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SCATTERING IN A MOLECULAR BEAM AS A RESULT OF INTRA-BEAM COLLISIONS

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ABSTRACT

Collisions between molecules in a molecular beam can be a more serious cause of scattering than collisions of the beam molecules with a background gas. The magnitude of this effect is species dependent and is capable of influencing experimental results, as is shown by means of examples from high temperature mass-spectrometry.

INTRODUCTION

Whether it is a desired effect, as in the determination of reaction cross sections, or whether it is a detriment, scattering of a molecular beam as a result of gas phase collisions is a subject of concern to experimenters in the field. Collisions between beam molecules and ambient gas molecules or molecules of another beam are discussed thoroughly in many monographs and papers,[1,2,3,4,5] but only a few of these mention collisions between molecules in the same beam, and the author is aware of only the one article by V. S. Troitskii which undertakes a quantitative treatment of the problem.[6]

In what follows, a relatively simple model is developed and used to show that intra-beam collisions can cause a significant attenuation of the beam, and that the degree of attenuation varies with each species, being a function of a collision cross-section, a mean relative velocity, and the beam composition.

DEVELOPMENT OF THE MODEL

The probability c_{AB} that a molecule A with velocity v_A will collide with a B molecule in the increment of time dt is given by the formula,[7]

$$c_{AB}(v_A,t)\ dt = \frac{\pi\sigma_{AB}^2}{\Omega}\ dt\ n_B \frac{4\alpha_B^3}{\pi^{\frac{1}{2}}} \int_{v_B}\int_{\theta}\int_{\phi} \exp(-\alpha_B^2\ v_B^2)\ v_B^2$$

$$(v_A^2 + v_B^2 - 2v_A v_B \cos\theta)^{1/2} \sin\theta\ d\phi\ d\theta\ dv_B \quad ,$$

where $\alpha_B = (m_B/2kT)^{1/2}$, σ_{AB} is the collision radius for an A-B collision, n_B is the density of B molecules at the point in question, θ and ϕ are the polar and azimuthal angles respectively between the velocity vectors $\vec{v}_A$ and $\vec{v}_B$, and Ω is the segment of solid angle over which θ and ϕ may range. For a molecule in an enclosed volume, $\Omega = 4\pi$, but for a molecule in a molecular beam, Ω is equal to ω_o, the solid angle subtended by the source orifice, which means Ω will be a function of x, the distance along the beam, as will n_B.

Distance, rather than time, is of interest, so the differential in time dt is converted to dx/v_A, to give the probability that a molecule A at x will sustain a collision with a B molecule in travelling the distance dx.

It is now desired to average this probability over all the A molecules arriving at point x. This is done by integrating over the range of v_A using the velocity distribution function,

$2\alpha_A^4 \exp(-\alpha_A^2 v_A^2) v_A^3 dv_A$, where $\alpha_A = (m_A/2kT)^{1/2}$. The mean collision probability C_{AB} is then expressed as the following:

$$C_{AB}(x)\, dx = \frac{\pi\sigma_{AB}^2}{\Omega}\, dx\, n_B \frac{8\alpha_A^H \alpha_B^3}{\pi^{1/2}} \int_{v_A} \int_{v_B} \int_{\theta} \int_{\phi} \exp(-\alpha_A^2 v_A^2) v_A^2$$

$$\exp(-\alpha_B^2 v_B^2) v_B^2 (v_A^2 + v_B^2 - 2v_A v_B \cos\theta)^{1/2} \sin\theta\, d\phi\, d\theta\, dv_B\, dv_A \,. \qquad (1)$$

For the case of the molecule in the isotropic environment of an enclosed volume, the multiple integral with its normalizing factor can be evaluated analytically to give $(1 + m_A/m_B)^{1/2}$, but in general such an evaluation is not possible for a molecular beam where Ω is restricted to ω_o. In the latter case the simplifying assumption can be made that θ is approximately zero, that is, that all the molecules are travelling in essentially the same direction. This assumption will give too low a collision probability, especially in the vicinity of the orifice, but the result can be considered a lower limit. Equation (1) then loses the dependence on θ and ϕ and assumes the form of Eq. (2).

