

Electron Ionization Cross-Sections of Polyatomic Oxide Molecules Determined by High-Temperature Mass Spectrometry

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Abstract—The ionization cross-sections of B₂O₃, NaBO₂, NaPO₃, and KPO₃ were determined by high-temperature mass spectrometry. It is shown that the use of the additivity rule for calculating the ionization cross-sections leads to underestimated partial pressures of the molecular forms of vapor above the objects being studied, even when appropriate correction factors are introduced.

Keywords: high-temperature mass spectrometry, vaporization, partial pressures, ionization cross-section

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The study of processes at high temperatures is of key importance in materials science, physical chemistry, and related fields of knowledge, since evaporation and thermal dissociation, accompanied by the formation of various gaseous products, occur under these conditions. An accurate description of such processes is impossible without reliable data on the qualitative and quantitative composition of vapor. High-temperature mass spectrometry, which is a combination of the classical Knudsen effusion method with mass spectrometric analysis of the vapor phase [1–4], has a number of advantages compared with other methods, since it allows high degree of reliability in determining both the qualitative and quantitative composition of vapor. The partial pressures of the molecular forms of vapor over the systems under study are usually determined by two methods: complete isothermal evaporation and comparison of ion currents. In this case, the pressure in the Knudsen cell is correlated with the measured ion current using the equation

$$p_i = kIT/\sigma_i. \quad (1)$$

Here and below, p is the vapor pressure, I is the intensity of ion current, T is the temperature, and σ is the ionization cross-section.

The complete isothermal evaporation method is based on the isothermal evaporation of a sample of a known mass for a certain period of time with simultaneous recording of the mass spectrum of ions. The sample evaporates completely, or the proportion of the vaporized substance is determined from the difference in the weight of the cell with the sample before and after the experiment. To determine the partial pressure

of the molecular forms of vapor, the Hertz–Knudsen equation is used:

$$p_i \text{ (Pa)} = 2285q\sqrt{T}/M_i s_{\text{eff}}^{-1} \left[\int_{\tau=0}^{\tau} \frac{I(\tau)d\tau}{I(\tau)^{-1}} \right]. \quad (2)$$

Here, q is the mass of the vaporized substance, M is the molecular weight, s_{eff} is the effective area of the effusion hole of the effusion chamber, and τ is the vaporization time.

The method of comparing the ion currents is based on the constancy of the geometrical and other physical characteristics of a device within the framework of the same experiment when two ion currents are measured in sequence, one of which refers to the standard with the known vapor pressure and the other, to the substance under study; the partial pressures of the molecular forms of vapor are determined by the equation

$$p_i = \frac{p_{\text{st}} I_i T_i \sigma_{\text{st}} \gamma a_{\text{st}}}{I_{\text{st}} T_{\text{st}} \sigma_i \gamma_i a_i}. \quad (3)$$

Here, γ is the conversion coefficient of the secondary electron multiplier, and a is the isotopic distribution coefficient. The indices i and st refer to the compound under study and the standard, respectively.

The transverse ionization section σ of atoms is usually taken from [5]; for molecules with a more complex composition, it is usually determined by the “additivity rule” (the sum of the transverse ionization sections of atoms). In the series element–monoxide–dioxide, the ionization cross-section increases. In some cases, correction factors are used [6, 7]. In their fundamental paper, Drowart et al. [8] showed that the additivity rule does not give correct results in most cases. The

review gives the experimental ionization cross-sections for both atoms and molecules. The information is presented in the form of $\sigma(A)/\sigma(B)$ ratios. It is noteworthy that the ionization cross-sections of atoms, their monoxides, and dioxides are arranged in the reverse order. In particular, it was experimentally established that $\sigma(M_2)/\sigma(M) = 1.25$, $\sigma(MO)/\sigma(M) = 0.65$, and $\sigma(MO_2)/\sigma(MO) = 0.5$. The obtained data, summarized in [8], refer only to a limited range of compounds; hence, for the overwhelming majority of polyatomic compounds there are no experimental values that can be used to determine the partial pressures by comparing the ion currents.

