ELSEVIER
Thermochimica Acta 290 (1997) 239–251
thermochimica acta

Quantitative interpretation of the evaporation coefficients for the decomposition or sublimation of some substances in vacuo

Boris V. L'vov*, Alexander V. Novichikhin

Department of Analytical Chemistry, St. Petersburg State Technical University, St. Petersburg 195251, Russia

Received 3 May 1996; revised 20 September 1996; accepted 21 October 1996

Abstract

An attempt is made at a quantitative interpretation of the low evaporation coefficients α (10^{-7}–10^{-1}) observed under thermal decomposition of 12 different compounds ($AgNO_3$, $BaSO_4$, $BaCO_3$, BN, Be_3N_2, Mg_3N_2, AlN, GaN, ZnO, CdS, CdSe and NH_4Cl) in vacuo under the conditions of free-surface evaporation after Langmuir. It is suggested that the main reason for the low evaporation coefficients lies in the difference between the true scheme of thermal decomposition of a given compound and in assuming its direct decomposition to the products corresponding to thermodynamic equilibrium. These differences consist, firstly, in a primary gasification of all decomposition products, including low-volatile components (metals and metal oxides) and, secondly, in a partial or total evolution of nitrogen, oxygen, sulfur, selenium and hydrogen chloride in the form of free atoms or H + Cl mixture rather than of molecules. The interpretation of the evaporation coefficients α for elemental red phosphorus, arsenic and antimony is based on the assumption that the sublimation of these substances occurs, accordingly, through a primary formation of P_2 molecules, or of $As_2 + As_4$ and $Sb_2 + Sb_4$ mixtures, rather than by direct formation of the P_4, As_4, or Sb_4 molecules corresponding to thermodynamic equilibrium, as is generally accepted. The proposed mechanisms of decomposition or sublimation are validated by a comparison of the experimental and calculated activation energies. © 1997 Elsevier Science B.V.

Keywords: Calculation of kinetics; Decomposition mechanism; Evaporation coefficient; Solid-state reactions

1. Introduction

As shown in a series of papers of L'vov et al. [1–6], the kinetics of reactions involving thermal decomposition of oxides [1–6] and hydroxides [4] in an argon environment, as well as oxide reduction by hydrogen [5], can be calculated theoretically based on the concepts of Hertz–Langmuir concerning evaporation of monatomic substances [6] and an equilibrium composition of the gaseous products formed in these processes. In most cases, calculated data agree fairly well with the results of kinetic studies by the electrothermal atomic absorption spectrometry [1–6].

In the case of solid-state reactions involving the formation of solid products, such as carbothermal reduction of metal oxides [7–9] and thermal decomposition of the nitrates of Ag, Cd and Pb in vacuum [10–13], an adequate description of the kinetics of the corresponding reactions has required introduction of an additional assumption, namely, that their mechanism involves primary gasification of all products with

---

*Corresponding author. Tel.: 7 812 552 7741; fax: 7 812 528 0281; e-mail:lvov@achem.hop.stu.neva.ru.

PII S0040-6031(96)03100-0

subsequent condensation of the components being in the condensed state in equilibrium. Since the composition of the primary products of these reactions differs from the equilibrium composition, the kinetic parameters of the corresponding processes differ substantially from the calculated parameters which would correspond to direct compound decomposition into the equilibrium products.

The difference in the kinetics of the processes occurring in equilibrium and nonequilibrium conditions is customarily taken into account by introducing into the Hertz–Knudsen–Langmuir equation an evaporation coefficient α, which is the ratio of the real gaseous-product flux J to the maximum possible flux $J_{\max}$, measured under the conditions of equilibrium evaporation from the effusion cell (after Knudsen)

$$\alpha = J/J_{\max} \tag{1}$$

There is a large number of references to substances with $\alpha \ll 1$ [14–16]. We are not aware, however, of any attempts at a quantitative correlation of the corresponding values of α with possible differences in the reaction mechanisms under equilibrium and nonequilibrium conditions. One of the obstacles in the way is that most experiments, even those conducted in vacuum, did not exclude collisions of atoms or molecules of the gaseous products with the reactant surface, which could result in accumulation, condensation, and/or association of the primary products in the reaction zone and, hence, in a shift of the measurement conditions toward equilibrium. Experiments performed with single crystals or densely pressed pellets of a compound, or with microgram amounts of substances distributed over the heater surface in the form of individual microparticles or, still better, of microdroplets (for substances with the melting point below the temperature of the experiment) appear more reliable, i.e. approaching closer to the conditions of nonequilibrium evaporation from a free surface (after Langmuir). One may expect that the evaporation rate approaches in these cases that from a free surface, J_{L}, and as a result the evaporation coefficient reaches here its lowest value

$$\alpha_{\min} = J_{\mathrm{L}}/J_{\max} \tag{2}$$

Based on the aforementioned considerations, we used in the calculation of the evaporation coefficients and in the search for the true mechanism of thermal decomposition the literature data for the kinetic parameters of thermal decomposition in vacuum of the following compounds: oxysalts ($AgNO_3$, $BaSO_4$ and $BaCO_3$), nitrides (BN, Be_3N_2, Mg_3N_2, AlN and GaN), an oxide (ZnO), a sulfide (CdS), a selenide (CdSe) and ammonium chloride (NH_4Cl). Besides, the same considerations were used to interpret the kinetics and mechanism of sublimation of red phosphorus, arsenic and antimony.

Basically, our method consists in a reasonable choice of such a nonequilibrium composition of the products of decomposition or sublimation of a substance with which the calculated pressure of one of the reaction products or the total pressure of all products would be close to the value of the corresponding parameter measured under the conditions of evaporation after Langmuir. The criterion of correctness of the chosen mechanism is taken to be the agreement between the calculated and experimental values of the activation energy E_{a}.

2. Theoretical

The flux J of a gaseous product (in moles) produced under the conditions of monatomic evaporation is given by the well-known Hertz–Knudsen–Langmuir equation

$$J = \frac{P}{(2\pi MRT)^{1/2}} \tag{3}$$

Here, P is the partial pressure of the gaseous product corresponding to a hypothetical equilibrium for the evaporation process, M the molar mass of the gaseous particles, R the gas constant, and T the temperature.

