

# Mass Spectrometric Study of Stability, Thermochemistry and Structures of the Gaseous Oxyacid Salts

Sergey I. Lopatin\* and Sergey M. Shugurov

St. Petersburg State University, Universitetskii pr., 26, St. Petersburg, 198504, Russia

**Abstract:** Experimental data obtained by Knudsen Effusion Mass Spectrometry and results of quantum-chemical calculations on the structure and thermodynamic properties of gaseous oxyacid salts were systematized. A criterion of thermal stability of these compounds was offered and regularities in the atomization enthalpies were established.

**Keywords:** Review, Knudsen Effusion Mass Spectrometry (KEMS), quantum chemistry, thermochemistry, molecular structure, high temperature, oxide systems, oxyacid salts.

## INTRODUCTION

The systematic studies on vaporization and thermodynamic properties of oxide systems have been carried out in our University in last 50 years. Vaporization studies on oxides provided a great body of facts concerning the qualitative and quantitative composition of the vapor and thermodynamic characteristic of vaporization and thermal dissociation reactions. The most valuable information was obtained by means of high temperature mass spectrometry allowing the partial pressures of vapor species to be measured within a wide concentration range. It was found that the composition of the vapor phase over oxides is not nearly so simple as it had supposed earlier. In the vapor over oxides monomeric molecules, dimers, trimers, tetramers and etc. were detected. The researcher's attention was first focused on the vaporization of individual oxides stable on passing in vapor. Afterwards systems in which vapor contains gaseous oxides not existing in the condensed state, for example  $\text{LnO}$ ,  $\text{BO}_2$ ,  $\text{AlO}$ ,  $\text{Al}_2\text{O}$ , etc., were studied. The experiments were carried out in wide temperature ranges: from 100 up to 3000 K. The resulting data were summarized in the exhaustive reviews [1-7]. Research on systems containing gaseous molecules consisting of three sorts of atoms was initiated. For the first time oxide associates were detected in the vapor over individual oxides vaporized from metallic cells. Aldrich [8] detected in the mass spectra of the vapor over barium oxide vaporized from tantalum, molybdenum, and tungsten cells at temperatures higher than 1600 K the ions  $\text{BaTaO}_2^+$ ,  $\text{BaTaO}_3^+$ ,  $\text{BaMoO}_4^+$ ,  $\text{BaMoO}_3^+$ ,  $\text{BaMoO}_2^+$ ,  $\text{BaWO}_4^+$ ,  $\text{BaWO}_3^+$ ,  $\text{BaWO}_2^+$ , and  $\text{BaWO}^+$ . The dissociation energies of magnesium, calcium, strontium, and tin, vaporized from molybdenum and tungsten cells, were determined in [9,10]. Molybdates and tungstates were detected in the vapor over alkaline-earth, beryllium, indium, and lithium oxides vaporized from molybdenum and tungsten cells [11-15]. Thus, experimental evidence was

obtained showing that compounds which were later named "oxyacid salts" [5, 7, 16] or "binary oxides" [4] are stable in vapor at high temperatures. Systematic studies in this field were initiated in early 1960s, and later the reviews [4-7, 17, 18] appeared devoted to the stability and thermodynamic properties of the gaseous oxyacid salts. Salts can be presented as products of the reaction between acidic and basic oxides. Our systematic study of the vaporization of oxide systems allowed us to reveal certain regularities, in particular, we found that the stability of a gaseous salt depends of the difference of acid-base properties of oxides formed this salt.

## CONCEPT OF RELATIVE ORBITAL ELECTRONEGATIVITY

The "basicity" or "acidity" of chemical elements and their compounds is one of the fundamental concepts of chemical science. The position of an element in the periodic table determines the whole set of its properties, both qualitative and quantitative. Using Mendeleev's periodic system of elements, we can predict, in the first approximation, whether an element in question forms an acidic or basic oxide. If the acid-base properties of oxides are expressed quantitatively, it is criteria which allow fairly correct predictions of the qualitative and quantitative composition of the vapor over oxide systems. The problem of quantitative assessment of the degree of acidity or basicity of oxides can be solved on the basis of the modern concept of electronegativity, i.e. on the basis of assessment of the amount of ionic character of bonds in molecules, both in the condensed and in the gas phase.

We suggested the relative orbital electronegativity of oxides (after Mulliken) forming a salt as the criterion of thermal stability of the gaseous oxyacid salt [19]. Mulliken [20], using the valence bond method, came to a definition of the absolute electronegativity, according to which the electronegativity is a half-sum of the ionization energy of a neutral atom ( $I$ ) and its electron affinity ( $F$ ). Expression (1) formed the basis for a new Mulliken electronegativity scale which is proportional to the thermochemical Pauling scale.

\*Address correspondence to this author at the St. Petersburg State University, Universitetskii pr., 26, St. Petersburg, 198504, Russia;  
Tel: (812) 4284067; Fax: (812) 423969;  
E-mail: sergeylopatin2009@yandex.ru

$$\chi = (I + F)/2 \quad (1)$$

The Mulliken's electronegativity reflected a certain averaged trend of the valence orbital of a neutral atom to retain its "own" electron and to acquire "another's" electron. Later Mulliken's conclusion was confirmed by the molecular orbital method, and the Mulliken's electronegativity was suggested to call the orbital electronegativity ( $\chi$ ). At present both the ionization energies and electron affinities of practically all elements of the periodic table are quite accessible reference data [21]. Therefore, there is not difficulty in constructing a scale of "absolute" electronegativities.

Viting [22] introduced the concept of the average orbital electronegativity of molecules, calculated by the additivity rule (Eq. 2).

$$\bar{\chi} = \frac{\sum n_i \chi_i}{\sum n_i} \quad (2)$$

Here  $\bar{\chi}$  is the average orbital electronegativity of a molecule;  $\chi_i$ , orbital electronegativity of atom; and  $n_i$ , number of atoms of this sort in the formula unit of this molecule. The  $\chi$  values for oxides are given in Table 1 in ascending order. The ratio of the relative orbital electronegativities of salt-forming oxides can serve as a measure of the enthalpy of this salt formation from the oxides.

### GASEOUS PHASE COMPOSITION OF OXIDE SYSTEMS: MOLECULAR STRUCTURES AND THEORETICAL STUDIES

To the present time more than a hundred of gaseous oxyacid salts have been identified and studied. It was found that the gaseous salts are so diverse that the nomenclature for crystalline salts is absolutely inapplicable to them. First of all this relates to compounds in nontraditional oxidation states of both the cation-and anion-forming elements. At present, in the absence of a legal IUPAC nomenclature, it is conventional in the literature to name gaseous salts as follows. The termination "ate" is added to an anion-forming element and the chemical formula of the compound is written, for example: barium molybdates  $\text{BaMoO}_4$ ,  $\text{BaMoO}_3$ ,  $\text{BaMoO}_2$ ,  $\text{Ba}_2\text{MoO}_5$ ,  $\text{Ba}_2\text{MoO}_7$ , etc.

To determine the molecular composition of vapor, the Knudsen effusion method with mass spectrometric analysis of vapor-phase products was developed. Over the past 50 years, a great number of mass spectrometry studies were carried out, and a significant number of previously unknown molecules were found and characterized. In some cases, these molecules are dominating vapor components. However, a number of properties, such as structure, internuclear distances, and vibration frequencies of molecules, cannot be determined by direct measurements by a mass spectrometer. These properties are studied by IR matrix-isolation spectroscopy, gas-phase electron diffraction, and photoelectron spectroscopy. As quantum-chemical calculation are developed and advanced, a possibility appears to calculate structures and mode frequencies for certain molecules.

At present a definite protocol has settled for the description of properties of high temperature vapor. Mass

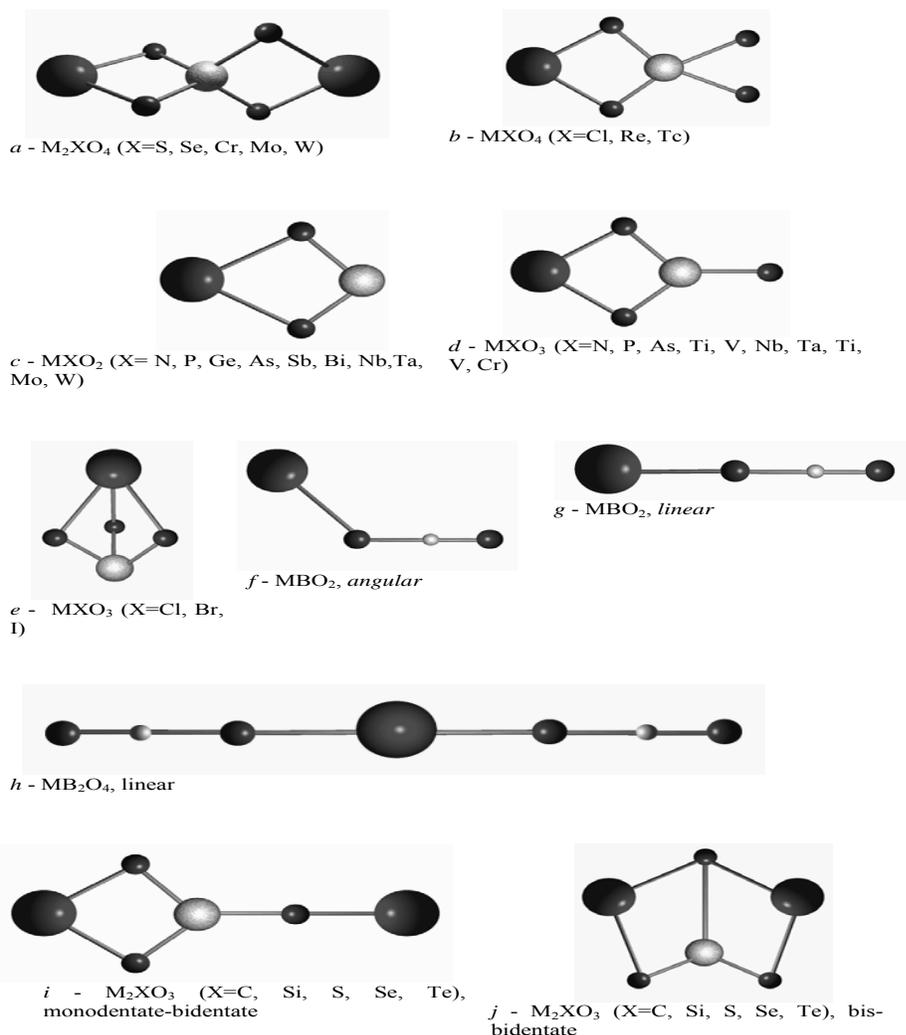
spectrometry provides information on its qualitative and quantitative composition, temperature range for studies, partial pressures of molecular species in the vapor. Based on the resulting data, one can further select conditions of experiment and interpret electron diffraction and spectral results. In turn, the structural and spectral data allow one to estimate thermodynamic function of the gaseous species detected by mass spectrometry and to determine their standard thermochemical properties, such as formation and atomization enthalpies. Unfortunately, because of the limited applicability of gas-phase electron diffraction and IR spectroscopy, connected with the fact that the experimental data in cases when several sorts of molecules present in vapor is difficult to interpret, structural parameters and normal mode frequencies can be obtained not for all gaseous salts. First of all, this relates to complex polyatomic molecules present in the vapor in insignificant amounts in mixtures with their dissociation products. Trying to estimate thermodynamic function of associates, experimenters resort to approximations based on analogies or to arbitrary combinations of structural fragments of molecules. In these cases, the role of quantum-chemical calculations increases, as they provide a decision criterion in the case of inconsistent or contradictory mass spectral data.

At present a rather definite notion of the molecular structures of gaseous oxyacid salts had been formed, interpreted in terms ion pair model [23-27]. According to the modern views based on the experimental evidence provided by gas-phase electron diffraction [28-58], IR matrix isolation spectroscopy [23-26, 59-95], molecular beams deflection technique [96], and quantum-chemical calculations [27,97-124], the structures of the overwhelming majority of gaseous salts present closed cycles with the cation most probably located to triangle side or tetrahedron edge and with bidentate cation-anion bond (Figs. 1 a-e, i-j). An exception are borates having a linear structure (Figs. 1 f-h).

The presently accepted structures of gaseous oxyacid salts point to preferentially ionic nature of the cation-anion bond. Comparison of electron diffraction data for similar molecules ( $\text{K}_2\text{SO}_4$ ,  $\text{Cs}_2\text{SO}_4$ , and  $\text{K}_2\text{CrO}_4$ ) showed [41] that these molecules are quite similar in that have similar structures of the acid residues, preserve their structure in the gas phase, and have similar geometric positions and specific features of bond between the alkali metals and remaining parts of the molecules. The accumulated experimental evidence revealed a number of common regularities in the geometric configurations and internuclear distances in molecules [41]:

(1) The valence angles in the structural unit of a chain atom  $X$  (anion-forming element) belonging to a certain group of the periodic table are determined by the valence state of the atom. In various molecules containing atom  $X$  in the certain valence state, the valence angles in the structural unit of this atom vary within a narrow range around constant average values, irrespective of the chemical individuality of atoms bound to atom  $X$  and to the remaining more distant part of the molecule. The overall structure of the atom  $X$  unit is preserved (linear, planar, tetrahedral, etc.).

(2) The internuclear distances for two directly bound atoms are determined by their chemical individuality, the



**Fig. (1).** Structures of the gaseous oxyacid salts.

multiplicity of the bond between them, and the valence state of each of them. In different molecules containing a bond between atoms of a certain chemical individuality (with the same bond multiplicity and valence states of each of the bound atoms), internuclear distances vary within a rather narrow range around a certain constant average value, irrespective of the chemical individuality of atoms in the nearest surrounding of the bond under consideration and of the structure of a more distant part of the molecule.

The above regularities which relate to the geometric configurations of and internuclear distances in molecules make it possible to assess with a fairly high accuracy the valence angles and internuclear distances in any molecule, provided experimental data for structural units containing atoms and bonds of the same type as those present in the molecule are available.

Electron diffraction results revealed some more empirical regularities. First, as shown in [58], essential displacements of metal ions relative to anion groups are characteristic of molecules built up as ion pairs. Such molecules characteristically combine a fairly rigid anion group and a significant delocalization of the metal ion relative to its equilibrium position. This finding suggests that the metal ion is bound to acid residue as a whole. Evidence for this

suggestion was provided by theoretical structural studies of inorganic molecules. Charkin *et al.* [117] showed that “mobile”  $M$  atoms (cations) migrate from one part of the molecular “framework” into another. Another very important regularity relates to the invariance of the cation-oxygen internuclear distance in the molecules of  $M_2XO_4$ ,  $MXO_4$ ,  $MXO_3$  (X = N, P), and  $MNO_2$  salts, which involve an M-O-O-X ring [44]. In the latter work, one more very interesting observation was made. Comparison of the M-O internuclear distances ( $M = Cs, Rb, K$ ) with the ionic crystal radii of  $M^+$  showed that the ionic radius of oxygen was constant and equal to 1.15 Å. The constancy of the resulting “ionic” oxygen radius provides a good method for estimating geometric parameters for unstudied compounds. Therewith, one can widely use the data in [125].

The above-listed regularities enable us to transfer structural parameters from analogous compounds when experimental data for particular salt molecules are lacking.

The possibility of internal rotation in the molecules gaseous salts results in the concept of “nonrigidity” of these compounds [126]. Variation in the mutual arrangement of atoms in nonrigid molecules does not result in bond cleavage and new bond formation. The possibility of intramolecular motions requires essential revision of the concept of

chemical bond. It was demonstrated on the example of the LiNC molecule that in certain phases of motion around the NC group the lithium atom gets closer alternatively to nitrogen or carbon [127]. A similar phenomenon is characteristic of all ionic molecules due to long-range Coulomb interactions [128].

Dronin and Gusarov [129] applied the electrostatic model to study the intramolecular motion in the  $K_2SO_4$  molecule and concluded that this molecule can exist as several isomers. The potential energy surfaces of such systems contain, along with an absolute minimum corresponding to the main isomer, local minima corresponding to isomers with higher energies. These minima are separated by potential barriers that prevent, to a certain extent, isomerization. Only minima of the same type can exist on the potential surface of. The possible equilibrium configurations are symmetrical and correspond to the ionic nature of the anion-cation bond. The salt  $K_2SO_4$  can exist as three isomers: A stable isomer of  $D_{2d}$  configuration and less stable isomers of  $C_{2v}$  and  $C_{3v}$  configurations.

The latter two configurations correspond to saddle points with a flat energy gradient, rather than minima on the potential energy surface.

One more important problem relates to study on the “nonrigidity” of the potassium sulfate molecule [129]. All previous calculations concerned molecules with one metal atom [128]. If there are two such atoms, as for example, is  $K_2SO_4$ , to describe the “nonrigidity” of such gaseous salt requires consideration of a qualitatively new type of motion, specifically simultaneous motion of two potassium atoms with respect to the  $SO_4^{2-}$  framework [128].

Earlier the vibration spectra of gaseous molecules were mainly studied by IR spectroscopy. Now an essential role is played also by Raman spectroscopy, which is connected with the advent of laser light sources and high-resolution spectral instruments. In the IR spectra those modes are active, which are accompanied by changes in dipole moment, whereas in the Raman spectra, vibrations accompanied by changes in molecular polarizability. For all molecules possessing a symmetry center, vibrations active in the IR spectrum are forbidden in the Raman spectrum and vice versa. For molecules of other types, a vibration can be simultaneously active in the both spectra. Owing to the specified features of the spectra of polyatomic molecules, study of Raman spectra supplements study of IR absorption spectra. Joint study of the both types of spectra makes it possible to determine the maximal number of principal modes and the molecular configuration.

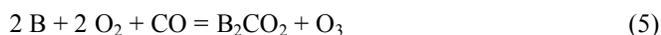
In a rarefied gas, intermolecular interactions can be neglected. The gas-phase vibration spectra of fairly simple molecules have a fine rotational structure, which allows determination of inertia moments and, therefore, internuclear distances and valence angles. Salts of oxygen-containing acids are solids at room temperature. Even though some of them vaporize without decomposition, their IR spectra are rather difficult to obtain by routine methods in high-temperature cells (furnaces). Furthermore, these spectra are difficult to interpret, as the role of rotational and vibrational “hot” bands grows. At present the high-temperature IR spectra of the metaborates of alkali metals [130-134] and

indium and thallium [135], cesium nitrite, cesium and thallium nitrates [134], as well as gallium, indium, and thallium molybdates [135] have been reported. The matrix isolation method is successfully applied for studying stable salts in vapor [59]. In this method, salts and inert gases (argon or nitrogen) are mixed in 1:500 or higher ratios and frozen on an IR-transparent window cooled to 10-15 K. As the molecules under study, captured by the matrix from an inert gas, are completely isolated from each other, the spectrum obtained by the matrix isolation method is similar to the gas-phase spectrum. It is free from splitting caused by the crystal field and also from lattice vibrations. The matrix spectrum is easier than the gas spectrum as it does not contain a rotational structure because of the rigid matrix surrounding at low temperatures. The absence of this structure and intermolecular interactions result in the fact that the spectra of solutions contain very narrow bands of individual molecules, and even isotope peaks of metals, located very closely to each other, can be resolved.

Along with experimental vibration modes, calculated and estimated values are used in various calculations. Certain frequencies of metal-oxygen stretching vibrations lay below  $150\text{ cm}^{-1}$  and thus cannot be measured experimentally on modern instruments. Therefore, they are calculated for a known salt structure on the ionic model basis. Equilibrium geometric parameters, normal mode frequencies and intensities can be calculated by various quantum-chemical methods. When neither experimental nor calculated mode frequencies of gaseous salts are available, estimates are used. In particular, one can estimate the mode frequencies of  $SeO_4^{2-}$ ,  $MoO_4^{2-}$ , and  $WO_4^{2-}$  in selenates, molybdates, and tungstates of alkali metals, alkaline-earth metals, and germanium. The mode frequencies of these salts were calculated on the basis of the mode frequencies of free  $SeO_4^{2-}$ ,  $MoO_4^{2-}$ , and  $WO_4^{2-}$  anions [136] with account for the splitting of the E and  $F_2$  terms, resulting from metal coordination to a free tetrahedral anion [68, 79, 137], and the experimental mode frequencies given in these publications. As shown in [85], coordination a free tetrahedral anion to a metal cation induces splitting of the  $\nu_3(F_2)$  mode due to transition from the  $T_d$  to  $D_{2d}$  symmetry, which gives rise to two peaks in the IR spectrum ( $B_2$  and E bands). The  $[\nu(B_2) - \nu(E)]$  splitting decreases as the anion mass increases. This regularity was found to be common for all gaseous salts of oxygen-containing acids. Comparison of the normal mode frequencies of the free  $SO_4^{2-}$  anion [136] and alkali metal sulfates [69] showed that the  $\nu_4(F_2)$  frequency is also split into  $B_2$  and E, and  $\nu_2(E)$ , into  $A_1$  and  $B_1$ , when the free tetrahedral anion coordinates to metal cations and the  $T_d$  symmetry transforms into  $D_{2d}$ . The splitting decreases on passing from  $Li_2SO_4$  to  $Cs_2SO_4$ . The  $\nu_1(A_1)$  frequency remains unchanged. We made use of the above data in estimating normal mode frequencies for the anions  $SeO_4^{2-}$ ,  $MoO_4^{2-}$ , and  $WO_4^{2-}$ . In this case, the fact that the splitting is cation-dependent was not taken into account, as the error of  $50\div 3100\text{ cm}^{-1}$  only slightly affects the  $\Phi^0(T)$  value at high frequencies.