The two integrals in the final expression can be integrated by parts to give Φ_{AB}, a measure of the relative velocities which depends only on the ratio of the masses:[6]

$$\Phi_{AB} = 2(1 + \mu_{AB})^{1/2} - \frac{\mu_{AB}}{(1 + \mu_{AB})^{3/2}} - 1 - \mu_{AB}^{1/2} \,,$$

$$C_{AB}(x)\,dx = n_B \pi \sigma_{AB}^2\,dx\,\frac{8\alpha_A^4\alpha_B^3}{\pi^{1/2}} \int_0^\infty \int_0^\infty \exp(-\alpha_A^2 v_A^2)\, v_A^2 \exp(-\alpha_B^2 v_B^2)\, v_B^2 \left|v_A - v_B\right| dv_B\, dv_A$$

$$= n_B \pi \sigma_{AB}^2\,dx \left[\frac{8\alpha_A^4\alpha_B^3}{\pi^{1/2}} \int_0^\infty \int_0^{v_A} \exp(-\alpha_A^2 v_A^2)\, v_A^2 \exp(-\alpha_B^2 v_B^2)\, v_B^2 (v_A - v_B)\, dv_B\, dv_A \right.$$

$$\left. + \frac{8\alpha_A^4\alpha_B^3}{\pi^{1/2}} \int_0^\infty \int_{v_A}^\infty \exp(-\alpha_A^2 v_A^2)\, v_A^2 \exp(-\alpha_B^2 v_B^2)\, v_B^2 (v_B - v_A)\, dv_B\, dv_A \right] . \qquad (2)$$

$$= n_B \pi \sigma_{AB}^2\,dx\,\Phi_{AB}$$

where $\mu_{AB} = m_A/m_B$. A plot of Φ_{AB} versus μ_{AB} is shown in Fig. I.

Equation (2) can now be reduced to the form,

$$C_{AB}(x)\, dx = \pi\sigma_{AB}^2\, \Phi_{AB}\, n_B(x)\, dx \;, \tag{3}$$

where the dependence on x of n_B is indicated. To a good approximation,

$$n_B(x) = n_{BO}\, \frac{\omega_o(x)}{4\pi} = \frac{p_B}{kT}\, \frac{\omega_o(x)}{4\pi} \;,$$

where n_{BO} is the concentration of B molecules inside the source, p_B is the partial pressure of B in the source, and ω_o has been defined above. The following expression, derived for a circular orifice of area a, is sufficiently accurate for the present purpose:

$$\omega_o(x) = 2\pi \left[1 - \left(\frac{2\pi x^2}{2\pi x^2 + a} \right)^{1/2} \right] .$$

These relations substituted into Eq. (3) give,

$$C_{AB}(x)\, dx = \pi\sigma_{AB}^2\, \Phi_{AB}\, \frac{p_B}{2kT} \left[1 - \left(\frac{2\pi x^2}{2\pi x^2 + a} \right)^{1/2} \right] dx \;.$$

Now to find $S_{AB}(L)$, the probability that an A molecule will successfully travel the beam length L without colliding with a B molecule, the logarithm of $1 - C_{AB}(x)\, dx$ is integrated from zero to L:

$$\ln \left[1 - C_{AB}(x)\, dx\right] \cong - C_{AB}(x)\, dx, \text{ so that}$$

$$\ln S_{AB}(L) = -\pi\sigma_{AB}^2\, \Phi_{AB}\, \frac{p_B}{2kT} \int_0^L \left[1 - \left(\frac{2\pi x^2}{2\pi x^2 + a}\right)^{1/2}\right] dx$$

$$= -\pi\sigma_{AB}^2\, \Phi_{AB}\, \frac{p_B}{2kT} \left[L + (a/\pi)^{1/2} - (L^2 + a/\pi)^{1/2}\right] .$$

Ordinarily L is much greater than $(a/\pi)^{1/2}$, so the expression in square brackets can be expanded in terms of $(1/L)(a/\pi)^{1/2}$, and, considering only first order terms, is approximated by $(a/\pi)^{1/2}\,[1 - (1/2L)(a/\pi)^{1/2}]$. In most cases even the first order terms can be disregarded, leaving only $(a/\pi)^{1/2}$.