In the case of compound S decomposing into gaseous products A, B, C, etc.

$$S(\mathrm{s/l}) \rightarrow a\mathrm{A(g)} + b\mathrm{B(g)} + c\mathrm{C(g)} + \ldots \tag{4}$$

the flux of product A in moles can be expressed through the partial pressure P_{A} of this product corresponding to the hypothetical equilibrium of reaction (4) in the form [6,16]

$$J_{\mathrm{A}} = \frac{P_{\mathrm{A}}}{(2\pi\bar{M}RT)^{1/2}} = \frac{a\gamma}{F^{1/\nu}(2\pi\bar{M}RT)^{1/2}} \exp\frac{\Delta S_T^0}{\nu R} \cdot \exp\left[-\frac{\Delta H_T^0}{\nu RT}\right] \tag{5}$$

where

$$F \equiv a^a \times b^b \times c^c \times \ldots \quad (6)$$

$$\nu \equiv a + b + c + \ldots \quad (7)$$

$$\overline{M} \equiv M_A^{a/\nu} \times M_B^{b/\nu} \times M_C^{c/\nu} \times \ldots \quad (8)$$

Here, S_T^0 and H_T^0 are the changes in entropy and enthalpy for reaction (4), and $\gamma = 1.01325 \times 10^5$ is the coefficient of conversion from atmospheres used to calculate partial pressures in chemical thermodynamics to pascals. When calculating the combined pressure of several products, the coefficient a in Eq. (5) should be replaced with the sum of the corresponding stoichiometric coefficients, and in the case of the total pressure P_t, with the coefficient ν.

An analysis of Eq. (5) permits the following two comments bearing on the comparison of the calculated and experimental values of α and E_a.

1. The value of the evaporation coefficient is determined not only by the differences in the equilibrium pressures P, but by those in the geometrical means of the molar masses $\overline{M}$ of gaseous products for the reactions being compared, i.e.

$$\alpha \equiv \frac{J_L}{J_{max}} = \frac{P_L}{P_{max}} \left[\frac{\overline{M}_{max}}{\overline{M}_L}\right]^{1/2} \quad (9)$$

   Here the subscripts L and 'max' indicate that the parameter in question relates to the case of evaporation from a free surface (after Langmuir) and from an effusion cell, respectively. The magnitude of this correction to the coefficient calculated from the P_L/P_{max} ratio does not exceed 20% in most of the cases considered below and will be disregarded subsequently.
2. In accordance with Eq. (5), the activation energy for dissociative evaporation of a compound can be written as

$$E_a = \Delta H_T^0/\nu \quad (10)$$

When deriving the value of E_a from the slope of the $\ln J = f(1/T)$ plot, one should bear in mind a slight decrease of the prefactor in Eq. (5) with temperature. This decrease results in a systematic underevaluation of the experimental value of E_a. As shown earlier [1], the magnitude of this underevaluation is $0.5R\overline{T}$, where $\overline{T}$ is the mean temperature for the interval of measurement. For $\overline{T} < 700$ K, this underevaluation does not exceed 3 kJ mol^{-1} and, bearing in mind much larger experimental errors, can be neglected.

3. Results and discussion

3.1. Decomposition of $AgNO_3$

The equilibrium path for the thermal decomposition of $AgNO_3$ corresponds to the following reaction [17]

$$AgNO_3(l) = Ag(s) + NO_2 + 0.5O_2 \quad (11)$$

Using the values of thermodynamic functions presented in Table 1 [18–20], we find 9.5×10^{-3} atm for the equilibrium partial pressure of NO_2 at 600 K.

The most comprehensive study of the $AgNO_3$ decomposition in vacuum is reported in our recent work [12]. We employed quadruple mass spectrometry in the evolved gas analysis of the products of thermal decomposition of $AgNO_3$. The dry residue of $AgNO_3$ deposited on a Ta platform in the form of a solution and containing 10 μg Ag was heated at a rate of 1 K s^{-1}. The gaseous products were studied with a multichannel quadruple mass analyzer. Fig. 1 presents background-corrected signals for all the ions measured, namely, NO^+, NO_2^+, O_2^+, Ag^+ and $AgNO_3^+$, in the 560–640 K range.

A quantitative analysis of the relative content of various ions in the gas phase, made with due inclusion of the molecule dissociation in the ionizer, showed [12] thermal decomposition of $AgNO_3$ to proceed in accordance with the reaction

$$AgNO_3(l) \rightarrow Ag(g) + NO_2 + 0.5O_2 \quad (12)$$

i.e. via gasification of all primary products of thermal decomposition, including metallic silver.

Taking into account the mass spectrometer calibration in units of pressure, the experimental data [12] show the NO_2 pressure at 600 K to be 2.3×10^{-8} atm. This value is in a fairly good agreement with a thermodynamic calculation of the equilibrium NO_2 pressure for reaction (12) yielding 3.7×10^{-9} atm. Thus the real evaporation coefficient turns out to be $\alpha \equiv 2.3 \times 10^{-8}/9.5 \times 10^{-3} = 2.4 \times 10^{-6}$, to be

Table 1
Thermodynamic functions used in the calculations

Species	T/K	State of aggregation	$_fH^0_T$/(kJ mol^{-1})	S^0_T/(J mol^{-1} K^{-1})	References
$AgNO_3$	600	l	−75.3±0.6	250.4	[18,19]
Ag	600	s	7.9	60.7	[18,19]
Ag	600	g	291.2±0.8	187.4	[18,19]
NO_2	600	g	59.9±0.5	269.0	[20]
O_2	600	g	17.6	226.3	[20]
$BaSO_4$	1500	s	−1236.9±2.5	369.5	[20]
BaO	1500	s	−469.8±5.0	159.2	[20]
BaO	1500	g	−72.7±8.5	293.4	[20]
SO_2	1500	g	−221.5±0.2	328.1	[20]
O_2	1500	g	49.3	258.0	[20]
O	1500	g	278.8±0.1	195.1	[20]
$BaCO_3$	1200	s	−1061.9±5.0	289.1	[20]
BaO	1200	s	−487.7±5.0	145.9	[20]
BaO	1200	g	−83.9±8.5	285.0	[20]
CO_2	1200	g	−339.3±0.1	279.3	[20]
BN	1800	s	−181.9±1.5	82.7	[20]
B	1800	s	37.3	44.9	[20]
B	1800	g	597.5±5.0	190.7	[20]
N_2	1800	g	57.6	248.2	[20]
Be_3N_2	1800	s	−377.2±1.3	241.8	[20]
Be	1800	g	357.2±5.0	173.5	[20]
N	1800	g	508.2±0.4	190.6	[20]
Mg_3N_2	1200	s	−330.1±2.0	246.0	[20]
Mg	1200	g	170.8±0.8	177.5	[20]
N_2	1200	g	36.8	234.1	[20]
N	1200	g	495.8±0.4	182.1	[20]
AlN	1700	s	−245.2±3.0	99.7	[20]
Al	1700	g	363.5±4.0	200.9	[20]
N_2	1700	g	54.1	246.2	[20]
N	1700	g	506.2±0.4	189.4	[20]
GaN	1300	s	−56.0±9.2	103.2	[18,19]
Ga	1300	g	302.4±4.0	206.3	[20]
N_2	1300	g	40.2	236.8	[20]
N	1300	g	497.8±0.4	183.8	[20]
ZnO	1400	s	−294.4±0.3	120.1	[18,19]
Zn	1400	g	153.4±0.2	193.0	[18,19]
O_2	1400	g	45.6	255.5	[20]
O	1400	g	276.7±0.1	193.7	[20]
CdS	1000	s	−119.4±4.2	134.9	[18,19]
Cd	1000	g	126.4±0.4	192.8	[18,19]
S_2	1000	g	162.5±0.3	270.7	[20]
S	1000	g	297.1±0.2	195.0	[20]
CdSe	1000	s	−102.7±2.1	151.5	[18,19]
Se_2	1000	g	171.9±8.4	296.4	[18,19]
Se	1000	g	242.6±11. 3	203.0	[18,19]
NH_4Cl	298	s	−314.4±2.0	95.9	[18]
NH_3	298	g	−45.9±0.4	192.7	[20]
HCl	298	g	−92.3±0.1	186.8	[20]
H	298	g	218.0	114.6	[20]
Cl	298	g	121.3±0.2	165.1	[20]
P(red)	600	s	−10.2±0.1	39.7	[18,19]
P_4	600	g	81.5±0.3	331.6	[20]
P_2	600	g	163.1±1.3	241.7	[20]

