On the Double Oven Method of Mass Spectrometer for Relative Partial Pressure Measurements*

MINORU TSUDA**

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The frit-type double oven method of mass spectrometer has been solved for molecular gas flow. The fragmentation coefficient and relative partial pressure are calculated for the monomer and dimer of alkali halides in the single component system. Simple formula for experiment is derived to determine relative partial pressure of monomer and dimer. In case of existence of monomer, dimer and trimer, relative partial pressures are also calculated.

1. Introduction

Concerning as mass spectrometric studies about the high temperature thermochemical property of substances^{1),2)}, the double oven method was proposed^{3),4)} and used⁵⁾ in connection with a study of polymeric species in equilibrium with alkali halides⁶⁾. From usual single oven measurements alone, it was impossible to determine the relative amounts of polymeric species, since the relative ionization cross-sections were unknown.

In the previous works^{3)~5)}, two ovens connected with a pipe freely established the same pressure. Then the vapor pressure in the upper oven was so limited as the mean free path of vapor should be larger than twenty times of the effusion hole diameter of the upper oven and smaller than the connected pipe diameter.

The existence of the lower and upper limits of the mean free path restricts the vapor pressure within the small range or there exists no suitable pressure range for usual effusion hole and pipe diameters, and then there exists no suitable temperature range of the upper oven. On the other hand, two ovens can be connected with small size of openings or frit⁷⁾. In this case the mean free path of upper oven vapor needs at least large compared with twenty times of the diameter of the effusion hole, but there is no restriction on the upper limit of the mean free path. The mean free path of lower oven vapor needs large compared with twenty times of the diameter of the frit openings in order to maintain molecular flow, and there is also no restriction on the upper limit. Accordingly, suitable temperature range of the upper oven may be found for temperatures of the lower oven, so that both gas flows from the lower to the upper oven and from the upper oven to the ion source of mass spectrometer are molecular flows. Hence, the ratios of the ionization constants and fragmentation coefficient of polymeric species can be determined for single component system by the frit-type double oven method.

2. Ratio of Ionization Constants for Monomer and Dimer

Let us assume that only monomers and dimers exist and the lower oven contains the condensed

* This work was studied at Argonne National Laboratory, Argonne, Ill., U.S.A.

**Mass Spectrometer Laboratory, Tokyo Institute of Technology (Ohokayama, Meguro-ku, Tokyo)

phase at temperature T_1 and vapor pressure P_1 , and that upper oven temperature T_2 is little higher than T_1 and upper oven pressure is P_2 . Then upper oven temperature is changed to T_2' little higher than T_2 at constant lower oven temperature. Let N_{12} is the mole number of gas flow per unit time from the lower oven to the upper one, N_{23} is the mole number of gas flow per unit time from the upper oven to outside of it, and each suffix m, d, 1, 2, and 3 to characterize monomer, dimer, the lower oven, the upper oven and outside of the upper oven respectively.

From mass conservation law in the steady state following equations are obtained.

$$N_{m12} + 2N_{d12} = N_{m23} + 2N_{d23} \quad (1)$$

$$= N_{m23}' + 2N_{d23}' \quad (2)$$

where N' represents the mole number of gas flow per unit time at upper oven temperature T_2' and constant lower oven temperature T_1 . Considering well known quantity of molecular flow Q^* is equal to PV and NRT where V and R are the volume of gas flow per unit time and gas constant respectively, N can be written as follows,

$$\left. \begin{aligned} N_{m23} &= K_{23} (1/T_2 M_m)^{1/2} (P_{m2} - P_{m3}) \\ N_{d23} &= K_{23} (1/T_2 M_d)^{1/2} (P_{d2} - P_{d3}) \\ N_{m23}' &= K_{23} (1/T_2' M_m)^{1/2} (P_{m2}' - P_{m3}') \\ N_{d23}' &= K_{23} (1/T_2' M_d)^{1/2} (P_{d2}' - P_{d3}') \end{aligned} \right\} \quad (3)$$

