



Thermodynamic properties of crystalline and gaseous lower niobium chlorides[☆]

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ABSTRACT

Thermodynamic functions of crystalline and gaseous niobium chlorides in lower state of oxidation are presented. The thermodynamic properties of solid niobium chlorides including their clusters Nb_3Cl_8 ($\text{NbCl}_{2.67}$) and $\text{Nb}_6\text{Cl}_{14}$ ($\text{NbCl}_{2.33}$) in the temperature range from 298 to 1300 K were calculated using experimental low temperature isobaric heat capacity measurements, thermogravimetric and tensimetric data on the process of their thermal decomposition and mass-spectrometric determination of vapor phase composition during this process.

The thermodynamic properties of gaseous lower niobium chlorides in the temperature range 298–2000 K were calculated using vibration frequencies of these molecules. The latter were obtained using suggested molecular structures by a method involving the application of the force constants estimated on the basis of vibration frequencies of vapors of titanium, zirconium and vanadium tetrachlorides in terms of modified valence force field.

The vibration frequencies were used to calculate the thermodynamic functions of gaseous niobium lower chlorides in terms of the rigid rotator-harmonic oscillator approximation.

The obtained thermodynamic data allowed us to calculate the composition of the vapor phase in the system $\text{Nb}=\text{NbCl}_5$ (vapor) in the temperature range from 700 to 2000 K for pressures 10^{-6} and 1 atm. The mechanism of thermal decomposition of niobium cluster $\text{Nb}_6\text{Cl}_{14}$ ($\text{NbCl}_{2.33}$) was determined under pressure of 1 atm and in vacuum.

1. Introduction

Since the discovery of the electrical superconductivity of metals at ultralow temperatures by Kamerlingh Onnes in 1911 [1], the goal of researchers has been to find a material that has superconducting properties at room temperatures. However, despite the theoretical (BCS) theory developed by Bardeen, Cooper and Schrieffer to explain the phenomenon of superconductivity [2], it was impossible to predict substances with such properties. Therefore, the discovery of a whole class of high-temperature superconductors (cuprates of alkaline earth metals) by Bednorz and Müller in 1978 [3] was rather accidental. Somewhat earlier Ginzburg [4] predicted that new superconductors should be sought among compounds with a layered structure consisting of electrically conductive layers separated by layers with dielectric

properties—the so-called "sandwich" structure. Based on this assumption, to date, more than a thousand substances have been studied for high-temperature superconductivity [5]. About three hundred of them actually turned out to be superconductors, but their superconducting transition temperature was not high enough. Among this group of substances, particular attention was drawn to compounds with double layers of metal atoms (titanium, zirconium, and hafnium), such as nitride chloride and their adducts with organic molecules [6–9]. From this point of view compounds with the ZrCl structure type (Fig. 1), containing double layers of metal atoms separated by double layers of halogen atoms [10], are very promising.

A single crystal of this compound has a metallic electrical conductivity along the metal layers and is an insulator in the perpendicular direction [11]. It should be noted that there is a strong metallic bond

[☆] In memory of Professor Leo Brewer (University of California, Berkeley). Prof. Leo Brewer (1919–2005) was a member of The Manhattan Project who headed a group that predicted the possible high-temperature properties of the then newly discovered plutonium and providing thermodynamic calculations for a cerium sulfide crucible that would resist molten plutonium without contaminating it.

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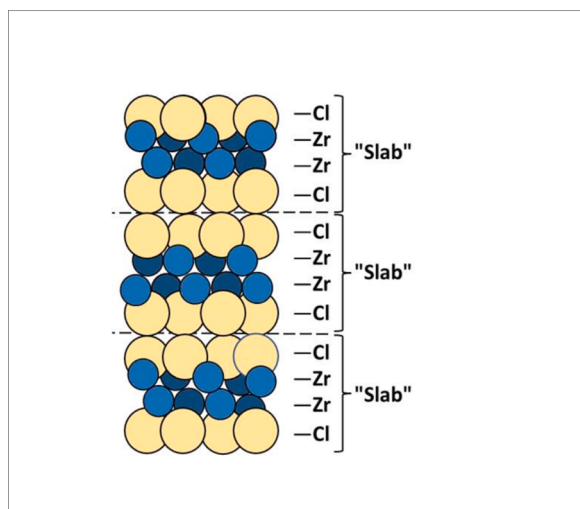


Fig. 1. Image of crystalline structure of ZrCl.

Table 1

Results of chemical analysis of lower niobium chlorides

Compound	Nb % found	calculated	Cl % found	calculated
NbCl ₄	39.40 ± 0.10	39.58	60.28 ± 0.11	60.42
NbCl _{3.13}	45.41 ± 0.10	45.50	54.33 ± 0.11	54.43
NbCl _{2.67}	49 ± 0.10	49.53	50.45 ± 0.10	50.47
NbCl _{2.33}	52.89 ± 0.10	52.94	46.99 ± 0.10	47.06

between the metal atoms in the layers, which leads to a significant reduction in the distance between the metal atoms in comparison with the metallic state, while between chlorine atoms there is only a weak van der Waals bond, which allows individual Cl-Zr-Zr-Cl layers or “slabs” to move along each other practically without friction.

Unfortunately, the presence of superconductivity in this compound was not tested and has not been investigated to date, probably due to the complexity of its preparation.

We assume that a not yet synthesized niobium monochloride with a similar to ZrCl structure could be a promising superconducting compound.

The assumption is based on the fact that of all metals, niobium has the highest superconducting transition temperature (9.2 K). Niobium is found in many superconductors currently in use, such as Nb₃Ge (critical temperature 23 K) [5]. Interestingly, when studying the low-temperature heat capacity of the niobium cluster NbCl_{2.67} (Nb₃Cl₈) an anomaly jump was found [15] in the heat capacity at temperature of

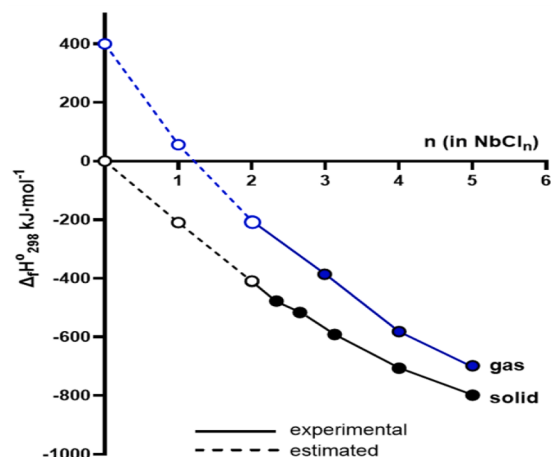


Fig. 3. Enthalpy of formation of solid and gaseous lower niobium chlorides at normal conditions (P=1 atm, T=298 K) (enthalpy of formation of gaseous metal niobium is taken from reference book [12]). Experimental data were taken from [13,16–19]