Table 1
(Continued)

Species	T/K	State of aggregation	${}_fH^0_T$/(kJ mol^{-1})	S^0_T/(J mol^{-1} K^{-1})	References
As	600	s	7.9	53.3	[19]
As_4	600	g	168.2±0.4	369.8	[19]
As_2	600	g	233.1±6.3	264.5	[19]
Sb	600	s	7.9	63.9	[19]
Sb_4	600	g	229.7±0.8	408.7	[19]
Sb_2	600	g	246.7±3.3	280.5	[19]

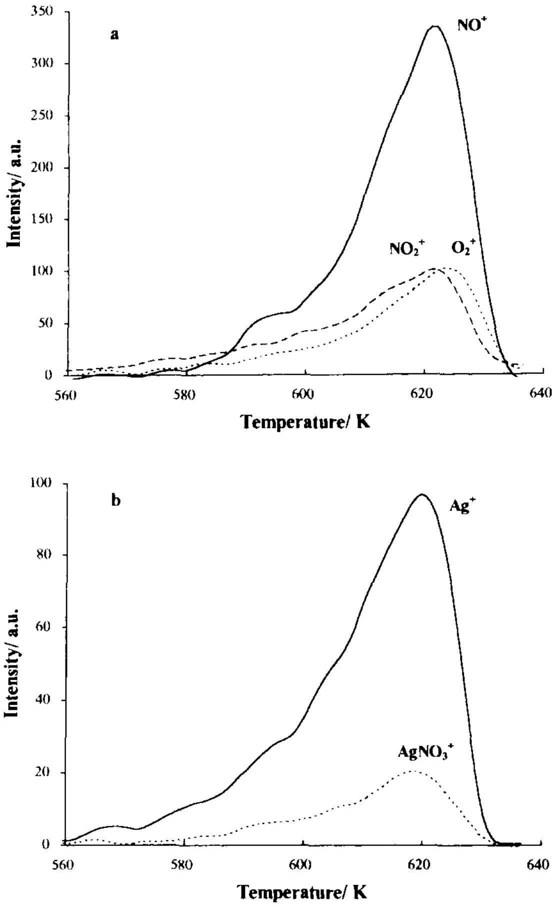

Fig. 1. Background-corrected mass spectral signals for 10 μg Ag as its nitrate salt heated on the Ta platform [12]: (a) volatile and (b) non-volatile species.

compared with the theoretical value $\alpha \equiv 3.7 \times 10^{-9}/9.5 \times 10^{-3} = 3.9 \times 10^{-7}$.

An additional argument for the correctness of this mechanism of thermal decomposition of $AgNO_3$ is a good agreement of the experimentally measured [12] activation (167 ± 3 kJ mol^{-1}) with the calculated energies (172 kJ mol^{-1}). We note for comparison that if the reaction followed the path (11), we would have $E_a = 99\,\text{kJ mol}^{-1}$. The value $E_a = 175 \pm 1\,\text{kJ mol}^{-1}$ obtained by Mu and Perlmutter [21] is also in a good agreement with the calculation. In the latter case, the kinetics of thermal decomposition was studied by thermogravimetry with 10–20 mg samples heated at a rate of 1 K min^{-1} in a flow of N_2. Since the analysis was made on a molten $AgNO_3$ sample, the area of the reaction practically coincided with that of the free sample surface, so that the decomposition should follow the Langmuir kinetics.

3.2. Decomposition of $BaSO_4$

The equilibrium pathway for the thermal decomposition of $BaSO_4$ corresponds to the reaction

$$BaSO_4(s) = BaO(s) + SO_2 + 0.5O_2 \qquad (13)$$

The SO_2 pressure calculated for 1500 K using the thermodynamic function of Table 1 is 2.9×10^{-5} atm.

The thermodynamics and kinetics of decomposition of $BaSO_4$ were experimentally studied by Mohazzabi and Searcy [22] using the torsion-effusion and torsion-Langmuir techniques. The values of the enthalpy and entropy found in [22] for reaction (13) yield 2.5×10^{-5} atm for the pressure of SO_2 at 1500 K, which practically coincides with our calculations.

The SO_2 pressure calculated for the case of evaporation, after Langmuir, turned out to be 5.3×10^{-7} atm, whence for the evaporation coefficient at 1500 K we obtain $\alpha \equiv 5.3 \times 10^{-7}/2.9 \times 10^{-5} = 1.8 \times 10^{-2}$. Assuming the decomposition of sulfates to proceed via gasification of all reaction products, as is the case with the nitrates, we can present the reaction of thermal decomposition in the following form:

$$BaSO_4(s) \rightarrow BaO(g) + SO_2 + 0.5O_2 \quad (14)$$

The values of the thermodynamic functions given in Table 1 yield 3.5×10^{-6} atm for the partial pressure of SO_2 at 1500 K, which is seven times the experimental results. If we also assume that the thermal decomposition of $BaSO_4$ involves oxygen evolution in the form of free atoms, i.e. by the reaction

$$BaSO_4(s) \rightarrow BaO(g) + SO_2 + O \quad (15)$$

we shall obtain 2.5×10^{-7} atm for the SO_2 partial pressure at 1500 K, with $\alpha \equiv 2.5 \times 10^{-7}/2.9\times 10^{-5} = 8.6 \times 10^{-3}$, which disagrees with experiment only within a factor two. The latter assumption appears reasonable if we recall that no molecular oxygen was found in thermal decomposition of the Cd and Pb nitrates as well [12].

The mean value $E_a = 384 \pm 8\,kJ\,mol^{-1}$ measured by Mohazzabi and Searcy [22] for $BaSO_4$ decomposition under the Langmuir conditions is somewhat lower than the value $E_a = 407\,kJ\,mol^{-1}$ calculated for reaction (15), while exceeding the $E_a = 358\,kJ\,mol^{-1}$ value for reaction (13).

3.3. Decomposition of $BaCO_3$

Equilibrium conditions of the thermal decomposition of $BaCO_3$ are realized in the reaction

$$BaCO_3(s) = BaO(s) + CO_2 \quad (16)$$

The values of the thermodynamic functions at 1200 K listed in Table 1 yield 7.7×10^{-4} atm for the equilibrium partial pressure of CO_2.

