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EFFECTS OF EFFUSING MOLECULES ON A SUSPENDED TARGET *

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ABSTRACT

Knowledge of the angular distribution of velocity vectors of molecules streaming from an office into vacuum in effusion experiments is important in a variety of applications Particular applications are in torsion–effusion experiments, where the recoil force depends on angular distribution, and in target-collection experiments, where the fraction of effusing vapor collected by the target depends on angular distribution Recently, commercial vapor pressure balances based on the target-collection principle have become available We present a theoretical analysis of the needed angular distribution for the general case of effusion orifices which are frustums of right circular cones, a case which includes cylinders We apply this analysis to target-collection problems in which the target, collimator, or collector is circular or ring-shaped and coaxial with the orifice Both mass effects and force effects are included We consider the case in which a fraction ν $(0 \leqslant \nu \leqslant 1)$ of the impinging molecules stick permanently to the target and in which reflected molecules have a different "temperature" than do the impinging ones We have available a FORTRAN program which calculates angular distributions and fractions of effusing molecules which strike a given target or collimator For the special case of cylindrical orifices, closed-form equations based on derivations by Clausing are presented for the target-collection probability

INTRODUCTION

The vapor pressure and/or chemical composition of the vapor of a substance, particularly at elevated temperatures, can be obtained by a modification of the Knudsen-effusion method [1,2] in which a fraction of the effusing vapor impinges on a cold target A variety of means are available [3] for analyzing effects on the target mass change [4], counting of radioactivity

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[5], X-ray fluorescence analysis [6], force imparted by impinging vapor [7], etc The method combined with mass spectrometry [8] renders it especially powerful Recently, an automatic target-collection apparatus incorporating a microbalance has been made available commercially [9]

Orifices used in Knudsen-effusion cells are usually circular in cross section, their defining sections are frustums of right circular cones [10,11], often the special case of a cylinder The target used, or the collimator used to define the part of the effusing vapor which strikes the target, is circular and coaxial with the orifice for simplicity of analysis Correlation of effects on the target with the vapor pressure in the effusion cell requires knowledge of the fraction of the effusing vapor which strikes the target. Additional factors of importance, particularly where the force exerted on the target is of interest, are the fraction of impinging molecules which stick to the target, the angular distribution of momentum vectors of the molecules striking the target and of any rebounding from the target, the temperature of the source of the effusing molecules, and the effective temperature of any molecules rebounding from the target A theoretical analysis including these factors is available [10] and is outlined here

THEORY

We consider the model described before and illustrated in Fig. 1 A Knudsen-effusion cell with an effusion orifice whose flow-rate limiting section is in the shape of a right circular conic frustum, included would be cylindrical orifices in which the semiapex angle of the cone is zero and ideal orifices in which the height of the frustum is zero Either diverging or

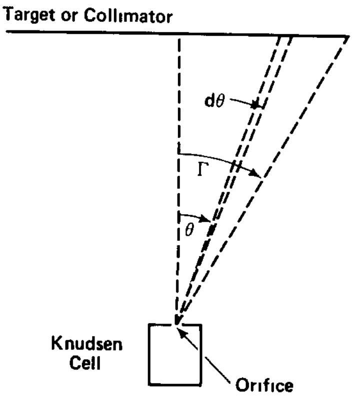

Fig 1 Geometric representation of an effusion-cell and target combination Γ is one-half of the angle subtended at the orifice by the target or collimator θ is the angle representing the direction of the velocity vector of an effusing molecule

converging conical orifices can be considered The target or collimator is circular, coaxial with the orifice, and sufficiently far removed from the orifice that the orifice appears effectively as a point source of effusing molecules The quantities of interest are the rate at which molecules impinge on the target and the force exerted on the target Each can be related to the vapor pressure in the effusion cell

We consider the cases in which all molecules striking the target condense permanently and in which a fraction of the molecules re-evaporate or are reflected We define the following terms

Γ = half the angle subtended at the orifice by a diameter of the target or collimator

ν = the fraction of effused molecules striking the target which re-evaporate or are reflected

G_Γ = the "transmission probability" of the orifice–target system, i e the fraction of molecules entering the effusion orifice which effuse and strike the target

f = the force exerted on the target

θ = the angle between a line originating at the center of the orifice exit and the common axis of the orifice and the target

P = the pressure of vapor within the effusion cell

$\mathrm{d}G_\theta$ = the fraction of molecules entering the effusion orifice which effuse and strike the target within an incremental ring between θ and $\theta + \mathrm{d}\theta$

It is convenient to express $\mathrm{d}G_\theta$ by

$$\mathrm{d}G_\theta = 2Q(\theta) \sin\theta \cos\theta \, \mathrm{d}\theta \tag{1}$$