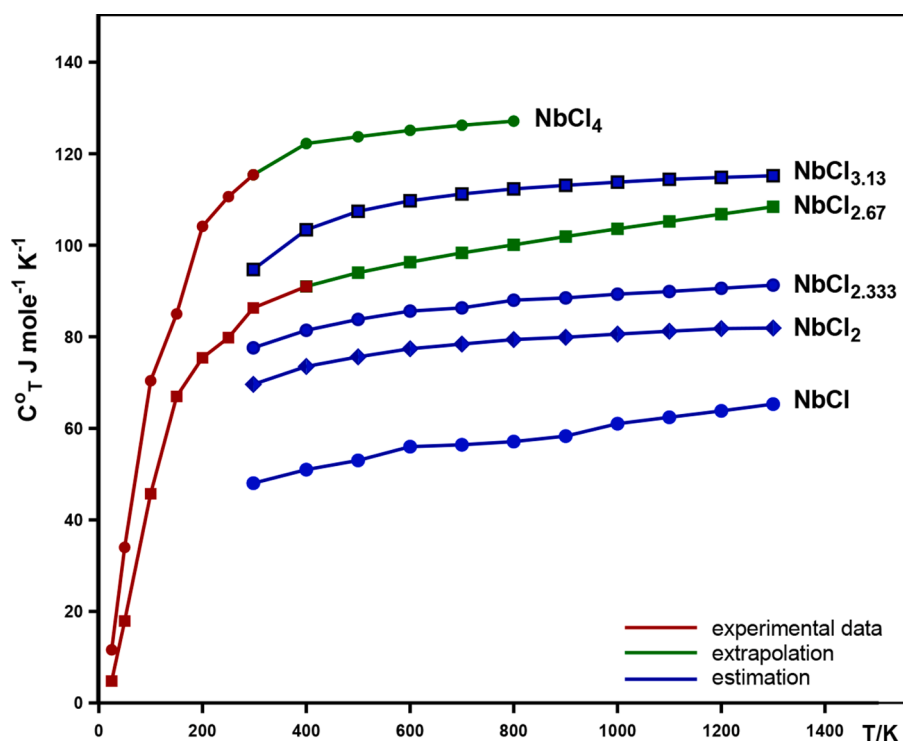


Fig. 2. Isobaric heat capacity of lower solid niobium chlorides dependence on temperature

* Experimental data for NbCl₄ and NbCl_{2.67} in temperature range 7–315 K were taken from [15]

Table 2

Thermodynamic Properties of Solid Lower Niobium Chlorides

(C_p^o - isobaric heat capacity, S^o - entropy, G^o - Gibbs thermodynamic potential, H_T^o-H₂₉₈^o, heat content, Δ_fH^o - enthalpy of formation)

NbCl ₄ T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H ^o
298	116.6±0.2	161.2±0.4	161.2±0.2	0	-705.1±2.0
400	122.2	196.4	165.9	12.2	-703.2
500	123.7	223.8	174.8	24.4	-700.5
600	125.1	246.5	184.9	36.9	-698.0
700	126.2	265.9	196.6	494	-695.7
800	127.1	282.8	205.1	621	-692.9

NbCl _{3,13} T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o kJ mol ⁻¹
298	94.7	127.6	127.6	0	-592.0±11.0
400	103.4	157.5	139.0	10.2	-590.1
500	107.4	181.0	147.6	20.7	-587.7
600	109.7	200.8	156.4	31.6	-585.2
700	111.2	217.9	164.3	42.6	-582.7
800	112.3	232.8	175.2	53.8	-579.8
900	113.1	246.1	173.2	54.1	-577.5
1000	113.8	258.0	181.0	76.4	-574.4
1100	114.4	268.9	188.4	87858	-571.7
1200	114.8	278.9	196.5	99319	-569.0
1300	115.2	281.1	202.7	110826	-566.3

NbCl _{2,67} (Nb ₃ Cl ₈) T(K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	86.3±0.2	105.5±0.3	105.5±0.2	0	-517.3±10.0
400	91.0	131.6	108.0	9.87	-514.3
500	94.0	152.3	115.6	18.1	-510.9
600	96.3	169.6	123.6	27.3	-506.9
700	97.3	184.6	131.0	37.6	-502.8
800	100.1	197.9	138.5	47.5	-498.4
900	101.9	209.7	145.7	57.5	-493.9
1000	103.6	220.6	152.7	67.9	-489.3
1100	105.2	230.5	159.3	78.3	-483.5
1200	106.8	239.7	165.6	88.9	-479.6
1300	108.4	248.4	171.7	99.7	-474.6

NbCl _{2,33} (Nb ₆ Cl ₁₄) T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	77.6±0.2	96.1±0.2	06.1±0.2	0	-479.0±10.0
400	81.4	120.9	102.2	9.00	-476.7
500	83.8	139.2	107.8	18.1	-474.3
600	85.8	155.0	115.3	27.4	-471.1
700	86.9	168.4	122.0	37	-468.9
800	88.0	180.6	130.9	46.6	-466.6
900	88.5	191.3	137.4	56.4	-464.4
1000	89.3	201.3	144.2	66.2	-461.2±10
1100	89.9	210.2	150.7	76199	-458.1
1200	90.5	218.5	156.8	86251	-455.6
1300	91.3	226.5	162.7	96393	-452.8

NbCl ₂ T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o kJ mol ⁻¹
298	73.6	88.0	88.0	0	-411.0
400	76.6	110.1	90.9	7.7	-409.4
500	78.3	127.5	96.6	15.4	-407.2
600	80.7	141.6	102.6	23.4	-406.1
700	82.5	154.5	109.4	31.6	-403.9
800	84.8	165.7	116.8	40	-402.3
900	85.9	179.7	121.9	48.4	-400.7
1000	87.5	184.8	127.7	57.1	-398.0±12.0
1100	89.1	193.2	133.2	65.9	-395.9
1200	90.7	201.1	138.6	74.9	-393.5
1300	92.4	208.4	143.7	84.1	-391.0

NbCl T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	48.0	58.0	58.0	0	-210.0

(continued on next page)

Table 2 (continued)

NbCl T (K)	C_p° $J\ mol^{-1}\ K^{-1}$	S°	G°	$H_f^\circ - H_{298}^\circ$ $kJ\ mol^{-1}$	$\Delta_f H_f^\circ$
400	51.0	72.6	59.9	5.1	-209.2
500	53.0	84.2	63.7	10.3	-208.3
600	55.9	94.0	67.9	15.7	-207.4
700	56.4	102.6	72.3	21.2	-206.2
800	57.9	102.2	76.5	26.9	-205.1
900	59.5	114.1	77.6	33.9	-204.2
1000	61.0	123.5	82.6	38.8	-202.5±15.0
1100	62.4	129.4	88.5	45	-201.0
1200	63.8	134.9	92.1	51.3	-199.4
1300	65.3	140.0	95.6	57.8	-197.8

*Standard uncertainty of estimated values of isobaric heat capacity, entropy, Gibbs thermodynamic potential and isobaric heat content is $\pm 2\%$ of the presented value.