If the beam is long enough to warrant this approximation, the probability that a molecule A can travel this length without colliding with a B molecule is given by the equation,

$$S_{AB} = \exp -\left[\frac{p_B}{2kT}\, \pi\sigma_{AB}^2\, \Phi_{AB}(a/\pi)^{1/2}\right] . \qquad (4)$$

The parameter L no longer appears in the expression, which means most of the collisions occur in the vicinity of the orifice, so that lengthening the beam beyond the point where L is much greater than $(a/\pi)^{1/2}$ will not significantly increase the number of collisions. If the pressure p_B is great enough so that every molecule sustains at least one collision, then the orifice can no longer be considered the source. Instead the source of the beam appears to be a diffuse

"cloud" of molecules just outside the orifice. Estermann mentions this phenomenon as having been observed by several investigators.[5]

Equation (4) can be combined with the usual formula for the intensity of a molecular beam to give an expression corrected for intra-beam scattering:[1,3,5]

$$J = \frac{p_A\, a}{\pi L^2 (2\pi m_A kT)^{1/2}} \exp\left[- \frac{p_A}{2kT} \pi\sigma_{AA}^2\, \Phi_{AA}\, (a/\pi)^{1/2} \right].$$

J is the beam flux-density at L, and the other symbols have already been defined. In this case the A and B molecules are identical as the subscripts indicate. Differentiation of this equation with respect to p_A leads to the prediction of a maximum in J at a value of p_A given by the relation,

$$p_A(\max) = \frac{2kT}{\pi\sigma_{AA}^2\, \Phi_{AA} (a/\pi)^{1/2}} .$$

Although the phenomenon of a maximum in the intensity as a function of pressure has been observed,[5] it does not appear to be the general case. Derivation of the formula above predicates molecular flow, but at $p_A(\max)$ the mean free path inside the source is about 0.1 $a^{1/2}$, that is, about an order of magnitude smaller than the dimensions of the orifice, which means that viscous flow is starting. Under these conditions the validity of the formula is marginal and depends on parameters not considered in the derivation, such as, perhaps, the geometry of the orifice, etc.

AN ILLUSTRATIVE EXAMPLE

Equation (4) contains three parameters which are dependent on the species: p_B, σ_{AB}, and Φ_{AB}. The interaction of these parameters can be illustrated by means of an example. Consider a beam containing three species: Species 1 is a monomer molecule; species 2 is a dimer of the same molecule, therefore having twice the mass and a somewhat greater size; species 3 is a molecule having the same mass as the dimer but the same size as the monomer. For each of these species the attenuation as a result of collisions can be calculated in each of two cases. Case I: the principal component of the beam is species 1, with species 2 and 3 present in minor quantities. Case II: the principal component is species 2, with species 1 and 3 minor constituents. Only collisions of the species in question with the major component will be considered. Then Φ_{AB} will have the following values, with the numerical subscripts indicating the identity of A and B respectively (e.g. Φ_{12} refers to the instance with species 1 as A and species 2 as B):

$$\Phi_{11} = \Phi_{22} = \Phi_{32} = 0.475, \quad \Phi_{12} = 0.470, \quad \Phi_{21} = \Phi_{31} = 0.665.$$

The remaining parameters are assigned reasonable values such as might be encountered at the high pressure limit of a mass-spectrometric determination of vapor species from a Knudsen cell:

$$T = 1000^{\circ}K, \quad p_B = 0.1 \text{ torr}, \quad a = 10^{-2} \text{ cm}^2,$$

$$\sigma_{11} = \sigma_{31} = 5 \times 10^{-8} \text{cm}, \quad \sigma_{12} = \sigma_{21} = \sigma_{32} = 6 \times 10^{-8} \text{ cm},$$

$$\sigma_{22} = 7 \times 10^{-8} \text{cm}.$$

Substitution of the above values in Eq. (4) will give the fraction of each species which travels the beam length without undergoing a collision. If it is assumed that each collision results in a loss of molecules, then the quantity $1 - S_{AB}$ is the fraction of each species lost as a result of scattering. Table I lists this fraction for each species in both cases. The attenuation is appreciable, ranging from about 10% to more than 18%.

For species 1, the monomer, the scattering is greatest in Case II. The increase over Case I is caused by the difference in σ, since $\Phi_{12} \cong \Phi_{11}$. Loss of the dimer, species 2, is approximately the same in both cases, but is slightly greater in Case I. Although σ is greater in Case II, it is more than offset by the smaller Φ.

