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Effusion of positive and negative ions from a Knudsen cell with weak electric field and ionic conductivity of the sample

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Abstract

The studies on absolute partial pressure measurements of ionic components of the high temperature vapors over inorganic fluorides by means of Knudsen cell mass spectrometry are summarized. The problems arising when the ions are extracted directly from the effusion cell with electric field are discussed. The conditions for correct determination of the equilibrium constants for gaseous reactions, involving both positive and negative ions, are established.

Keywords: High temperature mass spectrometry; Knudsen cell; Ion-molecular equilibrium; Thermal ionization; Inorganic fluorides; Cerium trifluoride; Superionic conductor

1. Introduction

It was reliably established early in the last century that both positive and negative ions can be emitted thermally from ionic salts and glasses (electrolytes). Alkali metal salts were found to be the strongest ion emitters [1]. Also in this period some regularities emerged in the emission phenomena [2]. In particular, a rule was formulated that salts containing solely positive or negative mobile ions can emit at appropriate temperatures solely positive or negative ions, respectively [3]. Generally, no quantitative relation was established between the emission intensity from the condensed phase and the conductivity. However, for a series of potassium alumosilicates (superionics on K^+) the K^+ ionic current was found to rise linearly with increasing conductivity [4].

In recent years, the kinetics of ionic sublimation of alkali halide polycrystals [5] and single crystals [6–8] has been studied using modern high-vacuum devices. The complicated shape of the temperature dependence of the ionic currents was explained by changes in the surface morphology and the properties of the double-layer electric field at the crystal–vacuum boundary. Dislocations on the single crystal surface were supposed to be the emission centers for alkali cations [9].

Ions are usually formed by equilibrium surface ionization in heated metals [10]. At low temperatures, when surface ionization is insignificant, one can also observe alkali cation emission (K^+) from unannealed tungsten wires. For this kind of ion emission as well as for ion emission from electrolytes, sharp increases of ion emission current after contact with water with subsequent decay of the emission is characteristic [11]. If the metal surface is covered with two or three ionic salt monolayers, the alkali cation emission pattern turns out to be similar to that from bulk salt [12].

The application of Knudsen cell mass spectrometry (KCMS) to the study of ion–molecule equilibrium (IME) was described in 1985 [13]. The designed apparatus based on magnetic sector instrument detected both the ionic and molecular components of the saturated vapor during a single experiment. Neutral species were detected in the conventional way through electron impact ionization and ionic components of the vapor were detected after being directly drawn out of the cell by a weak electrostatic field. In the experiments, the cell was partially filled with an ionic salt as usual. Therefore, both surface ionization from the inner metal surface and ion emission from the salt surface were possible. Unfortunately, the predominant emission mechanism cannot be experimentally determined under equilibrium

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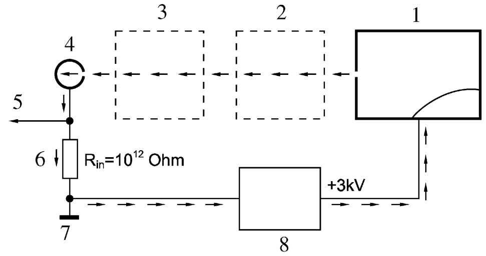

Fig. 1. Electrical scheme of thermal ions measurement (rows show the direction of current when positive thermal ions being measured): (1) Knudsen cell, (2) ion optics, (3) mass analyzer, (4) detector, (5) DC amplifier, (6) input resistance, (7) ground (ironwork), (8) accelerating voltage power supply.

conditions. However, one can expect that at salt pressures up to 1 Pa and temperatures of about 1000 K, the inner metal surface would be covered with a polymolecular salt layer, which would act as ion emitter.