The equilibrium vapor pressure of $BaCO_3$ and the vacuum decomposition rates of the single crystal were measured by Basu and Searcy [23] by the same torsion-effusion and torsion-Langmuir techniques that had been used earlier in $BaSO_4$ experiments [22]. The values of the enthalpy and entropy found in [23] for the equilibrium reaction (16) yield 4.8×10^{-4} atm for the CO_2 pressure at 1200 K, which is in agreement with our calculations. In the case of Langmuir evaporation, the CO_2 pressure at 1200 K should be 9.2×10^{-8} atm, whence for the evaporation coefficient at 1200 K we obtain $\alpha \equiv 9.2 \times 10^{-8}/7.7\times 10^{-4} = 1.2 \times 10^{-4}$. Assuming, as before, that thermal decomposition of carbonates occurs through gasification of all reaction products, we can write the reaction of the thermal decomposition of $BaCO_3$ in the following form:

$$BaCO_3(s) \rightarrow BaO(g) + CO_2 \quad (17)$$

Using the values of the thermodynamic functions presented in Table 1, we find 1.9×10^{-7} atm for the partial pressure of CO_2 at 1200 K, whence the calculated evaporation coefficient at 1200 K is $\alpha \equiv 1.9 \times 10^{-7}/7.7 \times 10^{-4} = 2.5 \times 10^{-4}$. The agreement between the experimental and calculated values of α appears quite satisfactory, which argues for the decomposition mechanism described by reaction (17).

At the same time one should not overlook the fact that the experimental value $E_a = 226 \pm 7\,kJ\,mol^{-1}$ [23] differs substantially from the calculated one, $E_a = 314\,kJ\,mol^{-1}$. We attribute it to the enhanced diffusion limitations preventing escape of the decomposition products from the surface of the $BaCO_3$ crystal as the BaO layer grows in thickness, and to the associated decrease in the slope of the $\ln P = f(1/T)$ graph. This is also supported by the incredibly low value of the apparent change in the reaction entropy ($S^0_{1200} = 53.5\,J\,mol^{-1}\,K^{-1}$), which corresponds to this graph. This value is 2.5 times smaller than that for reaction (16), and one fifth the value of ΔS^0_{1200} for reaction (17). Incidentally, thermogravimetric measurements of Judd and Pope [24] yield 283 ± 17 kJ mol^{-1} for the activation energy of thermal decomposition of $BaCO_3$ in vacuum, which lies substantially closer to the calculated figure of 314 kJ mol^{-1}.

3.4. Decomposition of BN

The equilibrium path for the thermal decomposition of BN corresponds to the reaction

$$BN(s) = B(s) + 0.5N_2 \quad (18)$$

Using the values of thermodynamic functions listed in Table 1, we find for 1800 K an equilibrium N_2 partial pressure 8.3×10^{-6} atm.

Langmuir free-evaporation rates for solid BN were measured by Dreger et al. [25] with a microbalance built inside a vacuum system. The BN samples consisted of thin plates sawed from a compressed BN block. The pressure of N_2 was measured in the 1600–2000 K range. At 1800 K, $P \approx 2 \times 10^{-8}$ atm, whence for the real evaporation coefficient we obtain $\alpha \equiv 2 \times 10^{-8}/8.3 \times 10^{-6} = 2.4 \times 10^{-3}$.

Assuming, as earlier, that the thermal decomposition of nitrides occurs through gasification of all products, we can present the process of BN decomposition in the following form:

$$BN(s) \rightarrow B(g) + 0.5N_2 \qquad (19)$$

Based on the thermodynamic functions of Table 1, we find 3.5×10^{-8} atm for the partial pressure of N_2 at 1800 K, which is in agreement with the experimental value of 2×10^{-8} atm. The calculated evaporation coefficient at 1800 K, $\alpha \equiv 3.5 \times 10^{-8}/8.3 \times 10^{-6} = 4.2 \times 10^{-3}$, is in agreement with the real evaporation coefficient of 2.4×10^{-3}.

When comparing the activation energy (532 kJ mol^{-1}) calculated for reaction (19) with experiment, one should bear in mind that the BN sample became coated in the course of decomposition by a boron layer which, according to Dreger et al. [25], impeded its further decomposition. As a result, the slope of the experimental relation

$$\log P_{N_2} = f(1/T)$$

just as in the case of $BaCO_3$, turned out to be substantially underevaluated. The value of E_a corresponding to this slope is only 448 ± 11 kJ mol^{-1}, which is considerably lower than that for the equilibrium reaction (18), namely 489 kJ mol^{-1}.

3.5. Decomposition of Be_3N_2

The equilibrium path for the decomposition of Be_3N_2 corresponds to the reaction

$$Be_3N_2(s) = 3Be(g) + N_2 \qquad (20)$$

Using the values of the thermodynamic functions in Table 1, we find 3.9×10^{-5} atm for the equilibrium pressure N_2 at 1800 K.

The equilibrium pressure of nitrogen evolving in the decomposition of Be_3N_2 was measured by Hoenig and Searcy [26] using the Knudsen technique, and the kinetics of the process, using the Langmuir method. In both cases, a vacuum automatic recording balance was employed. When using a Knudsen cell with an orifice of ϕ 0.91 mm, the partial pressure of nitrogen at 1800 K was found to be $\approx 3 \times 10^{-5}$ atm, which is in a good agreement with our calculations.

The measurements by Langmuir method were carried out with Be_3N_2 pellets formed by hot pressing. The pressed specimens had ~ 82% of the theoretical density. At 1800 K, the equivalent equilibrium pressure of N_2 was found to be 1.5×10^{-7} atm, which corresponds to $\alpha \equiv 1.5 \times 10^{-7}/3.9 \times 10^{-5} = 3.9 \times 10^{-3}$. To fit the calculated values of P_{N_2} and α to the experiment, we have to assume that thermal decomposition of Be_3N_2 proceeds with evolution of 70% of nitrogen in the form of free atoms, i.e. by the reaction

$$Be_3N_2(s) \rightarrow 3Be(g) + 1.4N + 0.3N_2 \qquad (21)$$

Under this assumption, the calculated total pressure of atomic and molecular nitrogen (2.3×10^{-7} atm) and the calculated evaporation coefficient ($\alpha \equiv 2.3 \times 10^{-7}/3.9 \times 10^{-5} = 5.9 \times 10^{-3}$) are in a good agreement with the experiment.

The activation energy found from the

$$\log P_{N_2} = f(1/T)$$

relation [26] is 428 ± 7 kJ mol^{-1}, which is in a fairly good agreement with the calculated value $E_a = 456$ kJ mol^{-1} for reaction (21), while exceeding by far the value $E_a = 370$ kJ mol^{-1} calculated for reaction (20).