In spite of extremely low temperatures, chemical reactions, including synthesis of salts of oxygen-containing acids, can occur in isolating matrices. Matrix reaction (3) was studied in [86].

Ogden and Williams [87], based on the fact that the found mode frequencies well fit those of alkali metal carbonates, assumed formation in a matrix of two isomers of thallium carbonate with  $C_{2v}$  structures (Figs. 1i and 1j). The reaction of  $Tl_2O$  with  $SO_2$  in an argon matrix yielded  $Tl_2SO_3$  and  $Tl_2S_2O_5$  [88]. Matrix reactions of boron and aluminum with small molecules gave  $B_2CO_2$ ,  $Al_2CO_2$ , and  $Al_2CO_3$  by mechanisms (4)-(8) [89].



Cyclic  $MCO_2$  molecules ( $M = Li, Na, K, Cs$ ) [90, 92, 94],  $KCO_3$  [93] of  $C_{2v}$  symmetry (Fig. 1c), and  $M_2CO_2$  ( $M = K, Cs$ ) with a  $W$ -shaped structure [90] were studied by the matrix isolation method. The salts all were obtained by co-condensation of beams of corresponding alkali metals and  $CO_2$ . The reactivity of alkali metals increases from lithium to cesium. The subsequent annealing of matrices can promote formation of more complicated salts  $M_xCO_2$  ( $x = 3$ ). The co-condensation of  $NO_2$ ,  $NO$ ,  $N_2O$  molecular beams and alkali metals in an argon matrix at 4 and 14 K results give rise to  $M_x^+NO^-$  and  $M_x^+NO_2^-$  ion pairs [95]. Analogous ion pair associates are formed by chemical reactions in isolated matrices of inert gases at extremely low temperatures and in effusion cells at high temperatures. It is not improbable that sooner or later the above carbonates and sulfates will also be obtained by gas-phase synthesis, provided conditions for coexistence of the oxides forming these salts in required concentrations will be created.

Unfortunately, experimental methods of determining normal mode frequencies for molecules of gaseous salts of oxygen-containing acids have quite objective limitations. These limitations are connected first of all with the necessity of creating high-density molecular flows, which is possible to reach rather rarely. In most cases the relative content of a salt in vapor is low. In this case, calculation methods are helpful.

The last two decades are characterized by qualitative changes in the position of quantum-chemical calculations among other methods of studying structures and properties of free molecules. The progress in computer equipment makes it possible to create and improve computer programs for quantum chemistry. Modern computers open out possibilities for quantum-chemical calculations by standard procedures.

Unempirical studies of molecular force fields are the most intensively developed direction of quantum chemistry. With known force field one can calculate the vibration spectrum, geometry, and other experimentally observable parameters of a molecule. In this case, a possibility appears to check the interpretation of electron diffraction and spectral data and to reveal experimental errors. Joint examination of *ab initio* and experimental data gives way to obtaining more reliable molecular parameters. The related problem successfully solved by quantum-chemical methods is the problem of isomerism of gaseous salts and of stability of isomers [116].

A systematic *ab initio* study of the force fields and vibration spectra of gaseous oxyacid salts was fulfilled in the following cycles of works [97-99, 102-108, 110-112, 122, 137, 138] and [100, 105, 116-121]. Separate works are devoted to quantum-chemical studies of the molecules  $LiBO_2$  [123],  $NaBO_2$  [139],  $LiNO_3$  and  $NaNO_3$  [95],  $NaPO_3$  [101],  $LiClO_3$  and  $NaClO_3$  [109],  $M(NO_3)_2$  ( $M = Be, Mg, Ca$ ) [112],  $Mg(NO_2)_2$ ,  $Cu(NO_2)_2$  and  $Cu(NO_3)_2$  [113],  $LiClO_4$  and  $Li_2SO_4$  [114],  $LiCO_2$  and  $NaCO_2$  [124], and lithium and sodium phosphates and nitrates [115]. The results of quantum-chemical calculations of molecular structures and normal mode frequencies nicely fit available experimental data.

The subjects of numerous experimental and theoretical studies were free molecules of compounds of *s*- and *p*-elements. As a result, an integral view of the stereochemistry of these compounds formed, which made it possible to predict reliably the structures of still unstudied molecules. The quality of *ab initio* calculations is higher the higher theory level is applied. Semiempirical methods make use of empirical parameters derived from spectroscopic data.

The structures of *d*-element compounds remain uncertain because both of experimental difficulties associated with high temperatures and of unknown vapor compositions. The quantum-chemical calculations [140] showed that the above-described regularities characteristic of gaseous salts of *s*- and *p*-elements are also valid for salts formed by *d*-elements.

## THERMODYNAMIC PROPERTIES OF THE OXIDE VAPOR SPECIES

At present a great body of standard enthalpies of formation of gaseous oxyacid salts are available, which has been generalized and systematized in [18, 140, 151]. The heats of gas-phase and heterophase reactions involving gaseous salts are calculated by Eqs. (9) and (10).

$$d \ln K_p / d T = \Delta_r H^0(T) / RT^2 \quad (9)$$

$$\Delta_r H^0(298 K) = - T \{ R \ln K_p(T) + \Delta [G^0(T) - H^0(298 K)]/T \} \quad (10)$$

According to the nomenclature accepted in high temperature mass spectrometry, the calculations by Eqs. (9) and (10) are referred to as calculations by the II and III laws of thermodynamics, respectively.

The term "calculation by the II law" is used in cases when experimental temperature dependence of equilibrium constant is available. In Eq. (9),  $\Delta_r H^0(T)$  is the reaction enthalpy at a mean experimental temperature. The  $\Delta_r H^0(T)$  is reduced to standard temperature by means of heat capacity functions  $H^0(T) - H^0(298)$ . To determine heats of vaporization or sublimation, which is a special case of Eq. (9), Clausius-Clapeyron equation (11) is applied.

$$\frac{d \ln p}{d T} = \frac{\Delta_r H^0(T)}{RT^2} \quad (11)$$

Integration of Eq. (11) on the assuming that  $\Delta_r H^0(T)$  is constant within a narrow temperature range gives the following expression.

$$\lg p = \frac{\Delta_r H^0(T)}{2.3 RT} + const \quad (12)$$

Therefore, the temperature dependence of vapor pressure is described by linear equation (13).

$$\lg p = \frac{-A}{T} + B \quad (13)$$

The major consequence of Eq. (13) is as follows: in thermodynamic formulas containing equilibrium constants calculated from partial pressures, for example in Eq. (11),  $p_i$  can be replaced by the proportional value  $I \cdot T$ . In mass spectral experiments, temperature dependences of ion current intensity are measured, and  $\log(I \cdot T) = f(1/T)$  plots are constructed. The slope of the straight line gives the reaction enthalpy. The calculation is usually carried out by the least-squares method.

The “calculation by the III law” is based on Eq. (10), which requires preliminary determination of  $\Delta S^0(T)$ . The calculation of absolute entropies is based on the Planck postulate asserting that the entropy of a ideal crystal is zero at 0 K. At present the so-called reduced Gibbs potential is widely used to calculate reaction heats, which allows reaction enthalpies at standard temperature, 298.15 or 0 K, to be calculated from the equilibrium constants measured at various temperatures. By definition, the reduced Gibbs potential is described by Eq. (14), and reaction enthalpies are calculated in this case by Eq. (15).

$$\Phi_r^0 \equiv \frac{(G_r^0 - H_0^0)}{T} \equiv -\frac{(H_r^0 - H_0^0 - TS_r^0)}{T} \quad (14)$$

$$\Delta H_0^0 = -RT \ln K_p + T \Delta \Phi_r^0 \quad (15)$$

Gas-phase reduced Gibbs potentials are calculated by statistical thermodynamics methods in the “rigid rotor-harmonic oscillator” approximation, using data on molecular structures and normal mode frequencies. For liquids and solids these values are found from heat capacity data.

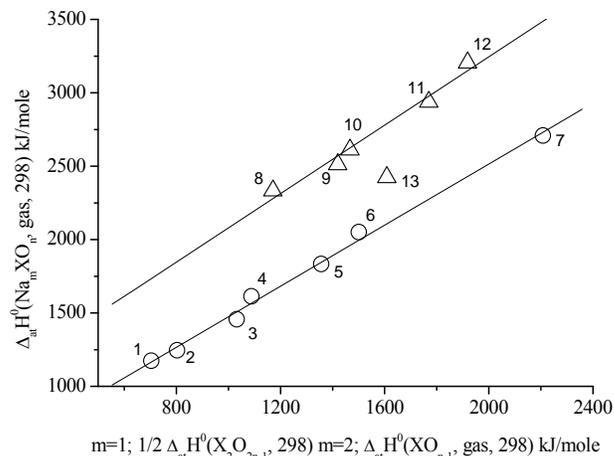
In particular, the approximate Landya method [152] is widely used.

In practice, researchers tend to combine calculations by the II and III laws in mass spectral studies for determination of heats of gas-phase and heterogeneous reactions. The criterion of validity of the resulting data is the coincidence of the reaction enthalpy found by the II and III laws. However, reaction enthalpies are far from always measurable by the II law. In particular, this relates to gas-phase reactions involving salts of oxygen-containing acids, when the relative contents of the latter in the vapor is 5% and lower, since for correct results one has to obtain temperature dependence of equilibrium constant within the temperature range of 100 K and more. If this is impossible, one has to restrict himself by calculations by the III law in a narrow temperature range.

Sometimes equilibrium constants are calculated, passing the stage of transition to absolute values of partial pressures. Selection and measurement of dimensionless equilibrium constants were applied for this aim. For example, for exchange reaction (16) we obtain Eq. (17) for equilibrium constant.



$$K_p = \frac{p(\text{InPO}_2) p(\text{PO}_2)}{p(\text{InPO}_3) p(\text{PO})} = \frac{\sigma(\text{InPO}_3) \sigma(\text{PO})}{\sigma(\text{InPO}_2) \sigma(\text{PO}_2)} \cdot \frac{\gamma(\text{InPO}_3) \gamma(\text{PO})}{\gamma(\text{InPO}_2) \gamma(\text{PO}_2)} \cdot \frac{I(\text{InPO}_3) I(\text{PO}_2)}{I(\text{InPO}_2) I(\text{PO})} \quad (17)$$



**Fig. (2).** Dependence of atomization enthalpies of gaseous sodium salts on the atomization enthalpies of gaseous anion-forming oxides (1 – NaBiO<sub>2</sub>; 2 – NaNO<sub>2</sub>; 3 – NaPO<sub>2</sub>; 4 – NaNO<sub>3</sub>; 5 – NaBO<sub>2</sub>; 6 – NaPO<sub>3</sub>; 7 – NaReO<sub>4</sub>; 8 – Na<sub>2</sub>MoO<sub>3</sub>; 9 – Na<sub>2</sub>SO<sub>4</sub>; 10 – Na<sub>2</sub>CrO<sub>4</sub>; 11 – Na<sub>2</sub>MoO<sub>4</sub>; 12 – Na<sub>2</sub>WO<sub>4</sub>; 13 – Na<sub>2</sub>CO<sub>3</sub>).

Direct measurement of the total intensities of ion currents formed by ionization of InPO<sub>3</sub>, InPO<sub>2</sub>, PO<sub>2</sub>, and PO molecules and consideration of ionization cross sections and secondary emission ratios allow the absolute equilibrium constant to be estimated without passing to partial pressures and without using pressure standards. If compounds under study contain several isotopes, correction for isotope composition should be applied. Sometimes the ratio of ionization cross section to secondary emission ratio can be taken equal to unit. According to calculations, these assumptions result in that the equilibrium constants are estimated to within a factor 1.5-2.0. As a result, the error in the reaction enthalpy is about 5-10 kJ at 1000 K. More severe errors arise in the case when fragment ions are more abundant than molecular.

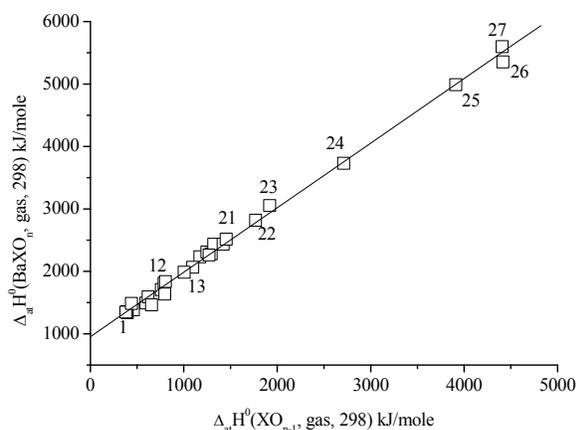
The ion pair model accepted for gaseous of oxyacid salts assumes that the structure of anions in isoanionic series and the nature of cation-oxygen bonds in isocationic series are preserved. In terms of the proposed model the atomization enthalpy of an anionic group is independent on the nature of the cation, and the dissociation energy of a cation-oxygen bond is independent on the nature of the anion.

If we consider trends to variation of the atomization enthalpy in groups of gaseous salts  $M_mXO_n$  ( $M$  is cation and  $X$  is anion-forming element, and  $m$  is 1 or 2) forming isoanionic and isocationic series, in the latter there is a well-defined linear dependence of the atomization enthalpies of salts on the atomization enthalpies of gaseous anion-forming oxides [Eq. (18)].

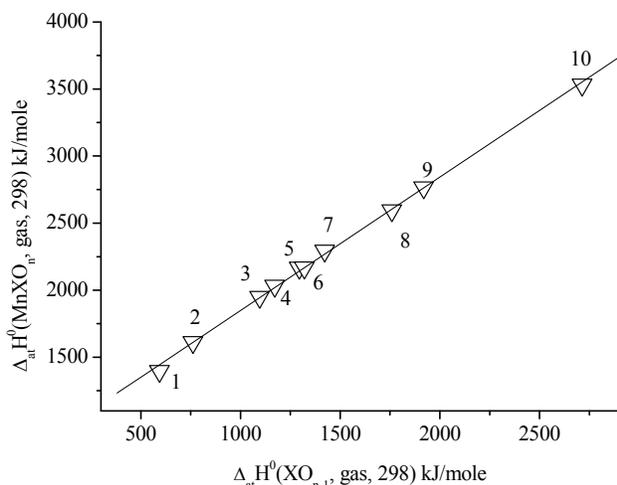
$$\Delta_{\text{at}}H^0(M_mXO_n, \text{gas}, 298) = k \Delta_{\text{at}}H^0(\text{anion-forming oxide, gas}, 298) + b \quad (18)$$

For example, the dependences of the atomization enthalpies of sodium, barium, and manganese salts on the atomization enthalpies of anion-forming oxides are given in Figs. (2-4).

The lower line in Fig. (2) refers to salts with a single sodium atom in the molecule, and the upper line, to salts

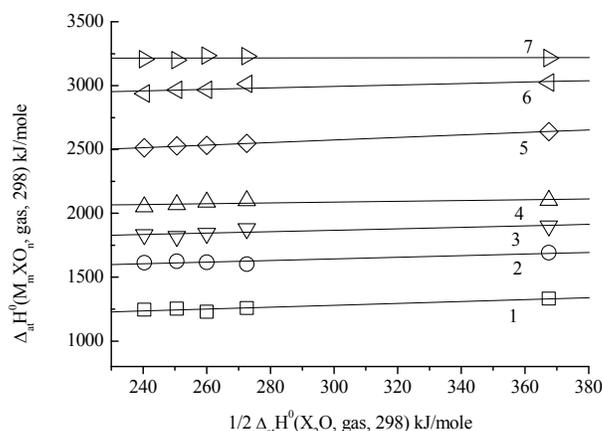


**Fig. (3).** Dependence of atomization enthalpies of gaseous barium salts on the atomization enthalpies of gaseous anion-forming oxides (1 – BaFeO<sub>2</sub>; 2 – BaNiO<sub>2</sub>; 3 – BaCoO<sub>2</sub>; 4 – BaCrO<sub>2</sub>; 5 – BaGeO<sub>2</sub>; 6 – BaBeO<sub>2</sub>; 7 – BaPO<sub>2</sub>; 8 – BaVO<sub>2</sub>; 9 – BaSiO<sub>2</sub>; 10 – BaNbO<sub>2</sub>; 11 – BaTaO<sub>2</sub>; 12 – BaBO<sub>2</sub>; 13 – BaCrO<sub>3</sub>; 14 – BaPO<sub>3</sub>; 15 – BaMoO<sub>3</sub>; 16 – BaSiO<sub>3</sub>; 17 – BaTiO<sub>3</sub>; 18 – BaVO<sub>3</sub>; 19 – BaNbO<sub>3</sub>; 20 – BaWO<sub>3</sub>; 21 – BaTaO<sub>3</sub>; 22 – BaMoO<sub>4</sub>; 23 – BaWO<sub>4</sub>; 24 – BaB<sub>2</sub>O<sub>4</sub>; 25 – BaNb<sub>2</sub>O<sub>6</sub>; 26 – BaRe<sub>2</sub>O<sub>8</sub>; 27 – BaW<sub>2</sub>O<sub>7</sub>).



**Fig. (4).** Dependence of atomization enthalpies of gaseous manganese salts on the atomization enthalpies of gaseous anion-forming oxides (1 – MnPO<sub>2</sub>; 2 – MnNbO<sub>2</sub>; 3 – MnPO<sub>3</sub>; 4 – MnMoO<sub>3</sub>; 5 – MnWO<sub>3</sub>; 6 – MnTiO<sub>3</sub>; 7 – MnNbO<sub>3</sub>; 8 – MnMoO<sub>4</sub>; 9 – MnWO<sub>4</sub>; 10 – MnB<sub>2</sub>O<sub>4</sub>).

with two sodium atoms. The enthalpies of formation and atomization of gaseous salts of alkali metals and Group III metals in the oxidation state +1 were found by measuring the vaporization or sublimation heats of the corresponding salts in the condensed state. Therefore, the validity of the resulting  $\Delta_f H^0$  (salt, gas, 298) and  $\Delta_{at} H^0$  (salt, gas, 298) values also depends on the correctness of the available published data on the standard enthalpies of formation of crystalline salts. The enthalpies of formation of the remaining salts were found by measuring the equilibrium constants of gas-phase synthesis of the salts from the corresponding gaseous oxides whose formation heats have been measured with a high accuracy [1]. Consideration of the trends in atomization enthalpies in groups of salts



**Fig. (5).** Dependence of atomization enthalpies of gaseous salts of alkali metals in isoanion series on the atomization enthalpies of gaseous cation-forming oxides (1 – NO<sub>2</sub><sup>-</sup>; 2 – NO<sub>3</sub><sup>-</sup>; 3 – BO<sub>2</sub><sup>-</sup>; 4 – PO<sub>3</sub><sup>-</sup>; 5 – SO<sub>4</sub><sup>2-</sup>; 6 – MoO<sub>4</sub><sup>2-</sup>; 7 – WO<sub>4</sub><sup>2-</sup>).

forming isocationic series allows one to estimate atomization and formation enthalpies for yet unstudied compounds, including oxides, and also to correct experimental data falling out the linear dependence.

If we postulate that the main validity criterion for the enthalpies of reactions involving gaseous salts of oxygen-containing acids, both measured and reduced to standard temperature, is the quality of fit of the atomization enthalpies of salts to linear dependence (18), it becomes relevant to select correctly the values of the formation and atomization enthalpies of gaseous anion-forming oxides from available published data. The recommended selected standard formation and atomization enthalpies of certain gaseous anion-forming oxides are given in Table 2. Selecting these values we were guided by the selection principles analogous to those used in the handbook [153].