The KCMS-IME method was applied to determine the formation enthalpies of negative and positive ions [14]. However, previous works in which absolute ion pressures were measured and stable intense negative ion currents were obtained are not nomerous. It was established earlier that NaF–Na_3AlF_6, KF–K_3AlF_6, and $Na_5Al_3F_{14}$–AlF_3 systems, heated in a clean Knudsen cell, give no negative ion signals, while with NaF–Na_3AlF_6 and KF–K_3AlF_6 systems such signals appeared after several “heating–cooling” cycles [15,16]. In the case of the $Na_5Al_3F_{14}$–AlF_3 system, this “heating–cooling” procedure was not effective, and the negative ion signals were detected only after fluorine–anion superionic CeF_3 was preliminarily heated in the cell at 1200 K for 3 h [17]. No difference in the neutral composition of vapor before and after several “heating–cooling” cycles and after CeF_3 evaporation was registered.

Essentially, solid salt electrolysis takes place during mass spectral studies of ion emission from Knudsen cells. Therefore, in the present work, we consider the Knudsen cell as a specific element of the electrochemical circuit involving two electrolytes, namely, the solid and gaseous phases (Fig. 1). The partial ion pressures in the gaseous electrolyte are mass spectrometrically measured. Reliable data can be obtained using the effusion (Knudsen) method only when sampling of the vapor phase has little effect on the partial pressures in the closed cell. In the present paper conditions when the sampling is negligible (we call it “closed cell” condition) will be formulated for the case when solely positive or negative ions are extracted from the cell with an electric field.

1.1. Effective effusion area in ion extraction

The effusion of neutral species is described by the Hertz-Knudsen equation

$$J = \frac{PS}{\sqrt{2\pi MRT}}, \tag{1}$$

where J is the effusion flow rate, P the partial pressure, M the molecular weight, and S is the effusion area. It is supposed that molecules in the vapor have a Maxwellian distribution and that the total pressure is low enough to allow collisionless flow from the orifice.

When an electric field is applied to extract ions from a partially ionized gas in an effusion cell, ions leaving the cell may have velocities far from their thermal values, and the resulting distribution function will not be the one in equilibrium. It is easy to estimate that the electrostatic potential at the center of the effusion orifice usually applied in the KCMS-IME method is about 3–7 V. Thus, the directional velocity of the ions has a value, corresponding to energies up to 7 eV, compared with thermal energies 0.1 eV at $T = 1000$ K. Moreover, the trajectories of effusing ions are nonlinear unlike neutrals. It is reasonable to think that Eq. (1) does not work under such conditions. Nevertheless, it has been shown [13] that Eq. (1) is applicable if S is simply replaced by the effective area of ion extraction S_U:

$$J_\pm = \frac{P_\pm S_U}{\sqrt{2\pi M_\pm RT}}. \tag{2}$$

Eq. (2) turns to be correct for effusion of thermal ions owing to three reasons: (a) The electric field penetrating into the cell decreases rapidly with distance from the hole, becoming almost zero in the immediate vicinity of the inner cell walls (Fig. 2). As one can see, the equipotential surface, corresponding to the energy $\sim kT$, is situated 1.5 mm from the hole. Therefore, the ions are emitted from the inner surface and back to the surface with thermal energies and Maxwellian distribution function. (b) Ions with different masses and equal charges (thermal ions are singly charged) go along the same trajectory in the electrostatic field if they have identical initial energy (kT) and identical initial velocity direction [18]. (c) In electrostatic field the time of flight for equal charges along trajectories (even nonlinear) is proportional to $M^{1/2}$ [18]. It appears from (a) and (b) that S_U does not depend on M and specified (has the same value) for all ions being extracted. It appears from (c) the total effusion flow rate of ions $J_\pm$ is proportional to $M^{-1/2}$. There is significant difference between S and S_U. The first is easily measured and stays constant during an effusion experiment, while the second depends