where K_{23} is a constant independent of the pressure, temperature and molecular weight of gases, but depend on the gas leak size. This Equation (3) is substituted in Equations (1) and (2). Considering $P_2 \gg P_3$ and $2M_m = M_d$ where P_{m2} , P_{m3} , M_m and M_d are monomer pressure in the upper oven and at outside of the upper oven, molecular weight of monomer and dimer respectively, one gets

$$(1/T_2)^{1/2} (P_{m2} + \sqrt{2} P_{d2}) = (1/T_2')^{1/2} (P_{m2}' + \sqrt{2} P_{d2}'). \quad (4)$$

It can be shown⁸⁾ from ideal gas theory that pressure P_i of a specy in the Knudsen cell is related to the measured ion intensity I_i by

$$P_i = k_i I_i T \quad (5)$$

where k_i is a proportionality constant assumed independent of temperature, but dependent on such as the beam geometry, the ionization cross-section, and the collection and detection efficiencies.

Equation (4) plus four equations similar to (5) constitute five equations in six unknowns, the unknowns being four pressures and two proportionality constants. Thus one can solve for the ratio of any two pressures or for the ratio of constants, obtaining

$$k_d/k_m = (I_m' T_2^{1/2} - I_m T_2'^{1/2}) / \sqrt{2} (I_d T_2^{1/2} - I_d' T_2'^{1/2}) \quad (6)$$

$$P_d/P_m = k_d I_d / k_m I_m. \quad (6a)$$

If the temperature change is small compared with ion intensity changes one can cancel the temperature terms in Equation (6) assuming $T_2^{1/2} \approx T_2'^{1/2}$.

Then the following equation is obtained.

$$k_d/k_m = (I_m' - I_m) / \sqrt{2} (I_d - I_d'). \quad (6b)$$

Ion currents I_m' and I_m in above formula can not be measured directly, because the fragment ions of the same mass come from dimer I_d' and I_d . So the fragmentation coefficient should be determined⁴⁾. When the temperature of the lower oven is raised up to T_1^* , the vapor pressures in the lower oven increase and the vapor pressure P_m , P_d in the upper oven increase to P_m^* , P_d^* . While the temperature T_2 of the upper oven remains constant, and following equilibrium is attained for the upper oven,

* $Q = K(T/M)^{1/2} (P_2 - P_3)$ dyne. cm/sec.

** For alkali halides 1° temperature change at 1000°K, i.e. 0.1% temperature change causes about 3% ion intensity change experimentally.

$$P_m^{*2} / P_d^* = P_m^2 / P_d = K_p \quad (7)$$

where K_p is the equilibrium constant between dimer and monomer pressures at constant temperature. Ion currents I_d^* and I_d , corresponding to dimer pressure P_d^* and P_d , are represented as

$$P_d^* / P_d = I_d^* / I_d = n. \quad (8)$$

From Equations (7) and (8), the following Equation (9) is obtained.

$$P_m^* / P_m (= I_m^* / I_m) = \sqrt{n}. \quad (9)$$

The fragmentation coefficient k is defined as follows

$$I_m = I_{md} - k \cdot I_d \quad (10)$$

$$I_m^* = I_{md}^* - k \cdot I_d^* \quad (11)$$

$$I_m' = I_{md}' - k \cdot I_d' \quad (12)$$

where suffix md refers to the total monomer ions from monomer molecules plus cracked one from dimers, and I^* and I refer to the ion currents at lower oven temperature T_1^* and T_1 respectively and upper oven temperature T_2 ,

The fragmentation coefficient k is obtained from Equations (10) and (11), using Equations (8) and (9), as follows,

$$\left. \begin{aligned} k &= (I_{md}^* - \sqrt{n} I_{md}) / I_d (n - \sqrt{n}) \\ \text{where} \\ n &= I_d^* / I_d. \end{aligned} \right\} \quad (13)$$

