RECEIVED BY TIC AUG 14 1974

IS T 649

The Effect of Geometry and
Surface Condensation on the
Behavior of a Torsion Effusion Cell

Dale Alan Fitzgibbons

M. S. Thesis Submitted to Iowa State University, May 1974

Ames Laboratory, USAEC
Iowa State University
Ames, Iowa 50010

Date Transmitted: August 1974

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

for

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
Department A
Springfield, VA 22151

Price: Microfiche **\$1.45**

RECEIVED BY TIG AUG 14 1974

iii

The effect of geometry and
surface condensation on the
behavior of a torsion effusion cell

by

Dale Alan Fitzgibbons

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Chemical Engineering and Nuclear
Engineering
Major: Chemical Engineering

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1974

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	Page
ABSTRACT	x
ACKNOWLEDGEMENTS	xi
NOMENCLATURE	xii
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. PREVIOUS WORK	14
CHAPTER 3. THEORY	22
Correction Factors for Torsion Effusion Cells	22
Formulation of Flux Model in Terms of Integral Equations	35
An Approximate Solution to the Closed-Cell Equations	44
CHAPTER 4. THE MONTE CARLO SIMULATION	63
The Spherical Sample	66
The Cylindrical Wall	73
The Planar End Surfaces	77
CHAPTER 5. RESULTS OF THE SIMULATION	81
CHAPTER 6. RECOMMENDATIONS FOR FUTURE STUDIES	88
APPENDIX A. MOLECULAR AVERAGE VELOCITIES	96
APPENDIX B. MOMENTUM OF A COSINE-DISTRIBUTED EFFUSION BEAM	100
APPENDIX C. THE ANGULAR DISTRIBUTION OF MOLECULES EFFUSING FROM AN IDEAL ORIFICE	107
APPENDIX D. BOUNDEDNESS OF THE KERNEL $K(s', s)$	111
APPENDIX E. FLUX INTENSITY FROM A UNIFORMLY EMITTING SPHERE	117
APPENDIX F. ATTRITION OF ENTRANCE FUNCTION MOLECULES BY THE SAMPLE	123

RECEIVED BY TIC AUG 14 1974

v

	Page
APPENDIX G. CALCULATION OF THE ANGULAR DISTRIBUTION FACTOR	128
APPENDIX H. FLOW DIAGRAM	131
APPENDIX I. PROGRAM LISTING	145
APPENDIX J. SPHERICAL-TO-SPHERICAL TRANSFORMATION	162
APPENDIX K. ENUMERATION OF RESULTS	167
APPENDIX L. ERROR ANALYSIS: VARIANCES of φ , P , ζ	207
BIBLIOGRAPHY	211

LIST OF FIGURES

	Page
Figure 1-1. Illustrating the use of the Monte Carlo method to estimate the area under the curve $y = f(x)$ in the interval $0 \leq X \leq a$.	8
Figure 1-2. Illustrating a refinement of the Monte Carlo estimate of the area under the curve $y = f(x)$.	12
Figure 3-1. A typical torsion effusion cell.	24
Figure 3-2. Configuration of the reduced vectors $\vec{p}$ and $\vec{h}$ with $\hat{u}$ in the proper direction to give a positive reaction.	31
Figure 3-3. Nomenclature for the various internal surfaces of the cell.	37
Figure 3-4. Nomenclature for the closed cell.	40
Figure 3-5. The relationship of the surface two-dimensional coordinate systems to the cell three-dimensional coordinate system.	58
Figure 4-1. Dimensional terminology for the Monte Carlo simulation.	64
Figure 4-2. Local coordinate system for points on the surface of the spherical sample.	68
Figure 4-3. Local-to-global coordinate transformation for the cylindrical surface.	74
Figure B-1. Coordinate geometry for an effusion beam.	101
Figure B-2. Geometrical arrangement for passage of the i -th molecule in an effusion beam.	104
Figure C-1. Molecular flux on point P by element dS' .	108
Figure C-2. Molecular flux on point P by element dS' through an element of orifice.	108

	Page
Figure D-1. Proximate points on two intersecting planes	113
Figure D-2. Proximate points on a cylinder.	115
Figure E-1. Configuration for a hemisphere transmitting molecules to an element dA .	118
Figure F-1. Relationship of a sphere to its apparent disk.	125
Figure F-2. Configuration for an element dA' transmitting molecules to a disk.	125
Figures H-1 through H-8. Main program.	132
Figure H-9. Subroutine SURF1.	140
Figure H-10. Subroutine SURF2.	141
Figure H-11. Subroutine SURF2A.	142
Figure H-12. Subroutine SURF3.	143
Figure H-13. Subroutine SURF4.	144
Figure J-1. Spherical-to-spherical transformation.	163
Figure J-2. Projection onto the x-y plane.	164
Figure J-3. Projection onto the $x'-z'$ plane.	165
Figure K-1. Phase I, Case 1.	169
Figure K-2. Phase I, Case 2.	170
Figure K-3. Phase I, Case 3.	171
Figure K-4. Phase I, Case 4.	172
Figure K-5. Phase I, Case 5.	173

