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Abstract

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A MASS-SPECTROMETRIC METHOD FOR DETERMINING PARTIAL VAPOR PRESSURES AND RELATIVE IONIZATION CROSS SECTIONS OF MOLECULES FROM ISOTHERMS OF COMPLETE EVAPORATION

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At present, in order to determine the molecular composition of vapor both over individual compounds and over binary systems, the mass-spectrometric method is being used with great success ([1]).

With the aid of this method it is possible to establish which molecules exist in the gas phase and to estimate the partial vapor pressure of each component. However, in the quantitative determination of partial pressures a number of difficulties arise, associated with the overlap of the mass spectra of the molecules contained in the vapor and with the absence of experimental data on the relative ionization cross sections of molecules of refractory compounds.

The method proposed in the present work makes it possible to carry out a complete interpretation of the mass spectrum, to determine relative ionization cross sections, and to determine the partial vapor pressures over multicomponent systems.

For simplicity let us consider a system consisting of components A and B.

1. Let molecules A and B be present in the gas phase at temperature T, giving, upon ionization, the ions A^+ and B^+. The experimentally obtained isotherm of complete evaporation of a charge q, containing q_1 of substance A and q_2 of substance B, is the dependence of the ion currents $A^+ – I_1$ and $B^+ – I_2$ on time.

As is known, the relation between the ion current I and the pressure p is expressed by the equation

$$p = kI/T \qquad (1)$$

To determine the proportionality coefficient k, we shall use the basic calculation equation of the Knudsen method ([2]):

$$q = ap\sqrt{\frac{M}{2\pi RT}}\,t$$

and transform it to the form:

$$q = a\sqrt{\frac{MT}{2\pi R}}\,k\int_0^t I\,dt = Bk\int_0^t I\,dt \tag{2}$$

by replacing the product pt by $\int p\,dt$ and substituting expression (1) for p, where q is the charge; a is the Clausing coefficient multiplied by the area of the effusion orifice; t is time; T is the absolute temperature; M is the molecular weight; R is the gas constant.

Applying (2) to the evaporation process of components A and B, we obtain

$$q_1 = B_1 k_1 \int_0^t I_1\,dt, \tag{2a}$$

$$q_2 = B_2 k_2 \int_0^t I_2\,dt. \tag{2 }$$

The areas under the curves of the dependence of the ion current on time,

$$s_1 = \int_0^t I_1\,dt$$

and

$$s_2 = \int_0^t I_2\,dt$$

can be found by graphical integration, which makes it possible to calculate the proportionality coefficients k_1 and k_2 from equations (2a) and (2b), and the ratio of the ionization cross sections of molecules A and B from the equation

$$\frac{\sigma_1}{\sigma_2} = \frac{k_2}{k_1}. \tag{3}$$

Using equation (1), one can calculate the partial vapor pressures of each component for any moment of time during the evaporation process. To pass from the time dependence to the concentration dependence and to construct the composition–partial pressure diagram, we divide the total area s_1 into a series of areas s_1'; s_1''; $s_1''' \ldots s_1^{(k)}$ by straight lines parallel to the ordinate axis. From equation

(2) it is seen that the ratio $\frac{s_1'}{s_1}$ is the fraction of substance evaporated by the time t_1, $\frac{s_1'+s_1''}{s_1}$ is the fraction of substance evaporated by the time t_2, etc. The amount of substance remaining in the charge by the time t_1 is

$$q_1' = g_1 - \frac{s_1'}{s_1} q_1,$$

and by the time t_2

$$q_1'' = q_1 - \frac{s_1'' + s_1'}{s_1} q_1,$$

etc. In an analogous manner, the amount of substance B in the charge at the times $t_1, t_2 \ldots t_n$ is determined and the composition of the condensate is calculated.

Thus, in the case of a two-component system with a simple vapor composition, the isotherm of total evaporation makes it possible to find the dependence of the partial pressures on the composition of the condensate and to determine the ratio of the ionization cross sections of the molecules present in the vapor. The possibility of using azeotropic mixtures with a known vapor composition to determine relative ionization cross sections has already been considered (3).