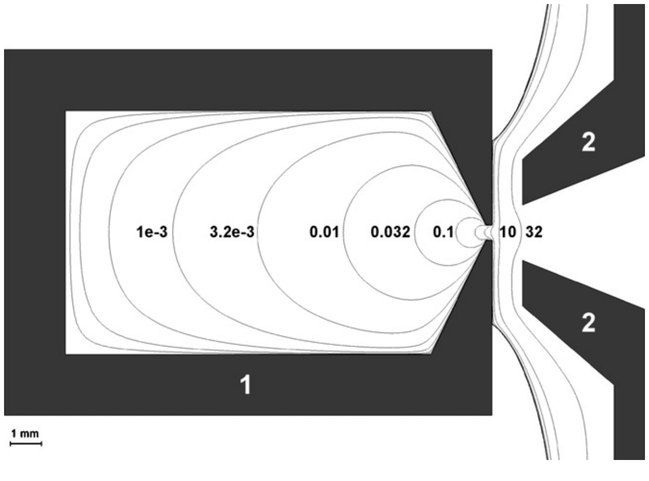

Fig. 2. Equipotential surfaces (V) between a cell (1) and a draw-out electrode (2) in our ion source calculated for vacuum conditions and potentials: $U(1) = 0$ V, $U = U(2) = 50$ V. The calculation is performed with the program FemLab [19].

on the extracting voltage, temperature, and ion pressure, *i.e.*, it is changeable during a run [15].

The value of S_U is generally unknown, but evidently may be calculated in numerical experiments involving the spatial dependence of the field, initial velocity function and trajectories of the ions. In the present work S_U was obtained experimentally from absolute ion partial pressure measurements with a mass spectrometer. When only relative partial ion pressures of ions of the same sign are of interest, the coefficient S_U cancels. The determination of the thermodynamic properties of charged gaseous compounds through the investigation of ion/molecule equilibrium has been the main application of Knudsen cell mass spectrometry during the past 20 years. Present work is aimed at determining the absolute partial pressures of charged species of both signs in the gas phase above hardly volatile inorganic salts. It is worth, then, to discuss the physical meaning and properties of the coefficient S_U under different experimental conditions.

It is known from plasma physics that the properties of an ionized gas (its behavior in an external electric field, in particular) strongly depend upon the relation between the characteristic dimension l of the volume containing gas (interior dimension of Knudsen cell) and the Debye length r_D. The last quantity is expressed as a function of ion volume concentrations (c_+, c_-) and temperature by the following formula:

$$r_D = \frac{1}{eN_a}\sqrt{\frac{\varepsilon_0 RT}{z_+^2 c_+ + z_-^2 c_-}}, \qquad (3)$$

where z are charge numbers of the ions (+1 and −1 for thermal ions), N_a the Avogadro number, and ε_0 is the electric constant. Let us first consider the case of low ion concentrations (pressures), *i.e.*, $r_D \gg l$ (in an effusion experiment l is typically 1 cm). In that case the extracting field penetrates into the cell as if it were empty. Thus, S_U depends only on extracting voltage U, $S_U = f(U)$. The gas volume is not necessary electrically neutral and the ion concentrations depend on electrical properties of emitting surface only. This situation is the most common in Knudsen cell mass spectrometry and corresponds to partial pressures of the charged species of the order 10^{-14} to 10^{-17} atm.

In the opposite case, $r_D \ll l$, the gas behaves as a plasma. This occurs at ion pressures of about 10^{-11} atm or higher. The interior part of the gas becomes electrically neutral. Extra charge is expelled to the inner boundaries of the cell, forming a layer with nonzero charge density, the thickness of which is the order of magnitude of r_D. This layer hinders the thermal emission of ions of one sign from the surface (metal or salt) and favors emission of ions with the opposite sign and ensures the electroneutrality of the volume. When an external field is applied, the plasma is partly destroyed by the directed motion of ions in the space, close to the effusion hole. Due to the screening effect the field tension, E becomes zero at a distance of, again, about r_D, *i.e.*, very far from the inner surface of the cell. The plasma boundary plays a role of S_U, acting as the area of ion emission with thermal energies. In the limit of high pressures ($r_D \to 0$) S_U tends to the area of the effusion hole ($S_U \to S$). Evidently, S_U must then be approximately a quadratic function of the Debye length.