In both cases more dimer than monomer is lost. In Case I both σ and Φ are greater for the dimer, and so the amount lost is almost twice that of the monomer. In Case II, $\Phi_{12} \cong \Phi_{22}$, so only the difference in σ is effective, and accordingly the values for the dimer and monomer are more nearly alike. Species 3, which differs from species 1 in Φ and from species 2 in σ, can be used to analyze the difference between the monomer and dimer in terms of these two

parameters. In Case I the difference between species 2 and 3 is greater than between species 1 and 3, but is of the same general magnitude, indicating that differences in both σ and Φ are important, with the effect of σ being the greater, for Case II the approximately equality between Φ_{12} and Φ_{32} (and therefore Φ_{22}) is evident in the similar values for species 1 and 3, whereas the difference in the values for species 2 and 3 reflects the differing values of σ responsible for the greater scattering of the dimer.

It has already been mentioned that the model developed here gives collision probabilities that are actually lower limits. A somewhat extreme upper limit may be found by substituting the value $(1 + \mu_{AB})^{1/2}$ for Φ_{AB} in Eq. (4), which would correspond to an isotropic distribution of velocity vectors with regard to orientation. The origin of this expression was discussed in connection with Eq. (1). On the average, the fractions scattered would increase by a factor of approximately three for the examples given here if this substitution is made. Hence the correct values are almost certainly within a factor of two of those given in Table I, and probably much closer.

In order for the scattering from the background gas to be comparable in magnitude to the intra-beam scattering in this example, the beam length would have to be of the order of a meter at a background pressure of 10^{-6} torr and a mean collision radius of 5×10^{-8} cm, and correspondingly longer at lower background pressures.[1,5]

DISCUSSION

The rather simple model developed here serves to show that intra-beam scattering can be quite significant at high beam pressures. For short beam lengths, as in mass-spectrometers with molecular beam sources, this type of scattering is likely to be of more importance than scattering from a background gas.

Indeed, Case I illustrates a hazard which may arise in a mass-spectrometric determination such as that mentioned above in the example: Vapor pressure measurements of minor polymeric species made at high source pressures are suspect, since under these conditions preferential scattering of the polymers from the beam is likely to occur. Roberts and Searcy have recently observed this effect in their measurements of cerium fluoride vapor pressure.[8] Their plot of the logarithm of the dimer pressure versus the inverse of the temperature, reproduced here as Fig. II, shows a downward deviation from linearity at the high pressure end. At a total source pressure of 10^{-3} atm and a temperature of about 1670°K, this deviation amounts to about a third of the expected dimer pressure. A round orifice 0.25 mm in diameter was used in this range. These values can be inserted into Eq. (4) with Φ_{AB} = equal to 0.665 and used to find σ_{AB} for the dimer-monomer collision. The value thus obtained is about 8×10^{-8} cm, which is reasonable. By comparison, a value of about 6×10^{-8} cm would be an acceptable value for the monomer-monomer collision radius. Substitution of this value for σ_{AB} and 0.475 for Φ_{AB} into Eq. (4),

with other parameters the same, results in a value of about 0.14 for the fraction of monomer scattered from the beam. The plotted monomer pressures show a barely discernible deviation from linearity at 1670°K of approximately the correct magnitude. Hence the data of Roberts and Searcy are consistent with their explanation of these deviations at high source pressures as being caused by intra-beam scattering.

Although this model was derived for thermal-velocity beams it can be generalized to other cases. The parameter Φ_{AB} will be the only one affected, since it alone depends on the velocity distribution. It is essentially equal to the quantity $|\vec{v}_A - \vec{v}_B|/v_A$ averaged over $\vec{v}_A$ and $\vec{v}_B$ for a thermal-velocity beam. Thus for beams having other velocity distributions the appropriate mean value of $|\vec{v}_A - \vec{v}_B|/v_A$ would have to be substituted. It should be kept in mind that $\vec{v}_B$ is averaged over the B molecules in a volume, whereas $\vec{v}_A$ is averaged over the A molecules passing through the beam.