Uncertainty of estimated values of enthalpy of formation of $NbCl_4(s)$ is $\pm 2\ kJ\ mol^{-1}$ of $NbCl_{3.13}(s)$ is $\pm 12\ kJ\ mol^{-1}$ of $NbCl_{2.67}(s)$ is $\pm 10\ kJ\ mol^{-1}$ of $NbCl_{2.33}(s)$ is $\pm 10\ kJ\ mol^{-1}$ of $NbCl_3(s)$ is $\pm 15\ kJ\ mol^{-1}$ of $NbCl(s)$ is $\pm 15\ kJ\ mol^{-1}$

9.2 K, corresponding to the temperature of transition to the superconducting state of metallic niobium, although X-ray phase analysis of the compound did not show the presence of metal [15]. The authors explain this anomaly by the fact that this cluster has a layered structure (type CdI_2), where the cadmium position is occupied by a group of three niobium atoms.

2. Materials and methods

Niobium pentachloride (purity 99.9%) and niobium powder (purity 99.0%) were purchased from Sigma-Aldrich. $NbCl_4$ was prepared by thermal reduction of $NbCl_5$ with niobium powder and niobium lower chlorides $NbCl_{3.13}$, $NbCl_{2.67}$ and $NbCl_{2.33}$ were prepared by thermal decomposition of $NbCl_4$ in molybdenum containers placed in sealed under vacuum quartz ampoules in a two-zone furnace.

The temperature of zones were chosen based on results of thermographic studies of this process (Appendix 5).

The composition of synthesized compounds was checked by chemical analysis [15]. The results with standard uncertainties are presented in Table 1.

Used methods: Calorimetry of dissolution was carried out on calorimeter LKB-8700 (Sweden) [13]. For low temperature calorimetry we used vacuum adiabatic calorimeter with electric impulse heating [15]. Tensimetric measurements of thermal decomposition of $NbCl_4$ were carried out in a two zone membrane quartz manometer [16]. Thermogravimetric measurements were carried out on derivatograph Q-1500 (Hungary) in inert gas, using special quartz vessels with capillary orifice.

3. Results

3.1. The thermodynamic functions of crystalline lower niobium chlorides

The thermodynamic properties of crystalline lower niobium chlorides (with the exception of monochloride) were presented earlier in the reference book [12], where these data were obtained by comparing and extrapolating similar experimental data obtained for elements situated nearby in the periodic table. Our data on isobaric specific heat capacity is based on experimental data of low-temperature heat capacity of niobium penta- and tetrachloride and clusters $NbCl_{2.67}$ (Nb_3Cl_8) [13] with extrapolation of these data to the high-temperature region. Isobaric heat capacity of studied lower niobium chlorides were determined in adiabatic calorimeter by the method of electric impulse heating in the temperature range 7–330 K on 70 – 100 temperature points. Average deviation of experimental values from smooth curves is 0.90% in the range 7–20 K and 0.10% from 20 to 330 K. The standard uncertainties in heat capacity of studied lower niobium chlorides at normal conditions ($P=1\ atm\ T=298\ K$) are $\pm 0.2\ J\ mole^{-1}\ K^{-1}$. The heat capacity of lower

niobium chlorides in temperature range from 298 to 1300 K was calculated by the method used in JANAF Thermochemical Tables [14] by deduction of chlorine atoms contribution calculated as $1/4 [C_p^\circ(NbCl_4)_{cr} - C_p^\circ(Nb_{cr})]$. The reliability of this method was checked by comparison of experimental and calculated value of heat capacity for niobium cluster $NbCl_{2.67}$ (Nb_3Cl_8):

$$C_{298}^\circ \text{ calculated} = 85.8 \pm 1.8\ J\ mol^{-1}\ K^{-1}$$

$$C_{298}^\circ \text{ experimental} = 86.3 \pm 0.2\ J\ mol^{-1}\ K^{-1}$$

The data on the heat capacity of solid lower niobium chlorides are presented in Fig. 2.

Values of entropies, heat contents and Gibbs thermodynamic potentials were calculated by integrating the obtained dependency of heat capacity on temperature.

Thermodynamic properties were calculated by equations presented in Appendix 1 using online program “Wolfram Integrator” with estimated error $\pm 2.0\%$ from presented values.

The enthalpy of formation of solid lower niobium chlorides in the temperature range from 298 to 1300 K are based on their experimentally determined enthalpy of formation [16–19] at certain temperatures by calculation using obtained thermodynamic functions in a wider temperature range.

The enthalpy of $NbCl_4$ formation at normal conditions ($P = 1\ atm., T = 298\ K$) which is basis for determination of other niobium lower chlorides enthalpy of formation was determined with minimal uncertainties using precision dissolution calorimeter LKB-8700 [13]. The obtained value is

$$\Delta_f H_{(298)}^\circ = -705.1 \pm 2.0\ kJ\ mol^{-1}$$

Enthalpy of formation of $NbCl_{3.13}$ and $NbCl_{2.67}$ was calculated from thermal decomposition reaction heats obtained by measuring equilibrium pressure of gaseous products in one- and two zone quartz membrane manometers [16–18]. The calculations was carried out using our and literature [12] data for heat content ($H_f^\circ - H_{298}^\circ$) for reaction products and metal niobium and chlorine. Enthalpy of formation of $NbCl_{2.33}$ was determined from thermal decomposition reaction heat by measuring dependence of equilibrium pressure of gaseous reaction products on temperature by effusion method with mass-spectral registration of composition and pressure of gas phase using mass-spectrometer MS-1201 reconstructed for thermodynamic research [19]. Standard uncertainties of $NbCl_{3.13}$, $NbCl_{2.67}$ and $NbCl_{2.33}$ enthalpy of formation at normal conditions were determined from experimental errors (RMSE) of measuring dependence of their thermal decomposition reaction gaseous products on temperature [19].

