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Abstract

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NEW COMPUTATIONAL METHODS IN MASS-SPECTROMETRIC STUDIES WITH A DOUBLE EFFUSION CELL AND THE THERMODYNAMIC PROPERTIES OF LITHIUM IODIDE

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A system of two cells connected by a channel, or a double effusion cell, was proposed for use in resolving the mass spectrum of vapors of complex composition into the spectra of individual compounds ([1]). Let us recall that in one of the cells, which we shall conventionally call the lower one, the substance under study is at temperature T_1; the cell is filled with saturated vapor. We shall restrict ourselves to the case in which the vapor contains only monomeric and dimeric molecules; the vapor pressures of the monomer and dimer in the lower cell are, respectively, p_m and p_d; the total pressure in the upper cell $p'_\mathrm{m} + p'_\mathrm{d}$ is equal to the pressure in the lower cell $p_\mathrm{m} + p_\mathrm{d}$ under viscous flow of the vapor through the connecting channel; in the case of molecular flow the equality ([2]) holds

$$\frac{p_\mathrm{m} + \sqrt{2}\,p_\mathrm{d}}{T_1^{1/2}} = \frac{p'_\mathrm{m} + \sqrt{2}\,p'_\mathrm{d}}{T_2^{1/2}}, \tag{1}$$

where T_2 is the temperature of the upper cell ($T_2 \geq T_1$). The composition of the vapor in the upper cell is determined by the equilibrium constant of the dimer dissociation reaction

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \tag{2}$$

at temperature T_2 and the total pressure. The vapor stream effusing from the upper cell through the effusion orifice is subjected to mass-spectrometric analysis. To decipher the complex mass spectrum, measurements of ion currents as functions of T_1 at $T_2 = \text{const}$ are necessary. As a result of the calculations, the coefficients of the mass spectrum may be obtained, i.e., the ratios of the line intensities in the mass spectrum of an individual compound to the intensity of one of them chosen as the reference. Knowledge of the individual mass spectra of the monomer and dimer makes it possible to determine the relative vapor composition $p_\mathrm{d}/p_\mathrm{m}$ from measurements of ion currents as functions of T_2 at $T_1 = \mathrm{const}$ (3). In the described variant of the use of the double effusion cell, the first stage of the work is an experiment on deciphering the complex spectrum (T_1 changes during the experiment, $T_2 = \mathrm{const}$), and the second is an experiment on determining the relative vapor composition ($T_1 = \mathrm{const}$, T_2 changes during the experiment). The indicated possibilities for using a double effusion cell were realized in studies of the vapors of sodium chloride and lithium fluoride (2) and cesium halides (4).

In order to reduce the time required and at the same time to increase the accuracy of the results, it is expedient to find such a way of carrying out the experiment and the calculations that all the information of interest to us may be obtained from a single series of measurements. This proves possible if measurements of the intensities of the dimer lines I_d and of each of the mixed intensities of the monomer and dimer

$$I_\mathrm{md} = I_\mathrm{m} + a_\mathrm{md} I_\mathrm{d}$$

are carried out in the following order of changing the temperature regime, described in (4): the maximum superheating of the upper cell is established, then its temperature T_2 is lowered stepwise at $T_1 = \mathrm{const}$; after the point $T_2 = T_1$ has been reached, the lowering is continued—