The function $Q(\theta)$ has been derived as a function of θ and tabulated [10] or can be calculated with an available computer program [14] G_Γ is then expressed as

$$G_\Gamma = 2\int_0^\Gamma Q(\theta) \sin\theta \cos\theta \, \mathrm{d}\theta \tag{2}$$

The same program [14] calculates G_Γ

Equation (2) for the special case of a cylindrical effusion orifice was treated by Clausing [12] and Freeman and Searcy [13] but numerical integrations were required Edwards [10] showed the linear approximations of Clausing [12] to be highly accurate and obtained a closed-form expression of G_Γ for cylindrical orifices, that expression is given here in the Appendix

The Knudsen equation [1,2,6] modified by G_Γ is used to calculate the vapor pressure P in the effusion cell

$$P = (\mathrm{d}g/\mathrm{d}t)(2\pi RT/M)^{1/2}/(G_\Gamma A) \tag{3}$$

in which $\mathrm{d}g/\mathrm{d}t$ is the rate of accumulation of mass on the target, A is the area of the entrance to the orifice from the effusion cell, T is the temperature of the cell, and M is the molecular weight of the effusing vapor If ν is other than zero, then the right side of eqn (3) would be divided by $(1-\nu)$

The force f_s exerted on the target when $\nu=0$ is expressed by

$$f_s=(3/2)PA\int_0^{\Gamma} Q(\theta)\sin\theta\cos^2\theta\, d\theta \tag{4}$$

If the force on the target is measured, say by a torsion balance [3,7], the vapor pressure in the cell can be expressed by rearrangement of eqn (4)

When ν is greater than zero, the effect on the force exerted is complicated and dependent, among other things, on the distributions of speeds and of direction of momentum vectors of the reflected or re-evaporated molecules In the case in which the molecules leaving the target have momentum vectors distributed according to the Knudsen cosine law [3,15] and a Boltzmann speed distribution, so they can be assigned an effective temperature T', the expression for the force f_t is

$$f_t=(1/2)PA\left[\left(3\int_0^{\Gamma} Q(\theta)\sin\theta\cos^2\theta\, d\theta\right)+\nu(T'/T)^{1/2}G_{\Gamma}\right] \tag{5}$$

Assumption of the Knudsen cosine law is usually accurate Equation (5) is most useful in cases in which the effusate possesses significant vapor pressure at the temperature of the target and thermal accommodation is sufficient to assign to the molecules leaving the target the temperature of the target.

The force exerted by molecules impinging on a target can be important even in cases in which the rate of mass accumulation is measured by a microbalance from which the target is suspended [3] That force can become apparent when the temperature of the effusion cell is changed or when the nature of the vaporization reaction changes For instance, if the furnace heating the effusion cell were turned off, effusion would stop, and the mass of the target would appear to increase due to loss of the upward force of impinging molecules A similar effect would be observed if a sudden decrease in pressure in the effusion cell occurred when a volatile phase in the cell was exhausted

APPENDIX

The transmission probability, G_{Γ} of a cylindrical-orifice and target system can be expressed accurately in closed form [10] Consider a cylindrical effusion orifice with length of L and radius of r Let

$$c=2r/L \tag{A1}$$

Further, consider the angle

$$\alpha=\tan^{-1}c \tag{A2}$$

When the target subtends at the orifice an angle greater than 2α, then some parts of the target at its rim are invisible to the interior of the Knudsen cell, all vapor striking that part of the target comes by reflection off the walls of the orifice Hence, two expressions for G_Γ are needed, one when $\Gamma \leqslant \alpha$ and another when $\Gamma > \alpha$

We define

$$a = 1 - \left[(c+1)(c^2+1)^{1/2} - 1\right] / \left[c(c^2+1)^{1/2} + c^2\right] \tag{A3}$$

Then G_Γ is given by the following expressions

$$\begin{aligned} G_\Gamma(\Gamma < \alpha) = {} & \sin^2\Gamma - 4(1-2a)\Big[\tan\Gamma(c^2+1)(c^2-\tan^2\Gamma)^{1/2}/ \\ & (1+\tan^2\Gamma) - (c^3/2)(\sin 2\Gamma + 2\Gamma) + 2\sin^{-1}(\tan\Gamma/c) \\ & + (c^2-2)(c^2+1)I\Big]/(3\pi c^2) - 2(1-a)\Big[2(c^2+1)I \\ & - (c^2+2+2\tan^2\Gamma)\sin^{-1}(\tan\Gamma/c)/(1+\tan^2\Gamma) \\ & - \tan\Gamma(c^2-\tan^2\Gamma)^{1/2}/(1+\tan^2\Gamma)\Big]/(\pi c^2) \end{aligned} \tag{A4}$$