A linear dependence of the atomization enthalpy of gaseous salt on the atomization enthalpy of gaseous cation-forming oxide is also observed for isoanionic series.

Fig. (5) depicts the dependence of the atomization enthalpies of gaseous salts of alkali metals on the atomization enthalpies of gaseous cation-forming oxides. Since the atomization enthalpies of cation-forming oxides are close to each other, precise enthalpies of formation and atomization of gaseous salts are of great importance for high-quality linear correlations.

Using the scale of average electronegativities of oxides (Table 1) one can predict the possibility of existence of various of oxyacids salts in vapor. In the beginning of the scale there are alkali and alkaline-earth metal oxides possessing exclusively basic properties and acting in the synthesis of gaseous salts only as cation-forming oxides. Salts formed by these oxides exhibit the highest thermal stability and in most cases evaporate congruently without decomposition. Oxides possessing strongly pronounced acid properties and playing the role of anion-forming oxides are located in the end of the electronegativity scale. In the middle of the scale there are oxides which, according to the electronegativity values, can act as both cation- and anion-

**Table 1. Average Orbital Electronegativity ( $\chi$ ) for Oxides**

Oxide	$\chi$	Oxide	$\chi$	Oxide	$\chi$	Oxide	$\chi$	Oxide	$\chi$
Cs <sub>2</sub> O	3.89	ZrO	5.59	CoO	5.97	SnO <sub>2</sub>	6.42	SO	6.88
Rb <sub>2</sub> O	3.99	VO	5.62	NiO	6.00	PbO <sub>2</sub>	6.43	CO	6.90
K <sub>2</sub> O	4.06	MgO	5.68	CuO	6.01	Sb <sub>4</sub> O <sub>6</sub>	6.44	PO <sub>2</sub>	6.91
Na <sub>2</sub> O	4.34	Sc <sub>2</sub> O <sub>3</sub>	5.68	BeO	6.05	V <sub>4</sub> O <sub>10</sub>	6.44	As <sub>4</sub> O <sub>10</sub>	6.94
In <sub>2</sub> O	4.51	Y <sub>2</sub> O <sub>3</sub>	5.69	Cr <sub>2</sub> O <sub>3</sub>	6.07	WO <sub>2</sub>	6.44	SeO <sub>2</sub>	6.99
Li <sub>2</sub> O	4.51	CrO	5.70	SiO	6.15	AsO	6.49	P <sub>4</sub> O <sub>10</sub>	7.00
Ga <sub>2</sub> O	4.65	In <sub>2</sub> O <sub>3</sub>	5.72	SbO	6.16	Nb <sub>2</sub> O <sub>5</sub>	6.53	TeO <sub>3</sub>	7.02
Al <sub>2</sub> O	4.67	La <sub>2</sub> O <sub>3</sub>	5.75	Bi <sub>2</sub> O <sub>3</sub>	6.17	Ta <sub>2</sub> O <sub>5</sub>	6.53	SO <sub>2</sub>	7.10
Tl <sub>2</sub> O	4.71	NbO	5.77	HfO <sub>2</sub>	6.17	PO	6.59	CO <sub>2</sub>	7.12
CaO	4.81	TaO	5.78	B <sub>2</sub> O <sub>3</sub>	6.18	Mn <sub>2</sub> O <sub>7</sub>	6.60	SeO <sub>3</sub>	7.12
SrO	4.82	Ga <sub>2</sub> O <sub>3</sub>	5.80	GeO	6.18	SiO <sub>2</sub>	6.61	SO <sub>3</sub>	7.21
BaO	4.80	Al <sub>2</sub> O <sub>3</sub>	5.82	TiO <sub>2</sub>	6.23	CrO <sub>3</sub>	6.62	I <sub>2</sub> O <sub>5</sub>	7.32
ScO	5.22	BiO	5.83	ZrO <sub>2</sub>	6.24	GeO <sub>2</sub>	6.63	NO	7.35
YO	5.22	Tl <sub>2</sub> O <sub>3</sub>	5.84	VO <sub>2</sub>	6.26	ReO <sub>3</sub>	6.66	N <sub>2</sub> O <sub>3</sub>	7.39
LaO	5.30	MoO	5.85	CrO <sub>2</sub>	6.32	As <sub>4</sub> O <sub>6</sub>	6.70	NO <sub>2</sub>	7.41
AlO	5.39	SnO	5.86	HgO	6.33	MoO <sub>3</sub>	6.70	N <sub>2</sub> O <sub>5</sub>	7.43
MnO	5.44	PbO	5.88	Au <sub>2</sub> O	6.35	WO <sub>3</sub>	6.72	Br <sub>2</sub> O <sub>5</sub>	7.56
Ag <sub>2</sub> O	5.47	WO	5.89	NbO <sub>2</sub>	6.36	Re <sub>2</sub> O <sub>7</sub>	6.75	Cl <sub>2</sub> O <sub>7</sub>	7.71
HfO	5.49	FeO	5.89	ReO <sub>2</sub>	6.36	RuO <sub>3</sub>	6.76	Cl <sub>2</sub> O <sub>5</sub>	7.76
Cu <sub>2</sub> O	5.50	Hg <sub>2</sub> O	5.93	TaO <sub>2</sub>	6.37	P <sub>4</sub> O <sub>6</sub>	6.82	Cl <sub>2</sub> O	8.05
TiO	5.58	CdO	5.95	MoO <sub>2</sub>	6.41	TeO <sub>2</sub>	6.85		

**Table 2. Standard Formation and Atomization Enthalpies of Anion-Forming Oxides**

Molecule	$-\Delta_f H^\circ(298)$ kJ / mole	$\Delta_{at} H^\circ(298)$ kJ / mole	Ref.	Molecule	$-\Delta_f H^\circ(298)$ kJ / mole	$\Delta_{at} H^\circ(298)$ kJ / mole	Ref.
BO	-9.9	804.4	[153]	TaO <sub>2</sub>	173.7	1454.6	[153]
B <sub>2</sub> O <sub>3</sub>	835.4	2713.2	[153]	VO <sub>2</sub>	232.6	1248.3	[153]
CO	110.5	1076.4	[153]	NbO	-211.0	761.3	[153]
CO <sub>2</sub>	393.5	1608.6	[153]	NbO <sub>2</sub>	201.2	1422.7	[153]
SiO	98.8	798.1	[153]	Nb <sub>2</sub> O <sub>5</sub>	1252.0±59	3913.0±59	[163]
SiO <sub>2</sub>	322.1	1270.5	[153]	Nb <sub>4</sub> O <sub>10</sub>	3281±71	8665±73	[158]
GeO	37.7	655.9	[153]	CrO	-186.2	460.1	[153]
N <sub>2</sub> O <sub>3</sub>	-86.6	1606.4	[153]	CrO <sub>2</sub>	108.0	1003.5	[153]
N <sub>2</sub> O <sub>5</sub>	-13.3	2178.1	[153]	CrO <sub>3</sub>	322.0	1467.0	[153]
PO	28.0	593.6	[153]	Cr <sub>2</sub> O <sub>3</sub>	327±25	1869±26	[159]
PO <sub>2</sub>	281.5	1096.3	[153]	MoO <sub>2</sub>	15.6	1171.6	[153]
P <sub>2</sub> O <sub>3</sub>	684.6	2065.0	[153]	MoO <sub>3</sub>	364.4	1769.6	[153]
P <sub>2</sub> O <sub>5</sub>	1124.4	3003.3	[153]	Mo <sub>2</sub> O <sub>6</sub>	2792.8	2810.4	[153]
As <sub>4</sub> O <sub>6</sub>	1196.7	3295.5	[154]	WO <sub>2</sub>	-29.1	1320.5	[153]
SbO	-18.7	396.0	[155]	WO <sub>3</sub>	1910.2	1918.5	[153]
Sb <sub>4</sub> O <sub>6</sub>	1216.9	3784.5	[154]	W <sub>2</sub> O <sub>6</sub>	4380.8	4408.0	[153]
Bi <sub>2</sub> O <sub>3</sub>	241.9	1407.9	[154]	ReO <sub>3</sub>	284.5±20.9	1808±22	[160]
SO <sub>3</sub>	395.9	1420.5	[153]	Re <sub>2</sub> O <sub>7</sub>	1121±2	4416.8±2.0	[160]
SeO <sub>2</sub>	129.4±4.2	850.6±4.2	[156]	FeO	-271.0	393.2	[161]
SeO <sub>3</sub>	92.0±4.2	1063.0±4.2	[156]	NiO	-303.3	373.9	[161]
TeO <sub>2</sub>	63.1	767.8	[157]	CoO	-285.5	389.3	[161]
TiO	-50.2	672.7	[153]	MnO	-161.7	371.1	[161]

Table 2. contd....

Molecule	$-\Delta_f H^0(298)$ kJ / mole	$\Delta_{at} H^0(298)$ kJ / mole	Ref.	Molecule	$-\Delta_f H^0(298)$ kJ / mole	$\Delta_{at} H^0(298)$ kJ / mole	Ref.
TiO <sub>2</sub>	322.8	1294.9	[153]	BeO	-133.9	439.3	[153]
VO	-148.6	617.9	[153]	RuO <sub>3</sub>	78.2	1476.8	[163]
TaO	-242.5	789.2	[153]				

Table 3. Standard Formation and Atomization Enthalpies of Gaseous Salt Present in Vapor Above Oxide Systems and Detected Experimentally

Salt	$-\Delta_f H^0(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^0(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^0(298)$ kJ/mole	Ref.
LiNO <sub>2</sub>	202.0±10.0	[153]	Cs <sub>3</sub> P <sub>3</sub> O <sub>9</sub>	3353±15	[243]	BPO <sub>3</sub>	734±7	[171]
LiNO <sub>3</sub>	311.6±10.0	[153]	Cs <sub>2</sub> Re <sub>2</sub> O <sub>8</sub>	1946±11	[244]	BPO <sub>4</sub>	1008±5	[171]
LiBO <sub>2</sub>	677.7±12.8	[153]	Cs <sub>2</sub> I <sub>2</sub> O <sub>6</sub>	887±20	[242]	BWO <sub>4</sub>	1051±29	[151]
LiPO <sub>3</sub>	879.2±11.4	[151]	BeBO <sub>2</sub>	482	[162]	AlBO <sub>2</sub>	541±17	[162]
LiReO <sub>4</sub>	798±20	[174]	BePO <sub>2</sub>	433±21	[169]	GaPO <sub>2</sub>	373±36	[212]
LiCrO <sub>2</sub>	342.7±4.2	[175]	BePO <sub>3</sub>	777±22	[169]	GaPO <sub>3</sub>	661±35	[212]
LiVO <sub>3</sub>	704±30	[176]	BeMoO <sub>3</sub>	432.4±3.1	[194]	Ga <sub>2</sub> MoO <sub>4</sub>	827±26	[240]
LiMoO <sub>3</sub>	589.1±15.1	[175]	BeTiO <sub>3</sub>	763±22	[195]	Ga <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub>	1578±32	[240]
Li <sub>2</sub> SO <sub>4</sub>	1048.0±6.0	[177]	BeWO <sub>3</sub>	424.1±3.7	[194]	Ga <sub>2</sub> WO <sub>4</sub>	843±26	[240]
Li <sub>2</sub> CrO <sub>4</sub>	1026±20	[178]	BeNbO <sub>3</sub>	658±4	[196]	Ga <sub>2</sub> W <sub>2</sub> O <sub>7</sub>	1525±34	[240]
Li <sub>2</sub> MoO <sub>4</sub>	1051±30	[151]	BeTaO <sub>3</sub>	596±25	[197]	InPO <sub>2</sub>	491±30	[213]
Li <sub>2</sub> WO <sub>4</sub>	1048±30	[151]	BeWO <sub>4</sub>	794.9±5.2	[194]	InPO <sub>3</sub>	717±25	[213]
Li <sub>2</sub> SiO <sub>3</sub>	1177±8	[175]	BeB <sub>2</sub> O <sub>4</sub>	1358±21	[162]	InBO <sub>2</sub>	520±24	[151]
Li <sub>2</sub> P <sub>2</sub> O <sub>6</sub>	2072±15	[243]	Be <sub>2</sub> WO <sub>4</sub>	973.4±6.7	[194]	In <sub>2</sub> MoO <sub>4</sub>	863±30	[214]
Li <sub>3</sub> P <sub>3</sub> O <sub>9</sub>	3331±31	[243]	MgBO <sub>2</sub>	589±10	[198, 241]	TlNO <sub>3</sub>	103	[215]
Li <sub>2</sub> Re <sub>2</sub> O <sub>8</sub>	1869±24	[244]	MgB <sub>2</sub> O <sub>4</sub>	1458±22	[241]	TlPO <sub>3</sub>	737±28	[216]
NaBiO <sub>2</sub>	359±11	[179]	MgMoO <sub>3</sub>	467±23	[199]	TlBO <sub>2</sub>	557	[151]
NaNO <sub>2</sub>	166.3±8.0	[153]	MgMoO <sub>4</sub>	803±22	[199]	TlReO <sub>4</sub>	675±67	[217]
NaNO <sub>3</sub>	285.5±5.0	[153]	MgWO <sub>3</sub>	435±22	[199]	Tl <sub>2</sub> MoO <sub>4</sub>	817	[214]
NaBO <sub>2</sub>	662.3±12.8	[153]	MgWO <sub>4</sub>	773±22	[199]	Tl <sub>2</sub> WO <sub>4</sub>	873	[214]
NaPO <sub>2</sub>	568±24	[180]	MgPO <sub>2</sub>	429±12	[199]	GePO <sub>3</sub>	676.3±5.7	[218]
NaPO <sub>3</sub>	879.0±11.4	[151]	MgPO <sub>3</sub>	712±11	[199]	GeMoO <sub>4</sub>	765±4	[219]
NaReO <sub>4</sub>	827±15	[174]	CaPO <sub>2</sub>	428±6	[200]	GeWO <sub>4</sub>	759.8±8.4	[167]
NaAsO <sub>2</sub>	295±20	[181]	CaVO <sub>2</sub>	285	[201]	GeW <sub>2</sub> O <sub>7</sub>	1530.5±16.7	[167]
NaSbO <sub>2</sub>	233.9	[182]	CaBO <sub>2</sub>	527±15	[172]	GeNbO <sub>3</sub>	665±4	[166]
NaMoO <sub>3</sub>	624±16	[183]	CaVO <sub>3</sub>	729±15	[201]	GeMoO <sub>3</sub>	484±3	[166]
NaClO <sub>4</sub>	167	[184]	CaTiO <sub>3</sub>	826±26	[195]	GeWO <sub>3</sub>	411±4	[166]
Na <sub>2</sub> SO <sub>4</sub>	1024±6	[177]	CaMoO <sub>3</sub>	535±8	[202]	SnPO <sub>2</sub>	326.0±5.2	[220]
Na <sub>2</sub> CrO <sub>4</sub>	1003±20	[178]	CaWO <sub>3</sub>	540±8	[202]	SnPO <sub>3</sub>	611±11	[220]
Na <sub>2</sub> MoO <sub>4</sub>	1071±10	[151]	CaNbO <sub>3</sub>	682±4	[196]	SnWO <sub>4</sub>	778±71	[221]
Na <sub>2</sub> WO <sub>4</sub>	1142±10	[151]	CaTaO <sub>3</sub>	739±30	[197]	SnW <sub>2</sub> O <sub>7</sub>	1571±105	[221]
Na <sub>2</sub> Re <sub>2</sub> O <sub>8</sub>	1852±9	[244]	CaMoO <sub>4</sub>	859±18	[202]	Sn <sub>2</sub> WO <sub>5</sub>	1084±126	[221]
KBiO <sub>2</sub>	359±20	[185]	CaWO <sub>4</sub>	906±10	[202]	SnMoO <sub>4</sub>	670±40	[239]
KNO <sub>2</sub>	192.5±5.1	[153]	CaB <sub>2</sub> O <sub>4</sub>	1427±18	[172]	Sn <sub>2</sub> MoO <sub>5</sub>	929±42	[239]
KNO <sub>3</sub>	315.8±5.0	[153]	CaRe <sub>2</sub> O <sub>8</sub>	1644±50	[203]	PbBO <sub>2</sub>	360±20	[222]
KBO <sub>2</sub>	666.8±8.8	[153]	CaCrO <sub>2</sub>	215±22	[204]	PbPO <sub>3</sub>	617	[223]
KPO <sub>2</sub>	600±24	[180]	CaCrO <sub>3</sub>	543±25	[204]	PbMoO <sub>4</sub>	701	[224]

Table 3. contd....

Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.
KPO <sub>3</sub>	916±10	[151]	CaCoO <sub>2</sub>	149±19	[205]	PbWO <sub>4</sub>	736	[224]
KReO <sub>4</sub>	892±15	[174]	CaBeO <sub>2</sub>	415±24	[169]	PbV <sub>2</sub> O <sub>6</sub>	1477±45	[225]
KSbO <sub>2</sub>	269	[182]	CaSiO <sub>2</sub>	475±20	[238]	BiPO <sub>3</sub>	544	[223]
KClO <sub>4</sub>	216	[184]	CaSiO <sub>3</sub>	715±24	[238]	VPO <sub>3</sub>	655±19	[226]
KIO <sub>3</sub>	306±11	[242]	SrPO <sub>2</sub>	475±7	[200]	VPO <sub>2</sub>	318±11	[226]
K <sub>2</sub> FeO <sub>2</sub>	598	[186]	SrVO <sub>2</sub>	344	[201]	CrMoO <sub>4</sub>	632.2±13.0	[209]
K <sub>2</sub> SeO <sub>3</sub>	659±9	[187]	SrBO <sub>2</sub>	571.0±4.1	[172]	CrMoO <sub>3</sub>	286.1±14.2	[209]
K <sub>2</sub> SeO <sub>4</sub>	855.3±5.6	[187]	SrMoO <sub>3</sub>	577±3	[202]	CrMoO <sub>5</sub>	965±23	[209]
K <sub>2</sub> VO <sub>3</sub>	853	[188]	SrVO <sub>3</sub>	801	[201]	CrWO <sub>4</sub>	645.3±9.0	[209]
K <sub>2</sub> SO <sub>4</sub>	1075.8±6.0	[177]	SrTiO <sub>3</sub>	868±27	[195]	CrWO <sub>3</sub>	265.1±5.2	[209]
K <sub>2</sub> CrO <sub>4</sub>	1058±20	[178]	SrWO <sub>3</sub>	584±4	[202]	CrWO <sub>5</sub>	966±23	[209]
K <sub>2</sub> MoO <sub>4</sub>	1134±21	[151]	SrNbO <sub>3</sub>	741±3	[196]	CrNbO <sub>3</sub>	509.2±10.5	[209]
K <sub>2</sub> WO <sub>4</sub>	1174±21	[151]	SrTaO <sub>3</sub>	770±30	[197]	CrTaO <sub>3</sub>	492.9±4.3	[209]
K <sub>2</sub> CO <sub>3</sub>	811.6	[153]	SrMoO <sub>4</sub>	912±4	[202]	CrPO <sub>3</sub>	598.9±8.2	[208]
K <sub>2</sub> P <sub>2</sub> O <sub>6</sub>	2102±12	[243]	SrWO <sub>4</sub>	962±9	[202]	CrPO <sub>2</sub>	275.2±9.1	[208]
K <sub>3</sub> P <sub>3</sub> O <sub>9</sub>	3245±20	[243]	SrB <sub>2</sub> O <sub>4</sub>	1425±18	[172]	MnTiO <sub>3</sub>	662±21	[140]
K <sub>2</sub> Re <sub>2</sub> O <sub>8</sub>	1951±9	[244]	SrRe <sub>2</sub> O <sub>8</sub>	1624±50	[203]	MnB <sub>2</sub> O <sub>4</sub>	1132±24	[140]
K <sub>2</sub> I <sub>2</sub> O <sub>6</sub>	825±13	[242]	SrCrO <sub>2</sub>	235±17	[204]	MnPO <sub>3</sub>	602±15	[140]
RbBiO <sub>2</sub>	387±13	[185]	SrCrO <sub>3</sub>	566±23	[204]	MnPO <sub>2</sub>	299±12	[140]
RbNO <sub>2</sub>	187.6±11.0	[153]	SrCoO <sub>2</sub>	149±20	[205]	MnMoO <sub>4</sub>	654.5±9.2	[140]
RbNO <sub>3</sub>	315.0±8.0	[153]	SrFeO <sub>2</sub>	165.3±5.9	[206]	MnMoO <sub>3</sub>	342.7±8.2	[140]
RbBO <sub>2</sub>	698.5±3.8	[153]	SrBeO <sub>2</sub>	436±24	[169]	MnWO <sub>4</sub>	634.9±12.6	[140]
RbPO <sub>3</sub>	942.8±8.1	[151]	SrSiO <sub>2</sub>	474±18	[207]	MnWO <sub>3</sub>	289.1±9.8	[140]
RbReO <sub>4</sub>	930±15	[174]	SrSiO <sub>3</sub>	841±20	[207]	MnNbO <sub>2</sub>	105±17	[140]
RbSbO <sub>2</sub>	306	[182]	BaPO <sub>2</sub>	504±6	[208]	MnNbO <sub>3</sub>	551±17	[140]
RbClO <sub>4</sub>	221.8	[184]	BaPO <sub>3</sub>	823±4	[208]	FeMoO <sub>4</sub>	559.5±7.3	[206]
RbVO <sub>3</sub>	755.4	[189]	BaVO <sub>2</sub>	398±15	[201]	FeWO <sub>4</sub>	543.3±7.7	[206]
RbIO <sub>3</sub>	313±13	[242]	BaGeO <sub>2</sub>	415.0	[168]	FePO <sub>3</sub>	470.1±7.0	[206]
Rb <sub>2</sub> SeO <sub>4</sub>	865.1±9.9	[187]	BaNbO <sub>2</sub>	306±7	[196]	FePO <sub>2</sub>	172.7±6.9	[206]
Rb <sub>2</sub> SO <sub>4</sub>	1096.6±6.0	[177]	BaTaO <sub>2</sub>	344±23	[197]	CoMoO <sub>4</sub>	519±8	[205]
Rb <sub>2</sub> CrO <sub>4</sub>	1074±20	[178]	BaBO <sub>2</sub>	594±5	[173]	CoWO <sub>4</sub>	477±17	[205]
Rb <sub>2</sub> MoO <sub>4</sub>	1147±12	[190]	BaMoO <sub>3</sub>	647±13	[202]	CoWO <sub>3</sub>	123.7	[205]
Rb <sub>2</sub> WO <sub>4</sub>	1225±14	[190]	BaVO <sub>3</sub>	867±10	[201]	CoPO <sub>3</sub>	404.7±5	[205]
Rb <sub>2</sub> Re <sub>2</sub> O <sub>8</sub>	1972±9	[244]	BaTiO <sub>3</sub>	886±22	[195]	CoPO <sub>2</sub>	123±7	[205]
Rb <sub>2</sub> I <sub>2</sub> O <sub>6</sub>	846±12	[242]	BaNbO <sub>3</sub>	784.4±20	[196]	NiMoO <sub>4</sub>	432±19	[210]
CsBiO <sub>2</sub>	417±14	[179]	BaWO <sub>3</sub>	659±13	[202]	NiWO <sub>4</sub>	479±17	[210]
CsNO <sub>2</sub>	210.3±10.0	[153]	BaTaO <sub>3</sub>	807±31	[197]	NiPO <sub>3</sub>	375±13	[210]
CsNO <sub>3</sub>	304.4±8.0	[153]	BaMoO <sub>4</sub>	985±11	[202]	NiPO <sub>2</sub>	86±10	[210]
CsBO <sub>2</sub>	739.7±3.7	[153]	BaWO <sub>4</sub>	1025±13	[202]	ZnPO <sub>3</sub>	468±15	[247]
CsPO <sub>3</sub>	958±13	[151]	BaB <sub>2</sub> O <sub>4</sub>	1424±28	[173]	EuCrO <sub>2</sub>	928±45	[227]
CsReO <sub>4</sub>	963±15	[174]	BaNb <sub>2</sub> O <sub>6</sub>	1868±24	[196]	EuPO <sub>2</sub>	506	[228]
CsSbO <sub>2</sub>	329	[182]	BaW <sub>2</sub> O <sub>7</sub>	1970	[202]	EuPO <sub>3</sub>	778	[228]
CsClO <sub>4</sub>	244	[184]	BaRe <sub>2</sub> O <sub>8</sub>	1630±50	[203]	EuNbO <sub>2</sub>	279	[229]
CsVO <sub>3</sub>	757.2	[189]	Ba <sub>2</sub> MoO <sub>5</sub>	1464±70	[202]	EuNbO <sub>3</sub>	756±33	[229]
CsIO <sub>3</sub>	351±8	[242]	Ba <sub>2</sub> Mo <sub>2</sub> O <sub>8</sub>	2393±90	[202]	EuNb <sub>2</sub> O <sub>6</sub>	1972±51	[229]

Table 3. contd...

Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.	Salt	$-\Delta_f H^\circ(298)$ kJ/mole	Ref.
Cs <sub>2</sub> SeO <sub>4</sub>	876±11	[187]	Ba <sub>2</sub> W <sub>2</sub> O <sub>8</sub>	2567±40	[246]	EuMoO <sub>3</sub>	594	[230]
Cs <sub>2</sub> SO <sub>4</sub>	1122.5±6.0	[177]	BaBeO <sub>2</sub>	485±21	[169]	EuMoO <sub>4</sub>	962	[230]
Cs <sub>2</sub> CrO <sub>4</sub>	1123±20	[178]	BaCrO <sub>2</sub>	305±16	[209]	EuWO <sub>3</sub>	625	[231]
Cs <sub>2</sub> TeO <sub>3</sub>	753.0	[191, 215]	BaCrO <sub>3</sub>	675±19	[209]	EuWO <sub>4</sub>	986	[231]
Cs <sub>2</sub> RuO <sub>4</sub>	714.9±5.5	[192]	BaFeO <sub>2</sub>	245.6±4.0	[206]	EuW <sub>2</sub> O <sub>7</sub>	1748	[231]
Cs <sub>2</sub> MoO <sub>4</sub>	1206±10	[151]	BaCoO <sub>2</sub>	250±16	[205]	EuTiO <sub>3</sub>	887	[232]
Cs <sub>2</sub> WO <sub>4</sub>	1234.1±7.8	[193]	BaNiO <sub>2</sub>	243±15	[210]	EuVO <sub>2</sub>	321	[233]
Cs <sub>2</sub> CO <sub>3</sub>	806±17	[153]	BaSiO <sub>2</sub>	510±15	[211]	EuVO <sub>3</sub>	762	[233]
Cs <sub>2</sub> P <sub>2</sub> O <sub>6</sub>	2185±8	[243]	BaSiO <sub>3</sub>	884±18	[211]	EuTaO <sub>3</sub>	765	[227]

Table 4. Coefficients *k* and *b* of Eq. (18)

M=	<i>m</i> (Number of Points)	<i>k</i>	<i>b</i>	M =	<i>m</i> (Number of points)	<i>k</i>	<i>b</i>
Li	1(6)	1.018±0.050	521.4±69.4	B	1(2)	1.110	1219.4
	2(4)	1.094±0.067	1106.4±111.4		Ga	1(2)	1.145
Na	1(7)	0.997±0.034	433.0±45.5	In		2(4)	0.963±0.028
	2(5)	1.165±0.102	914.5±160.6		Tl	1(3)	1.048±0.098
K	1(7)	1.073±0.034	404.3±44.7	Ge		1(4)	0.933±0.044
	2(8)	1.036±0.091	1107.8±122.5		Sn	1(4)	0.972±0.014
Rb	1(6)	1.086±0.033	403.6±45.2	Pb		1(4)	0.994±0.022
	2(5)	1.092±0.083	1033.3±129.5		Cr	1(5)	1.062±0.070
Cs	1(6)	1.095±0.025	410.7±34.4	Mn		1(8)	1.040±0.023
	2(7)	1.130±0.085	990.4±124.0		Fe	1(10)	0.996±0.014
Be	1(10)	1.036±0.019	981.0±28.3	Co		1(4)	1.055±0.010
Mg	1(8)	1.009±0.019	837.2±29.2		Ni	1(4)	1.051±0.007
Ca	1(17)	1.027±0.014	889.0±23.4	Eu		1(4)	1.031±0.025
Sr	1(20)	1.028±0.017	896.2±26.8			1(15)	1.032±0.017
Ba	1(27)	1.033±0.013	953.8±23.2				

forming oxides, i.e. they exhibit amphoteric properties. At present amphotericism is established for germanium oxide GeO whose germanium phosphate [164], molybdates [165, 166], niobate [166], and tungstates [166, 167] are known on the one hand, and barium germanate [168] on the other; beryllium oxide {beryllium phosphates, molybdates, and tungstates [169, 170] vs. alkaline-earth metal beryllates [169]; and also boron oxide B<sub>2</sub>O<sub>3</sub> {boron phosphates [171] vs. alkaline-earth metal metaborates [172, 173]}. Chromium(II), iron(II), cobalt(II), and nickel(II) oxides also have amphoteric properties [140].

The oxyacid salts detected in vapor to the present time and characterized from the thermodynamic viewpoint are listed in Table 3. To generalize and systematize the great body of odd and diverse experimental data, we have examined [151] and corrected published enthalpies of formation of gaseous salts, using the information on their structures and normal mode frequencies, both experimental

and calculated. Table 3 contains our recommended values for the formation and atomization enthalpies.

The experimental data obtained allowed us to deduce linear equations (18) for isocationic series of salts of main group I-IV elements and certain *d*-elements. The coefficients *k* and *b* of Eq. (18) are shown in Table 4.

Using Eq. (18), we estimated the enthalpies of atomization and formation of gaseous salts which have been detected in vapor but not characterized thermodynamically for some reasons, or are so far unknown, but, according to our calculated electronegativities of their forming oxides, should be stable in the gaseous state (Table 5). The necessary condition for such estimation is the availability of published enthalpy of formation of an anion-forming oxide. As new experimental data will be obtained, the coefficients *k* and *b* in Eq. (18), as well as the enthalpies of formation and atomization of salts may change.

**Table 5. Standard Formation and Atomization Enthalpies of Certain Gaseous Salts Estimated by Eq. (18)**

Salt	$\Delta_{at}H^0$ (298) kJ/mole	$\Delta_fH^0$ (298) kJ/mole	Salt	$\Delta_{at}H^0$ (298) kJ/mole	$\Delta_fH^0$ (298) kJ/mole	Salt	$\Delta_{at}H^0$ (298) kJ/mole	$\Delta_fH^0$ (298) kJ/mole
LiPO <sub>2</sub>	1572	598	BaCrO <sub>3</sub>	1996	672	CoB <sub>2</sub> O <sub>4</sub>	3593	1041
LiSbO <sub>2</sub>	1217	291	BaCrO <sub>2</sub>	1438	364	FeMoO <sub>3</sub>	2017	197
LiBiO <sub>2</sub>	1238	371	GaNO <sub>3</sub>	1525	33	FeWO <sub>3</sub>	2174	160
Li <sub>2</sub> VO <sub>3</sub>	2472	888	GaNO <sub>2</sub>	1198	-45	FeVO <sub>3</sub>	2098	418
Li <sub>2</sub> SeO <sub>3</sub>	2037	747	GaReO <sub>4</sub>	2807	762	FeTiO <sub>3</sub>	2147	510
Li <sub>2</sub> TeO <sub>3</sub>	1946	664	GaClO <sub>4</sub>	1570	180	FeNbO <sub>3</sub>	2282	396
Li <sub>2</sub> MoO <sub>3</sub>	2388	664	InNO <sub>3</sub>	1583	122	FeTaO <sub>3</sub>	2316	371
Li <sub>2</sub> WO <sub>3</sub>	2551	634	InNO <sub>2</sub>	1278	66	FeBO <sub>2</sub>	1630	152
Na <sub>2</sub> SeO <sub>3</sub>	1905	719	InReO <sub>4</sub>	2781	768	FeB <sub>2</sub> O <sub>4</sub>	3643	1101
Na <sub>2</sub> VO <sub>3</sub>	2369	889	InClO <sub>4</sub>	1626	268	CaFeO <sub>2</sub>	1283	192
Na <sub>2</sub> CO <sub>3</sub>	2788	1108	TiNO <sub>2</sub>	1200	48	NiMoO <sub>3</sub>	1935	102
Na <sub>2</sub> TeO <sub>3</sub>	1809	631	TIPO <sub>2</sub>	1414	348	NiWO <sub>3</sub>	2088	61
K <sub>2</sub> MoO <sub>3</sub>	2322	739	GeNbO <sub>3</sub>	2454	614	NiVO <sub>3</sub>	2014	321
K <sub>2</sub> WO <sub>3</sub>	2476	699	GeTaO <sub>3</sub>	2485	586	NiTiO <sub>3</sub>	2062	413
K <sub>2</sub> TeO <sub>3</sub>	1903	762	GeRe <sub>2</sub> O <sub>8</sub>	5365	1451	NiNbO <sub>3</sub>	2194	295
RbPO <sub>2</sub>	1525	629	SnNbO <sub>3</sub>	2394	622	NiTaO <sub>3</sub>	2227	269
Rb <sub>2</sub> SeO <sub>3</sub>	1973	840	SnTaO <sub>3</sub>	2431	600	NiBO <sub>2</sub>	1556	65
Rb <sub>2</sub> MoO <sub>3</sub>	2313	746	SnB <sub>2</sub> O <sub>4</sub>	3890	1462	NiB <sub>2</sub> O <sub>4</sub>	3524	969
Rb <sub>2</sub> VO <sub>3</sub>	2396	969	PbVO <sub>3</sub>	2037	577	CaNiO <sub>2</sub>	1263	159
Rb <sub>2</sub> TeO <sub>3</sub>	1872	747	PbMoO <sub>3</sub>	1956	356	SrNiO <sub>2</sub>	1288	201
CsPO <sub>2</sub>	1541	650	PbWO <sub>3</sub>	2114	320	CrBO <sub>2</sub>	1723	263
Cs <sub>2</sub> SeO <sub>3</sub>	1963	839	PbP <sub>2</sub> O <sub>6</sub>	3901	1578	CrB <sub>2</sub> O <sub>4</sub>	3708	1184
Cs <sub>2</sub> CO <sub>3</sub>	2808	1190	PbNbO <sub>3</sub>	2210	544	CrRe <sub>2</sub> O <sub>8</sub>	5480	2314
Cs <sub>2</sub> MoO <sub>3</sub>	2314	756	PbTaO <sub>3</sub>	2256	531	CrVO <sub>3</sub>	2184	522
Cs <sub>2</sub> WO <sub>3</sub>	2483	731	PbReO <sub>4</sub>	2631	663	CrTiO <sub>3</sub>	2233	615
Cs <sub>2</sub> VO <sub>3</sub>	2401	983	PbRe <sub>2</sub> O <sub>8</sub>	5402	1662	MnVO <sub>3</sub>	2096	548
MgWO <sub>3</sub>	2205	459	CoMoO <sub>3</sub>	1973	142	MnTaO <sub>3</sub>	2302	488
MgTiO <sub>3</sub>	2178	810	CoVO <sub>3</sub>	2053	363	MnBO <sub>2</sub>	1654	307
MgNbO <sub>3</sub>	2305	687	CoTiO <sub>3</sub>	2102	455	CaMnO <sub>2</sub>	1260	300
MgTaO <sub>3</sub>	2336	659	CoTaO <sub>3</sub>	2270	314	SrMnO <sub>2</sub>	1285	343
BaCrO <sub>4</sub>	2473	900	CoBO <sub>2</sub>	3593	98	BaMnO <sub>2</sub>	1345	343

Equation (18) can be also used for estimating unknown enthalpies of formation of anion-forming oxides from the enthalpies of atomization of salts formed by these oxides. For example, using the atomization enthalpy of gaseous sodium, potassium, rubidium, and cesium antimonites and the coefficients  $k$  and  $b$  of Eqs. (18) for salts of these metals, we estimated the enthalpies of atomization and formation of Sb<sub>2</sub>O<sub>3</sub> (gas) and V<sub>2</sub>O<sub>5</sub> (gas): 1367 and -92 and 3116 and -835 kJ mol<sup>-1</sup>, respectively [151].

There are not only monomeric but dimeric and even trimeric molecules in vapor above complex oxide systems at the various cases. The polymerization in the high temperature vapor is a unique phenomenon. The reason of

polymerization of gaseous oxyacid salts structure and molecular parameters of them are not known and thermodynamic functions of these species as rule are only estimated. The literature data analysis has shown that existence of polymeric salts is connected with the presence of dipole moment of monomers. By present time polymeric gaseous metaborates, phosphates, chlorates, perchlorates, perrhenates, bismuthates, iodates, nitrates and nitrites of alkali metals, potassium pertechnitate, copper perrhenate, lithium vanadate, thallium phosphate and metaborate are known. It was considered earlier that the relative abundance of polymer in vapor phase decreases from cesium to lithium salts. For example in vapor the dimer/monomer ratio above

perchlorates of alkali metals decreases from 0.73 (sodium perchlorate) to 0.04 (cesium perchlorate) [141]. The dimer was found in vapor over potassium pertechnetate but not over cesium pertechnetate [142]. Publications [143-150] are devoted to the problem of vaporization of alkali metals metaborates. The results of these publications indicate that there are monomeric, dimeric and even trimeric molecules in vapor. Reactions of polymerization and mixed dimerization of gaseous alkali metals metaborates were investigated and the standard formation enthalpies of polymeric molecules were estimated.

Gaseous alkali metals salts containing two metallic atoms and zero dipole moment do not polymerize. Sulphates, selenates, chromates, molybdates and tungstates belong to this group. The progress in quantum chemistry nowadays allows calculating not only structures of polymeric molecules but also thermodynamic functions. This fact gives the opportunity to convert the values of dimerization and trimerization reaction enthalpies to the standard temperature and to determine the values of standard formation enthalpies of gaseous polymers. Particularly reactions of dimerization of phosphates, perrhenates, iodates and antimonites of alkali metals were investigated by us. It was found that there is not the direct connection between the relative abundance of polymer in vapor and the dipole moment of monomer, i.e. the value of dipole moment can't be the only criterion of gaseous polymer's thermal stability. The size of cation- and anion-forming atoms and also the type of bonding (ionic or covalent) may be the additional criteria of thermal stability.

Structures of studied gaseous polymers are closed cycles of cation of alkali metal bonded with two oxygen atoms. These structures are similar with gaseous polymeric halides of alkali metals. Regardless of the nature of anion and its structure the cycle oxygen-metal-oxygen-nonmetal presents. These cycles may be as planar as distorted and distortion has maximum value for cesium salts. Interatomic distances in anion don't change practically while moving from monomer to dimer whereas cation-oxygen distances decrease. The ionic character of cation-oxygen bonding for dimeric molecules stays. The formation enthalpies of investigated gaseous polymers are shown in Table 3.

### REGULARITIES IN VAPORIZATION BEHAVIOR OF OXYACID SALTS

Systematic studies on vaporization of oxyacid salts and analysis of published data allowed a series of regularities to be revealed, which made possible correct predictions of the qualitative and, in part, quantitative compositions of the vapor over such salts [234]. The possibility of thermal dissociation or vaporization (sublimation) without decomposition or with partial decomposition was suggested to assess with account for the relative radial electronegativity and volatility of salt-forming oxides and positions of the cation- and anion-forming elements in the periodic table. Furthermore, vaporization conditions should also be taken into account.

If the oxide electronegativity ratio  $\chi_1/\chi_2$  is low, which is in case when the salt forming oxides much differ in electronegativity, the salt can vaporize (sublime) without decomposition. The probability of vaporization without

decomposition decreases as the  $\chi_1/\chi_2$  value approaches one. The most electronegative are the alkali metal oxides, and, therefore, the majority of alkali metal salts evaporate congruently without decomposition, or with partial dissociation.

The dependence of the stability of salts formed in vapor on the electronegativity of cation-forming oxides can be demonstrated on a series of examples. The electronegativity of oxides increases in the order  $\text{Cs}_2\text{O} < \text{Rb}_2\text{O} < \text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Li}_2\text{O}$ . The nitrates and nitrites of these metals (high electronegativity of anion-forming oxides) evaporate without decomposition. As the electronegativity of anion-forming oxides decreases, the thermal stability of alkali metal salts decreases. Cesium, rubidium, and potassium sulphates, molybdates, tungstates, chromates, antimonates, bismuthates, perrhenates, and perchlorates are basically thermally stable. Sodium and lithium salts are prone to thermal dissociation, but lithium salts are much less stable than sodium salts.

On passing from alkali to alkaline-earth metal oxides, the electronegativity of cation-forming oxides increases, and the thermal stability of salts of group IIA elements decreases, and, therefore, even salts of barium, which is the most electropositive element in this series, undergo thermal decomposition. Only calcium, strontium, and barium perrhenates, borates, molybdates, and tungstates evaporate partially. The existence of other gaseous salts of group IIA and IVA elements in the oxidation state +2 is more likely associated with interaction of dissociation products of condensed salts in vapor.