2. Let molecules A, B, and AB be present in the gas phase at temperature T, giving ions A^+, B^+, and AB^+ upon ionization. The experimentally obtained isotherm of total evaporation represents the dependence of the ion currents A^+—I_1, B^+—I_2, AB^+—I_3 on time. In this case the ion current A^+ has a dual origin: I_{13}, from the molecule AB, and I_{11}, from the molecule A. Similarly, $I_2 = I_{22} + I_{23}$, where I_{22} is the ion current B^+ from molecule B, and I_{23} is the ion current B^+ from molecule AB.

To interpret the mass spectrum, i.e., to determine the coefficients

$$a_{13} = \frac{I_{13}}{I_3} \quad \text{and} \quad a_{23} = \frac{I_{23}}{I_3},$$

it is sufficient, as when using a double effusion chamber (4,5), to measure the ion currents at constant temperature and at different pressures in the effusion chamber.

For two different compositions of the condensate we write:

$$I_1 = I_{11} + a_{13} I_3 \tag{4}$$

$$I_1' = I_{11}' + a_{13} I_3'.$$

System (4) contains three unknowns, a_{13}, I_{11}, and I'_{11}; the third equation is obtained from the condition that the equilibrium constant is independent of pressure at constant temperature:

$$K_p = \frac{p_1 p_2}{p_3} = \frac{p'_1 p'_2}{p'_3}.$$

or through ion currents

$$\frac{I_{11} \cdot I_{22}}{I_3} = \frac{I'_{11} \cdot I'_{22}}{I'_3}. \tag{5}$$

In the region rich in component B, $I_{22} \cong I_2$ and $I'_{22} = I'_2$, and equation (5) can be written in the form $I'_{11} = cI_{11}$, where $c = \dfrac{I_2 \cdot I'_3}{I_3 \cdot I'_2}$, a quantity determined experimentally. In an analogous way, a system of equations is drawn up for determining the coefficient a_{23}. With the aid of the coefficients a_{13} and a_{23}, we find the total ion current from the molecule AB and its complete mass spectrum. On the basis of the results of the interpretation of the mass spectrum, total-evaporation isotherms may be constructed for AB molecules from the sum of the ion currents I_3, I_{23}, I_{13}; for A molecules—from the ion current I_{11}; and for B molecules—from the ion current I_{22}, and the quantities are also found

$$s_{11} = \int_0^t I_{11} dt, \quad s_{22} = \int_0^t I_{22} dt, \quad s_3 = \int_0^t (I_3 + I_{23} + I_{13}) dt.$$

To determine the connection coefficients k_1, k_2, and k_3, we shall use equation (2) and write it, taking into account the fact that components A and B have partially evaporated in the form of AB molecules:

$$q_1 = q_1^0 - \frac{M_1}{M_3} q_3 = B_1 k_1 \int_0^t I_{11}\, dt,$$

$$q_2 = q_2^0 - \frac{M_2}{M_3} q_3 = B_2 k_2 \int_0^t I_{22}\, dt, \tag{6}$$

$$q_3 = B_3 k_3 \int_0^t (I_3 + I_{23} + I_{13})\, dt,$$

where: q_1^0 (q_2^0) is the amount of substance A (B) in the initial sample; $q_1(q_2)$ is the amount of substance that evaporated in the form of A (B) molecules; q_3 is the amount of substance that evaporated in the form of AB molecules. System (6) contains a fourth unknown, q_3. Since, upon complete evaporation at the end of the experiment, the less volatile component A should remain, as the fourth equation we write: $p_1 = k_1 I_{11} T$, where p_1 is the saturated-vapor pressure of component A. If the investigated two-component system forms an azeotrope of known composition, then the quantities q_1, q_2, and q_3 are determined from the system of equations:

$$q_1 + q_2 + q_3 = q_1^0 + q_2^0; \tag{7}$$

$$\frac{q_1 + \frac{M_1}{M_3} q_3}{q_1 + q_2 + q_3} = \frac{q_1^0}{q_1^0 + q_2^0} \quad \text{—composition of the initial sample;} \quad \frac{q_1' + \frac{M_1}{M_3} q_3'}{q_1' + q_2' + q_3'} = N \quad \text{—composition}$$

of the mixture at the end of evaporation (composition of the azeotrope). Solving system (7) gives the values of the quantities q_1, q_2, and q_3. From the equations of system (6), the coefficients k_1, k_2, and k_3 and the ratios of the ionization cross sections are calculated:

$$\frac{\sigma_2}{\sigma_1} = \frac{k_1}{k_2} \quad \text{and} \quad \frac{\sigma_3}{\sigma_1} = \frac{k_1}{k_3}.$$

The partial pressures are determined from equation (1), i.e.,

$$p_1 = k_1 I_{11} T, \quad p_2 = k_2 I_{22} T \quad \text{and} \quad p_3 = k_3 (I_3 + I_{13} + I_{23}) T.$$

The composition of the condensate is calculated according to the scheme set forth in the first section.

3. In an analogous manner, systems in the gas phase over which the molecules A_2, A, AB, B are present, giving upon ionization the ions A_2^+, A^+, AB^+, B^+, or A_2^+, A^+, B^+, and certain other systems, for example those containing in the vapor the molecules A_2, A, B and giving upon ionization the ions A_2^+, A^+, B^+, may be considered. In all cases the isotherms of complete evaporation make it possible to decipher the mass spectrum, find the ratio of ionization cross sections, and determine the partial pressures as a function of the composition of the condensate.

Using the method described, we investigated the system NaF—ZrF_4*. The mass spectrum of the $NaZrF_5$ molecule, the ratio of ionization cross sections, and the composition–partial pressure diagram are presented below and in Fig. 1.

Mass spectrum of the positive ions of the $NaZrF_5$ molecule at a temperature of 1167°K and an ionizing-electron energy of 80 eV.

Fig. 1. Composition-partial pressure diagram at 1167°K: 1 —pressure of NaF vapor, 2 —pressure of Na_2F_2 vapor, 3 —pressure of $NaZrF_5$ vapor, 4 —pressure of ZrF_4 vapor

Figure 1: Fig. 1. Composition-partial pressure diagram at 1167°K: 1 —pressure of NaF vapor, 2 —pressure of Na_2F_2 vapor, 3 —pressure of $NaZrF_5$ vapor, 4 —pressure of ZrF_4 vapor

Na^+	ZrF_3^+	ZrF_2^+	ZrF^+	Zr^+
234	100	19.8	15.4	9.4

Relative ionization cross sections

	NaF	ZrF_4	$NaZrF_5$
σ	1.0	1.8	2.5

Fig. 1. Composition—partial pressure diagram at 1167°K:
1 —pressure of NaF vapor, 2 —pressure of Na_2F_2 vapor, 3 —pressure of $NaZrF_5$ vapor, 4 —pressure of ZrF_4 vapor.

The dissociation enthalpies of the $NaZrF_5$ and Na_2F_2 molecules were found from the equation for the isobar of the chemical reaction and are $62.2 \pm 4.6\ \frac{\text{kcal}}{\text{mol}}$ and 54.9 ± 2.2, respectively.

In studying the NaF—ZrF_4 system it was established that, under conditions of molecular effusion, evaporation into vacuum without a change in composition occurs at a total pressure over the system different from the extremal one. This is explained by the fact that the extremum of the total pressure, in accordance with Konovalov’ s law, is observed at a vapor composition coinciding with the composition of the condensate, whereas distillation at constant composition under conditions of molecular effusion is possible only when the composition of the condensate coincides with the composition of the stream leaving the effusion chamber. As is known, for a viscous character of effusion the compositions of the vapor and of the stream coincide, while for molecular effusion they differ in the ratio of the square roots of the masses.

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* V. I. Belousov and V. B. Sholts took part in the experimental work.

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

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