These data are presented in Fig. 3 and in Table 2. The values in bold were obtained by experiment and used as basis for calculation of thermodynamic properties with their calculated standard uncertainties.

Table 3

Vibration frequencies of gaseous lower niobium chlorides (G - symmetry number, ν_1 – frequency).

Molecule	G	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}
NbCl ₄	12	405	90 (2)	370 (3)	105 (3)
NbCl ₃	2	414	124	366 (2)	160 (2)
NbCl ₂	2	376	136 (2)	406	
NbCl	4	542			

3.2. Thermodynamic functions of gaseous lower niobium chlorides

Data on the thermodynamic characteristics of gaseous lower niobium chlorides, with the exception of tetrachloride [12], have not been found in the literature. Therefore, to calculate their thermodynamic functions, we initially calculated the vibration frequencies of gaseous molecules. The calculations were carried out in the approximation of a modified valence-force field with transfer of the values of the force constants, estimated on the basis of their values for titanium, zirconium, hafnium, and vanadium tetrachlorides. The applicability of this approach was tested by comparing the frequencies calculated by this method and experimentally determined frequencies for the molecules of lower titanium chlorides presented in Appendix 2. The numerical values of the force constants (in mdyn/Å) of the Nb-Cl bonds are:

$$f_d = 2.45; f_{dd} = 0.19; f_a = 0.11; f_{aa} = 0.008$$

The geometric structure of the molecules of lower niobium chlorides was taken as follows: for tetrachloride is tetrahedron, for trichloride - trigonal pyramid, for dichloride - angular (angle—tetrahedral). The Nb-Cl distance in all molecules was taken to be equal to that in the niobium pentachloride molecule [19]. Obtained values of vibration frequencies are presented in Table 3.

- Vibration frequencies were calculated using equations presented in the book by Herzberg G., “Molecular Spectra and Molecular Structure. II Infrared and Raman spectra of Polyatomic molecules. Van Nestrand. New York. 1934.

(Russian translation. “Vibrational and Rotation Spectra of polyatomic molecules” (Book on demand), 2013

The calculation of the thermodynamic functions of gaseous molecules of lower niobium chlorides was carried out in the temperature range of 298 to 2000 K using standard programs on a Hewlett-Packard 9820A computer. The enthalpies of formation were estimated based on the experimentally determined values for gaseous NbCl₅, NbCl₄, and NbCl₃ and graphical extrapolation for the remaining lower chlorides. The uncertainty of calculated values of heat capacity, entropy, thermodynamic potential and heat content was determined by error in estimation of vibration frequencies of gaseous lower niobium chlorides depending on the estimated molecular structure and bond force constants. In our case the error in vibration frequencies as seen in Table 3 did not exceed 5%. So the accepted uncertainty is 7% from the presented value of thermodynamic functions. The uncertainty of lower niobium chloride enthalpy of formation was calculated from experimental errors in its determination for gaseous niobium tetra- and trichloride and error of enthalpy of formation of di- and monochloride obtained by graphical extrapolation. The data obtained are presented in Table 4.

3.3. Calculation of the equilibrium composition of the gaseous phase in the Nb-NbCl₅ System in the temperature range from 1000 to 2000 K

Our experimental studies are in agreement with others [19] and showed that the gas phase above crystalline lower niobium chlorides at high temperatures is complex and simultaneously contains different types of molecules. We made a quantitative assessment of their content

Table 4

Thermodynamic Properties of Gaseous Lower Niobium Chlorides

C_p^o - isobaric heat capacity, S^o - entropy, G^o Gibbs thermodynamic potential, H_T^o - H₂₉₈^o, heat content, Δ_fH^o - enthalpy of formation)

NbCl ₄					
T(K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	99.4	372.3	372.3	0	-581.8
400	103.0	402.0	376.2	10.3	-581.1
500	104.7	425.2	383.8	20.7	-580.4
600	105.7	444.4	392.3	31.2	-579.4
700	106.3	460.8	401.0	41.8	-578.8
900	107.0	487.6	417.4	63.2	-577.6
1000	107.2	498.8	424.9	73.9	-577.0
1200	107.5	518.4	438.9	95.4	-576.2
1400	107.6	535.0	451.5	116.9	-575.4
1600	107.7	549.4	462.9	135.4	-575.0
1800	107.8	561.2	473.2	160	-574.8
2000	107.9	573.4	482.7	181.5	-574.6
NbCl ₃					
T (K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	76.1	345.6	345.6	0	-386.0
400	79.0	368.4	348.6	7.4	-385.4
500	80.4	386.2	354.4	15.9	-384.9
600	81.20	400.9	361.0	24	-393.6
700	81.7	413.5	367.6	32.1	-393.2
800	82.0	424.4	374.0	40.3	-392.4
900	82.3	434.1	380.6	48.1	-381.9
1000	82.4	442.8	386.0	56.8	-381.5
1200	82.7	457.8	396.8	73.3	-381.2
1400	82.8	470.6	406.4	89.8	-381.0
1600	82.9	481.7	415.1	106.4	-380.9
1800	82.9	491.4	415.1	122.9	-380.8
2000	83.0	500.1	430.4	139.5	-380.8
NbCl ₂					
T(K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mol ⁻¹	Δ _f H _T ^o
298	53.4	302.6	302.6	0	-204.0
400	55.3	318.6	303.6	6	-203.9
500	56.3	331.1	307.1	12	-203.8
600	56.9	341.4	311.3	18.1	-203.6
700	57.2	350.2	315.6	24.2	-203.4
800	57.4	357.8	319.9	30.3	-203.1
900	57.6	364.6	324.1	36.5	-202.8
1000	57.7	370.7	328.0	42.7	-202.5
1200	57.9	381.2	335.3	55.1	-201.7
1400	58.0	390.1	341.9	67.5	-200.7
1600	58.0	398.0	347.9	80	-199.4
1800	58.1	404.7	353.4	92.4	-197.9
2000	58.1	410.8	358.4	104.8	-196.7
NbCl					
T(K)	C _p ^o J mol ⁻¹ K ⁻¹	S ^o	G ^o	H _T ^o -H ₂₉₈ ^o kJ mole ⁻¹	Δ _f H _T ^o
298	35.0	257.1	257.1	0	+56.0
400	35.5	267.5	258.5	3.6	+55.2
500	36.0	275.5	261.2	7.2	+54.4
600	36.3	281.6	263.6	10.8	+53.5
700	36.7	287.7	267.1	14.4	+52.6
800	37.0	292.6	270.0	18.1	+51.7
900	37.3	297.0	272.7	21.8	+50.8
1000	38.6	301.9	275.3	25.6	+50.0
1200	38.3	307.8	280.2	33167	+48.3
1400	38.9	313.8	284.6	40880	+46.5
1600	39.5	319.0	288.6	48717	+44.3
1800	40.1	323.7	292.2	56678	+42.2
2000	40.4	327.9	295.5	64762	+40.1

*Standard uncertainty of estimated values of isobaric heat capacity, entropy, Gibbs thermodynamic potential and heat content is $\pm 7\%$ of the presented value.