3.6. Decomposition of Mg_3N_2

The equilibrium path for the thermal decomposition of Mg_3N_2 corresponds to the reaction

$$Mg_3N_2(s) = 3Mg(g) + N_2 \qquad (22)$$

Using the values of thermodynamic functions listed in Table 1, we find for the total pressure of all gaseous products of reaction (22) at 1200 K, the value of 3.0×10^{-3} atm.

The torsion-Langmuir study of Mg_3N_2 decomposition was made by Blank and Searcy [27] with Mg_3N_2 pellets pressed in a stainless steel die of ϕ 6.35 mm at 7 tons of total load. At 1200 K, the total pressure P_t was found to be 1.3×10^{-6} atm, which corresponds to $\alpha \equiv 1.3 \times 10^{-6}/3.0 \times 10^{-3} = 4.3 \times 10^{-4}$. Assuming the thermal decomposition of Mg_3N_2 to occur with evolution of 50% of nitrogen in atomic form, i.e. in accordance with the reaction

$$Mg_3N_2(s) \rightarrow 3Mg(g) + N + 0.5N_2 \qquad (23)$$

we shall obtain 1.1×10^{-6} atm for the value of P_t at 1200 K. The resultant calculated evaporation coefficient $\alpha \equiv 1.1 \times 10^{-6}/3.0 \times 10^{-3} = 3.7 \times 10^{-4}$ is in a good agreement with the experiment.

The activation energy derived from the

$$\log P_t = f(1/T)$$

relation in [27] is 238 kJ mol^{-1}, which is substantially lower than the value 297 kJ mol^{-1} calculated for reaction (23), while being somewhat higher than that for reaction (22), namely 215 kJ mol^{-1}.

3.7. Decomposition of AlN

The equilibrium path for the thermal decomposition of AlN corresponds to the reaction

$$AlN(s) = Al(g) + 0.5N_2 \qquad (24)$$

Using the values of thermodynamic functions listed in Table 1, we find for the decomposition temperature at 1700 K a total equilibrium pressure is 1.2×10^{-5} atm.

Langmuir free-evaporation rates for solid AlN over the 1590–1870 K range were measured by Dreger et al. [25] with a microbalance built inside a vacuum system. The AlN sample was a pellet of pure compressed powder. The total pressure of gaseous products at 1700 K was found to be 3.8×10^{-8} atm. For the corresponding evaporation coefficient we find $\alpha \equiv 3.8 \times 10^{-8}/1.2 \times 10^{-5} = 3.2 \times 10^{-3}$. We can obtain similar values of P_t and α by assuming that AlN decomposition involves evolution of 60% of nitrogen in the form of free atoms, i.e. by the reaction

$$AlN(s) \rightarrow Al(g) + 0.6N + 0.2N_2 \qquad (25)$$

Under these conditions, the total pressure P_t of gaseous products calculated at 1700 K is 2.0×10^{-8} atm, yielding for the evaporation coefficient $\alpha \equiv 2.0 \times 10^{-8}/1.2 \times 10^{-5} = 1.7 \times 10^{-3}$.

The activation energy derived from the relation $\log P_t = f(1/T)$ given in [25] is 542 ± 8 kJ mol^{-1}, which is in a good agreement with the calculated value of 506 kJ mol^{-1} for reaction (25), while exceeding by far the value $E_a = 417$ kJ mol^{-1} for reaction (24).

3.8. Decomposition of GaN

The equilibrium path for the thermal decomposition of GaN corresponds to the reaction

$$GaN(s) = Ga(g) + 0.5N_2 \qquad (26)$$

Using the values of thermodynamic functions listed in Table 1, we find for the total pressure of gaseous products P_t at 1300 K, the value of 6.6×10^{-3} atm.

The torsion-Langmuir study of GaN decomposition was made by Munir and Searcy [28] with GaN wafers prepared at room temperature in the ultrahigh-pressure apparatus. Microscopic examination [28] at 200 magnification showed no pores at the surface of wafers. At 1300 K, the total pressure was found to be 1.9×10^{-6} atm, so that $\alpha \equiv 1.9 \times 10^{-6}/6.6 \times 10^{-3} = 2.8 \times 10^{-4}$. Similar values of P_t and α can be calculated by assuming that the GaN decomposition occurs with evolution of 40% of nitrogen in the form of free atoms, i.e. by the reaction

$$GaN(s) \rightarrow Ga(g) + 0.4N + 0.3N_2 \qquad (27)$$

In this case, the calculated total pressure will be 3.7×10^{-6} atm, yielding $\alpha \equiv 3.7 \times 10^{-6}/6.6 \times 10^{-3} = 5.6 \times 10^{-4}$.

The activation energy corresponding to the decomposition of GaN is 305 kJ mol^{-1} [28]. The calculated values of E_a for reactions (26) and (27) are, respectively, 248 and 330 kJ mol^{-1}.

3.9. Decomposition of ZnO

The equilibrium path for the thermal decomposition of ZnO corresponds to the reaction

$$ZnO(s) = Zn(g) + 0.5O_2 \qquad (28)$$

Using the values of thermodynamic functions listed in Table 1, we find for the total pressure of gaseous products P_t at 1400 K, the value of 3.6×10^{-5} atm.

The kinetics of thermal decomposition of ZnO (after Langmuir) was studied by Hoenig [29] by the technique used with Be_3N_2 [26]. At 1400 K, the total pressure of gaseous products for decomposition of ZnO crystals is 6.0×10^{-7} atm [16,29], which yields for the evaporation coefficient $\alpha \equiv 6.0 \times 10^{-7}/3.6 \times10^{-5} = 1.7 \times 10^{-2}$.

Assuming, just as we did for $BaSO_4$, that oxygen evolves in the decomposition of ZnO in the form of free atoms, i.e. by the reaction

$$ZnO(s) \rightarrow Zn(g) + O \qquad (29)$$

we obtain for the total pressure of gaseous products at 1400 K the value 5.6×10^{-7} atm and for the calculated evaporation coefficient $\alpha \equiv 5.6 \times 10^{-7}/3.6\times 10^{-5} = 1.6 \times 10^{-2}$, which practically coincides with the experiment.

The activation energy derived from the data of [16] is 368 kJ mol^{-1}, and that found from [30], 375 ± 8 kJ mol^{-1}, which is in a good agreement with the value $E_a = 356$ kJ mol^{-1} calculated for reaction (29), while markedly exceeding the value $E_a = 308$ kJ mol^{-1} calculated for reaction (28).

Another significant argument for reaction (29) is the absence of any effect of adding up to 10^{-6} atm O_2 to the reaction system on the ZnO decomposition kinetics [31]. If oxygen evolves as O_2 molecules, the presence of an excess of O_2 in the system (which exceeded by an order of magnitude the equivalent equilibrium pressure of the decomposition products at 1380 K) should have reduced the rate of ZnO decomposition. A similar effect was clearly observed, in particular, in the case of CdS decomposition in the presence of S_2 vapor [14].