temperature of the upper chamber (in this part of the experiment the value of the temperature of the lower chamber is, generally speaking, immaterial; in particular, it may be kept constant). In what follows, the course of measurements just described will be denoted as an experiment at $T_1 = \mathrm{const}$. The calculation for such an experiment is based on the fact that, over a not too wide temperature interval, the logarithm of the equilibrium constant of reaction (1), $K_c = C_m^2/C_d$, and consequently also the logarithm of the quantity proportional to it, $K_c^* = I_m^2/I_d$, depend linearly on $1/T_2$. At the same time, owing to the presence of the dimer contribution to the intensity of the line I_{md}, the dependence of the quantity I_{md}^2/I_d on $1/T_2$ undergoes a break at the point $T_2 = T_1$, the slope of the line in the region $T_2 > T_1$ being smaller than the slope in the region $T_2 < T_1$. The break is due to the fact that at the indicated point the character of the temperature dependence of the pressures of the monomer and dimer changes discontinuously and, correspondingly, so does the contribution of the dimer to the line intensity I_{md}: in the region $T_2 > T_1$, as T_2 decreases, the dimer pressure increases and the monomer pressure decreases; in the region $T_2 < T_1$, the pressures of both compounds decrease. In principle, to determine the coefficient a_{md} it is sufficient to measure the ion currents at two temperature points lying on different sides of the point $T_2 = T_1$ and at an arbitrary third point; a_{md} is calculated from the requirement that the dependence of $\ln[(I_{md} - a_{md} I_d)^2/I_d]$ on $1/T_2$ be linear.

With a larger number of measurements, the optimum value of the coefficient a_{md} can be found by the method of least squares. For convenience in further calculations we shall operate with the quantity $(K_c^*)^{1/2} = I_m/I_d^{1/2}$. Putting $a_{md} = a^0_{md} + \Delta a_{md}$, where a^0_{md} is an approximate value of the coefficient sought, we obtain

$$\ln(I_m/I_d^{1/2}) = l + \ln(1 - \Delta a_{md} m), \tag{3}$$

where $l = \ln[(I_{md} - a^0_{md} I_d)/I_d^{1/2}]$, $m = I_d/(I_{md} - a^0_{md} I_d)$. To reduce the calculation to the solution of a system of linear equations, we expand the second term in expression (3) in a series, retaining only the first term of the expansion,

$$\ln(I_m/I_d^{1/2}) = l - \Delta a_{md} m. \tag{4}$$

Let us find such a value of Δa_{md} that the dependence of $\ln(I_m/I_d^{1/2})$ on $1/T_2$ is best approximated by the straight line $y = \alpha x + \beta$, where $x = 1/T_2$. From the requirement of the least-squares method,

$$\sum_1^n \Delta^2 = \sum_1^n (l - \Delta a_{md} m - \alpha x - \beta)^2 = \min,$$

where n is the number of measurements; differentiating with respect to Δa_{md}, α, and β, and setting the derivatives equal to zero, we obtain the system of normal equations

$$\begin{gathered} \beta n + \alpha \sum x + \Delta a_{md} \sum m = \sum l, \\ \beta \sum x + \alpha \sum x^2 + \Delta a_{md} \sum mx = \sum lx, \\ \beta \sum m + \alpha \sum mx + \Delta a_{md} \sum m^2 = \sum lm. \end{gathered} \tag{5}$$

The solution of this system gives the values of Δa_{md}, α, and β in the first approximation, since in the series expansion the terms of the second and higher orders were discarded. Therefore the calculation must be repeated, taking as a^0_{md} for the second approximation the value of a_{md} from the first approximation, and so on, until Δa_{md} becomes a sufficiently small quantity, such that

$$\Delta a_{md} \frac{I_d}{I_{md} - a^0_{md} I_d} \ll 1.$$

Simultaneously with the value of the coefficient a_{md}, the solution of system (5) gives ΔE_d, the heat of dissociation of the dimer molecules:

$$\alpha = -\Delta E_d/2R. \tag{6}$$

Measurements carried out in the region $T_2 \geqslant T_1$ make it possible to calculate the relative composition of the vapor. From the condition of equilibrium between the chambers (2) it follows that, at $T_1 = \text{const}$ and an arbitrary value of $T_2 \geqslant T_1$,

$$(p'_\mathrm{m} + \sqrt{2}p'_\mathrm{d})/T_2^{1/2} = \text{const}. \tag{7}$$

Making the substitution $p'_\mathrm{m} = k_\mathrm{m} I_\mathrm{m} T_2$, $p'_\mathrm{d} = k_\mathrm{d} I_\mathrm{d} T_2$, and dividing by k_m, we obtain

$$J_\mathrm{m} + \delta J_\mathrm{d} = b = \text{const}, \tag{8}$$

where $J_\mathrm{m} = I_\mathrm{m} T_2^{1/2}$, $J_\mathrm{d} = I_\mathrm{d} T_2^{1/2}$, $\delta = \sqrt{2}\, k_\mathrm{d}/k_\mathrm{m}$.