Uncertainty of estimated values of enthalpy of formation of NbCl₄ (g) is $\pm 8 \text{ kJ mol}^{-1}$ of NbCl₄ (g) is $\pm 12 \text{ kJ mol}^{-1}$ of NbCl₂ (g) is $\pm 15 \text{ kJ mol}^{-1}$ of NbCl (g) is $\pm 20 \text{ kJ mol}^{-1}$

Table 5Enthalpy of formation and entropies of reaction components in the system Nb- NbCl₅

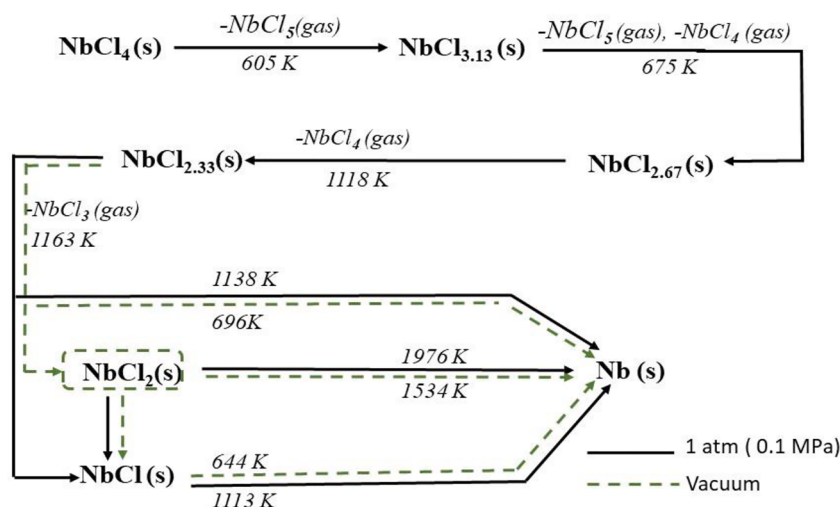
Component	$\Delta_f H_{298}^{\circ} \text{kJ mol}^{-1}$	$S_{298}^{\circ} \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta_f H_{1000}^{\circ} \text{kJ mol}^{-1}$	$S_{1000}^{\circ} \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
NbCl ₅ (gas)	-705.7	388.7	-706.0	607.0
NbCl ₄ (gas)	-581.8	372.3	-577.5	498.8
NbCl ₃ (gas)	-386.0*	345.6*	-381.5*	442.8*
NbCl ₂ (gas)	-204.0*	302.6*	-202.5*	370.7*
NbCl (gas)	+56.0*	257.1*	+50.0*	301.9*
Cl ₂ (gas)	0	222.8	0	266.4
Cl (gas)	120.8	165.0	123.9	192.1
Nb (s)	0	36.5	0	67.9

* our assessments

using values of enthalpy of formation and entropies of crystalline and gaseous lower niobium chlorides obtained by us and available in the literature [12,14]. The thermodynamic data used for the calculations are presented in Table 5.

The calculation was carried out by jointly solving the equations of dependence of equilibrium constants for formation of gaseous lower niobium chlorides from metallic niobium and its pentachloride on temperature. The reaction constants were calculated from the enthalpy of formation of compounds and their entropies at average temperature of the selected interval, i.e. at 1000 K. The equations of the reaction constants are presented in Table 6. The details of calculations are described in Appendix 3. The results obtained are presented in graphical

thermal decomposition of niobium tetrachloride in the gas phase lower chlorides of different oxidation states (penta-, tetra-, tri- and dichloride) are successively formed. In this case, upon decomposition in vacuum, the solid decomposition product of the NbCl_{2.33} (Nb₆Cl₁₄) cluster is NbCl₂ and at atmospheric pressure this phase was not detected, and the decomposition product is a metal or its mixture with monochloride (the chemical composition of the product corresponds to the formula NbCl_{0.4-0.5} (although X-ray phase analysis did not show the presence of metal, possibly due to its amorphous state. The mechanism of thermal decomposition of niobium tetrachloride proposed on the base of obtained thermodynamic data is presented on the scheme below.



form in Fig. 4 and are in good agreement with the experimental data.

Thus, in the range of mass-spectral pressures 10^{-6} atm it can be seen that with sequential thermal decomposition of crystalline niobium tetrachloride the molecules of penta-, tetra- and niobium trichloride are formed successively, and at higher temperatures (not yet studied) formation of gaseous di- and mono- niobium chloride are predicted. The presence of the first of these components was recorded in a mass-spectral study [18]. At atmospheric pressure, the main gaseous product of thermal decomposition of the crystalline niobium cluster NbCl_{2.67} (Nb₃Cl₈) is gaseous niobium tetrachloride, and during the decomposition of the NbCl_{2.33} (Nb₆Cl₁₄) cluster it is gaseous trichloride.

3.4. Mechanism of thermal decomposition of the niobium tetrachloride NbCl₄

As a result of thermographic [16], manometric [17] and mass-spectral studies [18], it was found that during the sequential

Derivatogram of thermal decomposition of niobium tetrachloride at atmospheric pressure is given in Appendix 5.

