Mass spectrometric determination of partial pressures of ions in the saturated vapor over the NaF–Na$_3$AlF$_6$ system

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Abstract

Mass spectrometric determination of absolute partial pressures of basic charged species Na$_2$F$^+$ and AlF$_4$$^-$ in the saturated vapor over the NaF–Na$_3$AlF$_6$ system (1:1 molar ratio) was carried out in the 974–1090 K temperature range. The ion pressures were 5–8 orders of magnitude lower than the pressures of basic molecular components NaAlF$_4$ and NaF. Particular attention was given to the equality of device sensitivity constants for positive and negative ions. Absolute device calibration was carried out using the measured ion currents Na$_2$F$^+$ and AlF$_4$$^-$ and the equilibrium constant of heterolytic dissociation available in the literature.
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1. Introduction

In the earlier 1950s, the new scientific direction—Knudsen cell mass spectrometry (KCMS) was developed. In this period, the attention was drawn to the presence of both neutral and charged species in the high temperature vapors over inorganic compounds [1–4]. Thus, Drowart and Honig have detected the neutral clusters C, C$_2$, C$_3$ and negative ions C$^-$, C$_2$$^-$, C$_3$$^-$ among the species emitted from the heated graphite wire. It has allowed to the authors to determine the electron affinities of these particles. Chupka has studied the vapors over several alkali halides (NaCl, KCl, KBr, RbCl) and has determined the enthalpies of the corresponding reactions M$_2$X$^+$(g) = M$^+$(g) + MX(g). These works have established the basis for studies, the positive and negative ions in the vapors of hardly volatile compounds. In the 1980s, a new procedure of high temperature mass spectral analysis was developed called the ion–molecule equilibrium method [5]. It allowed one to analyze both neutral and electrically charged species in saturated vapors of inorganic compounds and to measure directly the equilibrium constants of ion–molecule reactions involving negative and positive ions (note that absolute partial pressures can be determined only for neutral species, while in the case of charged species, a ratio of partial pressures of similarly charged ions can be obtained). To successfully use this method, measurable concentrations of either positively or negatively charged thermal ions should be present in vapors of the system under investigation. This can be provided by controlling the electron work function of the inner surface of an effusion cell. Normally, the concentration of ions is 5–8 orders of magnitude lower than the concentrations of neutral species. To calculate the vapor pressures of ions formed due to heterolytic dissociation of inorganic salts or in other reactions, two conditions are required to be fulfilled: the vapor should be electrically neutral and all necessary thermodynamic data should be available. However, if the Debye shielding radius is comparable to the linear size of an effusion cell, the vapor is not neutral, and the ratio of pressures of positive and negative species is determined by the work function. It is rather difficult to calculate the concentrations of ions under these conditions; therefore, direct measurements have to be carried out. In this work, an attempt was made to improve the procedure of measuring the absolute values of ion pressures that, in general, could make it possible to control the work function of the inner surface of effusion cell. The NaF–AlF$_3$ system was used as a model, because for this system, the thermodynamic functions of neutral and ion components of the vapor are available in the literature, and positive and negative ions can be measured within the scope of one experiment.

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2. Experimental

The experiments were carried out using MI-1201 magnetic mass spectrometer with a combined ion source. Experimental setup consisted of a magnetic sector mass analyzer (ordinary focusing, radius of beam curvature 200 mm, beam rotation angle 90°) and two detectors, namely, a Faraday cup and a secondary electron multiplier. With the Faraday cup the current was measured in the 10^{-15} to 10^{-10} A range, and with the multiplier, in the 10^{-17} to 10^{-12} A range. Mass resolution of this instrument ($m/\Delta m$) was about 300 (valley definition 5%) at the accelerating voltage of 3 kV and the mass range of 2–1200. The width of the outlet slit of the ion source was 0.3 mm. The source was equipped with reversers for changing the operating modes and the magnet poles. The reversing time was less than 20 s.

An ion source allowing one to study both positive and negative thermal ions and neutral species in a vapor within the scope of one experiment was described in detail in [5]. In our case, a draw out electrode was placed at a distance of about 1 mm from the effusion cell. There is a shielding electrode located between the draw out electrode and the ionization chamber. The shielding electrode was at the same potential as the draw out electrode. A movable shutter incorporated in the shielding electrode can completely switch off the beams emerging from the cell. Owing to the shielding electrode, defocusing conditions for analysis of thermal ions can be realized at low draw out field intensities.