The most common example of a non-thermal-velocity beam is that generated by a supersonic nozzle. In this case the dispersion in velocities $|\vec{v}_A - \vec{v}_B|$ is smaller relative to v_A than it is for a thermal-velocity beam, so higher beam intensities are possible before scattering becomes a problem.

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Table I.

Species	Case	
	I	II
1	0.097	0.135
2	0.185	0.181
3	0.134	0.136

Fraction lost as a result of intra-beam collisions.

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FIGURE CAPTIONS

Fig. I. Plot of Φ_{AB} versus μ_{AB}.

Fig. II. Vapor pressures of cerium fluoride monomers and dimers as measured by Roberts and Searcy, reference 8.

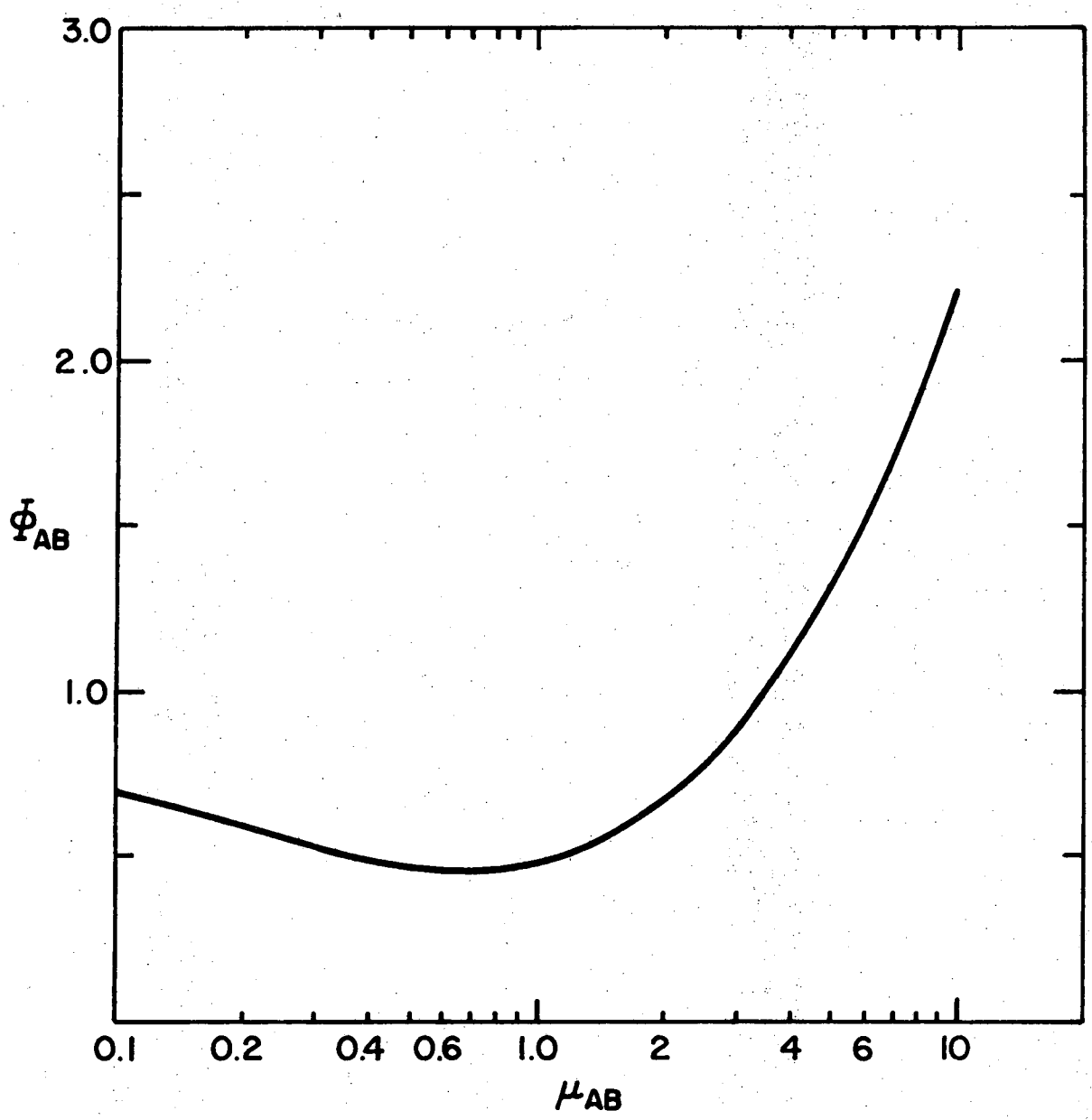

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Fig. I.

