCl_{3.13}$ and there is a breakpoint. The following experimental points (part BL) present the $NbCl_5$ vapor pressure over the homogenous region $NbCl_{3.13-2.67}$. At point 'G' the working chamber temperature became higher than the temperature of the membrane that is equal 573 K. After point 'G' the pressure first increased with temperature increase to the next experimental point, but at this point it began to decrease (at constant temperature). The rate of this decrease was small (approximately 1–2 mm Hg per hour), and it was almost constant. Upon the next stop of temperature increase (20–25 K) to the next point the picture was repeated. This was the difference in the results for this experiment from the previous one with the ordinary manometer.

These phenomena can be explained in the following manner. Because in point 'G' the working chamber temperature becomes higher than that of the membrane chamber gaseous $NbCl_4$ which is formed as a result of $NbCl_{2.67}$ interaction with gaseous $NbCl_5$ (reaction 2), is condensed in the membrane chamber where the temperature is lower. This is the cause of pressure decrease in the system. In point 'L' the temperature was kept constant (640 K) during 120 h and the pressure dropped to point L ($\sim$ 120 mm Hg). After that the membrane chamber temperature was increased at a constant rate 3° per min. up to 840 K. When the temperatures of the working and membrane chambers became equal (640 K) their temperatures were increased simultaneously. In this case the dependence of the pressure on temperature is expressed by curve LM. At point 'M' there is a breakpoint and the following experimental points are on curve MN which is exactly the curve of the ideal gas thermal expansion. The pressure at point 'M' is the same as the one calculated for gaseous $NbCl_4$ formed from the sample placed in the manometer. One can suppose that the curve LM expresses the dependence of $NbCl_4$ saturated vapor pressure on temperature because at the given rate of temperature increase the process of solid decomposition is very slow in comparison to the process of its sublimation. Moreover the phase ($NbCl_{3.13}$) formed in the decomposition process is unstable at these conditions and decomposes to the phase $NbCl_{2.67}$ which reacts with the $NbCl_5$ formed producing gaseous $NbCl_4$. It is possible to check the reliability of this hypothesis by calculating the enthalpy of $NbCl_4$ sublimation on the basis of experimental points on curve LM[1]. We made this calculation using both our, and literature data for the $(H_T - H_{298})$ of solid and gaseous $NbCl_4$. The result obtained for the standard conditions is:

$$\Delta_s H^\circ(NbCl_4,\ 298.15\,K) = 128.4 \pm 7.1\,kJ\,mol^{-1}$$

Hence the formation enthalpy of gaseous $NbCl_4$ is

$$\Delta_f H^\circ(NbCL_4, g,\ 298.15\,K) = -577.1 \pm 8.5\,kJ\,mol^{-1}$$

This value is larger that the literature one ($-561 \pm 10\,kJ\,mol^{-1}$) [10] but if one keeps in mind that our experimental value for the enthalpy of solid $NbCl_4$ formation obtained by the calorimetric method [8] is 10 kJ larger than the literature data, then the agreement is acceptable.

3. Conclusions

On the basis of tensimetric data obtained using both an ordinary and a two-zone membrane manometers it was shown that solid $NbCl_4$ decomposes upon heating to the solid niobium trichloride (which has the homogeneity region in the range $NbCl_{3.13-2.67}$) with formation of the $NbCl_5$ as a gaseous product. The phase $NbCl_{3.13}$ decomposes bivariantly also with formation of gaseous $NbCl_5$. After complete decomposition of this phase to its lower border ($NbCl_{2.67}$) in the closed system the process of gaseous $NbCl_4$ formation takes place. In the case of a rapid temperature increase it is possible to measure the $NbCl_4$ saturated vapor pressure because the decomposition process is slower than the sublimation. Some thermodynamic characteristics for intermediate compounds of the thermal decomposition process for $NbCl_4$ were calculated from the experimental data:

$$\Delta_f H^\circ(NbCl_{3.13}, 298.15\,K) = -599 \pm 10\,kJ\,mol^{-1}$$

$$\Delta_f H^\circ(NbCl_{2.67}, 298.15\,K) = -536.4 \pm 10.2\,kJ\,mol^{-1}$$

$$\Delta_f H^\circ(NbCl_4, g, 298.15\,K) = -577.1 \pm 8.5\,kJ\,mol^{-1}$$

$$\Delta_s H^\circ(NbCl_4, 298.15\,K) = 128.4 \pm 7.1\,kJ\,mol^{-1}$$

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[1] Note: the saturated vapor dependence on temperature for $NbCl_4$ calculated on the basis of literature data [10] is expressed by the curve QML in Fig. 3 and is close to our experimental data.

Acknowledgements

We are very grateful to Prof. Leo Brewer (University of California, Berkeley) for useful discussions of the problem and to Prof. Patrick Gallagher (Ohio State University) for initially reviewing the manuscript.

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