For condensed salts, the most characteristic oxidation state of group IIIA elements in cation-forming oxides is +3. The only exception are Tl(III) and Tl(I) salts which both are stable in the condensed state. In the gas phase, salts in which the element is present in the oxidation state +1 are more stable, except for boron whose B(III) salts are thermally stable ( $\text{BPO}_3$  and  $\text{BPO}_4$ , for example). When heated, salts of gallium, indium, and thallium in the oxidation state +3 undergo high temperature reduction-oxidation of the cation-forming oxide. Therewith, in condensed phase gallium and indium salts the metal oxidation state is preserved, and the vapor contains oxygen and gallium(I) and indium(I) salts. Thallium(III) salts lose oxygen and convert into Tl(I) salts already in the condensed phase, and at higher temperatures they evaporate practically without decomposition. The electronegativities of  $\text{M}_2\text{O}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$ ) are similar to those of alkali metal oxides, and, therefore, gaseous gallium(I), indium (I), and thallium(I) salts are rather stable, and the relative contents of dissociation products are low. The vapor over gallium and indium phosphates contents not more than 5 % of atomic metals. The thermal stability of aluminum salts is described below.

The oxidation state +4 in cation-forming oxides is characteristic for crystalline salts of silicon and germanium, for tin it is +4 and +2, and for lead, +2. Gaseous germanium, tin, and lead salts are thermally stable in the case of the oxidation state +2. Gaseous silicon salts are unknown. Germanium salts dissociate on heating, preserving the oxidation state of the cation-forming element in the condensed phase. Dissociation products and Ge(II) salts are

present in the vapor, their relative contents being insignificant, for example the content  $\text{GePO}_3$  in vapor does not exceed 2 mol.%, and that of  $\text{GeMoO}_4$ , 3%. Tin(IV) and lead(IV) salts detach oxygen on heating to transform in tin(II) and lead(II) salts, respectively, which in turn, pass in vapor with substantial dissociation. The relative content of salt in vapor passing from Ge to Pb increases (with the decrease of the electronegativity of the cation-forming oxide); for example, the content of  $\text{SnPO}_3$  in vapor is  $> 5\%$ , and that of  $\text{PbPO}_3 > 9\%$ .

The electronegativity ratio of salt-forming oxides is not an absolute criterion allowing precise prediction of the vaporization behavior of the crystalline salt. A no less relevant, though secondary, criterion of the probability of the existence an oxyacid salt in the vapor over condensed salt or a complicated oxide system is the relative volatility of the oxide forming this salt. In this case, the volatility is not a fugacity (the pressure required for a real system to exert the same effect as an ideal system) but the capacity of a substance to evaporate noticeably at some temperature. The volatility of an oxide is suggested to be measured by a temperature at which the vapor pressure of the oxide is 10 Pa (upper applicability limit of the Knudsen method) [151, 234]. The partial pressures of components of the vapor over oxides can be calculated using reference data [1, 153]. If salt-forming oxides much differ in volatility ("10 Pa" temperatures for gaseous oxide or its dissociation products differ by 400 and more degrees), the salt may undergo thermal dissociation even if the salt-forming oxides much differ in electronegativity. The more the oxides differ from each other in volatility, the lower probability of salt vaporization. Carbonates, sulfites, sulfates, zirconates, and metaborates of alkali metals can serve as examples. The electronegativity of the anion-forming oxides increases in the order  $\text{B}_2\text{O}_3 < \text{ZrO}_2 < \text{SO}_2 < \text{CO}_2 < \text{SO}_3$ . The volatility of these oxides decreases in the order  $\text{CO}_2$  (140 K)  $> \text{SO}_2$  (180 K)  $> \text{SO}_3$  (260 K)  $> \text{B}_2\text{O}_3$  (1470 K)  $> \text{ZrO}_2$  (2800 K). The volatilities of alkali metal oxides span the range 800-1200 K, except for  $\text{Li}_2\text{O}$  (1600 K). However, alkali metal metaborates evaporate without decomposition, whereas sulfites and zirconates completely dissociate, and in the vapor over sulfites,  $\text{SO}_2$  was identified and over zirconates, monatomic metal and oxygen, i.e. in all cases the condensed phase is enriched with a less volatile oxide. Carbon dioxide is more volatile than  $\text{SO}_2$ , but the  $\text{CO}_2$  electronegativity is higher than that of  $\text{SO}_2$ ; therefore, in the vapor over alkali metal carbonates  $\text{M}_2\text{XO}_3$  molecules were detected, and they are absent in the vapor over sulfites. The volatility of aluminum oxide is anomalously low in the series of group IIIA element oxides (2000 K), and, therefore, at present time only gaseous borate  $\text{AlBO}_2$  is known. Other aluminum salts completely dissociate, and  $\text{Al}_2\text{O}_3$  is accumulated in the condensed phase.

When estimating the qualitative and quantitative compositions of the vapor over a condensed salt, it is necessary to consider positions of the cation- and anion-forming element in the periodic table. This mainly concerns main group elements. The stability of higher oxidation states of elements decreases going down a group, and the stability of lower states increases. Therefore, salts formed by oxides of elements in higher oxidation states can undergo high temperature red-ox reactions on heating. In this case, the

cation- or anion-forming elements decrease their oxidation state. Liberation of molecular or atomic oxygen from salts is observed, for example, on heating of selenates, tellurates, antimonates, and bismuthates of alkali metals, in which the anion-forming oxide is in the highest oxidation state. These salts even in the condensed phase convert into selenites, tellurites, antimonites, and bismuthites, respectively, which evaporate at higher temperatures or undergo thermal dissociation. Cation-forming subgroup IIIA and IVA elements can reduce from the oxidation states +3 and +4 to +1 and +2, respectively. The temperature of high temperature reduction-oxidation generally decreases by going down in a group.

The vaporization behavior of salts of oxygen-containing acids is also affected by vaporization conditions. As a rule, vaporization studies are performed either in neutral (vaporization from platinum cells) or in reductive conditions (vaporization from molybdenum, tungsten, tantalum, and nickel cells). In neutral conditions, the oxidation state of salt-forming oxides either does not change or decreases due to high temperature reduction-oxidation. In reductive conditions, the oxidation state of oxides largely decreases. For example, on the vaporization of alkali metal phosphates from molybdenum, nickel, and tantalum cells the oxidation state of phosphorus decreases from +5 to +3, and in vapor, except for  $\text{MPO}_3$ , there are  $\text{MPO}_2$  molecules whose relative content depends on the reductive properties of cell material. We observed reduction of tin, boron, indium, and gallium phosphates in the case of the vaporization from a molybdenum cell. Our study on reactions of alkali and alkaline-earth metal phosphates with reductive metals [235] showed that the vapor composition largely depends on the nature of the reducing agent. Such a strong reducing agent as aluminum is able to reduce phosphates to elemental phosphorus, and a significant content of  $\text{P}_2$  was detected in the vapor.

Not less important is the choice of temperature range for study. The dissociation degree of barium metaborate is much dependent on temperature: at 1500 K it evaporates practically congruently, in the range 1550-1800 K dissociation products are also present in the vapor, and their relative contents increase with temperature. As mentioned above, temperature also affects reduction of cation- and anion-forming oxides, for example, the reduction degree of cesium and rubidium selenates to selenites depends on temperature.

The composition of the vapor over a salt can also depend on heating rate. When heated at a rate of about  $1 \text{ deg s}^{-1}$ , lead nitrate dissociates into solid  $\text{PbO}$  and gaseous  $\text{NO}_2$  and oxygen, whereas at the heating rate of  $1000 \text{ deg s}^{-1}$  it sublimates without decomposition [236].

Summing up the aforesaid, it is safe to state that only a combination of all the abovementioned listed criteria allow us to predict precisely the vaporization behavior of oxyacid salts.

## ION – MOLECULAR GASEOUS EQUILIBRIA

High temperature mass spectrometry is successfully applied not only for studying processes involving neutral gas particles, but also for determining equilibrium constants of

ion-molecular reactions. As a result, both the molecular and ionic compositions of the gas phase and also the enthalpies of formation of ions are determined. With the enthalpies of formation of positive ions one can calculate the ionization energies of the corresponding molecules and, for negative ions, electron affinities. High temperature mass spectrometry is especially efficient for molecules and radicals with a high electron affinity.

The interest in thermodynamic properties of charged particles is caused by a considerable practical significance of weakly ionized gases which take part in a great number of processes and technologies. The presence of a small amount of charged particles in vapor affects only slightly such properties as pressure, heat capacity, etc., but converts the gas from a dielectric to a conductor. The conductivity of a vapor is determined by the concentration of charged particles, which can be calculated when information on the properties of positive and negative ions is available.

Slow negative ions formed in the plasma of MHD generators decreases the conductivity of the plasma. In the case of thermo electron transducers, small electronegative additions lead to improved cathode and anode characteristics. The negatively charged ions  $\text{CO}_3^-$ ,  $\text{CO}_4^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  play an important role in the chemistry of the ionosphere *D*-layer. Sulfate anions formed on the combustion of fuel with sulfur admixtures give rise to a disastrous corrosion attack of gas turbines. To simulate the high temperature processes involving positively and negatively charged ions, it is necessary to know their energy characteristics.

The method of ion-molecular equilibrium has been considered in most details in [237]. When studying ion-molecule reactions, the equilibrium constants of exchange reactions, containing only ratios of partial pressures of ions, are measured. All the reactions can be classed under four types (19)-(22).



Reaction (19) involves electron transfer from molecule *A* to molecule *B*. The enthalpy of this reaction, reduced to standard temperature, gives the difference of the electron affinities of molecules *A* and *B*. Reaction (20) involves anion transfer. If the affinity of molecule *A* to anion *B* is known, the heat of the reaction allows determination of the affinity of molecule *C* to anion *B*. The equilibrium constants of reactions (19) and (20) are dimensionless, and for their determination one should measure the relative pressures of ions and molecules. In reaction (21), the electron transfer is accompanied by dissociation of the parent ion, the equilibrium constant becomes dimensional, and a pressure standard is required for its determination. Using the enthalpy of reaction (21), one can calculate the heat of formation of anion *B* if the heats of formation of *B*, *AC*, *A*, and *C* are known. In all three cases, measuring the reaction enthalpy makes it possible to find the enthalpy of formation of an

anion (*B*, *BC*), provided that the enthalpies of formation of the other reaction participants are known. To determine the equilibrium constant of heterolytic dissociation (22) in the gas phase, it is necessary to measure the absolute partial pressures of ions and neutral particles. Thus the enthalpy of formation of negative ions is obtained, as the enthalpies of formation of positive ions are generally known. The calculations of reaction heats from experimental equilibrium constants are carried out in the same way as for reactions involving no charged particles.

The concentration of charged particles formed in equilibrium vapor due to thermal processes is lower than the concentration of neutral particles by 4-5 orders of magnitude. Therewith, the probability of ion formation largely depends on physical properties of the inner surface of the reactor. The concentration of negative ions is largely lower than the concentration of positive ions and can be increased by elevating the temperature. This approach is not always reasonable, especially when one deals with thermally unstable ions. Various procedures for overcoming these impediments have been suggested [237]. Addition of alkali metal salts allows an ionized vapor to be generated in high-temperature systems, which does not contain ions in measurable amounts without salt additives.

The method of ion-molecular equilibrium has made possible a principally new approach to measuring the partial pressures of oxygen in the vapor over oxide systems [180]. The essence of this approach is reduced to measuring the intensity ratio of negative ions, provided that the equilibrium constant can be calculated from reference data. For example, the partial pressure of oxygen for equilibrium (23) can be calculated from Eq. (24), where *I* is the ion current intensity and *K*, equilibrium constant of reaction (24).



$$P(\text{O}_2) = I(\text{PO}_3^-)/K \cdot I(\text{PO}_2^-) \quad (24)$$

Table 6 lists the standard formation enthalpies of cations and anions of oxyacid salts, determined by the method of ion-molecular equilibrium. In many cases, in the vapors of oxygen-containing inorganic compounds, except for ions listed in Table 6, complex associates, such as  $\text{KBeMoOF}_7$ , were detected [248].

## CONCLUSION

In spite of the fact that a great deal of structural and thermochemical experimental and calculated data on gaseous salts is available, the subject is still not covered completely. Thermochemical characteristics of salts of subgroup IIIA and IVA elements in the oxidation states +1 and +2, respectively, are few in number. The low electronegativity of  $\text{Al}_2\text{O}$  points to a high probability of existence of gaseous Al(I) salts. The absence of reliable thermochemical data for copper, silver, gallium, indium, and thallium salts is connected with the absence of reliable data on the standard enthalpies of formation of crystalline salts. The complete absence of data for *f*-element salts is due to experimental difficulties.

The progress in quantum-chemical calculations opens up the possibility of systematic research on polymerization of

**Table 6. Formation Enthalpies of Cations and Anions of Oxyacid Salts [5, 7, 153, 237].**

Ion	$-\Delta_f H^0(0)$ kJ/mole	Ion	$-\Delta_f H^0(0)$ kJ/mole	Ion	$-\Delta_f H^0(0)$ kJ/mole	Ion	$-\Delta_f H^0(0)$ kJ/mole
KBO <sub>2</sub> <sup>+</sup>	357±12	HfO <sup>+</sup>	-803.8	CsSO <sub>4</sub> <sup>-</sup>	998±13	BO <sub>2</sub> <sup>-</sup>	709±16
CsBO <sub>2</sub> <sup>+</sup>	402±20	ScO <sup>+</sup>	-555.8	CrO <sub>3</sub> <sup>-</sup>	669.0	ReO <sub>4</sub> <sup>-</sup>	934±23
K <sub>3</sub> (BO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	1254±40	YO <sup>+</sup>	-535.7	CrO <sub>4</sub> <sup>-</sup>	783±11	Na <sub>2</sub> B <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1628±37
Cs <sub>3</sub> (BO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	1273±40	LaO <sup>+</sup>	-390.2	NaCrO <sub>4</sub> <sup>-</sup>	973±14	K <sub>2</sub> B <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1625±34
K <sub>3</sub> CO <sub>3</sub> <sup>+</sup>	538±15	ThO <sup>+</sup>	-570.9	KCrO <sub>4</sub> <sup>-</sup>	998±16	Na <sub>3</sub> S <sub>2</sub> O <sub>8</sub> <sup>-</sup>	2312±41
Cs <sub>3</sub> CO <sub>3</sub> <sup>+</sup>	601±15	ThO <sub>2</sub> <sup>+</sup>	-388.0	MoO <sub>3</sub> <sup>-</sup>	637±11	K <sub>3</sub> S <sub>2</sub> O <sub>8</sub> <sup>-</sup>	2377±40
K <sub>3</sub> SO <sub>4</sub> <sup>+</sup>	756±20	UO <sup>+</sup>	-576.6	MoO <sub>4</sub> <sup>-</sup>	800±11	K <sub>3</sub> Cr <sub>2</sub> O <sub>8</sub> <sup>-</sup>	2373±39
Cs <sub>3</sub> SO <sub>4</sub> <sup>+</sup>	841±20	UO <sub>2</sub> <sup>+</sup>	-48.8	NaMoO <sub>4</sub> <sup>-</sup>	1035±17	Cr <sub>2</sub> O <sub>6</sub> <sup>-</sup>	1444±63
Li <sub>2</sub> O <sup>+</sup>	-433.5	PuO <sup>+</sup>	-500.0	KMoO <sub>4</sub> <sup>-</sup>	1064±15	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> <sup>-</sup>	1820±55
Na <sub>2</sub> O <sup>+</sup>	-517.3	PuO <sub>2</sub> <sup>+</sup>	-489.0	CsMoO <sub>4</sub> <sup>-</sup>	1060±1	NaP <sub>2</sub> O <sub>6</sub> <sup>-</sup>	2060±37
K <sub>2</sub> O <sup>+</sup>	-366.6	SO <sub>3</sub> <sup>-</sup>	602±6	WO <sub>3</sub> <sup>-</sup>	695±11	NaP <sub>2</sub> O <sub>5</sub> <sup>-</sup>	1780±50
Cs <sub>2</sub> O <sup>+</sup>	-282.8	SO <sub>4</sub> <sup>-</sup>	743±9	WO <sub>4</sub> <sup>-</sup>	881±11	NaP <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1489±72
CaO <sup>+</sup>	-674.1	LiSO <sub>3</sub> <sup>-</sup>	904±34	NaWO <sub>4</sub> <sup>-</sup>	1139±15	K <sub>3</sub> CrSO <sub>8</sub> <sup>-</sup>	2383±57
SrO <sup>+</sup>	-597.7	LiSO <sub>4</sub> <sup>-</sup>	1041±12	KWO <sub>4</sub> <sup>-</sup>	1172±18	UO <sub>2</sub> <sup>-</sup>	566.2
BaO <sup>+</sup>	-541.5	NaSO <sub>4</sub> <sup>-</sup>	976±13	CsWO <sub>4</sub> <sup>-</sup>	1180±15	UO <sub>3</sub> <sup>-</sup>	1295.0
TiO <sup>+</sup>	-679.8	KSO <sub>4</sub> <sup>-</sup>	992±12	PO <sub>2</sub> <sup>-</sup>	645±18		
ZrO <sup>+</sup>	-714.8	RbSO <sub>4</sub> <sup>-</sup>	982±19	PO <sub>3</sub> <sup>-</sup>	943±16		

gaseous oxyacid salts. To reveal the regularities of polymerization and establish a quantitative criterion of its probability, one has to study the dependence of the polymerization degree of a salt on the dipole moment of the monomeric molecule, nature of the cation-forming element, and structure of the anion.

The authors believe that the systematized experimental results on the thermodynamics of gaseous oxyacid salts, the proposed criteria of the thermodynamic stability of gaseous oxyacid salts and also the method for estimating the standard enthalpies of formation of these salts will form a basis for development of a general theory of thermal stability of gaseous inorganic compounds.

### CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

### ACKNOWLEDGEMENT

Declared none.

### REFERENCES

- [1] E.K. Kazenas, and Yu.V. Tsvetkov, *Vaporization of oxides*, Nauka: Moscow, 1997.
- [2] M. Inghram, and J.Drowart, "Application of mass spectrometry in high temperature chemistry", In: *International Symposium on High Temperature Technology*, 1959.
- [3] J. Drowart, "Mass spectrometric studies of the vaporization of inorganic substances at high temperatures", In: *Condensation and Evaporation of Solids*, E. Rutner, P. Goldfinger, J.P. Hirth, Eds. Gordon & Breach: New York, 1964.
- [4] P.W. Gilles, "Ternary species at high temperatures", *Pure and Applied Chemistry*, pp. 543-546, May 1962.
- [5] G.A. Semenov, and V.L. Stolyarova, *Mass Spectrometric Study of the Vaporization of Oxide Systems*, Nauka: Leningrad, 1990.
- [6] K. Hilpert, "Chemistry of Inorganic Vapors". In: *Structure and bonding*. M. J. Clarke, Ed., Springer: Berlin, 1990.
- [7] V.L. Stolyarova, and G.A. Semenov, V.L. Stolyarova, and G.A. Semenov., *Mass Spectrometric Study of the Vaporization of Oxide Systems*, Chichester, J.Wiley: New York, 1994.
- [8] L.T. Aldrich "The evaporation products of barium oxide from various base metals and of strontium oxide from platinum", *Journal of Applied Physics*, vol. 22, pp. 1168-1174, September 1951.
- [9] J. Drowart, G. Exteen and G. Verhaegen, "Mass spectrometric determination of the dissociation energy of the molecules MgO, CaO, SrO and Sr<sub>2</sub>O", *Transactions of the Faraday Society*, vol. 60. no. 503. Pt. 11. pp. 1920-1933, 1965.
- [10] R. Colin, G.Verhaegen, and J. Drowart, "Mass-spectrometric study of the vaporization of tin oxides. dissociation energy of SnO", *Transactions of the Faraday Society*, vol. 61. no. 511. Pt. 7. pp. 1364. 1965.
- [11] W.A. Chupka, J. Berkowitz, and C.F. Giese "Vaporization of berillium oxide and its reaction with tungsten", *Journal of Chemical Physics*, vol. 30, pp. 827-834, March 1959.
- [12] R.P. Burns, G. De Maria, J. Drowart, and M.G. Inghram, "Mass spectrometric investigation of the vaporization In<sub>2</sub>O<sub>3</sub>", *Journal of Chemical Physics*, vol. 38, pp. 1035-1036, April 1963.
- [13] A. Büchler, G.L. Stauffer, W. Klemperer, and L. Wharton, "Determination of the geometry of lithium oxide, Li<sub>2</sub>O(g), by Electric Deflection" *Journal of Chemical Physics*, vol. 39, pp. 2299-2303, September 1963.
- [14] S. Kambayashi, and E.Kato, "A thermodynamic study of (magnesium oxide + silicon oxide) by mass spectrometry at 1973 K", *The Journal of Chemical Thermodynamics*, vol. 16, pp. 241-, March 1984.
- [15] K.N. Marushkin, A.S. Alikhanyan, J.N. Grinberg, B.T. Melekh, S.R. Shirokov, and V.I. Gorgoraki, "Vapor composition in the BaO – WO<sub>3</sub> system", *Russian Journal of Inorganic Chemistry*, vol. 32, pp. 3036-3042, December 1987.
- [16] G.A. Semenov, "About stability of the ternary oxide systems in the gas phase", In *Study of structure and energy properties of molecules*. Ivanovo, 1986.