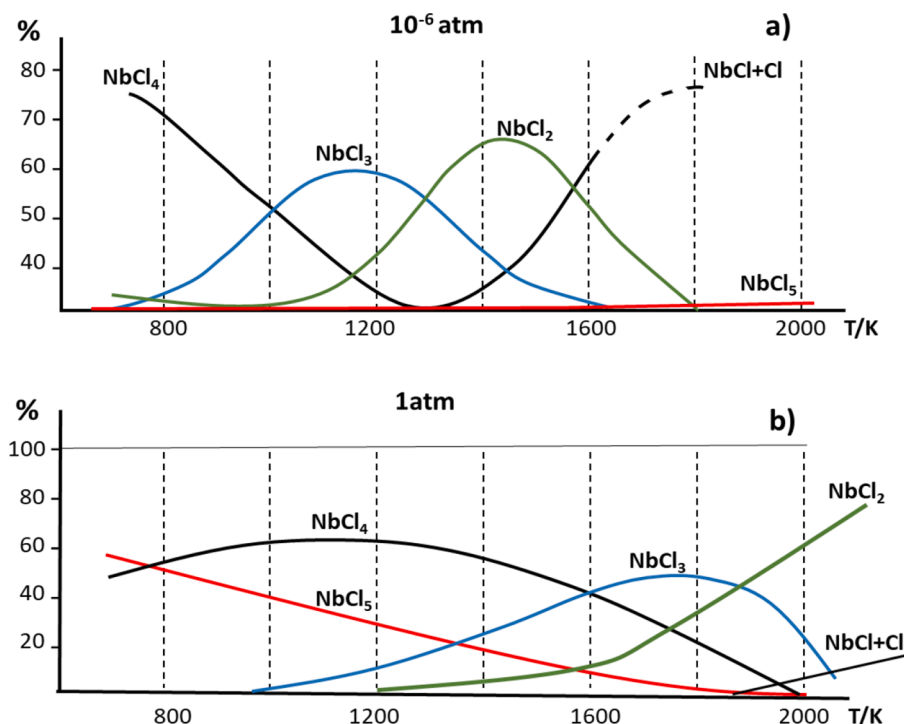
This means that niobium cluster NbCl_{2.33} (Nb₆Cl₁₄) can decompose with formation of various crystalline phases that depends on the pressure of the formed gaseous products. Our thermodynamic data allowed us to calculate the conditions of these phases formation. The calculated thermodynamic parameters and equations for the dependence of the equilibrium constants of these reactions are presented in Table 7.

4. Discussion

Based on the obtained thermodynamic data, we conclude that the process of thermal decomposition of the niobium cluster NbCl_{2.33} (Nb₆Cl₁₄) at atmospheric pressure proceeds simultaneously with the formation of solid niobium monochloride and metallic niobium, bypassing the stage of niobium dichloride formation, as shown in Fig. 5

Table 6Equations of the dependence of the reaction constants on temperature ($\Delta_r H_{1000}^\circ$ - reaction enthalpy, $\Delta_r S_{1000}^\circ$ - entropy of reaction)

N ^o	Reactions	$\Delta_r H_{1000}^\circ/\text{kJ mole}^{-1}$	$\Delta_r S_{1000}^\circ/\text{J mole}^{-1}\text{K}^{-1}$	Equations
1	$1/5\text{Nb} + 4/5 \text{NbCl}_5 (\text{gas}) = \text{NbCl}_4$	12.7	96.5	$\log K_1 = -6635/T + 5.05$
2	$2/5\text{Nb} + 3/5 \text{NbCl}_5 (\text{gas}) = \text{NbCl}_3$	42.1	51.4	$\log K_2 = -2198/T + 2.68$
3	$3/5\text{Nb} + 2/5 \text{NbCl}_5 (\text{gas}) = \text{NbCl}_2$	78.9	87.6	$\log K_3 = -4172/T + 4.59$
4	$4/5\text{Nb} + 1/5 \text{NbCl}_5 (\text{gas}) = \text{NbCl}$	91.2	121.4	$\log K_4 = -4762/T + 6.55$
5	$2/5\text{NbCl}_5 (\text{gas}) = 2/5\text{Nb} + \text{Cl}_2$	282.4	50.8	$\log K_5 = -14767/T + 2.66$
6	$1/5\text{NbCl}_5 (\text{gas}) = 1/5\text{Nb} + \text{Cl} (\text{gas})$	265.1	84.4	$\log K_6 = -13862/T + 4.41$

**Fig. 4.** Composition of gas phase in the Nb – NbCl₅ system in dependence on temperature at 1 atm and 10^{−6} atm.**Table 7**Dependence of equilibrium pressure of gaseous reaction products of thermal decomposition of NbCl_{2.33} (Nb₆Cl₁₄) on temperature ($\Delta_r H_{1000}^\circ$ - enthalpy of reaction, $\Delta_r S_{1000}^\circ$ - entropy of reaction)

N ^o	Reactions	Equation of equilibrium pressure of gaseous reaction products on temperature	$\Delta_r H_{1000}^\circ/\text{kJ mole}^{-1}$	$\Delta_r S_{1000}^\circ/\text{J mole}^{-1}\text{K}^{-1}$	T ₁ , K	T ₂ , K
1	$3\text{NbCl}_{2.33} = 2\text{NbCl}_2(\text{s}) + \text{NbCl}_3(\text{g})$	$\log P_{\text{atm}} = -10762/T + 8.04$	206.1	158.9	1338	751
1	a $3\text{NbCl}_{2.33} = \text{NbCl}(\text{s}) + 2\text{NbCl}_3(\text{g})$	$\log P_{\text{atm}} = -10917/T + 8.48$	208.1	161.7	1187	754
1	b $1.3\text{NbCl}_{2.33} = 0.3\text{Nb}(\text{s}) + \text{NbCl}_3(\text{g})$	$\log P_{\text{atm}} = -11389/T + 10.49$	218.1	205.9	1085	691
2	$2\text{NbCl}_2(\text{s}) = \text{NbCl}(\text{s}) + \text{NbCl}_3(\text{g})$	$\log P_{\text{atm}} = -19034/T + 10.27$	364.5	196.7	1853	1170
2	a $3\text{NbCl}_2(\text{s}) = \text{Nb}(\text{s}) + 2\text{NbCl}_3(\text{g})$	$\log P_{\text{atm}} = -20600/T + 10.43$	394.5	199.6	1976	1534
3	$2\text{NbCl}(\text{s}) = \text{Nb}(\text{s}) + \text{NbCl}_2(\text{g})$	$\log P_{\text{atm}} = -10574/T + 10.43$	202.5	199.7	1013	644

T₁, K—temperature of the thermal decomposition (endothermic effect in thermography) at the pressure of gaseous decomposition products 1 atm.

T₂, K—temperature of the thermal decomposition at the pressure of gaseous decomposition products 10^{−6} atm (area of mass-spectral studies)

Temperature of NbCl_{2.33} thermal decomposition at atmospheric pressure was determined by thermal analysis as 1164 ± 10 K. This value is close to the temperatures calculated for reactions 1a and 1b and confirms the reliability of our lower niobium chlorides thermodynamic properties estimation.

This is confirmed by experimental data of the final decomposition product corresponding to the formula NbCl_{0.4-0.5}, which is confirmed by experimental data [18]. This product did not lose chlorine [19] when heated to 1300 K. When NbCl_{2.67} (Nb₃Cl₈) was heated in vacuum, the decomposition product is niobium dichloride, which was confirmed by the results of mass-spectral studies.[18]

5. Conclusion

Niobium dichloride upon heating at atmospheric pressure or vacuum decomposes to metal niobium, probably with some presence of niobium monochloride (Fig. 6).