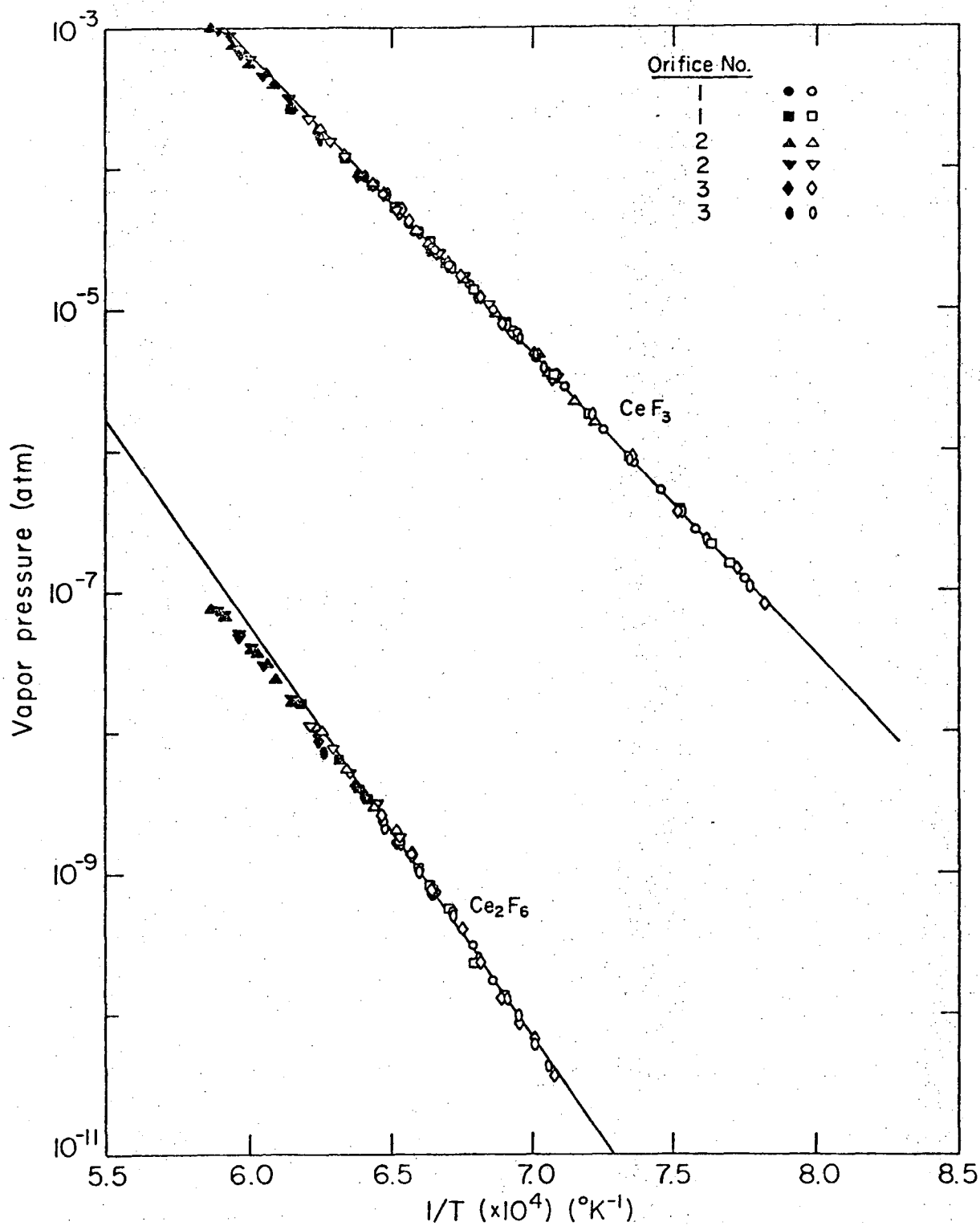

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Fig. II.

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