The requirements of the method of least squares lead to the system

$$bn_1 - \delta \sum J_\mathrm{d} = \sum J_\mathrm{m}, \qquad b \sum J_\mathrm{d} - \delta \sum J_\mathrm{d}^2 = \sum J_\mathrm{m} J_\mathrm{d}, \tag{9}$$

where n_1 is the number of measurements in the region $T_2 \geqslant T_1$. After calculating δ, the relative composition of the vapor at any temperature point can be found:

$$\frac{p_\mathrm{d}}{p_\mathrm{m}} = \frac{\delta}{\sqrt{2}} \frac{I_\mathrm{d}}{I_\mathrm{m}}. \tag{10}$$

Finally, let us use the method of least squares to determine the coefficients of the mass spectrum of the dimer from experimental data at $T_2 = \text{const}$. Writing the condition $(K_c^*)^{1/2} = \text{const}$ in the form

$$I_\mathrm{md}/I_\mathrm{d}^{1/2} - a_\mathrm{md} I_\mathrm{d}^{1/2} = b_1 = \text{const},$$

we obtain, in the usual way, a system of normal equations with respect to the unknowns b_1 and a_md:

$$\begin{aligned} b_1 n + a_\mathrm{md} \sum I_\mathrm{d}^{1/2} &= \sum I_\mathrm{md}/I_\mathrm{d}^{1/2}, \\ b_1 \sum I_\mathrm{d}^{1/2} + a_\mathrm{md} \sum I_\mathrm{d} &= \sum I_\mathrm{md}. \end{aligned} \tag{11}$$

The relations derived above were used in analyzing data obtained in experiments with lithium iodide. An anhydrous preparation was used, obtained by a procedure close to that described by I. V. Tananaev et al. ([5]).* The work was carried out on an MS-4 mass spectrometer equipped with an ion source with a double effusion chamber. With minor exceptions, the apparatus and the experimental conditions were the same as in ([2,4]). The differences between the double effusion chamber and that described earlier are that the upper chamber was made of tungsten; the diameter of the connecting channel was reduced to 1.0 mm.

To take into account the background of the instrument and scattering of the molecular beam by parts of the heating unit, a movable shutter in the form of a narrow strip was used, cutting off access to the ionization region chiefly for those molecules that had flown directly out of the effusion orifice. Measurements of the intensities of the ion currents of the monomer and dimer were carried out at an accelerating voltage of 3.2 kV; when recording the complete mass spectrum, the accelerating voltage was reduced to 1.3 kV. The ionizing voltage was about 40 V. Table 1 gives the mass spectrum of lithium iodide; the ion currents of all isotopic molecules are summed.

Table 1

Mass spectrum of lithium iodide; $T_1 = 719°\text{K}$; $T_2 = 722°\text{K}$

Li^+	J^+	LiJ^+	Li_2J^+	J_2^+	$Li_2J_2^+$	$Li_3J_2^+$	$Li_4J_3^+$
60.0	19.7	38.6	100.0	0.55	0.44	1.64	0.05

From the data of Table 1 it follows that monomeric, dimeric, trimeric, and tetrameric molecules are present in lithium iodide vapors, with dimeric Li_2J_2 molecules predominating. The concentration of the tetramer in the vapor, apparently,

* The author expresses his gratitude to V. I. Belousov for the synthesis of the anhydrous preparation.

is negligibly small, and the concentration of trimer is also insignificant; therefore the spectrum of the monomer—dimer—trimer system cannot be decoded with sufficient accuracy. Nevertheless, it is possible to determine the coefficient a_{23}, equal to the ratio of the ion currents $Li_2J^+/Li_3J_2^+$ in the mass spectrum of the trimer: $a_{23} = 2.2 \pm 1.7$ (weighted mean from 2 experiments at $T_1 = \text{const}$ and $T_2 = \text{const}$; here and below the ± sign indicates root-mean-square errors). The calculations were carried out using equations derived analogously to equations (5) and (11).