- [17] G.A. Semenov, "Gaseous oxyacid salts. Formation enthalpies", In *Problems of modern chemistry of coordination compounds*. Leningrad. Issue 3. 1970.
- [18] E.K. Kazenas *Thermodynamics of Vaporization of the Binary oxides*, Nauka: Moscow, 2004.
- [19] S.I. Lopatin, "Stability of the gaseous oxyacid salts", *Russian Journal of Inorganic Chemistry*, vol. 69, pp. 1417-1420, September 1999.
- [20] R.S. Mulliken, "New electronegativity scale; together with data on valence states and on valence ionization potentials and electron affinities," *Journal of Chemical Physics*, vol. 2, pp. 782-793, May 1934.
- [21] V.N. Rondrat, Ed. *Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinities*, Handbook. Kondrat'ev V.N., Ed. Nauka: Moscow, 1974.
- [22] L.M. Viting, *High-Temperature Solution-Melts*, MGU: Moscow, 1991.
- [23] G. Ritzhaupt, and J. P. Devlin, "Infrared spectra of  $\text{tl}^+\text{no}_3^-$  ion pairs variably hydrated or ammoniated in an argon matrix", *The Journal of Physical Chemistry*, vol. 81, pp. 67-71, January 1977.
- [24] G. Ritzhaupt, and J.P. Devlin, "Infrared spectra of alkali metal perchlorate ion pairs", *Journal of Chemical Physics*, vol. 62, no. 5, pp. 1982-1986, May 1975.
- [25] J. Draeger, G. Ritzhaupt, J.P. Devlin, "Matrix spectra, force constants, and structures for  $\text{m}+\text{clo}_4^-$  and hydrated alkali metal perchlorates ion pairs", *Inorganic Chemistry*, vol. 18, pp. 1808-1811, July 1979.
- [26] G. Ritzhaupt, H.H. Richardson, and J.P. Devlin, "Coordination Geometries of Ion Pairs in the Vapors of Alkali Metal Chlorates", *High Temperature Science*, vol. 19, pp. 163-172, January 1985.
- [27] J.S. Francisko, and I.H. Williams, "Structural and spectral consequences of ion pairing. II. A theoretical study of  $\text{ClO}_3^- \text{Li}^+$  and  $\text{ClO}_3^- \text{Na}^+$ ", *Chemical Physics*, vol. 114, pp. 339-345, March 1987.
- [28] N.I. Tuseev, E.Z. Zazorin, and V.P. Spiridonov, "Determination of the molecular structure of the cesium nitrite by electron diffraction method" *Russian Journal of Inorganic Chemistry*, vol. 20, pp. 587-591, April 1979.
- [29] V.A. Kulikov, V.V. Ugarov, and N.G. Rambidi, "Structure of the  $\text{RbNO}_2$  and  $\text{CsNO}_2$  molecules", *Russian Journal of Inorganic Chemistry*, vol. 22, pp. 183-185, May 1981.
- [30] A.N. Khodchenkov, V.P. Spiridonov, and P.A. Akishin, "Electron diffraction study of the structure of lithium and sodium nitrates in the vapor", *Russian Journal of Inorganic Chemistry*, vol. 6, pp. 765-766, May 1965.
- [31] V.A. Kulikov, V.V. Ugarov, and N.G. Rambidi, "Structure of the  $\text{RbNO}_3$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 22, pp. 196-198, February 1981.
- [32] V.A. Kulikov, V.V. Ugarov, and N.G. Rambidi, "Structure of the  $\text{CsNO}_3$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 22, pp. 168-171, March 1981.
- [33] R.E. LaVilla, and S.H. Bauer, "The structure of gaseous copper (ii) nitrate as determined by electron diffraction" *Journal of the American Chemical Society*, vol. 85, pp. 3597-3600, July 1963.
- [34] A.A. Istchenko, E.Z. Zazorin, and V.P. Spiridonov, "Electron diffraction study of the structure of copper nitrate in the vapor," *Koordinatsionnaya Khimiya (Russia)*, vol. 2, pp. 1203-1207, September 1976.
- [35] A.A. Istchenko, "Electron Diffraction study of the structure of  $\text{TlNO}_3$  and  $\text{Cu(NO}_3)_2$  in the gas phase", *Canadian Science Dissertation Chemistry*, Moscow, 1976.
- [36] V.A. Kulikov, V.V. Ugarov, and N.G. Rambidi, "Structure of the  $\text{TlNO}_3$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 22, pp. 166-168, March 1981.
- [37] S. Shibata, and K. Iijima, "Molecular structure of gaseous copper nitrate as studied by electron diffraction", *The Journal of Molecular Structure*, vol. 117, pp. 45-50, January 1984.
- [38] K.P. Petrov, A.I. Kolesnikov, V.V. Ugarov, and N.G. Rambidi, "Electron diffraction study of the structure of gaseous metaphosphates molecules. I. Cesium metaphosphate", *Russian Journal of Inorganic Chemistry*, vol. 21, pp. 198-200, April 1980.
- [39] K.P. Petrov, V.V. Ugarov, and N.G. Rambidi, "Electron diffraction study of the structure of gaseous metaphosphates molecules. II. Sodium metaphosphate", *Russian Journal of Inorganic Chemistry*, vol. 22, pp. 158-159, April 1981.
- [40] G.V. Girichev, and N.I. Giricheva, "Structure of the potassium metaphosphate molecule", *Russian Journal of Inorganic Chemistry*, vol. 28, pp. 189-191, April 1987.
- [41] V.P. Spiridonov, "The study of the inorganic substances by the electron diffraction method and some regularity of its structures", Doctoral Science Dissertation Chemistry, Moscow, 1968.
- [42] V.V. Ugarov, "Electron diffraction study of the some oxyacids structures", Canadian Science Dissertation Chemistry, Moscow, 1973.
- [43] V.V. Ugarov, Ju.S. Ezhov, and N.G. Rambidi, "Molecular Structures of Inorganic compounds of low volatility. I. Salts of Oxygen acids of the Type  $\text{M}_2\text{XO}_4$ ", *The Journal of Molecular Structure*, vol. 25, pp. 357-367, March 1975.
- [44] V.A. Kulikov, V.V. Ugarov, and N.G. Rambidi, "Electron diffraction study of the  $\text{Cs}_2\text{SO}_4$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 23, pp. 184-186, January 1982.
- [45] K.P. Petrov, V.V. Ugarov, and N.G. Rambidi, "Electron diffraction study of the  $\text{Tl}_2\text{SO}_4$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 21, pp. 159-161, January 1980.
- [46] V.A. Kulikov, "Determination of molecular structure constants of the alkali metal salts in the high temperature vapor", Canadian Science Dissertation Chemistry, Moscow, 1982.
- [47] S.B. Lapshina, L.I. Ermolaeva, G.V. Girichev, and V.P. Spiridonov, "Electron diffraction study of the  $\text{HfClO}_4$  molecule in the gas phase", *Russian Journal of Inorganic Chemistry*, vol. 37, pp. 487-493, March 1996.
- [48] S.M. Tolmachev, and N.G. Rambidi, "Electron diffraction study of the  $\text{Tl}_2\text{MoO}_4$  molecules in the gas phase", *Russian Journal of Structural Chemistry*, vol. 13, pp. 3-6, January 1972.
- [49] S.M. Tolmachev, and N.G. Rambidi, "Electron diffraction study of the  $\text{Tl}_2\text{WO}_4$  molecules in the gas phase", *Russian Journal of Inorganic Chemistry*, vol. 12, pp. 203-206, February 1971.
- [50] V.M. Petrov, N.I. Giricheva, V.N. Petrova, and G.V. Girichev, "The study of structure of the  $\text{KNO}_3$  molecule by electron diffraction method", *Russian Journal of Inorganic Chemistry*, vol. 32, pp. 51-55, April 1991.
- [51] N.N. Roddatis, S.M. Tolmachev, V.V. Ugarov, and N.G. Rambidi, "About structure of the thallium perchlorate in the vapor", *Russian Journal of Structural Chemistry*, vol. 15, pp. 693-695, April 1974.
- [52] K.P. Petrov, V.V. Ugarov, and N.G. Rambidi, "Electron diffraction study of the  $\text{CsReO}_4$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 21, pp. 189-192, March 1980.
- [53] G.V. Girichev, N.I. Giricheva, E.A. Kuligin, and K.S. Krasnov, "Structure of the  $\text{Cs}_2\text{CrO}_4$  molecule", *Russian Journal of Inorganic Chemistry*, vol. 24, pp. 63-69, January 1983.
- [54] V.V. Ugarov, Yu.S. Ezhov, and N.G. Rambidi, "Electron diffraction study of the  $\text{Cs}_2\text{MoO}_4$  and  $\text{Cs}_2\text{WO}_4$  molecules", *Russian Journal of Inorganic Chemistry*, vol. 14, pp. 359-360, February 1973.
- [55] A.P. Sarvin, and Yu.S. Ezhov, "Electron diffraction study of the  $\text{Rb}_2\text{MoO}_4$  molecule," *Russian Journal of Inorganic Chemistry*, vol. 21, pp. 34-39, May 1980.
- [56] Yu.S. Ezhov, and A.P. Sarvin, "Electron diffraction study of the  $\text{Rb}_2\text{WO}_4$  molecule," *Russian Journal of Inorganic Chemistry*, vol. 21, pp. 40-45, May 1980.
- [57] K.P. Petrov, "Electron diffraction study of structure some salts and complex halogenaluminate molecules," *Canadian Science Dissertation Chemistry*, 1981.
- [58] S.A. Komarov, "Electron diffraction study of the rubidium, cesium, and thallium metaborates", Canadian Science Dissertation Chemistry, Moscow, 1979.
- [59] A.J. Barnes, Ed., *Matrix Isolation Spectroscopy*. D. Reidel Publ. Comp., Dordrecht: Holland. 1981.
- [60] R. Teghil, B. Janis, and L. Bencivenni, "Matrix-isolation ir studies on alkali metal  $\text{M}(\text{XO}_2)$  species. bonding and structure of  $\text{Li}(\text{CO}_2)$ ,  $\text{M}(\text{ClO}_2)$  and  $\text{M}(\text{BO}_2)$  molecules", *Inorganica Chimica Acta*, vol. 88, pp. 115-124, February 1984.
- [61] L. Bencivenni, H.M. Nagarathna, K.A. Gingerich, and R. Teghil, "Matrix-isolation studies on metal coordinated oxyanions. The shape of molecular  $\text{MClO}_4$ ,  $\text{MClO}_3$ ,  $\text{MReO}_4$ , and  $\text{EuWO}_4$  systems", *Journal of Chemical Physics*, vol. 81, pp. 3415-3423, August 1984.
- [62] I.R. Beattie, J.S. Ogden, and D.D. Price, "The Use  $^{18}\text{O}$  enrichment to determine the mode of co-ordination in  $\text{MXO}_3$  species via infrared frequency and intensity patterns: the shape of matrix-isolated  $\text{KNO}_3$ ", *Journal of the Chemical Society Dalton Transactions*, pp. 1460-1464, October 1979.
- [63] S.N. Jenny, and J.S. Ogden "Matrix-isolation Studies on Alkali-metal Phosphates. Part I. The Characterization of Molecular  $\text{NaPO}_3$ ", *Journal of the Chemical Society Dalton Transactions*, pp. 1465-1467, October 1979.

- [64] J.S.Ogden, and S.J. Williams "Matrix Isolation Studies on Alkali-metal Phosphites, Arsenites and Antimonites. The Characterization of Molecular  $\text{NaPO}_2$ ,  $\text{CsAsO}_2$  and  $\text{KSbO}_2$ ", *Journal of the Chemical Society Dalton Transactions*, pp. 825-831, April 1982.
- [65] L. Bencivenni, and K.A. Gingerich, "Matrix-isolation Study of the infrared spectra of alkali  $\text{MPO}_3$ ,  $\text{MNO}_3$  and  $\text{MPO}_2$  Molecules", *The Journal of Molecular Structure*, vol. 98, pp.195-200, March 1983.
- [66] R.M. Atkins, and K.A. Gingerich, "Matrix-isolation and Raman Studies of the Molecules  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ", *Chemical Physics Letter*, vol. 53, pp. 347-349, February 1978.
- [67] M. Spoliti, L. Bencivenni, S. Nunziante Cesaro, R. Teghil, and M. Maltese, "Infrared Spectra of Matrix-isolated Gaseous Ternary Oxides. Part VI. The infrared spectra of lithium, cesium and thallium sulfates and indium and thallium molybdates", *The Journal of Molecular Structure*, vol. 74, pp. 297-299, February 1981.
- [68] H.M. Nagarathna, L. Bencivenni, and K.A. Gingerich, "IR and Raman spectra of matrix isolated  $\text{Cs}_2\text{XO}_4$  (X = S, Cr, Mo, W) molecules. The use of the isotopic shifts and IR band intensity relationships in the evaluation of the bond angles in the  $\text{D}_{2h}$   $\text{Cs}_2\text{XO}_4$  molecules", *Journal of Chemical Physics*, vol. 81, pp. 591-598, February 1984.
- [69] L. Bencivenni, L. Vitalini-Sacconi, and M. Pelino, "Thermodynamic Functions of Gaseous Lithium, Sodium, Potassium, Rubidium and Caesium Sulfates", *Thermochemica Acta*, vol. 106, pp. 51-55, January 1986.
- [70] A.K. Brisdon, R.A. Gomme, and J.S. Ogden, "Matrix Isolation Studies of the Vaporization of Alkali Metal Oxoselenium Salts: Characterization of Molecular  $\text{M}_2\text{SeO}_4$ ,  $\text{M}_2\text{SeO}_3$ , and  $\text{MSeO}_2$ ", *The Journal of Physical Chemistry*, vol. 95, pp. 2927-2931, July 1991.
- [71] J.R. Beattie, and J.E. Parkinson, "Structural Studies of Matrix-isolated Alkali Metal Chlorates; an Example of Tridentate Coordination by the Chlorate Ion", *Journal of the Chemical Society Dalton Transactions*, pp. 1185-1188, June 1983.
- [72] N. Smyrl, and J.P. Devlin, "Vibrational spectra of matrix isolated alkali metal chlorate ion pairs", *Journal of Chemical Physics*, vol. 60, pp. 2540-2546, June 1974.
- [73] G. Ritzhaupt, H.H. Richardson, and J.P. Devlin, "Coordination geometries of ion pairs in the vapors of alkali metal chlorates", *High Temperature Science*, vol. 19, pp. 163-172, January 1985.
- [74] L. Bencivenni, H.M. Nagarathna, K.A. Gingerich, and R.Teghil, "Matrix-isolation studies on metal coordinated oxyanions. The shape of molecular  $\text{MClO}_4$ ,  $\text{MClO}_3$ ,  $\text{MReO}_4$ , and  $\text{EuWO}_4$  systems", *Journal of Chemical Physics*, vol. 81, pp. 3415-3423, August 1984.
- [75] K.R. Biggs, R.A. Gomme, J.T. Graham, and J.S. Ogden, "Characterization of Molecular Alkali Metal Iodates by Mass Spectrometry and Matrix Isolation IR Spectroscopy", *Journal of Physical Chemistry*, vol. 96, pp. 9738-9741, December 1992.
- [76] L. Bencivenni, H. Nagarathna, and K.A. Gingerich, "The use of  $^{18}\text{O}$  substitution in the characterization of  $\text{MReO}_4$  molecules", *Chemical Physics Letters*, vol. 99, pp. 258-261, March 1983.
- [77] L. Bencivenni, H. Nagarathna, D. Wilhite, and K.A. Gingerich, "Matrix-isolation of alkali-metal and thallium perhenate and dimerization of  $\text{MReO}_4$  species", *Inorganic Chemistry*, vol. 23, pp. 1279-1285, September 1984.
- [78] S.A. Arthers, I.R. Beattie, and R.A. Gomme, "Matrix-isolation studies of alkali metal perhenates: the shape and vibrational assignments of caesium perhenate", *Journal of the Chemical Society, Dalton Transactions*, pp. 1461-1464, July 1983.
- [79] I.R. Beattie, J.S.Ogden, and D.D. Price, "Matrix-isolation Studies on Molecular  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{MoO}_4$ , and  $\text{K}_2\text{WO}_4$ ", *Journal of the Chemical Society, Dalton Transactions*, pp. 505-510, April 1982.
- [80] L. Bencivenni, and K.A. Gingerich, "The infrared and raman spectra of matrix-isolated m-v-o systems. the characterization of  $\text{MVO}_3$  and  $\text{MVO}_2$  molecules", *Journal of Molecular Structure*, vol. 96, pp. 197-202, March 1983.
- [81] K.R. Biggs, R.A. Gomme, J.T. Graham, and J.S. Ogden, "Characterization of molecular alkali metal iodates by mass spectrometry and matrix isolation ir spectroscopy", *Journal of Physical Chemistry*, vol. 96, pp. 9738-9741, December 1992.
- [82] L. Bencivenni, H. Nagarathna, and K.A. Gingerich, "The use of  $^{18}\text{O}$  substitution in the characterization of  $\text{MReO}_4$  molecules. The IR spectrum of matrix-isolated  $\text{CsReO}_4$ ", *Chemical Physics Letters*, vol. 99, pp. 258-261, March 1983.
- [83] L. Bencivenni, H. Nagarathna, D. Wilhite, and K.A. Gingerich, "Matrix-isolation of alkali-metal and thallium perhenate and dimerization of  $\text{MReO}_4$  species", *Inorganic Chemistry*, vol. 23, pp. 1279-1285, September 1984.
- [84] S.A. Arthers, I.R. Beattie, and R.A. Gomme, "Matrix-isolation studies of alkali metal perhenates: the shape and vibrational assignments of caesium perhenate", *Journal of the Chemical Society Dalton Transactions*, pp. 1461-1464, July 1983.
- [85] L. Bencivenni, and K.A. Gingerich, "Infrared spectra of matrix-isolated gaseous ternary oxides  $\text{M}_2\text{XO}_4$ ", *Journal of Chemical Physics*, vol. 76, pp. 53-56, January 1982.
- [86] S.J. David, and B.S. Ault, "Oxide Salt Reaction in Matrix Isolation. Infrared Spectrum of the  $\text{Ti}_2^+\text{CO}_3^{2-}$  Triple Ion in Argon Matrices", *Journal of Physical Chemistry*, vol. 86, pp. 4618-4622, December 1982.
- [87] J.S. Ogden, and S.J. Williams, "Matrix isolation studies on  $\text{Cs}_2[\text{CO}_3]$ ,  $\text{Rb}_2[\text{CO}_3]$ , and  $\text{K}_2[\text{CO}_3]$ . The shape of molecular  $\text{K}_2[\text{CO}_3]$ ", *Journal of the Chemical Society Dalton Transactions*, pp. 456-462, February 1981.
- [88] S.J. David, and B.S. Ault, "Oxide Salt Reactions in Matrix Isolation: Infrared Spectra of the  $\text{Ti}_2^+\text{SO}_3^{2-}$  and  $\text{Ti}_2^+\text{S}_2\text{O}_5^{2-}$  Triple Ions", *Inorganic Chemistry*, vol. 23, pp. 1211-1215, September 1984.
- [89] G.V. Chertikhin, L.V. Serebrennikov, and V.F. Shenel'kov, "Formation of the aluminum carbonates in argon matrix", *In: Structure and Property of Molecules*, Ivanovo. Chem. Technol. Inst: Ivanovo 1988.
- [90] L. Bencivenni, L. D'Alessio, and F. Ramondo, "Vibrational Spectra and Structure of  $\text{M}(\text{CO}_2)$  and  $\text{M}_2(\text{CO}_2)$  Molecules", *Inorganica Chimica Acta*, vol. 121, pp.161-166, February 1986.
- [91] M.E. Jacox, and D.E. Milligan, "Matrix isolation study of the vibration spectrum and structure of  $\text{CO}_2^-$  in argon matrix", *Chemical Physics Letters*, vol. 28, pp. 163-, February 1974.
- [92] M.E. Jacox, and D.E. Milligan, "Study of the vibrational spectrum and structure of the  $\text{CO}_3^-$  radical anion", *Journal of Molecular Spectroscopy*, vol. 52, N 3, pp. 363-379, March 1974.
- [93] J.E. Bennett, B. Mile, and A. Thomas, "Electron Spin resonance Spectrum of the  $\text{CO}_2^-$  Radical Ion at 77  $^\circ\text{K}$ ", *Transactions of the Faraday Society*, vol. 61, no. 515, Pt. 11, pp. 2357-2364, November 1965.
- [94] M. Barbeschi, L. Bencivenni, and F. Ramondo, "IR Matrix Spectra of  $\text{CsNO}_2$ ,  $\text{RbNO}_2$ ,  $\text{KNO}_2$  and  $\text{NaNO}_2$ . The Structure of  $\text{CsNO}_2$ ", *Chemical Physics*, vol. 112, pp. 387-392, March 1987.
- [95] D.E. Milligan, and M.E. Jacox, "matrix-isolation study of the interaction of electrons and alkali metal atoms with various nitrogen oxides. Infrared Spectra of the Species  $\text{NO}^-$ ,  $\text{NO}_2^-$ , and  $\text{N}_2\text{O}_2^-$ ", *Journal of Chemical Physics*, vol. 55, pp. 3404-3418, July 1971.
- [96] A. Büchler, J.L. Stauffer, and W. Klemperer, "electric-deflection studies of the geometry of some molecules containing cesium", *Journal of Chemical Physics*, vol. 46, pp. 605-608, February 1967.
- [97] V.G. Solomonik, "Theoretical study of structure of the  $\text{LiNO}_2$  molecule", *In Structure and Property of Molecules*, Ivanovo. Chem. Technol. Inst: Ivanovo, 1988.
- [98] V.G. Solomonik, and S.P. Konovalov, "Ab initio study of powder field and vibration spectra of the  $\text{LiNO}_3$  molecule", *Russian Journal of Structural Chemistry*, vol. 24, pp. 10-16, May 1983.
- [99] S.P. Konovalov, and V.G. Solomonik, "Ab initio study of geometry, powder field and vibration spectra of the  $\text{LiBO}_2$  molecule", *Russian Journal of Structural Chemistry*, vol. 29, pp. 1655-1660, July 1984.
- [100] V.G. Zakrzhevskii, A.I. Boldyrev, and O.P. Charkin, "Theoretical study of structure and stability of the  $\text{LiPO}_3$ ", *Russian Journal of Structural Chemistry*, vol. 25, pp. 2614-2618, October 1980.
- [101] K.D. Sen, "On the geometry of  $\text{NaPO}_3$ ", *Journal of Chemical Physics*, vol. 75, pp. 1043-1044, February 1981.
- [102] S.P. Konovalov, and V.G. Solomonik, "Ab initio study of geometry  $\text{Li}_2\text{CO}_3$  molecule", *Russian Journal of Structural Chemistry*, vol. 24, pp. 163-164, February 1983.
- [103] S.P. Konovalov, and V.G. Solomonik, "Ab initio study of vibration spectra of the  $\text{Li}_2\text{CO}_3$  molecule", *Russian Journal of Structural Chemistry*, vol. 26, pp. 15-21, January 1985.
- [104] V.G. Solomonik, "Unempirical study of powder fields, vibrational spectra and structure of the inorganic molecules and ions", Doctor of Sciences Dissertation (Chemistry), Moscow, 1993.
- [105] D.O. Charkin, M.L. McKee, and O.P. Charkin, "Unempirical study of structure and stability of the carbonates, silicates, nitrates, phosphates, borates and aluminates  $\text{L}_2\text{AO}_3$  и  $\text{MAO}_3$  (L = Li, Na; M