3.10. Decomposition of CdS

The equilibrium path for the thermal decomposition of CdS corresponds to the reaction

$$CdS(s) = Cd(g) + 0.5S_2 \qquad (30)$$

Using the values of thermodynamic functions listed in Table 1, we find for the total pressure of gaseous products P_t at 1000 K, the value of 4.2×10^{-5} atm.

The kinetics of thermal decomposition of single-crystal CdS was studied [31,32] by the torsion-Langmuir technique in both cases. At 1000 K, the total pressure of gaseous products for (0001) basal face-oriented crystals was found to be $\sim 3 \times 10^{-6}$ [32] and 6×10^{-6} [31] atm. For the mean value $P_t = 4.5 \times 10^{-6}$ atm, we obtain the evaporation coefficient $\alpha \equiv 4.5 \times 10^{-6}/4.2 \times 10^{-5} = 0.11$. Similar values of P_t and α can be calculated, if we assume that the decomposition of CdS occurs with evolution of 30% of sulfur in the form of free atoms, i.e. by the reaction

$$CdS(s) \rightarrow Cd(g) + 0.3S + 0.35S_2 \qquad (31)$$

The calculated values of P_t and α will now be 4.9×10^{-5} atm and 0.12, respectively.

The activation energy of CdS decomposition under the free-evaporation conditions was found to be 238 ± 6 [31] and 247 ± 2 kJ mol^{-1} [32], which is in a good agreement with the value $E_a = 234$ kJ mol^{-1} calculated for reaction (31), while exceeding the value $E_a = 214$ kJ mol^{-1} obtained for reaction (30).

As shown by measurements of Somorjai and Jepsen [33], introduction of sulfur vapor into the reaction system in the form of S_2 molecules resulted in a change of the CdS decomposition rate in proportion to $P_{S_2}^{-1/2}$. A decrease in the rate of decomposition, while less noticeable, was also observed when Cd vapor was admitted to the system. These results are in agreement with the conclusions of L'vov et al. [2–6] concerning the effect of excess vapor of one of the gaseous products on the decomposition rate and the existence of two kinetically different evaporation modes, equimolar and isobaric. Regrettably, the accuracy with which the CdS decomposition rate was measured as a function of S_2 vapor content is not high enough to permit revealing the comparatively small difference between the relative contents of S_2 molecules (100 or 70%) in the decomposition products of reactions (30) and (31).

3.11. Decomposition of CdSe

The equilibrium path for the thermal decomposition of CdSe corresponds to the reaction

$$CdSe(s) = Cd(g) + 0.5Se_2 \qquad (32)$$

Using the values of thermodynamic functions listed in Table 1, we find for the total pressure of gaseous products at 1000 K, the value of 8.0×10^{-5} atm.

The kinetic parameters characterizing thermal decomposition of single-crystal CdSe are given in the review by Searcy [16]. The total pressure of gaseous products at 1000 K is 8.1×10^{-6} atm and the evaporation coefficient $\alpha \equiv 8.1 \times 10^{-6}/8.0\times 10^{-5} = 0.10$. Similar values for P_t and α can be obtained if we assume CdSe to decompose with evolution of 70% of Se in the form of free atoms, i.e. by the reaction

$$CdSe(s) \rightarrow Cd(g) + 0.7Se + 0.15Se_2 \quad (33)$$

Using the values of the thermodynamic functions listed in Table 1, we come to $P_t = 6.8 \times 10^{-6}$atm and $\alpha = 0.085$.

According to Searcy [16], the activation energy for decomposition of CdSe is 234 kJ mol^{-1}, which is in a good agreement with the calculated value $E_a = 226$ kJ mol^{-1} for reaction (33), and is considerably in excess of $E_a = 206$ kJ mol^{-1} for reaction (32).

3.12. Decomposition of NH_4Cl

Equilibrium decomposition of NH_4Cl should proceed by the reaction

$$NH_4Cl(s) = NH_3(g) + HCl(g) \quad (34)$$

Using the values of thermodynamic functions [20,34] listed in Table 1, we find at 600 K an equilibrium pressure $P_t = 5.2 \times 10^{-2}$ atm.

The kinetic characteristics of the thermal decomposition of NH_4Cl studied in [34,35] (apparent enthalpy and entropy of activation) are given in a review paper of Searcy [16]. Using these characteristics, we find at 600 K the experimental values $P_t = 6.6 \times 10^{-5}$atm and $\alpha \equiv 6.6 \times 10^{-5}/5.2 \times 10^{-2} = 1.3 \times 10^{-3}$. Similar values for P_t and α can be obtained if we assume that the decomposition of NH_4Cl under free-surface evaporation is accompanied by evolution of 22% HCl in the form of free H and Cl atoms, i.e. by the reaction

$$NH_4Cl(s) \rightarrow NH_3(g) + 0.22(H + Cl) + 0.78HCl(g) \quad (35)$$

Here we shall have $P_t = 7.2 \times 10^{-5}$atm and $\alpha \equiv 7.2 \times 10^{-5}/5.2 \times 10^{-2} = 1.4 \times 10^{-3}$.

At the same time, the temperature dependence of the rate of decomposition proceeding by reaction (35) turns out to differ substantially from the one obtained experimentally. Calculation yields 130 kJ mol^{-1} for the value of E_a for reaction (35), whereas measurements give only 56 kJ mol^{-1} which is lower by far than ever the value E_a=95 kJ mol^{-1} calculated for reaction (34).

We believe that this could be due to an increase in the fraction of dissociated HCl with increasing temperature. If we assume that at 700 K this fraction increases to 31%, i.e.

$$NH_4Cl(s) \rightarrow NH_3(g) + 0.31(H + Cl) + 0.69HCl(g) \quad (36)$$

then the values $P_t = 3.6 \times 10^{-4}$atm and $\alpha = 4.6 \times 10^{-4}$ calculated for 700 K would agree well with the experimental values $P_t = 3.3 \times 10^{-4}$atm and $\alpha = 4.2 \times 10^{-4}$.

The activation energy corresponding to the aforementioned case of NH_4Cl decomposition, with the fraction of dissociated HCl increasing with increasing temperature, can be calculated from the obvious expression

$$E_a = \frac{R\ln(P_2/P_1)}{T_1^{-1} - T_2^{-1}} \quad (37)$$

Substituting the values of P_t thus found at 600 and 700 K, we obtain $E_a = 56$ kJ mol^{-1}, in complete agreement with the experimental value. To facilitate comparison, Table 2 lists the final results of our analysis.