Then, Equations (10) and (12) are substituted into Equation (6b), finally Equation (14) for k_d/k_m is obtained as following relation,

$$\left. \begin{aligned} k_d / k_m &= 1 / \sqrt{2} \{ (\Delta I_{md} / - \Delta I_d) + k \} \\ \text{where} \\ \Delta I_{md} &= I_{md}' - I_{md} \\ \Delta I_d &= I_d' - I_d. \end{aligned} \right\} \quad (14)$$

Using the relation shown in Equation (13), the fragmentation coefficient k can be experimentally determined by changing lower oven temperature at constant temperature of the upper oven. While, the ratio I_{md}/I_d in Equation (14) can be experimentally determined from the following procedure. After that the thermal equilibrium was attained between the upper oven and its heating system, the heater resistance of the upper oven is slightly decreased and the resulted variation of the peak heights of the total monomer ion currents I_{md} and the dimer ion currents I_d are recorded at the same time. The slope ratio of the peak heights caused by the transient temperature increase in few degrees of the upper oven gives $\Delta I_{md}/-\Delta I_d$ shown in Equation (14). Consequently, one can determine the ratio of the proportionality constants k_d/k_m using Equation (14).

3. Ratios of Ionization Constants for Monomer, Dimer and Trimer

Analogously, when there are not only monomer and dimer but trimer—the quantities concerned to trimer are denoted by the suffix t—the ratios of the proportionality constants can be determined by changing upper oven temperatures from T_2 to T_2' and T_2'' . The following two molecular flow equations at each respective temperature are obtained,

$$\left. \begin{aligned} N_{m23} + 2N_{d23} + 3N_{t23} &= N_{m23}' + 2N_{d23}' + 3N_{t23}' \\ N_{m23} + 2N_{d23} + 3N_{t23} &= N_{m23}'' + 2N_{d23}'' + 3N_{t23}'' \end{aligned} \right\} \quad (15)$$

where N_{23} , N_{23}' and N_{23}'' denote the mole numbers of the molecular flow per unit time from the upper oven to outside of it at upper oven temperatures T_2 , T_2' and T_2'' , respectively. These mole

numbers may be represented by equations similar to Equation (3), and each pressure may be represented by following nine equations,

$$\left. \begin{aligned} P_m &= k_m I_m T & P_m' &= k_m I_m' T' & P_m'' &= k_m I_m'' T'' \\ P_d &= k_d I_d T & P_d' &= k_d I_d' T' & P_d'' &= k_d I_d'' T'' \\ P_i &= k_i I_i T & P_i' &= k_i I_i' T' & P_i'' &= k_i I_i'' T'' \end{aligned} \right\} \quad (16)$$

where P , P' and P'' are upper oven pressures of each molecular species corresponding to upper oven temperatures T , T' and T'' . The equations similar to Equation (3) and concerned to N_{23} , N_{23}' and N_{23}'' are substituted into Equation (15), and eleven equations from Equations (15) and (16) are obtained with twelve unknowns which are nine pressures and three ionization constants. Thus one may solve for the ratios of the ionization constants or partial pressures from similar way as mentioned above for two kinds of molecular species,

$$\left. \begin{aligned} k_d/k_m &= \{ (I_m T_2^{1/2} - I_m' T_2'^{1/2})(I_i T_2^{1/2} - I_i'' T_2''^{1/2}) \\ &\quad - (I_m T_2^{1/2} - I_m'' T_2''^{1/2})(I_i T_2^{1/2} - I_i' T_2'^{1/2}) \} / \\ &\quad \sqrt{2} \{ (I_d T_2^{1/2} - I_d'' T_2''^{1/2})(I_i T_2^{1/2} - I_i' T_2'^{1/2}) - \\ &\quad (I_d T_2^{1/2} - I_d' T_2'^{1/2})(I_i T_2^{1/2} - I_i'' T_2''^{1/2}) \} \\ P_d/P_m &= k_d I_d / k_m I_m \end{aligned} \right\} \quad (17)$$