The complete isothermal evaporation method, in which the values of cross-sections are not used, is applicable, unfortunately, only to the case of the monomolecular composition of vapor. In those cases when the vapor contains two or more species, knowledge of the mass of the substance that vaporized in a certain form is required. This, in turn, is also associated with the use of ionization cross-sections. In the case of the monomolecular composition of the vapor above the compound, the relative value of $\sigma(A)/\sigma(B)$ can be obtained by the equation

$$\frac{\sigma_{st}}{\sigma_i} = \frac{q_i \sqrt{T_i/M_i} \gamma_i a_i I_{st} T_{st} \tau_{st}}{q_{st} \sqrt{T_{st}/M_{st}} \gamma_{st} a_{st} I_i T_i \tau_i} \quad (4)$$

by jointly solving Eqs. (2) and (3).

In the present work, this procedure was performed for polyatomic molecules B_2O_3 , $NaBO_2$, $NaPO_3$, and KPO_3 , which pass into vapor congruently without dissociation [9, 10]. The reagents B_2O_3 , $NaBO_2$, $NaPO_3$, and KPO_3 with at least 99.9% purity were used as the starting reagents.

The study was carried out by Knudsen effusion mass spectrometry on an MS-1301 mass spectrometer. The samples were evaporated from a molybdenum effusion chamber heated by electron bombardment. The temperature of the chamber with the sample was measured using an EOP-66 optical pyrometer with an accuracy of ± 10 K. Ionization of molecules effusing from the chamber was performed with slow electrons with an energy of 30 eV. Silver as a standard with a known ionization cross-section [5] equal to 5.05×10^{-16} cm² was placed in the chamber with the substance being studied. The ion appearance energies were determined by the vanishing ion current method with an accuracy of ± 0.3 eV. The equipment was pre-calibrated against the CaF_2 vapor pressure [11]. Starting from the temperature of ~ 1270 K, the mass spectrum of vapor above the mixture of B_2O_3 and silver contained Ag^+ ions with an appearance energy of 7.6 eV. The $B_2O_3^+$ ions with an appearance energy of 14.0 eV appeared in the mass spectrum of vapor at a temperature of 1350 K. The appearance energies of $B_2O_3^+$ and Ag^+ indicate that both of these ions are the

products of direct ionization of the corresponding molecules [12]. At a temperature of 1389 K, the intensity of the Ag^+ ion current was 430 arb. units, and the intensity of the $B_2O_3^+$ ion current at 1557 K was 290 arb. units. The ratio $\sigma(Ag)/\sigma(B_2O_3)$, determined by Eq. (4), was 2.94, and $\sigma(B_2O_3)$ was 1.72×10^{-16} cm². The ionization cross-section of B_2O_3 , calculated by the additivity method with a correction factor of 0.7 [6], is 6.31×10^{-16} cm².

The mass spectrum of vapor above the mixture of $NaBO_2$ and silver at ~ 1300 K contained the peaks of Na^+ , $NaBO_2^+$, $Na_2BO_2^+$, and Ag^+ ions with appearance energies of 9.8, 9.9, 11.7, and 7.6 eV, respectively. The values of the ion appearance energies in the mass spectrum indicate that $NaBO_2^+$ and Ag^+ are molecular ions [12–14], while Na^+ and $Na_2BO_2^+$ are the products of dissociative ionization of the $NaBO_2$ and $Na_2B_2O_4$ molecules [13, 14]. At 1374 K, the ion intensities were 72 (Na^+), 72 ($NaBO_2^+$), 45 ($Na_2BO_2^+$), and 9 (Ag^+) arb. units. When determining the σ_{st}/σ_i ratio, the intensities of the Na^+ and $NaBO_2^+$ ion currents were summed with a correction for γ . When determining the mass of the sample that passed into vapor in the form of $NaBO_2$, the dimerization process was taken into account. The $\sigma(Ag)/\sigma(NaBO_2)$ ratio, determined by Eq. (4), was 1.86, and $\sigma(NaBO_2)$ was 2.73×10^{-16} cm². The ionization cross-section of $NaBO_2$, calculated by the additivity method with a correction of [6], is 6.41×10^{-16} cm².