	Page
Figure K-6. Phase I, Case 6.	174
Figure K-7. Phase I, Case 7.	175
Figure K-8. Phase I, Case 8.	176
Figure K-9. Phase I, Case 9.	177
Figure K-10. Phase I, Case 10.	178
Figure K-11. Phase I, Case 11.	179
Figure K-12. Phase I, Case 12.	180
Figure K-13. Phase I, Case 13.	181
Figure K-14. Phase I, Case 14.	182
Figure K-15. Phase I, Case 15.	183
Figure K-16. Phase I, Case 16.	184
Figure K-17. Phase II, Case 1.	186
Figure K-18. Phase II, Case 1.	187
Figure K-19. Phase II, Case 2.	188
Figure K-20. Phase II, Case 2.	189
Figure K-21. Phase II, Case 3.	190
Figure K-22. Phase II, Case 3.	191
Figure K-23. Phase II, Case 4.	192
Figure K-24. Phase II, Case 4.	193
Figure K-25. Phase II, Case 5.	194
Figure K-26. Phase II, Case 5.	195
Figure K-27. Phase II, Case 6.	196
Figure K-28. Phase II, Case 6.	197

	Page
Figure K-29. Phase II, Case 7.	198
Figure K-30. Phase II, Case 7.	199
Figure K-31. Phase II, Case 8.	200
Figure K-32. Phase II, Case 8.	201

LIST OF TABLES

	Page
Table I-1. Definitions of identifiers used in the program.	145
Table K-1. Phase I: parameter settings and sample sizes for the sixteen cases.	168
Table K-2. Phase II: parameter settings and sample sizes for the eight cases.	185
Table K-3. Phase II: standard deviation about the mean for each flux curve, Cases 1 and 2.	202
Table K-4. Phase III: parameter settings and sample sizes for the eight cases.	204
Table K-5. Phase III: output data.	205
Table K-6. Phase III: comparison of theoretical escape probability, P_{th} , with that calculated by the simulation.	206

ABSTRACT

A detailed investigation of the sources of certain non-idealities inherent in the behavior of a torsion effusion cell has been performed. Integral equations have been approximately solved with the aid of Monte Carlo computations to establish a model which predicts molecular flux on the inside walls of a typical configuration. Further, Monte Carlo calculations have confirmed the model-predicted consequences of variations in geometrical dimensions and the existence of molecular adsorption on the walls.

The results confirm the findings of earlier investigators that molecular escape probability is strongly affected by the existence of flux gradients within the cell. However, another outcome is that the cell reaction torque is influenced significantly by the angular distribution of effusing molecules, itself a function of internal flux distribution.

ACKNOWLEDGEMENTS

For guidance and helpful criticism during the early stages of the study much credit is due Dr. F. Dee Stevenson. For assistance with the preparation of the manuscript, credit is also due Dr. Frank O. Shuck. Thanks are especially due Dr. Thomas D. Sandry whose enthusiasm and technical wisdom saved the author much wasted effort. Thanks are given to Dr. Herbert T. David of the Iowa State University Statistical Laboratory for assistance with the statistical analyses in Appendix L and to Mr. William S. Frazier, Jr. for guiding the author through the quicksand of IBM OS/360 Job Control Language. Finally, the author acknowledges the patience and skill of Donna Baldwin who typed the manuscript.

NOMENCLATURE

Notation in this work is used in a somewhat fluid manner. Symbols are often tailored to a specific discussion, resulting in many of them assuming several different meanings depending on the immediate context. Where confusion is likely to occur, parenthesized numbers in the following list of the more important symbols refer to chapters in which the symbols assume the designated meanings. Some seldom used symbols, as well as most of the highly specialized symbols appearing in derivations in the appendices, have been omitted.

A	Channel cross-sectional area (2).
A	Cell radius (4,5).
A	Inside surface area of enclosure (5).
A_1, A_2, A_0	Orifice areas (3).
ΔA_i	Area of the i -th bin (5).
A_s	Sample surface area (5,6).
A_{S_i}	Area of surface S_i (3).
a	Channel radius (2).
a	Dimensionless cell parameter, L/R (3).
a, b, c	Direction cosines (4).
B	Cell half length.
b	Dimensionless cell parameter, R_s/R (3).
c	Molecular speed (2).
$\bar{c}_p$	Mean molecular speed across a plane.