in which

$$\begin{aligned} I = {} & \frac{1}{(c^2+1)^{1/2}}\left[\tan^{-1}\left(\frac{\tan\Gamma}{\left[(c^2+1)^{1/2} - c\right]\left[c + (c^2-\tan^2\Gamma)^{1/2}\right]}\right)\right. \\ & \left. + \tan^{-1}\left(\frac{\tan\Gamma}{\left[(c^2+1)^{1/2} + c\right]\left[c + (c^2-\tan^2\Gamma)^{1/2}\right]}\right)\right] \end{aligned} \tag{A5}$$

and

$$\begin{aligned} G_\Gamma(\Gamma > \alpha) = {} & a\sin^2\Gamma - 4(1-2a)\big[\pi + (c^2-2)(c^2+1)I' \\ & - (c^3/2)(\sin 2\Gamma + 2\Gamma)\big]/(3\pi c^2) - 2(1-a)\big[2(c^2+1)I' \\ & - (\pi/2)(c^2+2)\big]/(\pi c^2) \end{aligned} \tag{A6}$$

in which

$$I' = \pi/2(c^2+1)^{1/2} \tag{A7}$$

Table A1 gives a test of eqns (A4) and (A6) The first column gives the value of L/r of the effusion orifice The second column gives the angle Γ subtended at the orifice by the target The third column gives the correct value of G_Γ calculated by accurate numerical integrations of exact equations with the available computer program [14] mentioned earlier The fourth column gives values of G_Γ calculated with eqns (A4) and (A6) The values of Γ were chosen for convenience in applying the numerical integrations as well as for the purposes of this test

It is seen that only for large values of Γ and for $L/r > 4$ do any inaccuracies in equations (A4) and (A6) appear that could be of experimen-

TABLE A1

G_Γ for cylindrical orifices

L/r	Γ (°)	G_Γ from numerical integrations	G_Γ from eqs (A4) and (A6)
1 000	10 57	0 03234	0 03234
	21 14	0 1198	0 1198
	31 72	0 2428	0 2428
	42 29	0 3774	0 3774
	52 86	0 4991	0 4991
	63 43	0 5881	0 5881
	70 08	0 6261	0 6261
	81 14	0 6635	0 6636
	90 00	0 6720	0 6721
2 000	11 25	0 03488	0 03488
	22 50	0 1218	0 1218
	30 00	0 1937	0 1937
	41 25	0 2997	0 2997
	52 50	0 3872	0 3873
	60 00	0 4340	0 4343
	71 25	0 4842	0 4847
	82 50	0 5097	0 5103
	90 00	0 5142	0 5147
4 000	11 07	0 03085	0 03085
	19 92	0 08253	0 08253
	31 85	0 1576	0 1576
	42 42	0 2200	0 2199
	47 71	0 2482	0 2481
	58 28	0 2962	0 2960
	68 86	0 3306	0 3304
	79 43	0 3504	0 3502
	90 00	0 3565	0 3563
6 000	10 75	0 02663	0 02663
	18 43	0 06131	0 06129
	30 36	0 1174	0 1172
	42 29	0 1710	0 1702
	48 25	0 1951	0 1940
	60 18	0 2350	0 2334
	72 11	0 2615	0 2596
	78 07	0 2694	0 2675
	90 00	0 2754	0 2734
8 000	10 52	0 02329	0 02328
	20 37	0 05925	0 05910
	33 03	0 1073	0 1065
	39 36	0 1304	0 1291
	52 02	0 1714	0 1692
	58 35	0 1882	0 1855
	71 01	0 2125	0 2093
	77 34	0 2198	0 2165
	90 00	0 2252	0 2218

TABLE A1 (contınued)

L/r	Γ (°)	G_Γ from numerıcal ıntegratıons	G_Γ from eqs (A4) and (A6)
10 00	10 37	0 02056	0 02055
	17 87	0 04326	0 04309
	30 98	0 08510	0 08402
	37 54	0 1056	0 1039
	50 65	0 1422	0 1394
	57 21	0 1573	0 1540
	70 33	0 1793	0 1753
	76 88	0 1859	0 1817
	90 00	0 1909	0 1866
20 00	12 73	0 01714	0 01692
	19 76	0 02932	0 02861
	26 78	0 04198	0 04061
	40 83	0 06668	0 06382
	47 86	0 07777	0 07421
	61 90	0 09557	0 09087
	68 93	0 1018	0 09671
	82 98	0 1086	0 1031
	90 00	0 1094	0 1038

tal ımportance In any expected, practıcal case Γ would be less than 45° and L/r would be less than 10 In such cases, eqns (A4) and (A6) wıll always be accurate wıthın 2% When L/r ıs 4 or less, these equatıons can be consıdered exact Of far greater concern should always be conformıty of condıtıons of the experıment to the model [10] on whıch derıvatıon of eqns (A4) and (A6) as well as those ın the computer program [14] ıs based

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