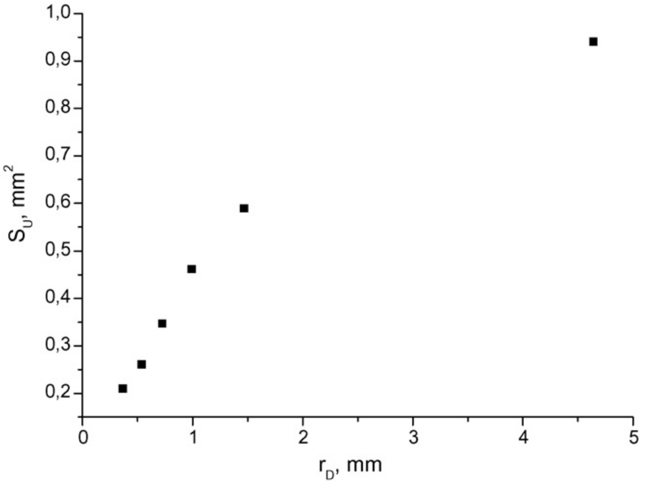

Fig. 3. Experimental dependence of S_U on r_D ($S = 0.2\ \mathrm{mm}^2$) on the data obtained in Ref. [15].

Since pressure grows exponentially (*i.e.*, rapidly) with temperature, the two regimes of ion extraction, described above, can be met in the course of a single experiment. Fig. 3 shows the dependence of S_U upon r_D, evaluated from the absolute partial pressures of Na_2F^+ and AlF_4^-, measured in the saturated vapor above the system NaF–Na_3AlF_6 in the temperature range 974–1090 K [15]. The form of the curve corresponds to the two extreme cases and supports the above speculations.

1.2. Closed and open cell conditions

Mass spectrometric effusion experiments, aimed at measurements of the equilibrium constants of heterolytic ion/molecule reactions, necessarily involve the registration of ions with both signs. The problem is that ion currents, corresponding to positive and negative ions, are measured in turn, not simultaneously. Let us assume that the equilibrium constant for the reaction of the heterolytic dissociation of

$$\mathrm{NaAlF_4(g) = Na^+(g) + AlF_4{}^-(g)}, \qquad K_P = \frac{P_{\mathrm{Na^+}} P_{\mathrm{AlF_4{}^-}}}{P_{\mathrm{NaAlF_4}}} \qquad (4)$$

is to be measured. By applying a positive extracting voltage to register thermal anions, we cut off the cation flow from the cell and *vice versa*. Thus, it is very important to know to what extent the extraction of ions with one sign can influence the partial pressures of ions with the same as well as with the opposite sign.

In the classic Knudsen method (neutral species) a similar problem is solved quite simply: effusion of the vapor will not disturb the equilibrium if the rate of evaporation of the sample inside the cell is much greater than the rate of effusion. Usually it is sufficient to ensure that the relation $S_{ev} \gg S$ holds, where S_{ev} is the area of the sample surface. In the case of ion extraction this condition should be replaced by $J_{\pm em} \gg J_\pm$, where $J_{\pm em}$ is the rate of emission from the sample surface and $J_\pm$ is the rate of effusion. However, $J_{\pm em}$ depends not only on the area, but also on the conductivity of the sample, because the charge deficit, created by the extraction, must be compensated and the electric circuit, consisting of the extracting plate, the cell and the supplying wire, maintaining a constant potential of the cell, must be closed (Fig. 1).