$$\left. \begin{aligned} k_i/k_m &= \{ (I_m T_2^{1/2} - I_m' T_2'^{1/2})(I_d T_2^{1/2} - I_d'' T_2''^{1/2}) - \\ &\quad (I_m T_2^{1/2} - I_m'' T_2''^{1/2})(I_d T_2^{1/2} - I_d' T_2'^{1/2}) \} / \\ &\quad \sqrt{3} \{ (I_i T_2^{1/2} - I_i'' T_2''^{1/2})(I_d T_2^{1/2} - I_d' T_2'^{1/2}) - \\ &\quad (I_i T_2^{1/2} - I_i' T_2'^{1/2})(I_d T_2^{1/2} - I_d'' T_2''^{1/2}) \} \\ P_i/P_m &= k_i I_i / k_m I_m \end{aligned} \right\} \quad (18)$$

where I , I' and I'' are the ion currents corresponding to upper oven temperatures T_2 , T_2' and T_2'' respectively.

On the other hand, there is free connection between the lower oven and upper one, instead of the frit to obtain the pressure equilibrium in both ovens at constant lower oven pressure. The upper oven temperatures T_2 , T_2' and T_2'' are slightly differed, following Equation (19) can be deduced instead of Equation (15),

$$\left. \begin{aligned} P_m + P_d + P_i &= P_m' + P_d' + P_i' \\ P_m + P_d + P_i &= P_m'' + P_d'' + P_i'' \end{aligned} \right\} \quad (19)$$

Then the ratios of the proportionality constants are obtained from eleven equations from Equation (16) plus Equation (19) as follows.

$$\left. \begin{aligned} k_d/k_m &= \{ (I_m T_2 - I_m' T_2')(I_i T_2 - I_i'' T_2'') - (I_m T_2 - I_m'' T_2'')(I_i T_2 - I_i' T_2') \} / \\ &\quad \{ (I_d T_2 - I_d'' T_2'')(I_i T_2 - I_i' T_2') - (I_d T_2 - I_d' T_2')(I_i T_2 - I_i'' T_2'') \} \\ P_d/P_m &= k_d I_d / k_m I_m \end{aligned} \right\} \quad (20)$$

$$\left. \begin{aligned} k_i/k_m &= \{ (I_m T_2 - I_m' T_2')(I_d T_2 - I_d'' T_2'') - (I_m T_2 - I_m'' T_2'')(I_d T_2 - I_d' T_2') \} / \\ &\quad \{ (I_i T_2 - I_i'' T_2'')(I_d T_2 - I_d' T_2') - (I_i T_2 - I_i' T_2')(I_d T_2 - I_d'' T_2'') \} \\ P_i/P_m &= k_i I_i / k_m I_m \end{aligned} \right\} \quad (21)$$

When the influence of trimer should be taken into consideration, Equations (17) and (18) or Equations (20) and (21) may be used in order to determine the ratios of the proportionality constants of monomer, dimer and trimer.

4. Discussion

When simple formula (14) is used instead of Equation (6) to obtain the ratio of the ionization constants k_d / k_m , the slope ratio $\Delta I_{md} / -\Delta I_d$ can be measured at one time. This eliminates or diminishes the experimental errors caused from variations of the frit size of the oven by contamination, ionization efficiency, background of ion source and detecting efficiency of ions in time interval on two separated measurements at different temperatures. For Equation (14) chemical equilibrium of dimer and monomer is unnecessary, but existence of the conservation law in steady state shown in Equations (1) and (2) is necessary. If steady state conditions (1) and (2) do not exist time in time, Equations (6), (10), (12) and (13) should be used in place of Equation (14) to obtain the ratio of the ionization constants k_d / k_m .

In case of monomer and dimer, the fragmentation coefficient is obtained by Equation (13). By similar way the fragmentation coefficients may be calculated for coexistence of monomer, dimer and trimer.

In Sections 2 and 3 calculations were made for one component system. By similar treatments, calculations for multi-component system may be done, but resulting equations may become considerably complicated.

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