Note that the defocusing mode is preferable, because it makes it possible to reduce the influence of ions formed due to the ionization of the substance on the surface of an effusion cell. In this case, an effusion orifice turns out to be the only source of both positive and negative ions. In addition, the defocusing mode is more stable and reproducible upon alternating measurement of ions different in sign.

Inversion of electrode potentials was carried out by changing the sign of the accelerating voltage. A fine adjustment was performed through the focusing, correction potentials, and the voltage between deflecting plates.

When positive and negative ions were measured, the accelerating voltage was equal to $+3$ and -3 kV, respectively. The draw out voltage was chosen on the basis of the maximum signal and was similar for complex ions with opposite signs. It was virtually unchanged during each experiment but varied from 40 to 100 V in different experiments. The potentials of the focusing and correction electrodes determining mostly the ion beam collimation were symmetrical: -200 and $+80$ V for positive ions and $+200$ and -80 V for negative ions. Therefore, the sensitivity of instrument with respect to both positive and negative ions was similar ($K_+ = K_- = K_\pm$).

A nickel cell covered with a fitted lid was used in the experiments. The effusion orifice had a diameter of 0.47 mm; the effusion channel length was about 0.2 mm; the ratio of the inner surface of the cell to the effusion area was not less than 1000. The temperature was measured to within ± 2 K

using a Pt/Pt–Rh (10%) thermocouple calibrated against KCl melting point (mp = 1049 K). Reagent grade NaF and melted cryolite Na_3AlF_6[1] (>99%) were used through out this work. The samples of NaF–Na_3AlF_6 (1:1 molar ratio) system were prepared from a mechanical mixture of sodium fluoride and melted cryolite.

The instrument was calibrated using the equilibrium constants of heterolytic dissociation:

$$NaAlF_4(g) + NaF(cr) = Na_2F^+(g) + AlF_4^-(g) \qquad (1)$$
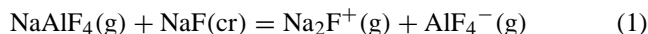
and ion currents of Na_2F^+ and AlF_4^- measured in this work. The equilibrium constants for reaction (1) were calculated from data in the literature on the equilibrium constants for reactions $Na_2F^+(g) = Na^+(g) + NaF(cr)$ [6] and $NaAlF_4(g) = Na^+(g) + AlF_4^-(g)$ [7]. The activities of NaF and Na_3AlF_6 were assumed to be one. Using the assumptions, the $p(Na_2F^+) \times p(AlF_4^-)$ values were calculated for the temperature range 974–1090 K. The Na_2F^+ and AlF_4^- ion currents and pressures are known to be related by the following equations [8]:

$$p(Na_2F^+) = K_\pm \times S_u^{-1} \times I(Na_2F^+) \times M(Na_2F^+)^{1/2} \times T^{1/2}$$
$$p(AlF_4^-) = K_\pm \times S_u^{-1} \times I(AlF_4^-) \times M(AlF_4^-)^{1/2} \times T^{1/2}$$

where p is ion pressure; $K_\pm$ is sensitivity constant; S_u is the effective area of ion collection (analogous to the effusion orifice area for neutrals); I is measured ion current; M is relative molar mass; T is absolute temperature. S_u is determined by the geometry of the draw out electrode and cell effusion channel, and by the draw out potential, temperature, and concentration of charged species. When temperature and draw out potentials of positive and negative ions are constant (as in our experiments), the S_u value is considered to be constant, independent of the ion sign. This made it possible to calculate the $p(Na_2F^+) \times p(AlF_4^-)$ ratio using equation [8]:

$$\frac{p^+}{p^-} = \frac{I^+}{I^-} \left(\frac{M^+}{M^-} \right)^{1/2}$$

We have the $p(Na_2F^+) \times p(AlF_4^-)$ values calculated from the literature data and the experimental $p(Na_2F^+)/p(AlF_4^-)$ ratios. Further, solving the system for two unknown terms, we determined the pressures $p(Na_2F^+)$, $p(AlF_4^-)$ in themselves and calculated the $K_\pm/S_u$ values.