As an illustration, let us consider the results, obtained in a recent work [17]. In the first series of experiments, a salt mixture, $Na_5Al_{13}F_{14}$–AlF_3, was evaporated from a cleaned Ni cell. In the second series with the same system, the inner surface of the cell was preliminarily subjected to heating (at 1200 K for 3 h) in presence of CeF_3. As cerium trifluoride is much less volatile, the saturated vapor composition of the neutral components was found to be the same and was represented by the $NaAlF_4$ and $Na_2Al_2F_8$ molecules [17]. However, the results for the thermal ions were quite different. With the pure cell, the $NaAl_2F_8{}^-$, $AlF_4{}^-$, and $Al_2F_7{}^-$ signals in the range of 720–920 K were absent. With the modified surface, the same anions were already easily measurable at 856 K. It can be estimated that the negative ion current increased at least by a factor of 440, while for Na^+ the ion current decreased only by one order. Obviously, conductivity is provided by CeF_3, which is known to be a superionic conductor.

In the negative ion mode of operation, the excess positive charge, accumulating in the gas phase, must somehow be removed from the cell. Otherwise the circuit would not work and measurements would not be possible. It is conceivable that this was the case with the cleaned effusion cell in the first series of experiments, described above. In the absence of anion conductivity, negative charge flow could be provided by the flow of positive ions in the opposite direction with a subsequent discharge on the Ni surface. The positive ion conductivity of $Na_5Al_3F_{14}$ salt is rather higher than the negative one (Table 1). At the same time transport of Na^+ through the solid requires a certain overvoltage, well known in electrochemistry. Our experiments show that the overvoltage is evidently insufficient for electrolysis, involving transport of positive ions. The circuit may be closed only due to fast enough chemical reaction (discharging) at the salt–vapor interface, for example

$$Na^+(g) + F^-(s) = NaF(s), \tag{5}$$

stimulating the movement of negative ions from the salt–nickel boundary through the bulk. A sufficient rate of the reaction is achieved if the F^--conductivity of the solid phase is high enough. Therefore, one may think that the role of CeF_3 was to ensure high negative ion conductivity and provide neutralization of the excess positive ions.

Let I_+ and I_- be the alternately measured ion currents from the cell, I(C) and I(A)–cation and anion currents flowing through the electrolyte cross section at the inner surface of the cell. Due to the steady state of the charge flow

$$I_+ = I(C), \tag{6}$$

$$I_- = I(A). \tag{7}$$

At high rates of electrode processes (neutralization reactions, in particular), actual pressures of the ions are controlled by the relation between the sampled current and the maximum current (at a given extracting voltage U), provided by the conductivity of the solid sample:

$$I_+ \ll I_{\max}(C) \rightarrow P_+ = f(T), \tag{8}$$

$$I_- \ll I_{\max}(A) \rightarrow P_- = f(T), \tag{9}$$

$$I_+ = I_{\max}(C) \rightarrow P_+ = f[T, I_{\max}(C)], \tag{10}$$

$$I_- = I_{\max}(A) \rightarrow P_- = f[T, I_{\max}(A)]. \tag{11}$$

Relations (8) and (9) give the conditions when a Knudsen cell can be considered as closed (sampling does not affect ion pressures or very small orifice for classical case). If these conditions are violated at least for ions of one sign, the measured pressure reduces to a value, corresponding to the upper limit of the cation or anion current through the sample. Therefore, measurement of the equilibrium constant (4) will yield a conservative result.

It is worth noting that when the conditions (8) and (9) are not met, the experiment will not give the actual partial pressures of ions even without any extracting voltage (spontaneous effusion), but those pressures, which took place in the absence of the effusion hole. At the same time the equilibrium constant for the reaction of heterolytic dissociation will be measured correctly because of conservation of the product P_+P_- due to chemical equilibrium.