3.13. Sublimation of P (red), As and Sb

Equilibrium sublimation of red phosphorus, arsenic and antimony should proceed by the following reactions

$$4P(s) = P_4(g) \quad (38)$$

$$4As(s) = As_4(g) \quad (39)$$

$$4Sb(s) = Sb_4(g) \quad (40)$$

Table 2
The evaporation coefficient for NH_4Cl decomposition in vacuum [a]

Equilibrium reaction	Implied reaction	$\bar{T}$/K	$\bar{\alpha}$	
			Calculation	Experiment
$NH_4Cl(s) = NH_3 + HCl$	$NH_4Cl(s) \rightarrow NH_3 + 0.22(H + Cl) + 0.78HCl$	600	1.4×10^{-3}	1.3×10^{-3} [16]
$NH_4Cl(s) = NH_3 + HCl$	$NH_4Cl(s) \rightarrow NH_3 + 0.31(H + Cl) + 0.69HCl$	700	4.6×10^{-4}	4.2×10^{-4} [16]

[a] Calculated and experimental [16] activation energies are equal in value (56 kJ mol^{-1}).

Table 3
The evaporation coefficient and activation energy for P (red), As and Sb sublimation in vacuum

Equilibrium reaction	Implied reaction	$\bar{T}$/K	$\bar{\alpha}$		E_a/(kJ mol^{-1})	
			Calculation	Experiment	Calculation	Experiment
$4P(s) = P_4(g)$	$2P(s) \rightarrow P_2(g)$	600	1×10^{-6}	1×10^{-6} [36]	184	218 [36]
$4As(s) = As_4(g)$	$6As(s) \rightarrow As_2(g) + As_4(g)$	550	3×10^{-4}	5×10^{-4} [37] 5×10^{-5} [38]	177	180 [37] 183 [38]
$4Sb(s) = Sb_4(g)$	$6Sb(s) \rightarrow Sb_2(g) + Sb_4(g)$	650	1×10^{-1}	2×10^{-1} [38]	214	207 [38]

The equilibrium vapor pressures found for the mean sublimation temperatures of these elements, with due account of the thermodynamic functions given in Table 1, are 2.9×10^{-2} atm at 600 K for phosphorus, 1.5×10^{-5} atm at 550 K for arsenic, and 1.2×10^{-8} atm at 650 K for antimony.

The sublimation kinetics of red phosphorus was studied in [36,37], arsenic in [37,38] and antimony in [38]. Single-crystal evaporation at Langmuir conditions was used in all cases. The sublimation rates for all elements were found to be substantially lower than those expected for equilibrium conditions, yielding for the evaporation coefficients [16]$\approx 10^{-6}$ for P at 600 K, 5×10^{-4} [37] and 5×10^{-5} [16] for As at 550 K, and 2×10^{-1} for Sb at 650 K. To obtain similar values for α, we would have to assume that sublimation of these elements occurs by the following reactions

$$2P(s) \rightarrow P_2(g) \tag{41}$$

$$6As(s) \rightarrow As_2(g) + As_4(g) \tag{42}$$

$$6Sb(s) \rightarrow Sb_2(g) + Sb_4(g) \tag{43}$$

The values of P_t for these reactions calculated using the data of Table 4 are 3.5×10^{-8} atm for P at 600 K, 5.1×10^{-9} atm for As at 550 K, and 1.1×10^{-9} atm for Sb at 650 K. Note that the calculated values of α, namely, 1.2×10^{-6} for P, 3.4×10^{-4} for As and 9.2×10^{-2} for Sb turn out to be fairly close to the experimental data.

The activation energies for reactions (41)–(43), respectively, are 184, 177 and 214 kJ mol^{-1}. They are quite close to the experimental values of E_a: 218 kJ mol^{-1} [36] for P, 180 ± 13 kJ mol^{-1} [37] and 183±6 kJ mol^{-1} [16,38] for As, and 207 ± 9 kJ mol^{-1} [16,38] for Sb. We note for comparison, that the activation energies for reactions (38)–(40), namely, 122 kJ mol^{-1} for P, 137 kJ mol^{-1} for As, and 198 kJ mol^{-1} for Sb, lie considerably below the experimental values.

For convenience, the main results of the present analysis are summed up in Table 3.

4. Conclusions

To facilitate an overall analysis of the results, Table 4 presents the experimental and calculated values of the evaporation coefficients and activation energies for all the aforementioned cases of thermal decomposition, with the exception of NH_4Cl. Their analysis, combined with the results listed in Tables 2 and 3, permits the following conclusions.

1. The calculation of the activation energies in all cases, except for the thermal decomposition of NH_4Cl, was made under an implicit assumption that the fraction of the dissociated product remains constant under variation of temperature. In order to explain the anomalously low value of E_a in the NH_4Cl case, however, we have to assume that the fraction of dissociated HCl molecules increases with increasing temperature. This contradiction requires a further analysis.
2. The error in the calculation of the activation energies, as can be deduced from the data in Table 1, did not exceed 2 kJ mol^{-1} for $AgNO_3$, Mg_3N_2, ZnO and CdO and 5 kJ mol^{-1} for all other substances. The error of the experimental determination of the E_a values averages ~ 10 kJ mol^{-1}.
3. Taking into account these uncertainties, the calculated values of activation energies E_a for the assumed reactions (in the range between 172 and 532 kJ mol^{-1}) agree quite well, on the whole, with their experimental values. The noticeable discrepancy in the cases of $BaCO_3$, $BaSO_4$ and

BN can be accounted for by an underevaluation of the experimental values of E_a, which originates from a decrease of the evaporation area in the course of measurements as a result of BaO(g) and B(g) condensing on the sample surface. The discrepancy between the calculated and experimental E_a values for Mg_3N_2 can be explained, as in the NH_4Cl case, by the change of the composition of dissociated products with temperature. If we assume that at 1 800 K nitrogen evolves, as in the case of Be_3N_2, in the form of $1.4N + 0.3N_2$, the calculated E_a value decreases up to 238 kJ mol^{-1}.

4. The approach proposed here has turned out to be adequate as a whole for the interpretation of the low values of α (10^{-7} to 10^{-1}) in all the cases considered, including the situations where the choice of decomposition paths was fairly limited by possible variations in the composition of the products ($BaCO_3$, $BaSO_4$, BN and ZnO), or was predetermined by direct observations of primary decomposition products ($AgNO_3$). Taking into account that the choice of the proposed mechanisms of decomposition or sublimation was based on the values of α, the agreement between the calculations and experiment with respect to the activation energy provides a weighty argument for the validity of these mechanisms.
5. The interpretation of the evaporation coefficients and of the decomposition and sublimation mechanisms made here is not more than tentative and, as such, requires checking and refinement, preferably by invoking direct methods of measurement of the decomposition products, as this was done with $AgNO_3$. We would like to hope that the proposed approach will find continuation and development in studies of other workers.