In the mass spectrum of vapor above the mixture of $NaPO_3$ and silver, starting from a temperature of ~ 1300 K, the peaks of Na^+ , $NaPO_3^+$, and Ag^+ ions were recorded. The appearance energies of Na^+ and Ag^+ were 10.2 and 7.6 eV, respectively. The appearance energy of $NaPO_3^+$ was not measured because of the low intensity of the ion current. The $NaPO_3^+$ and Ag^+ ions are molecular [12, 15, 16], and Na^+ is the product of dissociative ionization of $NaPO_3$ [15, 16]. At 1344 K, the ion intensities were 44 (Na^+) and 6.6 (Ag^+) arb. units. The $\sigma(Ag)/\sigma(NaPO_3)$ ratio, determined by Eq. (4), was 1.43, and $\sigma(NaPO_3)$ was 3.51×10^{-16} cm². The ionization cross-section of $NaPO_3$, calculated by the additivity method with a correction factor of 0.7 [6], is 7.60×10^{-16} cm².

The mass spectrum of vapor above the mixture of KPO_3 and silver, starting from ~ 1320 K, contains the peaks of K^+ and Ag^+ ions. The appearance energies of K^+ and Ag^+ were 9.8 and 7.6 eV, respectively. The Ag^+ ion is molecular [12], and K^+ is the product of dissociative ionization of KPO_3 [15, 16]. At 1491 K, the ion intensities were 66 (K^+) and 3.0 (Ag^+) arb. units. The

Table 1. Ionization cross-sections of polyatomic molecules

Compound	$\sigma \times 10^{-16} \text{ cm}^2$		
	I	II	III
B ₂ O ₃	1.72 ± 0.22	6.31	—
NaBO ₂	2.73 ± 0.25	6.41	3.01
NaPO ₃	3.51 ± 0.18	7.60	2.83
KPO ₃	4.43 ± 0.31	8.23	4.29

(I) experimental data, this work; (II) estimation by the additivity method [5] including correction factors; (III) estimation from the experimentally determined ionization cross-sections of binary oxides according to the recommendation of [17].

$\sigma(\text{Ag})/\sigma(\text{KPO}_3)$ ratio, determined by Eq. (4), was 1.14, and $\sigma(\text{KPO}_3)$ was $4.43 \times 10^{-16} \text{ cm}^2$. The ionization cross-section of KPO₃, calculated by the additivity method with a correction factor of 0.7 [6], is $8.23 \times 10^{-16} \text{ cm}^2$.

The results indicate that the ionization cross sections of the studied polyatomic molecules do not obey the additivity rule even if the correction factors are taken into account, which is consistent with the data presented in the review [8]. At the same time, an increase in the ionization cross-section in the series NaBO₂–NaPO₃–KPO₃ corresponds to the tendency of its variation associated with the increase in the ionic radius and accordingly the atomic ionization cross-section [5] on passing from boron to phosphorus and from sodium to potassium.

In [17] it was proposed that the ionization cross-sections of oxygen-containing acid salts be calculated by representing them as the products of interaction of basic and acidic oxides, and using the recommendations given in [8]. At the same time, NaBO₂ can be represented as the product of interaction of NaO and BO, and NaPO₃ and KPO₃ as the products of interaction of Na(K)O and PO₂. In this case, the ionization cross-sections of NaBO₂, NaPO₃, and KPO₃ are ($\times 10^{-16} \text{ cm}^2$) 3.01, 2.83, and 4.29. These values differ from those obtained experimentally in the present study, but the differences are much smaller than the values calculated by the additivity method. The Table 1 presents data on the ionization cross-sections of the molecules under study, obtained by various methods.