According to our calculations niobium monochloride can be obtained by thermal decomposition of the NbCl_{2.67} (Nb₃Cl₈) cluster at

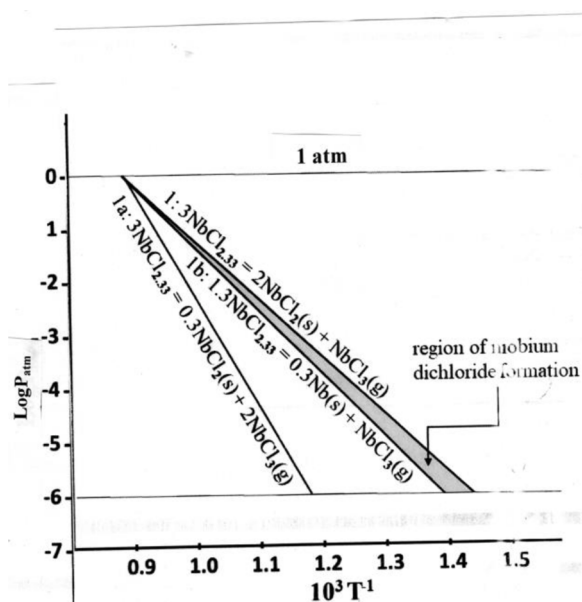


Fig. 5. Dependence of $\text{NbCl}_{2.33}$ thermal decomposition products on pressure and temperature below 1 atm.

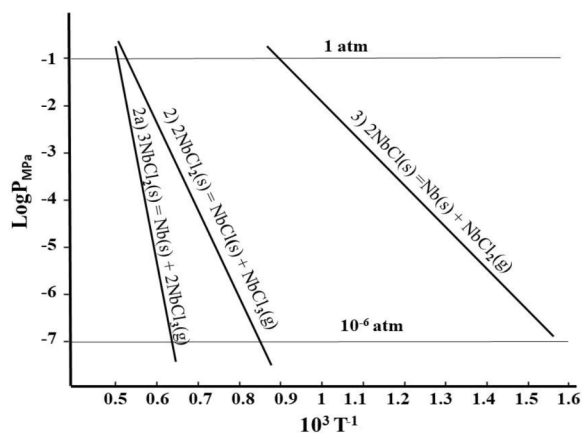


Fig. 6. Dependence of NbCl_2 and NbCl thermal decomposition products on temperature and pressure below 1 atm.

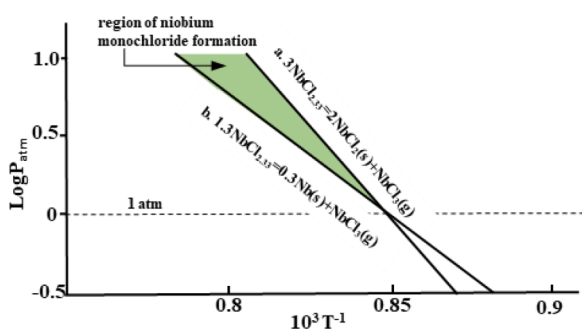


Fig. 7. Dependence of NbCl_2 and NbCl thermal decomposition products on temperature and pressure above 1 atm.

elevated pressure (more than 4 atm) (Fig. 7).

At atmospheric pressure niobium monochloride decomposes approximately at 1850 K. Crystalline niobium dichloride and monochloride can also be synthesized according to thermodynamic data by solid-phase reduction of the $\text{NbCl}_{2.67}$ (Nb_3Cl_8) cluster with metallic niobium powder in a closed system at 1000–1050 K.

It should be noted that the thermodynamic characteristics of crystalline niobium di- and monochloride were obtained by graphical extrapolation, which implies a rather large uncertainty. For a more reliable prediction of the thermal behavior of these phases, it would be desirable to have experimental thermogravimetric data on the process of thermal decomposition and mass-spectral analysis of the resulting gaseous products of niobium dichloride thermal decomposition up to a temperature of 1400 K.

Associated content

Supporting information

Supporting information is available free of charge at

1, <http://janaf.nist.gov>

NIST JANAF Thermochemical Tables. (PDF)

2, <http://books.google.com>

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Not allocable.

List of symbols

C_{op} J · mol⁻¹ K⁻¹ isobaric heat capacity

S_o J · mol⁻¹ K⁻¹ entropy

G^0 J · mol⁻¹ K⁻¹ Gibbs thermodynamic potential

$H^0 T - H^0 298$ J · mol⁻¹ heat content

$\Delta_f H_f^0$ kJ · mol⁻¹ heat of formation f_d m dyn · Å⁻¹ stretch force constant

of Nb - Cl bond f_{dd} m dyn · Å⁻¹ force constant of Nb - Cl bonds interaction

f_α m dyn · Å bending force constant of Cl - Nb - Cl bonds $f_{\alpha\alpha}$ m dyn · Å

bending force constant of Cl - Nb - Cl bonds interaction

CRediT authorship contribution statement

Viatcheslav I. Tsirelnikov: Conceptualization, Methodology, Writing – review & editing. **Lidia M. Bazhanova:** Data curation, Investigation. **Boris V. Lokshin:** Software, Validation.

Declaration of Competing Interest

None

Data Availability

Data will be made available on request.

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Appendix 1

$$\begin{aligned}
 H_T^\circ - H_{298}^\circ &= \int_{298}^T C_P^\circ dT; \\
 S_T^\circ &= S_{298}^\circ + \int_{298}^T \frac{C_P}{T} dT; \\
 F_T^* &= \frac{H_T^\circ - H_{298}^\circ}{T} - S_T^\circ; \\
 \Delta H_{fT}^\circ &= \Delta H_{f298}^\circ + (\Delta H_T^\circ - \Delta H_{298}^\circ)
 \end{aligned}$$

Appendix 2**Vibration frequencies of gaseous lower titanium chlorides**

Molecule	ν_1	ν_2	ν_3	ν_4
TiCl ₃ —exp*	—	110±12	505±10	135 ±12
calculation**	530	270	590	260
our calculation	477	130	495	121
TiCl ₂ —exp*	—	122 ± 12	486 ± 30	
calculation**	279	196	439	
our calculation	309	120	430	
TiCl—exp*	450±20			
calculation**	379			
our calculation	449			

*Kasuo Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds.