Table 4
The evaporation coefficient at the mean temperature and activation energy for some decomposition reactions in vacuo

Reactant	Products		$\bar{T}$/K	$\bar{\alpha}$		E_a/(kJ mol^{-1})	
	Equilibrium reaction	Implied reaction		Calculation	Experiment	Calculation [a]	Experiment
$AgNO_3$	$Ag(s) + NO_2 + 0.5O_2$	$Ag(g) + NO_2 + 0.5O_2$	600	3.9×10^{-7}	2.4×10^{-6} [12]	172	167 [12] 175 [21]
$BaSO_4(s)$	$BaO(s) + SO_2 + 0.5O_2$	$BaO(g) + SO_2 + O$	1500	8.6×10^{-3}	1.8×10^{-2} [22]	407	384 [22]
$BaCO_3(s)$	$BaO(s) + CO_2$	$BaO(g) + CO_2$	1200	2.5×10^{-4}	1.2×10^{-4} [23]	314	226 [23] 283 [24]
BN(s)	$B(s) + 0.5N_2$	$B(g) + 0.5N_2$	1800	4.2×10^{-3}	2.4×10^{-3} [25]	532	448 [25]
$Be_3N_2(s)$	$3Be(g) + N_2$	$3Be(g) + 1.4N + 0.3N_2$	1800	3.9×10^{-3}	5.9×10^{-3} [26]	456	428 [26]
$Mg_3N_2(s)$	$3Mg(g) + N_2$	$3Mg(g) + N + 0.5N_2$	1200	3.7×10^{-4}	4.3×10^{-4} [27]	297	238 [27]
AlN(s)	$Al(g) + 0.5N_2$	$Al(g) + 0.6N + 0.2N_2$	1700	1.7×10^{-3}	3.2×10^{-3} [25]	506	542 [25]
GaN(s)	$Ga(g) + 0.5N_2$	$Ga(g) + 0.4N + 0.3N_2$	1300	5.6×10^{-4}	2.8×10^{-4} [28]	330	305 [28]
ZnO(s)	$Zn(g) + 0.5O_2$	$Zn(g) + O$	1400	1.6×10^{-2}	1.7×10^{-2} [16]	356	368 [16]375 [30]
CdS(s)	$Cd(g) + 0.4S_2$	$Cd(g) + 0.3S + 0.35S_2$	1000	1.2×10^{-1}	1.1×10^{-1} [31,32]	234	238 [31] 274 [32]
CdSe(s)	$Cd(g) + 0.5Se_2$	$Cd(g) + 0.7Se + 0.15Se_2$	1000	8.5×10^{-2}	1.0×10^{-1} [16]	226	234 [16]

[a] Corrected for 0.5 *RT* value (see Section 2).

Acknowledgements

We are grateful to Dr. L.K. Polzik (The St.Petersburg State Technical University) and to Dr. A. Galwey (The Queen's University of Belfast) for helpful suggestions made in the process of the manuscript preparation. This work was supported in part by BSW Perkin–Elmer.

References

[1] B.V. L'vov, P.A. Bayunov and G.N. Ryabchuk, Spectrochim. Acta Part B, 36 (1981) 397.

[2] B.V. L'vov and G.N. Ryabchuk, Zh. Anal. Khim., 36 (1981) 2085.

[3] B.V. L'vov and G.H.A. Fernandes, Zh. Anal. Khim., 39 (1984) 221.

[4] B.V. L'vov, G.N. Ryabchuk and G.H.A. Fernandes, Zh. Anal. Khim., 39 (1984) 1206.

[5] B.V. L'vov, G.N. Ryabchuk and G.H.A. Fernandes, Zh. Anal. Khim., 40 (1985) 792.

[6] B.V. L'vov, Spectrochim. Acta Part B, 52 (1997) 201.

[7] B.V. L'vov, Izv. Vuzov. Chern. Metallurgiya, 1 (1986) 4.

[8] B.V. L'vov and A.V. Ilyukhin, Izv. Vuzov. Chern. Metallurgiya, 9 (1988) 10.

[9] B.V. L'vov, Spectrochim. Acta Part B, 44 (1989) 1257.

[10] B.V. L'vov, Zh. Analit. Khim., 45 (1990) 2144.

[11] B.V. L'vov, Mikrochim. Acta (Wien), 2 (1991) 299.

[12] B.V. L'vov and A.V. Novichikhin, Spectrochim. Acta Part B, 50 (1995) 1427.

[13] B.V. L'vov and A.V. Novichikhin, Spectrochim. Acta Part B, 50 (1995) 1459.

[14] G.A. Somorjai and J.E. Lester, Progress in Solid State Chemistry, 4 (1967) 1.

[15] J.P. Hirth and G.M. Pound, Condensation and Growth Kinetics, Pergamon, Oxford (1963).

[16] A.W. Searcy, Chemical and Mechanical Behavior of Inorganic Materials, Wiley, New York (1970) Chap. 4 and 6.

[17] K.H. Stern, J. Phys. Chem. Ref. Data, 1 (1972) 751.

[18] V.P. Glushko (ed.), Thermodynamic Constants of Substances, Akad. Nauk SSSR, Moscow (1962–1982). Handbook in 10 volumes (in Russian).

[19] V.A. Kireev, Methods of Calculations in Thermodynamics of Chemical Reactions, Khimiya, Moscow, 1975 (in Russian).

[20] L.V. Gurvich, I.V. Veits, V.A. Medvedev et al., Thermodynamic Properties of Individual Substances, Nauka, Moscow, 1978–1982 (in Russian).

[21] J. Mu and D.D. Perlmutter, Thermochim. Acta, 56 (1982) 253.

[22] P. Mohazzabi and A.W. Searcy, J. Chem. Soc. Faraday Trans. I, 72 (1976) 290.

[23] T.K. Basu and A.W. Searcy, J. Chem. Soc. Faraday Trans. I, 72 (1976) 1889.

[24] M.D. Judd and M.J. Pope, J. Therm. Anal., 4 (1972) 31.

[25] L. Dreger, V.V. Dadape and J.L. Margrave, J. Phys. Chem., 66 (1962) 1556.

[26] C.L. Hoenig and A.W. Searcy, J. Amer. Ceram. Soc., 50 (1967) 460.

[27] B.A.H. Blank and A.W. Searcy, J. Phys. Chem., 72 (1968) 2241.

[28] Z.A. Munir and A.W. Searcy, J. Chem. Phys., 42 (1965) 4223.

[29] C.L. Hoenig, Ph. D. Thesis, University of California (1964).

[30] R.J. Galluzzo and A.W. Searcy, High Temp. Sci., 3 (1971) 491.

[31] R.B. Leonard and A.W. Searcy, J. Appl. Phys., 42 (1971) 4047.

[32] Z.A. Munir, High Temp. Sci., 2 (1970) 58.

[33] G.A. Somorjai and D.W. Jepsen, J. Chem. Phys., 41 (1964) 1389.

[34] R.D. Schultz and A.O. Dekker, J. Phys. Chem., 60 (1956) 1095.

[35] R.F. Chaiken, D.J. Sibett, J.E. Sutherland, D.K. Van de Mark and A. Wheeler, J. Chem. Phys., 37 (1962) 2311.

[36] J.S. Kane, Ph. D. Thesis, University of California, Berkeley (1955).

[37] L. Brewer and J.S. Kane, J. Phys. Chem., 59 (1995) 105.

[38] G.M. Rosenblatt, P. Lee and M.B. Dowell, J. Chem. Phys., 45 (1966) 3454.