Table 1
Specific ionic conductivity of solid phases at experiment temperatures

Solids	Cationic conductivity	Anionic conductivity
NaF, KF [20]	More than 10^{-5} S/cm	More than 10^{-5} S/cm
Na_3AlF_6, $Na_5Al_3F_{14}$, K_3AlF_6 [21]	More than 10^{-3} S/cm	–
AlF_3 [22]	–	–
CeF_3 [23]	–	More than 10^{-3} S/cm

2. Conclusion

In summary, it was shown that in order to make mass spectrometric determinations of the equilibrium partial pressures of positive and negative ions it is necessary to provide cationic and anionic conductivity of the salt layer covering the inner surface of a Knudsen cell. Cationic conductivity alone does not ensure neutralization of the positive charge, making anion current measurements impossible. Treatment of the effusion cell with superionic F^--conductor made possible the correct measurements of the absolute partial pressures of ions, both positive and negative, and the correct equilibrium constant for the reaction of heterolytic dissociation was obtained in the present work.

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References

[1] O.W. Richardson, Emission of Electricity from Hot Bodies, 2nd ed., Longmans, Green & Company, New York, 1921.
[2] A.L. Reimann, Thermionic Emission, John Wiley & Sons, New York, 1934.
[3] G.C. Schmidt, Ann. Phys. 75 (1924) 337.

[4] U.I. Malov, L.S. Leonova, S.E. Nadhina, N.G. Bukun, E.A. Ukshe, Jurn. Fiz. Him. (Russ. J. Phys. Chem.) 56 (8) (1982) 1879.
[5] M.F. Butman, J. Nakamura, H. Kawano, Appl. Surf. Sci. 78 (1994) 421.
[6] M.F. Butman, A.A. Smirnov, L.S. Kudin, Appl. Surf. Sci. 126 (1998) 185.
[7] M.F. Butman, L.S. Kudin, A.A. Smirnov, Z.A. Munir, Int. J. Mass Spectrom. 202 (2000) 121.
[8] M.F. Butman, A.A. Smirnov, L.S. Kudin, Z.A. Munir, Surf. Sci. 458 (2000) 106.
[9] H. Dabringhaus, M.F. Butman, Surf. Sci. 560 (2004) 167.
[10] E.Ya. Zandberg, N.I. Ionov, Poverhnostnaya ionizatsiya (Surface Ionization), Nauka, Moscow, 1969.
[11] V.I. Batkin, O.Ya. Savchenko, Techn. Phys. 47 (5) (2002) 604.
[12] M.V. Knat'ko, M.N. Lapushkin, V.I. Paleev, Techn. Phys. 50 (4) (2005) 498.
[13] L.N. Sidorov, L.V. Zhuravleva, I.D. Sorokin, Mass Spectrom. Rev. 5 (1986) 73.
[14] L.N. Sidorov, Int. J. Mass Spectrom. 118–119 (1992) 739.
[15] S.V. Abramov, N.S. Chilingarov, A.Ya. Borshchevskiy, L.N. Sidorov, Int. J. Mass Spectrom. 231 (2004) 31.
[16] S.V. Abramov, N.S. Chilingarov, L.N. Sidorov, Russ. J. Electrochem. 5 (2007), in press (English translation available).
[17] S.V. Abramov, N.S. Chilingarov, J.V. Rau, A.Ya. Borshchevskiy, L.N. Sidorov, Int. J. Mass Spectrom. 245 (2005) 90.
[18] M. Szilgyi, Electron and Ion Optics, Plenum Press, New York, 1988.
[19] FemLab–Software for Multiphysics Modeling (http://www.comsol.com/).
[20] A.R. West, Basic Solid State Chemistry, 2nd ed., John Wiley & Sons, 1999.
[21] S. Hull, Rep. Prog. Phys. 67 (2004) 1233.
[22] A.M. Phahle, A.E. Hill, J.H. Calderwood, Thin Solid Films 22 (1974) 67.
[23] C. Hoff, H.-D. Wiemhöfer, O. Glumov, I.V. Murin, Solid State Ionics 101–103 (1997) 445.