Temperature dependence of $K_\pm/S_u$ is given in Fig. 1. Experimental data can be well approximate by the linear dependence: $\log 10 (K_\pm/S_u) = -[(6.6 \pm 0.4) \times 10^3/T] + (3.3 \pm 0.4)$.
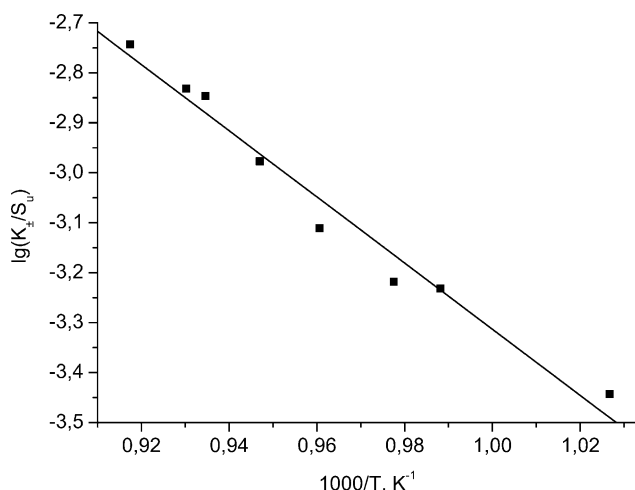
Fig. 1. Calculated values $K_{\pm}/S_u$ at the different temperatures in the scope of one experiment.

3. Results and discussion

3.1. Composition of vapor

The Na^+, Na_2F^+, K^+, $KNaF^+$, and AlF_4^- ions were the main ions detected in the vapor of the system under study (the presence of potassium was due to impurity of KF in the samples of NaF and Na_3AlF_6). In addition, $Na_3F_2^+$, $Na_4F_3^+$, and $Na_5F_4^+$ ions were unambiguously detected. Low intensity signals of Cs^+, Rb^+, $CsNaF^+$, $RbNaF^+$, $CsKF^+$, $RbKF^+$, K_2F^+, $KNa_2F_2^+$, $K_2NaF_2^+$, $KNa_3F_3^+$, $KNa_4F_4^+$, due to impurities in the samples, were also observed in the mass spectrum. Note that $Na_5F_4^+$ and $CsKF^+$ ions are characterized by a similar mass number ($m/e = 191$). The signal detected at $m/e = 193$ indicates the presence of $CsKF^+$. However, its low intensity at high temperatures $I(m/e = 193)/I(m/e = 191) \approx 0.015 < W(^{41}K)/W(^{39}K) \approx 0.073$ (natural isotope ratio) evidences that $Na_5F_4^+$ is also present. This was confirmed by the fact that another pentameric ion, $KNa_4F_4^+$, was also detected. A weak peak at $m/e = 233$ can be assigned to $Na_6F_5^+$ or, more likely, to a triple complex ion $CsKNaF_2^+$. Unfortunately, the low intensity of the signal did not allow the isotopic composition to be distinguished. Among the negative ions, $NaAl_2F_8^-$ and the weak signal of $NaAlF_5^-$ and $Na_2Al_2F_9^-$ were also measured. The signals of ions containing cesium, rubidium, and potassium slowly decreased with temperature treatment of the sample.

In the case of complex ions (e.g., Na_2F^+ and $KNaF^+$), dependence of ion current intensity on deflecting plate voltage (Fig. 2) exhibited a single maximum at $+15$ V, and in the case of the AlF_4^- ion, a single maximum at -16 V. However, a wide distribution with several maxima was typical for atomic ions Na^+, K^+, Cs^+, and Rb^+. This provided evidence that the mentioned ions were mainly formed outside the cell. Therefore, they are ignored in the subsequent discussion.
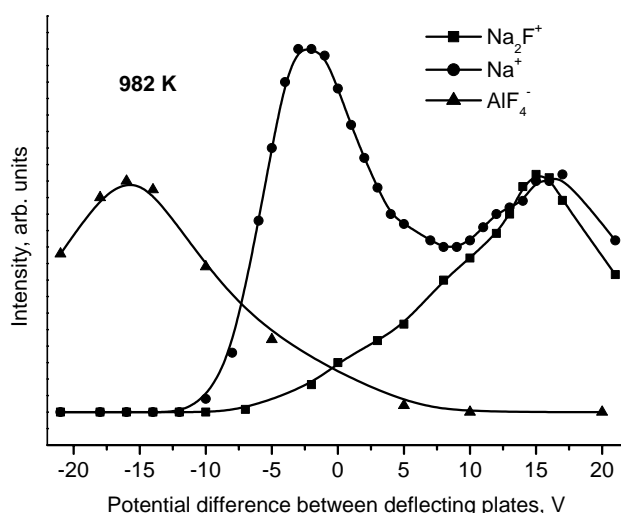

Fig. 2. The dependence of the Na^+, Na_2F^+, and AlF_4^- signals (normalized) on the voltage between deflecting plates. For all ions draw out voltage is constant and equals to 45 V.