- = Be, Mg; A = C, Si, N<sup>+</sup>, P<sup>+</sup>, B<sup>-</sup>, Al<sup>-</sup>”, *Russian Journal of Structural Chemistry*, vol. 43, pp. 1694-1709, October 1998.
- [106] V.V. Sliznev, and V.G. Solomonik, “Structure and vibration spectra of the M<sub>2</sub>SO<sub>4</sub> (M = Li, Na, K) molecules”, *Koordinatsionnaya Khimiya (Russia)*, vol. 22, pp. 699-705, September 1996.
- [107] V.G. Solomonik, A.V. Marenich, and V.V. Sliznev, “Unempirical study of structure and vibrational spectra of the alkali metal sulphites, and selenites”, *Koordinatsionnaya Khimiya (Rus)*, vol. 24, pp. 488-498, July 1998.
- [108] V.G. Solomonik, and A.V. Marenich, “Structure, powder fields and vibrational spectra of the alkali metal tellurites by *ab initio* calculations”, *Russian Journal of Structural Chemistry*, vol. 40, pp. 431-443, March 1999.
- [109] J.S. Francisko, and I.H. Williams, “Structural and spectral consequences of ion pairing. II. A theoretical study of ClO<sub>3</sub><sup>-</sup>Li<sup>+</sup> and ClO<sub>3</sub><sup>-</sup>Na<sup>+</sup>”, *Chemical Physics*, vol. 114, pp. 339-345, March 1987.
- [110] V.G. Solomonik, T.P. Pogrebnyaya, and V.V. Sliznev, “Unempirical study of powder fields, vibrational spectra and structure of the LiClO<sub>3</sub> molecule”, *Russian Journal of Structural Chemistry*, vol. 37, pp. 440-449, March 1996.
- [111] V.G. Solomonik, and T.P. Pogrebnyaya, “Unempirical study of structure, isomers, and vibrational spectra of the LiClO<sub>3</sub>, NaClO<sub>3</sub> и KClO<sub>3</sub> molecules”, *Russian Journal of Structural Chemistry*, vol. 39, pp. 35-45, January 1998.
- [112] V. Rossi, C. Sadum, L. Bencivenni, and R. Caminiti, “Ab initio HF-SCF studies of the equilibrium structures and vibrational spectra of the Be(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> molecules”, *Journal of Molecular Structure*, vol. 314, pp. 247-260, March 1994.
- [113] L. Rodrigues-Santiago, X. Solans-Monfort, M. Sodupe, and V. Branchadell, “Coordination of NO<sub>2</sub> to Cu and Mg in M(NO<sub>2</sub>)<sub>2</sub> Complexes. A Theoretical Study”, *Inorganic Chemistry*, vol. 37, pp. 4512-4517, September 1998.
- [114] F. Ramondo, L. Bencivenni, R. Caminiti, and C. Sadum, “Ab initio study on LiClO<sub>3</sub> and Li<sub>2</sub>SO<sub>4</sub> molecules: geometries and vibrational frequencies”, *Chemical Physics*, vol. 151, pp. 179-186, February 1991.
- [115] F. Ramondo, L. Bencivenni, R. Caminiti, and F. Grandinetti, “Coordination structures and vibrational frequencies of Li and Na metaphosphates and nitrates. Ab initio SCF study”, *Chemical Physics*, vol. 145, pp. 27-35, January 1990.
- [116] O.P. Charkin, “Problems of theoretical study of stability and structure of inorganic isomers”, *Russian Journal of Structural Chemistry*, vol. 24, pp. 87-98, February 1983.
- [117] O.P. Charkin, M.L. McKee, N.M. Klimenko, and P.R. Shloer, “Unempirical study of isomery in salt molecules LAB<sub>2</sub> with 18 and 20 valence electrons”, *Russian Journal of Inorganic Chemistry*, vol. 43, pp. 294-302, February 1998.
- [118] D.O. Charkin, M.L. McKee, and O.P. Charkin, “Unempirical study of structure and stability of the carbonates, silicates, nitrates, phosphates, borates and aluminates L<sub>2</sub>AO<sub>3</sub> and MAO<sub>3</sub> (L = Li, Na; M = Be, Mg; A = C, Si, N<sup>+</sup>, P<sup>+</sup>, B<sup>-</sup>, Al<sup>-</sup>)”, *Russian Journal of Inorganic Chemistry*, vol. 43, pp. 1694-1709, October 1998.
- [119] D.O. Charkin, “Unempirical study of ortho-meta isomery of beryllium and magnesium carbonates and silicates molecules”, *Koordinatsionnaya Khimiya (Rus)*, vol. 22, pp. 706-708, September 1996.
- [120] D.O. Charkin, M.L. McKee, K.J. Mardsen, and O.P. Charkin, “Unempirical study of ortho-meta isomery of beryllium and magnesium carbonates and silicates molecules”, *Russian Journal of Inorganic Chemistry*, vol. 42, pp. 1508-1522, September 1997.
- [121] O.P. Charkin, M.L. McKee, and P.R. Shloer, “Unempirical study of isomery in salt molecules LAB<sub>2</sub> with 16 valence electrons”, *Russian Journal of Inorganic Chemistry*, vol. 43, pp. 280-293, February 1998.
- [122] A.V. Marenich, and V.G. Solomonik, “Structure, powder fields and vibrational spectra of XO<sub>4</sub><sup>2-</sup> (X=S, Se, Te, Cr, Mo, W) ions: unempirical calculations by CISD+Q method. *Russian Journal of Inorganic Chemistry*, vol. 46, pp. 462-466, March 2001.
- [123] Nguen Minh Tho, “The structure and bonding of the lithium metaborate (LiBO<sub>2</sub>) molecule. An ab initio study”, *Journal of Molecular Structure (THEOCHEM)*, vol. 136, pp. 371-379, March 1986.
- [124] Y. Yoshioka, and K.D. Jordan, “Stabilities and structures of the Li-CO<sub>2</sub> and Na-CO<sub>2</sub>”, *Chemical Physics Letters*, vol. 84, pp. 370-374, February 1981.
- [125] R.D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides”, *Acta Crystallographica*, vol. 32 A, pp. 751-767, May 1976.
- [126] V.V. Ugarov, “Electron diffraction study of structure of the oxyacid salt and complex halogenide molecules”, *Russian Journal of Structural Chemistry*, vol. 31, pp. 22-28, Yuly 1990.
- [127] E. Clementi, H. Kistenmacher, and H. Popkie, “Study of electron structure of molecules. Interaction between a lithium atom and cyano”, *Journal of Chemical Physics*, vol. 58, pp. 2460-2466, June 1973.
- [128] N.G. Rambidi, “High temperature inorganic molecular species with polytopic bonds. I. Deccription in terms of potential energy surfaces”, *Journal Molecular Structure*, vol. 28, pp. 77-88, January 1975.
- [129] A.A. Dronin, and A.V. Gusarov, “Inside molecular motion and isomerization in the K<sub>2</sub>SO<sub>4</sub> molecule”, *Koordinatsionnaya Khimiya (Russia)*, pp. 1498-1502, October 1980.
- [130] A. Büchler, and E.P. Marram, “The vibrational spectrum of gaseous cesium metaborate”, *Journal Chemical Physics*, vol. 39, pp. 292-295, February 1963.
- [131] R.J.M. Konings, A.S. Booij, and E.H.P. Cordfunke, “The vibrational spectrum of gaseous cesium metaborate”, *Journal of Molecular Spectroscopy*, vol. 145, pp. 451-453, February 1991.
- [132] A.M. Shapovalov, V.F. Shevel’kov, and A.A. Maltsev, “On structure of gaseous alkali metal metaborates”, *Vestnik Moskovskogo University, Chemistry (Russia)*, vol. 16, pp. 153-154, February 1975.
- [133] A.M. Shapovalov, V.F. Shevel’kov, and A.A. Maltsev, “Infrared spectra of vapor over the indium and thallium metaborates”, *Russian Journal of Structural Chemistry*, vol. 14, pp. 560-561, March 1973.
- [134] A.M. Shapovalov, V.F. Shevel’kov, and A.A. Maltsev, “Infrared spectra of the vapor over CsNO<sub>2</sub>, CsNO<sub>3</sub>, and TlNO<sub>3</sub> molecules”, *Vestnik Moskovskogo University, Chemistry (Russia)*, vol. 14, pp. 151-154, February 1973.
- [135] V.F. Shevel’kov, and A.A. Maltsev, “Infrared spectra of vapor and structure of gallium, indium and thallium molybdates”, *Vestnik Moskovskogo University, Chemistry (Russia)*, vol. 9, pp. 100-101, June 1969.
- [136] K. Nakamono, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Chichester: Wiley, 1986.
- [137] M. Spoliti, V. Piacente, L. Bencivenni, D. Ferro, and N. Cesaro, “Infrared spectra of matrix-isolated gaseous ternary oxides. IV. IR spectra of Li, Na, K and Tl chromates and Li and Cs molybdates and tungstates”, *High Temperature Science*, vol. 12, pp. 215-228, February 1980.
- [138] V.G. Solomonik, and V.L. Bugaenko, “Powder fields and vibration spectra of the LiNC, LiBO<sub>2</sub> и LiNO<sub>2</sub> molecules”, *Russian Journal of Structural Chemistry*, vol. 31, pp. 17-23, March 1990.
- [139] F. Ramondo, L. Bencivenni, and C. Sadum, “Ab initio SCF study of the BO<sub>2</sub><sup>-</sup> ion and the NaBO<sub>2</sub> and HBO<sub>2</sub> molecules”, *Journal of Molecular Structure (THEOCHEM)*, vol. 209, pp. 101-109, January 1990.
- [140] S.M. Shugurov, “Thermodynamic properties of gaseous oxyacid salts based on the some 3-d elements oxides”, *Candidate Science, or PhD Thesis. Dissertation (Chemistry)*, Saint-Petersburg, 2005.
- [141] E.N. Nikolaev, K.V. Ovchinnikov, and G.A. Semenov, “Mass spectrometric study of vapor composition over alkali metal perchlorates”, *The Russian Journal of General Chemistry*, vol. 51, pp. 1710-1715, August 1981.
- [142] J.K. Gibson, “Mass Spectrometric Identification of Gaseous Potassium and Cesium Perchlorates and Bimetallic Technetium-Rhenium Oxide Dimers”, *Radiochem. Acta*, vol. 62, pp. 127-132, March 1993.
- [143] A. Büchler, and J.B. Berkowitz-Mattuck, “Gaseous Metaborates. I. Mass Spectrometric Study of the Vaporization of Lithium and Sodium Metaborates”, *Journal Chemistry Physics*, vol. 39, pp. 286-291, February 1963.
- [144] A.V. Gusarov, A.V. Makarov, and O.T. Nikitin, “Study of thermodynamic properties of dimmer molecules in vapor of alkali metal metaborates”, *Available from VINITI*, Cherkasy, 1976, no. 3722-3776.
- [145] M. Asano, T. Kou, and Y. Yasue, “Mass spectrometric study of vaporization of cesium-containing borosilicate glasses”, *Non-cryst. Solids*, vol. 92, pp. 245-260, February 1987.

- [146] M. Asano, T. Harada, and Y. Mizutani, "Vaporization of borosilicate glasses containing all the alkali metals", *Physical Chemistry Glass*, vol. 32, pp. 174-179, August 1991.
- [147] M. Asano, T. Harada, and Y. Mizutani, "Vaporization of glasses in the  $R_2O-Cs_2O-B_2O_3-SiO_2$  ( $R = Li, Na, K, \text{ and } Rb$ ) system", *The Journal of Materials Science*, vol. 26, pp. 399-406, March 1991.
- [148] M. Asano, Y. Kato, T. Harada, and Y. Mizutani, "Thermodynamic quantities for reactions of alkali metaborate monomer and dimer vapors", *Mass Spectroscopy*, vol. 40, pp. 9-15, February 1992.
- [149] M. Asano, and Y. Yasue, "Mass spectrometric study of the vaporization of sodium borosilicate glasses", *The Journal of Nuclear Materials*, vol. 138, pp. 65-72, January 1986.
- [150] Y. Yasue, M. Asano, and K. Kubo, "Thermodynamic quantities for reactions of rubidium metaborate monomer and dimer vapors", *Bulletin of the Institute of Atomic Energy. (Kyoto, Japan)*, vol. 66, pp. 40-45 January 1984.
- [151] S.I. Lopatin, "Thermodynamic properties of gaseous oxyacid salts", Doct. Sci. Dissertation (Chem.), Saint-Petersburg, 2001.
- [152] N.A. Landiya, *Calculation of high temperature heat capacities of inorganic substances from standard entropy*, Izd. Akad. Nauk. Gruze. SSR: Tbilisi, 1962.
- [153] V.P. Glushko, Ed., *Thermodynamic properties of individual substances*. Nuka: Moscow, 1978-1984. Vol's. 1-4.
- [154] E.K. Kazenas, and A.A. Petrov, "Mass spectrometric study of vaporization processes and dissociation of the phosphorus, arsenic, and bismuth oxides", Available from *VINITI*, Cherkasy, 1989, N 5527-B89.
- [155] G.A. Semenov, "Determination of formation enthalpy of the gaseous antimony monoxide by mass spectrometry method", *Russian Journal Physical Chemistry*, vol. 59, pp. 1520-1521, June 1985.
- [156] R.B. Dobrotin, A.V. Suvorov, and S.M. Gadzhiev, "Thermodynamics of gaseous selenium oxides and hydroxides", in *Problems of Modern Chemistry of Coordination Compounds*, vol. 2, Leningrad, 1968.
- [157] D.W. Muenov, J.W. Hastie, R. Hauge, R. Bautista, and J.L. Margrave "Vaporization, thermodynamics and structures of species in the tellurium + oxygen systems", *Transactions of the Faraday Society*, vol. 65, pp. 3210-3214, December 1969.
- [158] G. Balducci, G. Gigli, and M. Guido, "Determination of the atomization energies of the gaseous molecules  $Nb_2O_4$ ,  $Nb_2O_5$ ,  $Nb_4O_9$  and  $Nb_4O_{10}$ ", *Journal of Chemical Physics*, vol. 85, pp. 5955-5960, October 1986.
- [159] M.I. Milushin, I.I. Nazarenko, "Vapor composition over chromium oxide  $Cr_2O_3$ . Formation enthalpies of the  $Cr_2O$ ,  $Cr_2O_2$ , and  $Cr_2O_3$  molecules", In *XI All-Union Conference on Calorimetry and Chemical Thermodynamics*, pt. 2, 1986, pp. 120-121.
- [160] G.A. Semenov, E.N. Nikolaev, and K.V. Ovchinnikov, "Mass spectrometric study of bond energy determination in  $Re_2O_7$  molecule", *Russian Journal of General Chemistry*, vol. 45, pp. 65-68, January 1975.
- [161] Bank of Thermodynamic Vagnitudes IVTANTERMO, the electronic version.
- [162] JANAF Thermochemical Tables. 3-d ed. National Institute of Standards and Technology. U.S., 1985.
- [163] V.P. Glushko, Ed., *Thermodynamic constants of substances*. vol's 1-10, Moscow: 1965-1981.
- [164] S.I. Lopatin, and G.A. Semenov, "Vaporization processes of the silicon and germanium diphosphates", *Russian Journal of General Chemistry*, vol. 65, pp. 1060-1064, June 1995.
- [165] S.I. Lopatin, G.A. Semenov, and Pilyugina T.S. "Thermochemical study of the gaseous oxiaicid salts. III. Germanium molybdate  $GeMoO_4$ ", *Russian Journal of General Chemistry*, vol. 70, pp. 529-531, April 2000.
- [166] S.I. Lopatin, G.A. Semenov, and S.M. Shugurov, "Thermodynamic properties of gaseous  $GeNbO_3$ ,  $GeMoO_3$ , and  $GeWO_3$ ", *Vestn. S.-Peterb. Gos. University, Ser. 4*, no. 2, pp. 50-53, December 2003.
- [167] V. Plies, "Zur Thermochemie von gasförmigem  $GeWO_4$  und  $GeW_2O_7$ ", *Zeitschrift für anorganische and allgemeine Chemie*, vol. 484, pp. 165-172, January 1982.
- [168] G.A. Semenov, "Thermodynamic properties of the gaseous barium germinate from high temperature mass spectrometry", *Russian Journal of Physical Chemistry*, vol. 70, pp. 997-998, June 1996.
- [169] S.M. Shugurov, and S.I. Lopatin, "Thermochemical study of the gaseous oxiaicid salts. XX. Beryllium phosphates and alkali earth metal beryllates", *Russian Journal of General Chemistry*, vol. 76, pp. 910-914, June 2006.
- [170] S.I. Lopatin, and G.A. Semenov, "Thermochemical study of the gaseous oxiaicid salts. VIII. Beryllium molybdate and tungstate", *Russian Journal of General Chemistry*, vol. 71, pp. 1294-1298, August 2001.
- [171] S.I. Lopatin, and G.A. Semenov, "A mass spectrometric study of the vaporization of boron phosphate ( $BPO_4$ )", *Rapid Communication in Mass Spectrometry*, vol. 13, pp. 1398-1400, December 1999.
- [172] S.I. Lopatin, G.A. Semenov, V.I. Baranovskii, S.M. Shugurov, and V.V. Sizov, "Thermochemical study of the gaseous oxiaicid salts. IX. Calcium and strontium metaborates", *Russian Journal of General Chemistry*, vol. 71, pp. 1422-1426, September 2001.
- [173] S.I. Lopatin, G.A. Semenov, and S.M. Shugurov, "Thermochemical study of the gaseous oxiaicid salts. VI. Barium metaborates", *Russian Journal of General Chemistry*, vol. 71, pp. 68-73, January 2001.
- [174] G.A. Semenov, K.E. Frantseva, K.V. Ovchinnikov, and A.M. Starodubtsev, "Thermodynamic properties of the gaseous alkali metal perenatrs", *Vestn. S.-Peterb. Gos. University, Ser. 4*, issue 3, pp. 44-49, March 1988.
- [175] S.I. Lopatin, and G.A. Semenov, "Thermochemical study of the gaseous oxiaicid salts. IV. Lithium cromite, molybdate (V) and silicate", *Russian Journal of General Chemistry*, vol. 70, pp. 1233-1236, August 2000.
- [176] L.S. Kudin, and A.M. Pogrebnoi, "Mass spectrometric study of lithium-vanadium bronze vaporization", *Russian Journal of Physical Chemistry*, vol. 70, pp. 1758-1763, October 1996.
- [177] K.H. Lau, R.H. Lamoreaux, and D.L. Hildenbrand, "Studies of the Vaporization/Decomposition of Alkali Sulfates", *The Journal of The Electrochemical Society*, vol. 132, pp. 3041-3048, December 1985.
- [178] L.A. Kuligina, and G.A. Semenov, "Mass spectrometric determination of thermodynamic properties of the gaseous alkali metal chromates", *Vestn. S.-Peterb. Gos. University, Ser. 4*, vol. 18, pp. 39-45, Marth 1985.
- [179] S.I. Lopatin, G.A. Semenov, T.S. Pilyugina, and D.O. Kirsanov, "Mass spectrometric study of vaporization of the sodium and cesium bithmutites", *Russian Journal of General Chemistry*, vol. 69, pp. 1283-1287, August 1999.
- [180] O.M. Vovk, and E.B. Rudny, "Determination of oxygen pressure by ion-molecular equilibrium", Available from *VINITI*, Moscow, 1985. 8374-B85.
- [181] G.A. Semenov, O.V. Romanova, M.N. Zhambekov, and A.S. Isabaev, "Mass spectrometric study of some alkali metal arsenates", In *iii all-union conference on the chemistry and technology of chalcogens and chalcogenides*, 1986, p. 50.
- [182] G.A. Semenov, and L.N. Smirnova, "Mass spectrometric study of the gaseous alkali metal antimonites", *Doklady Physical Chemistry (Russia)*, vol. 284, pp. 175-178, January 1983
- [183] U.V. Choudary, K.A. Gingerich, and J.E. Kingcade, "Mass spectrometric determination of the thermodynamic stabilities of gaseous molybdenum oxides and sodium molybdates and predicted stabilities of gaseous group ia tungstates, molybdates, chromates and sulfates", *Journal of the Less Common Metals*, vol. 42, pp. 111-126, January 1975.
- [184] E.N. Nikolaev, G.A. Semenov, and S.V. Glushkov, "Formation enthalpy of the alkali metal perchlorates", *Russian Journal of General Chemistry*, vol. 54, pp. 1447-1449, July 1984.
- [185] S.I. Lopatin, "Thermochemical study of the gaseous oxiaicid salts. X. Potassium and rubidium bithmutites", *Russian Journal of General Chemistry*, vol. 71, pp. 1427-1430, September 2001.
- [186] M. Farber, S. P. Harris, and R. D. Srivastava, "Iron and rhenium additives in unseeded and potassium-seeded molecular hydrogen/molecular oxygen flames", *Combustion Flame*, vol. 22, pp. 191-196, February 1974.
- [187] S.I. Lopatin, and G.A. Semenov, "Thermochemical study of the gaseous oxiaicid salts. XII. Alkali metal selenates", *Russian Journal of General Chemistry*, vol. 72, pp. 1963-1967, December 2002.
- [188] M. Farber, and R.D. Srivastava, "Mass-spectrometric investigation of reactions involving tungsten and molybdenum with potassium-seeded molecular hydrogen/oxygen flames", *Combustion Flame*, vol. 20, pp. 33-42, January 1973.
- [189] G.A. Semenov, N.V. Kozzyukova, B.V. Slobodin, and V.M. Ushakov, "Mass spectrometric study of vaporization behavior