According to the table 1, the use of the additivity rule leads to significantly overestimated σ values compared to the experiment, whereas the calculation method of [17] gives results closer to reality.

In the present work, the ionization cross-sections for polyatomic oxide molecules B₂O₃, NaBO₂, NaPO₃, and KPO₃ were experimentally determined by high-temperature mass spectrometry. The results showed that the σ values differ significantly from the calculated values obtained according to the additivity

rule even when correction factors are included in calculation, which leads to underestimated partial pressures.

The present study confirmed that, on the one hand, for polyatomic molecules the ionization cross-section does not obey the additivity rule. On the other hand, to calculate the ionization cross-sections of complex molecules using the ionization cross-sections of atoms, it is necessary to obtain as many experimental data as possible to complement the data presented in [8].

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CONFLICT OF INTEREST

The author of this work declares that he has no conflicts of interest.

REFERENCES

1. G. A. Semenov, E. N. Nikolaev, and K. E. Frantseva, *Application of Mass Spectrometry in Inorganic Chemistry* (Khimiya, Leningrad, 1976) [in Russian].
2. L. N. Sidorov, M. V. Korobov, and L. V. Zhuravleva, *Mass Spectral Thermodynamic Studies* (Mosk. Gos. Univ., Moscow, 1985) [in Russian].
3. V. L. Stolyarova and G. A. Semenov, *Mass Spectrometric Study of the Vaporization of Oxide Systems* (Wiley, Chichester, 1994).
4. L. N. Sidorov and S. I. Lopatin, in *The Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Ed. by J. C. Lindon, G. E. Tranter, and D. Koppenaal (Elsevier, Amsterdam, 2017), p. 95.
5. J. B. Mann, *J. Chem. Phys.* **46**, 1646 (1967).
6. M. Guido and G. Gigli, *High Temp. Sci.* **7**, 122 (1975).
7. R. T. Meyer and A. W. Lynch, *High Temp. Sci.* **5**, 192 (1973).
8. J. Drowart, C. Chatillon, J. Hastie, and D. Bonnell, *Pure Appl. Chem.* **77**, 683 (2005).
9. E. K. Kazenas and Yu. V. Tsvetkov, *Vaporization of Oxides* (Nauka, Moscow, 1997) [in Russian].
10. E. K. Kazenas and Yu. V. Tsvetkov, *Thermodynamics of Evaporation of Binary Oxides* (Nauka, Moscow, 2004) [in Russian].

11. *Thermodynamic Properties of Individual Substances, Reference Book*, Ed. by V. P. Glushko (Nauka, Moscow, 1978–1982), Vols. 1–4 [in Russian].
12. S. G. Lias, J. E. Bartmess, J. F. Liebman, et al., *J. Phys. Chem. Ref. Data* **17** (Suppl. 1), 1 (1988).
13. A. Büchler and J. B. Berkowitz-Mattuck, *J. Chem. Phys.* **39**, 286 (1963).
14. L. N. Gorokhov, A. V. Gusarov, A. V. Makarov, and O. T. Nikitin, *Teplofiz. Vys. Temp.* **9**, 1173 (1971).
15. A. S. Alikhanyan, A. V. Steblevskii, V. I. Gorgoraki, and I. D. Sokolova, *Dokl. Akad. Nauk SSSR* **222**, 629 (1975).
16. A. V. Steblevskii, A. S. Alikhanyan, I. D. Sokolova, and V. I. Gorgoraki, *Zh. Neorg. Khim.* **22**, 23 (1977).
17. S. I. Lopatin, S. M. Shugurov, A. I. Panin, and E. A. Vasil'eva, *Rapid Commun. Mass Spectrom.* **31**, 1559 (2017).

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