The plots of ion current intensities on draw out voltage (defocusing curves) are shown in Fig. 3. The curves for positive and negative cluster ions exhibit one maximum in the 40–50 V range. For atomic ions, an addition a sharp maximum appears in the range of 2–15 V. These curves agree with previous data [3,9], the only difference being different positions of the maxima. Thus, in [9] the maximum of the ion current intensity was found at 80–100 V.

The fact that the curves obtained for Na_2F^+ and AlF_4^- coincide in the range of the defocusing maxima indicates that these ions are identically captured from the effusion cell and confirms that, as in the case of AlF_4^-, the contribution of extraneous ions to the ion current of Na_2F^+ is negligible.

3.2. Partial pressures of ions

A series of experiments was carried out to study the NaF–Na_3AlF_6 system. Each heating–cooling cycle lasted several hours. After the sample was heated to a given temperature, the highly intense spectrum of positive ions was measured. However, negative ions were absent. When the sample was further heated and allowed to stand at a high temperature, the intensity of positive ions smoothly decreased and the signal of AlF_4^- appeared. Such a phenomenon has been described in the literature [10] and was explained by the accumulation of the alkali metal on the surface due to the decomposition of alkali–metal halide, and corresponding decrease in the surface work function.

After the ion current of AlF_4^- was measured, we applied the above-described calculation procedure of ion vapor pressures. The results obtained were as follows. First, the work function was found to decrease with prolongation of thermal treatment of the sample. Secondly, in different experiments, the $I(Na_2F^+) \times I(AlF_4^-)$ values measured at similar tem-

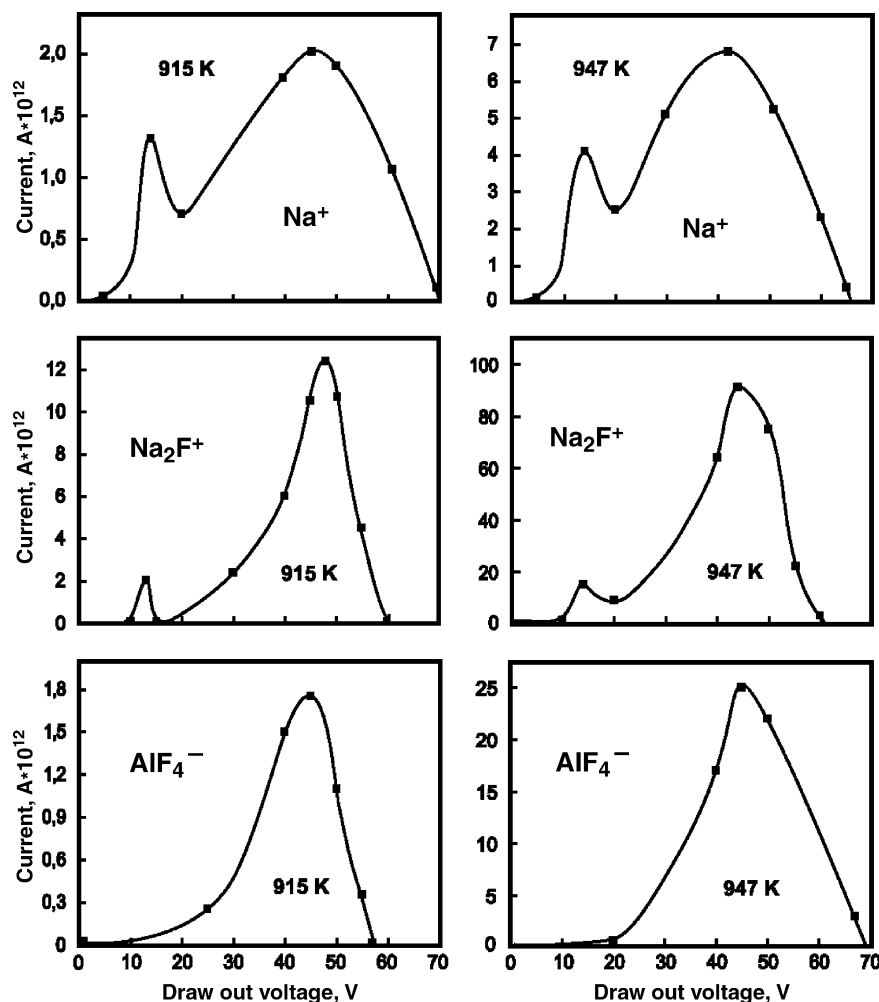Fig. 3. The intensities of the Na^+, Na_2F^+, and AlF_4^- ion currents vs. draw out voltage (defocusing curves). Scanning only with draw out field, the other electrodes potentials correspond to the signal maxima.

peratures were equal within the experimental errors, in spite of the change $I(Na_2F^+)/I(AlF_4^-)$ ratio up to 10 times.