2009 Wiley Publication, 6-th edition

**J.W Hastie, R.H.Hauge, J.L.Margrave, Infrared Spectra and Geomerics for the Dichlorides of Ca, Sc, Ti, V, Cr, Mn, Fe, Ni. 1971, High temp. Sci., 7, 257

Appendix 3

for monochloride

$$w_l^2 = 4\pi^2 c^2 \frac{m_x + m_y}{m_x m_y} \cdot f_d.$$

for dichloride

$$\begin{aligned}
 \lambda_1 &= \frac{f_d + f_{dd}}{m_y}; \\
 \lambda_2 &= 2 \left(1 + \frac{2m_y}{m_x} \right) \frac{1}{m_y} \cdot \frac{f_\alpha}{l^2}; \\
 \lambda_3 &= \left(1 + \frac{2m_y}{m_x} \right) \frac{f_d - f_{dd}}{m_y}.
 \end{aligned}$$

for trichloride

$$\begin{aligned}
 \lambda_1 + \lambda_2 &= \left(1 + 3 \frac{m_y}{m_x} \cos^2 \beta \right) \frac{f_d + 2f_{dd}}{m_x} + \left(1 + 3 \frac{m_y}{m_x} \sin^2 \beta \right) \frac{12 \cos^2 \beta}{1 + 3 \cos^2 \beta} \cdot \frac{f_\alpha + 2f_{\alpha\alpha}}{m_y l^2}; \\
 \lambda_1 \lambda_2 &= \frac{12 \cos^2 \beta}{1 + 3 \cos^2 \beta} \left(1 + 3 \frac{m_y}{m_x} \right) \frac{f_d + 2f_{dd}}{m_y^2} \cdot \frac{f_\alpha + f_{\alpha\alpha}}{l^2}; \\
 \lambda_3 + \lambda_4 &= \left(1 + \frac{3m_y}{2m_x} \sin^2 \beta \right) \frac{f_d - f_{dd}}{m_y} + 3 \frac{1 + \cos^2 \beta + \frac{3m_y}{2m_x} \sin^4 \beta}{1 + 3 \cos^2 \beta} \cdot \frac{f_\alpha - f_{\alpha\alpha}}{m_y l^2}; \\
 \lambda_3 \lambda_4 &= 3 \frac{1 + \cos^2 \beta + 3 \frac{m_y}{m_x} \sin^2 \beta}{m_y^2} \cdot \frac{f_d - f_{dd}}{m_y^2} \cdot \frac{f_\alpha - f_{\alpha\alpha}}{l^2}.
 \end{aligned}$$

Appendix 4

The composition of the gas phase with the introduction of 1 mole of niobium pentachloride and an excess of metallic niobium into the system is expressed by the following ratio:

$I = X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7$ where:

X_1 - amount of unreacted niobium pentachloride in moles

X_2 - X_5 - amounts of tetra-, tri-, di- and monochloride of niobium in the gas phase

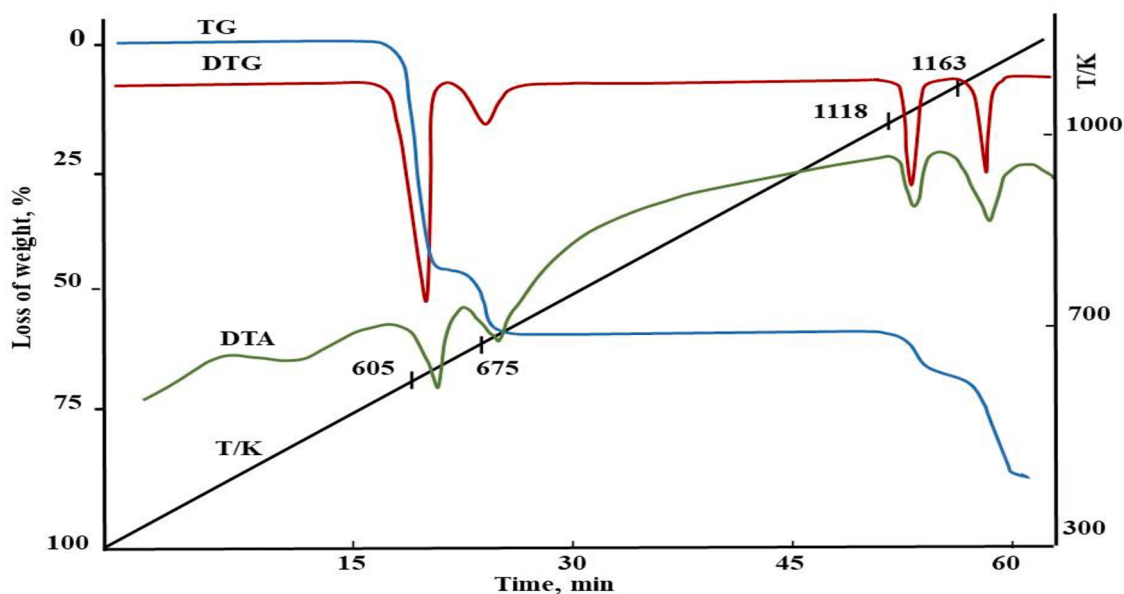
X_6 , X_7 - the number of moles of molecular and atomic chlorine in the gas phase. The general composition of the gas phase can be expressed in terms of the amount of niobium pentachloride consumed for the formation of this lower niobium chloride:

$I = X_1 + 0.8A^{-0.2}K_1X_1^{0.8} + 0.6A^{-0.4}K_2X_1^{0.6} + 0.4A^{-0.4}K_3X_1^{0.6} + 0.4A^{-0.6}(K_3 + K_5)X_1^{0.4} + 0.2A^{-0.8}(K_4 + K_6)X_1^{0.2}$ where:

A is the coefficient of transition from partial pressures to molar fractions, equal to P_0T/P_0T_0 , (P_0 is a given initial pressure at 273 K.)

Grouping similar terms and making the substitution $t = 1/5X$, we get the equation: $t^5 + 0.8A - 0.2K_1t^4 + 0.6A \cdot 0.4K_2t^3 + 0.4A \cdot 0.6(K_3 + K_5)t^2 + 0.2A \cdot 0.8(K_4 + K_6)t - 1 = 0$ which is solved by the iteration method, setting $0 < t > 1$. The end of the process of successive iterations was considered as the condition: the value obtained after substitution of the last value gives a deviation from I equal to ± 0.0001 , which is equal to the accuracy of the molar fraction of the component $\pm 0.001\%$.

Appendix 5



Derivatogramm of thermal decomposition of niobium tetrachloride at atmospheric pressure

Derivations:

TG - thermogravimetry

DYG - differential thermogravimetry

DTA - differential analysis

T (K) - temperature

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