- of molten cesium and rubidium metavanadates”, In: *XIV International Mass Spectrometric Conference*, 1997, p. 234.
- [190] S.I. Lopatin, G.A. Semenov, D.O. Kirsanov, and S.M. Shugurov, “Thermochemical study of the gaseous oxiacid salts. II. Rubidium molybdate and tungstate”, *Russian Journal of General Chemistry*, vol. 70, pp. 383-385, March 2000.
- [191] G.A. Semenov, L.A. Fokina, and R.A. Mouldagalieva, “Mass spectrometric study of cesium tellurate and tellurite”, *Journal of Nuclear Materials*, vol. 210, pp. 167-171, February 1994.
- [192] E.H.P. Cordfunke, R.J.M. Konings, and S.R.M. Meysen, “Vapor pressures of some cesium compounds. II.  $\text{Cs}_2\text{MoO}_4$  and  $\text{Cs}_2\text{RuO}_4$ ”, *The Journal of Chemical Thermodynamics*, vol. 24, pp. 725-728, July 1992.
- [193] S.I. Lopatin, G.A. Semenov, and T.S. Pilyugina, “Thermochemical study of the gaseous oxiacid salts. V. Cesium tungstate”, *Russian Journal of General Chemistry*, vol. 70, pp. 1590-1592, October 2000.
- [194] S.I. Lopatin, and G.A. Semenov, “Thermochemical study of the gaseous oxiacid salts. VIII. Beryllium” molybdate and tungstate, *Russian Journal of General Chemistry*, vol. 71, pp. 1294-1298, August 2001.
- [195] S.I. Lopatin, and G.A. Semenov, “Thermochemical study of the gaseous oxiacid salts. XI. Alkali earth metal titanates *Russian Journal of General Chemistry*, vol. 71, pp. 1607-1611, October 2001.
- [196] G.A. Semenov, and S.I. Lopatin, “Thermochemical study of the gaseous oxiacid salts. VII. Alkali earth metal niobates”, *Russian Journal of General Chemistry*, vol. 71, pp. 884-888, June 2001.
- [197] S.I. Lopatin, G.A. Semenov, and T.S. Pilyugina, “Thermochemical study of the gaseous oxiacid salts. I. Alkali earth metal tantalates”, *Russian Journal of General Chemistry*, vol. 69, pp. 1761-1765, November 1999.
- [198] A.V. Gusarov, “Determination of stability of the gaseous magnesium metaborates”, *Teplofizika vysokikh temperatur (Russia)*, vol. 8, pp. 1186-1191, June 1970.
- [199] S.I. Lopatin, and S.M. Shugurov, “Thermochemical study of the gaseous oxiacid salts. XVII. Magnesium salts”, *Russian Journal of General Chemistry*, vol. 75, pp. 1057-1062, July 2005.
- [200] S.I. Lopatin, and G.A. Semenov, “Calcium, strontium, and barium gaseous phosphites”, *Physical Chemistry Doklady (Russia)*, vol. 287, pp. 380-381, February 1986.
- [201] G.A. Semenov, S.I. Lopatin, N.V. Kozyukova, and L.A. Kuligina, “Thermodynamics of formation of the gaseous ternary oxide compounds of alkaline-earth metals at high temperatures”, *High Temperature-High Pressure*, vol. 20, pp. 637-641, April 1988.
- [202] S.I. Lopatin, G.A. Semenov, and S.M. Shugurov, “Thermochemical study of the gaseous oxiacid salts. XIII. Alkali metal molybdates and tungstates”, *Russian Journal of General Chemistry*, vol. 73, pp. 187-193, February 2003.
- [203] G.A. Semenov, E.N. Nikolaev, K.V. Ovchinnikov, and A.M. Starodubtsev, “Thermodynamical properties of the gaseous alkali metal perrenates”, *Vestn. Saint-Petersberg Gos. University, Ser. 4*, vol. 25, pp. 44-49, May 1985.
- [204] S.I. Lopatin, S.M. Shugurov, and V.N. Savel'ev, “Gaseous calcium and strontium chromates”, in III-d Scientific Session UNTsKh, 2004.
- [205] S.M. Shugurov, S.I. Lopatin, G.A. Semenov, and V.L. Stolyarova, “Thermochemical study of the gaseous oxiacid salts. XVIII. Cobalt salts”, *Russian Journal of General Chemistry*, vol. 75, pp. 1252-1258, August 2005.
- [206] S.M. Shugurov, S.I. Lopatin, G.A. Semenov, and V.L. Stolyarova, “Thermochemical study of the gaseous oxiacid salts. XVI. Iron salts”, *Rus. J. Gen. Chem.*, vol. 75, pp. 357-363, March 2005.
- [207] V.L. Stolyarova, S.I. Lopatin, Shugurov S.M., and N.G. Turnina, “Thermodynamic properties of the gaseous strontium silicates”, *Physical Chemistry Doklady (Russia)*, vol. 411, pp. 220-222, November 2006.
- [208] S.I. Lopatin, S.M. Shugurov, and G.A. Semenov, “Thermochemical study of the gaseous oxiacid salts. XIV. Barium and chromium phosphates”, *Russian Journal of General Chemistry*, vol. 73, pp. 1972-1975, December 2003.
- [209] S.I. Lopatin, S.M. Shugurov, and G.A. Semenov, “Thermodynamic Study of Some Chromium-containing Gaseous Molecules by High Temperature Mass Spectrometry”, *Rapid Communication in Mass Spectrometry*, vol. 18, pp. 112-116, January 2004.
- [210] S.M. Shugurov, S.I. Lopatin, and V.L. Stolyarova, “Thermochemical study of the gaseous oxiacid salts. XIX. Nickel salts”, *Russian Journal of General Chemistry*, vol. 76, pp. 359-364, March 2006.
- [211] S.I. Lopatin, S.M. Shugurov, V.L. Stolyarova, and Z.G. Tyurnina, “Thermodynamic properties of the gaseous barium silicates  $\text{BaSiO}_2$  and  $\text{BaSiO}_3$ ”, *Journal Chemistry Thermodynamic*, vol. 38, pp. 1706-1710, December 2006.
- [212] S.I. Lopatin, G.A. Semenov, and A.F. Selevich, “Mass spectrometric study of the vaporization of gallium phosphates”, *Phosphorus Research Bulliten*, vol. 10, pp. 199-202, August 1999.
- [213] S.I. Lopatin, G.A. Semenov, and A.F. Selevich, “Vaporization of indium phosphates”, *Russian Journal of General Chemistry*, vol. 76, pp. 1783-1787, November 1997.
- [214] K.V. Ovchinnikov, G.A. Semenov, O. Kaposhi, and L. Lelik, “Formation enthalpies of the gaseous indium and thallium molybdates and thallium tangstate”, In: XI All-Union Conference on Calorimetry and Chemical Thermodynamic, 1986.
- [215] D. Cubicciotti, “Vaporization of thallos nitrate”, *High Temperature Science*, vol. 2, pp. 131-139, February 1970.
- [216] S.I. Lopatin, G.A. Semenov, and A.F. Selevich, “Mass spectrometric study of vaporization of the thallium phosphates”, *Russian Journal of General Chemistry*, vol. 68, pp. 892-894, June 1998.
- [217] Semenov G.A., E.N. Nikolaev, and K.V. Ovchinnikov, “Mass spectrometric study and thermodynamic properties of the thallium perrenate”, *Vestn. S.-Peterb. Gos. University, Ser. 4*, pp. 103-105, February 1989.
- [218] S.I. Lopatin, and G.A. Semenov, “Vaporization processes of the silicon and germanium diphosphates”, *Russian Journal of General Chemistry*, vol. 65, pp. 1060-1064, July 1995.
- [219] S.I. Lopatin, G.A. Semenov, and T.S. Pilyugina, “Thermochemical study of the gaseous oxiacid salts. III. Germanium molybdate  $\text{GeMoO}_4$ ”, *Russian Journal of General Chemistry*, vol. 70, pp. 529-531, April 2000.
- [220] S.I. Lopatin, and G.A. Semenov, “Mass spectrometric study of the  $\text{Sn}_2\text{P}_2\text{O}_7$  vaporization”, *Russian Journal of General Chemistry*, vol. 66, pp. 180-183, February 1996.
- [221] M.N. Bulova, A.S. Alikhanyan, and A.M. Gas'kov, “High temperature thermodynamic study of micro- and nanocrystalline  $\text{SnO}_2\text{-WO}_3$  systems”, *Inorganic Materials (Russia)*, vol. 38, pp. 831-836, July 2002.
- [222] V.I. Semenikhin, I.D. Sorokin, L.F. Yurkov, and L.N. Saidorov, “Molecular composition and component activities of  $\text{PbO-B}_2\text{O}_3$  system melts”, *Fizika I khimiya stekla (Russia)*, vol. 13, pp. 542-547, September 1987.
- [223] G.A. Semenov, K.E. Frantseva, and V.A. Urich, “Mass spectrometric study of vaporization processes of the lead and bithmus phosphates”, In: *VI All-Union Conference on phosphates*, 1984.
- [224] A.G. Nalivaiko, “*Thermodynamics of vaporization processes of the binary oxide systems  $\text{PbO-EO}_3$ ,  $\text{E} = \text{Cr, Mo, W}$* ”, Canadian Science Dissertation. Minsk, 1983.
- [225] S.I. Lopatin, I.Y. Mittova, F.S. Gerasimov, S.M. Shugurov, V.F. Kostryukov, and S.M. Skorokhodova, “Vaporization and thermodynamic properties of the  $\text{PbO-V}_2\text{O}_5$  system”, *Russian Journal of Inorganic Chemistry*, vol. 51, pp. 1749-1756, October 2006.
- [226] S.I. Lopatin, S.M. Shugurov, “Thermodynamics of gaseous phosphates of some polyvalent metals”, In *V International Symposium Inorganic Phosphate Materials*, 2005.
- [227] G. Balducci, G. De Maria, G. Gigli, and M. Guido, “Stability of Gaseous Ternary Compounds of the System  $\text{Eu-X-O}$  ( $\text{X} = \text{IV, V, or VIA Group Elements}$ )”, *High Temperature Science*, vol. 22, pp. 145-157, January 1986.
- [228] G. Balducci, G. Gigli, and M. Guido, “Thermochemical properties of gaseous  $\text{EuPO}_2$  and  $\text{EuPO}_3$  molecules”, *Journal of Chemical Physics*, vol. 70, pp. 3146-3148, June 1979.
- [229] G. Balducci, G. Gigli, and M. Guido, “Thermochemical Study of the Gaseous Molecules  $\text{EuNbO}_3$ ,  $\text{EuNbO}_2$ ,  $\text{EuNb}_2\text{O}_6$  and the Niobium Oxides  $\text{NbO}$  and  $\text{NbO}_2$ ”, *richte der Bunsen-Gesellschaft für Physikalische Chemie*, vol. 91, pp. 635-641, June 1987.
- [230] G. Balducci, G. Gigli, and M. Guido, “Thermodynamic Study of Gaseous Ternary Europium-Molybdenum-Oxygen Molecules”, *High Temperature Science*, vol. 9, pp. 149-164, March 1977.

- [231] G. Balducci, G. Gigli, and M. Guido, "Thermodynamic study of gaseous ternary europium-tungsten-oxygen molecules", *Journal of Chemical Physics*, vol. 67, pp. 147-151, January 1977.
- [232] G. Balducci, G. Gigli, and M. Guido, "Mass spectrometric study of the thermochemistry of gaseous  $\text{EuTiO}_3$  and  $\text{TiO}_2$ ", *Journal of Chemical Physics*, vol. 83, pp. 1909-1912, April 1985.
- [233] G. Balducci, G. Gigli, and M. Guido, "Thermodynamic study of gaseous ternary oxide molecules. The europium-vanadium-oxygen systems", *Journal of Chemical Physics*, vol. 79, pp. 5623-5627, November 1983.
- [234] S.I. Lopatin, "Regularities of vaporization of the oxyacid salts", *Fizika I khimiya stekla (Rus.)*, vol. 29, pp. 542-550, July 2003.
- [235] S.I. Lopatin, "Vaporization processes of phosphates which interact with some reducing metals", *Russian Journal of Applied Chemistry*, vol. 70, pp. 909-912, June 1997.
- [236] T.P. Radus, H.R. Udseth, and L. Friedman, *Journal of Physical Chemistry*, vol. 83, pp. 2969-2975, November 1979.
- [237] L.N. Sidorov, M.V. Korobov, and L.V. Zhuravleva, *Mass spectrometric thermodynamic investigations*. MGU: Moscow, 1985.
- [238] S.I. Lopatin, S.M. Shugurov, and V.L. Stolyarova, "Thermodynamics of the gaseous calcium silicates", *Physical Chemical Doklady (Russia)*, vol. 418, pp. 205-206, February 2008.
- [239] S.I. Lopatin, and S.M. Shugurov, "Thermochemical study of the gaseous oxiaacid salts. XXII. Tin molybdates", *Russian Journal of General Chemistry*, vol. 78, pp. 705-711, May 2008.
- [240] S.I. Lopatin, S.M. Shugurov, and A.O. Gunina, "Thermodynamic properties of the gaseous gallium molybdates and tungstates", *Journal of Physical Chemistry: A*, vol. 113, no. 48, pp. 13469-13474, November 2009.
- [241] S.I. Lopatin, S.M. Shugurov, and V.L. Stolyarova, "Thermochemical study of the gaseous oxiaacid salts. XXV. Magnesium borates", *Russian Journal of General Chemistry*, vol. 80, pp. 353-358, March 2010.
- [242] S.M. Shugurov, and S.I. Lopatin, "Thermochemical study of the gaseous oxiaacid salts. XXVI. Alkali metal iodates", *Russian Journal of General Chemistry*, vol. 80, pp. 705-710, May 2010.
- [243] S.M. Shugurov, S.I. Lopatin, and A.O. Gunina, "Thermochemical study of the gaseous oxiaacid salts. XXI. Lithium, potassium, and cesium phosphate polymers", *Russian Journal of General Chemistry*, vol. 77, N 9, pp. 1411-1418, September 2007.
- [244] S.M. Shugurov, S.I. Lopatin, "Thermochemical study of the gaseous oxiaacid salts. XXIV. Alkali metal perrenate polymers", *Russian Journal of General Chemistry*, vol. 78, pp. 1644-1650, October 2008.
- [245] G.A. Semenov, L.A. Fokina, and R.A. Mouldagalieva, "Mass spectrometric study of cesium tellurate and tellurite", *Journal of Nuclear Materials*, vol. 210, pp. 167-171, February 1994.
- [246] V.B. Lazarev, A.S. Alikhanjan, K.N. Marushkin, and J.H. Greenberg, "p-T-x Phase Diagram and Thermodynamics of Barium - Tungsten Oxides", *Thermochimica Acta*, vol. 93, pp. 457-459, March 1985.
- [247] S.I. Lopatin, V.A. Sinyuev, and S.M. Shugurov, "Mass spectrometric study of condensed phosphate vaporization", *KAKhAK (Kazakhstan)*, vol. 2(13), pp. 22-29, February 2005.
- [248] V.B. Sholtz, and L.N. Sidorov, "Dissociation enthalpies, mass spectra and structures of some complex fluorides", *Vestnik Mosk University (Russia)*, vol. 13, pp. 371-382, April 1972.

---

Received: September 28, 2010

Revised: November 05, 2011

Accepted: November 19, 2011

© Lopatin and Shugurov; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.