The experimental and calculated pressures of major ions and molecules in the NaF–Na_3AlF_6 system at 974–1090 K are listed in Table 1. These data were obtained under stationary conditions established after the heating–cooling cycles were repeated until reproducible results were obtained. As seen from table (sixth column), the effective area of ion collection decreases by a factor of 5 with a 100-fold in-

creasing in ion pressure. This is in good agreement with the effect of increasing shielding of the draw out field that is produced due to the Debye shielding radius (r_D) decreasing with increasing ion pressures (r_D is equal to 3.5 mm at 974 K and 0.3 mm at 1090 K). Perhaps, the effect of draw out field shielding becomes apparent in decreasing of $K_\pm/S_u$ with temperature (Fig. 1). The correctness of this suggestion will check in the future investigations with other systems. The fact that at low pressures, when $r_D = 3.5$ mm

Table 1
Absolute partial pressures of basic neutral $NaAlF_4$, NaF and charged Na_2F^+, AlF_4^- species in the saturated vapor over the NaF–Na_3AlF_6 system

T (K)	$p(NaAlF_4)$ (atm)	$p(NaF)$ (atm)	$p(Na_2F^+)$ (atm)	$p(AlF_4^-)$ (atm)	$K_\pm/S_u$ (atm/A K)	r_D (mm)
974	2.2×10^{-7}	1.5×10^{-7}	1.4×10^{-14}	1.4×10^{-14}	3.6×10^{-4}	3.4
1012	8.1×10^{-7}	5.3×10^{-7}	1.0×10^{-13}	8.3×10^{-14}	5.9×10^{-4}	1.4
1023	1.2×10^{-6}	7.4×10^{-7}	1.7×10^{-13}	1.4×10^{-13}	6.0×10^{-4}	1.1
1041	2.0×10^{-6}	1.3×10^{-6}	3.8×10^{-13}	3.3×10^{-13}	7.8×10^{-4}	0.7
1056	3.2×10^{-6}	2.0×10^{-6}	7.7×10^{-13}	6.3×10^{-13}	1.1×10^{-3}	0.5
1070	4.9×10^{-6}	3.0×10^{-6}	1.7×10^{-12}	9.7×10^{-13}	1.4×10^{-3}	0.4
1075	5.7×10^{-6}	3.4×10^{-6}	1.8×10^{-12}	1.4×10^{-12}	1.5×10^{-3}	0.4
1090	8.7×10^{-6}	5.1×10^{-6}	3.7×10^{-12}	2.4×10^{-12}	1.8×10^{-3}	0.3

and the vapor is not necessarily electrically neutral, the concentration of positive and negative ions is the same appears to be somewhat surprising. Unfortunately, the pressures of sodium and fluorine in the system under study were not measurable; only their product could be calculated. Therefore, the electron work functions calculated for the various ratios of $p(\text{Na})/p(\text{F})$ varying from 10^{-2} to 10^{2} give work function in the range 5.1–4.7 eV (in the case of pure nickel, the work function is equal to 5.0 eV). The ion pressures given in Table 1 and pressures of atomic sodium and fluorine are of the same order of magnitude. Therefore, the flow of sodium and fluorine emerging from the effusion cell is not noticeably affected by draw out of similarly charged species. Accumulation of nonstoichiometric amounts of sodium and decreasing in the work function can be provided only due to heating the $\text{NaF–Na}_3\text{AlF}_6$ system for a long time.

4. Conclusion

In the present work, the absolute partial pressures of ions in the volume of Knudsen cell and the temperature dependence of sensitivity constant were firstly obtained. The goal of the further experiments will be to confirm used suggestions. The investigation of another inorganic salt systems and the accumulation of the new data will allow to understand deeply the physical regularities of ion collecting from the saturated vapor by electrostatic field, especially, to make clear all peculiarities in dependence of instrument sensitivity constant upon temperature and ions pressure. The successful decision of these tasks will allow to start the next step in the investigations, namely: the determination of electron work function of salt surface from the partial pressures of ions in saturated vapor.

Acknowledgements

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