Table 2 gives the results of calculations of the coefficients a_{02} and a_{12}, representing the ratios of the intensities Li^+/Li_2J^+ and LiJ^+/Li_2J^+ in the dimer spectrum (the contribution of the trimer to the intensities was not taken into account).

Figure 1 shows, in semilogarithmic coordinates, the dependence of the ion currents $I_1(LiJ^+)$ and $I_2(Li_2J^+)$ on the temperature T_2, obtained in one of the experiments at $T_1 = \text{const}$. The same figure gives the temperature dependence of the quantity I_1^2/I_2, with a break at the point $T_2 = T_1$, and the temperature dependence of I_{11}^2/I_2 ($I_{11} = I_1 - a_{12}I_2$), which is well described by a straight line.

Table 2

Coefficients of the mass spectrum of lithium iodide dimer

Fig. 1. Temperature dependence of experimental and calculated quantities: 1 $-I_2$; 2 $-I_1$; 3 $-I_1^2/I_2$; 4 $-I_{11}^2/I_2$

Figure 1: Fig. 1. Temperature dependence of experimental and calculated quantities: 1 $-I_2$; 2 $-I_1$; 3 $-I_1^2/I_2$; 4 $-I_{11}^2/I_2$

Accelerating voltage, kV	$T_1 = \text{const}$, 1.3 a_{02}	$T_1 = \text{const}$, 1.3 a_{12}	$T_1 = \text{const}$, 3.2 a_{02}	$T_1 = \text{const}$, 3.2 a_{12}
$T_1 = \text{const}$	0.32 ± 0.02	0.16 ± 0.02	0.42 ± 0.01	0.15 ± 0.01
$T_2 = \text{const}$	0.30 ± 0.02	0.13 ± 0.01	0.43 ± 0.02	0.16 ± 0.01

Fig. 1. Temperature dependence of experimental and calculated quantities: 1 $-I_2$; 2 $-I_1$; 3 $-I_1^2/I_2$; 4 $-I_{11}^2/I_2$.

From the experimental data at $T_1 = \text{const}$, the temperature dependence of $\ln I_{11}/I_2^{1/2}$ gave the heat of dissociation of the dimer near the melting point (722°K): $\Delta E_d = 41.6 \pm 0.3$ kcal/g-mol (weighted mean from 4 determinations). From the temperature dependence of $\ln I_{11}I_2/I_3$ (I_3 is the ion current of the trimer Li_3J_2^+), the heat of dissociation of the trimer into dimer + monomer was found: $\Delta E_t = 32.7 \pm 0.6$ kcal/g-mol (weighted mean from 2 determinations). Using formulas (9)–(10), the ratio of the vapor pressures of the dimer and monomer was calculated: $p_d/p_m = 6$. Below the melting point this quantity depends only weakly on temperature, since the heats of sublimation of the monomer and dimer are close: $\Delta H_1 = 42.9 \pm 0.6$, $\Delta H_2 = 43.2 \pm 0.4$ kcal/g-mol (found from the temperature dependences of $\ln(I_{11}T)$ and $\ln(I_2T)$ in the interval 626–722°K; the results are close to those obtained earlier by Friedman (6)). Calibration of the sensitivity of the instrument with silver made it possible to estimate the absolute vapor pressure of the monomer at the melting point (722°K): $p_m = 3 \cdot 10^{-3}$ mm Hg.

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Note: Figure translations are in progress. See original paper for figures.