D	Distance from sample center (3).
D	Orifice diameter (4).
d	Transit distance.
F	Flow conductance (2).
F	Reaction force (3).
f	Reaction force correction factor (3).
f_0	Entrance distribution (3).
f_i	i -th flux coefficient (3,5,6).
$\vec{G}$	Cell angular impulse.
$\vec{G}_m$	Molecular angular impulse.
$\vec{G}_T$	Angular impulse imparted by an effusion beam.
$G_u(i)$	Useful angular impulse contributed by the i -th effusing molecule.
$\hat{i}, \hat{j}, \hat{k}$	Cartesian unit vectors.
$K(S', S)$	Probability kernel of integration.
$K_c(S', S)$	Combined transmission kernel.
k	Boltzmann's constant (2,3)
k	Corrected Clausing factor.
k_c	Uncorrected Clausing factor.
L	Cell half length.
$\vec{L}$	Angular momentum.
l	Length coordinate.
M	Molecular weight
m	Molecular mass.
$\bar{m}$	Mean molecular mass.

m_s	Evaporated mass of sample.
N_1, N_2, N_0	Number of molecules effusing.
N_c	Number of molecules condensing on the sample.
N_i	i-th bin tally.
N_k	Knudsen number.
N_s	Number of molecules evaporating.
N_w	Number of molecules condensing on the wall.
n_e	Sample emission intensity.
P	Transmission (escape) probability.
p	Local pressure.
p_s	Thermodynamic vapor pressure of the sample.
Q	Volumetric flow rate.
q	Orifice moment arm.
R	Universal gas constant (3).
R	Cell radius (3).
R	Sample radius (4).
R_s	Sample radius.
R_1, R_2	Random numbers.
r	Radius coordinate.
$\vec{r}$	Radius vector.
S	Arbitrary surface.
S_0	Orifice surface.
S_1	Sample surface.
S_2	Cylinder and end planes, exclusive of orifices.
S_3	Union of S_0 and S_2 .

T	Absolute temperature.
$\hat{u}$	Unit pivotal axis vector.
$\vec{v}$	Velocity vector.
x, y, z	Global coordinates.
x', y', z'	Local Coordinates.
$\alpha, \alpha_s, \alpha_w$	Condensation coefficients.
γ	Actual reaction torque.
γ_{id}	Ideal reaction torque.
ϵ	Truncation error.
ζ	Normalized directional distribution factor.
$\hat{\eta}$	Unit velocity vector.
θ	Cell angular displacement.
θ	Angle of incidence.
θ'	Angle of departure.
$\lambda, \lambda_s, \lambda_w$	Reflection coefficients.
$\vec{\rho}$	Reduced radius vector.
τ	Hooke's law constant for torsion
φ	Generalized torque correction factor.
$\psi(S)$	Molecular flux on surface S.
$\bar{\psi}$	Average flux.
$\psi_o(S)$	Closed cell flux.
$\psi_p(S)$	Perturbation flux.

$\psi_p^o(s)$

Normalized or reduced perturbation flux.

 ω

Unnormalized directional distribution coefficient.

CHAPTER 1.

INTRODUCTION

In the measurement of thermodynamic properties (e.g. vapor pressure and activity coefficient of solid and liquid metals it is generally required to measure the time rate at which molecules evaporate from the surface of a sample into free space or into an enclosure containing vapor. Free surface evaporation is called Langmuir vaporization (1); molecules are emitted from the surface into an infinite condenser never to return to the sample surface. The rate of evaporation is then related to the thermodynamic vapor pressure by theoretical consideration. The practical problems inherent in this technique have caused experimentalists to adopt some form of the Knudsen technique (2).

In this method, which normally is used only for extremely low vapor pressures (10^{-2} Torr or less), the sample is surrounded by some form of enclosure with a small aperture allowing a fraction of the molecules to escape into an infinite condenser. If this aperture or effusion orifice is small enough, barring the losses within the enclosure, the pressure inside the enclosure near the orifice will be close to the true thermodynamic vapor pressure, and the rate of molecular escape through the orifice, the effusion rate, can be related to the thermodynamic vapor pressure of the sample by a theoretical analysis similar to that used in the Langmuir technique. In this context, the term "infinite condenser" means the thermodynamic

surroundings of the sample and its enclosure; it further implies that the surroundings constitute a perfect sink for molecules, thereby preventing any of them from returning to the enclosure or the sample. While an infinite condenser is properly only a theoretical concept, it is practically approached very closely in actual systems by conducting the experiments under extremely high vacuum and (additionally) by providing targets which trap molecules chemically or thermally.

The necessity of measuring the mass flow rate of molecules escaping from the system has resulted in the evolution of a number of different practical approaches. The majority of these may be divided into two categories: (a) devices which detect a change in the steady state mass of the system and (b) devices which measure the momentum of the molecular beam from the orifice. The usual Knudsen cell, typical of the first category, is a small chamber (1 - 2 cm. being a typical dimension) of some comparatively inert material in which a quantity of the metal (shavings, turnings, wire, or the like) has been placed. A small (1 mm. or less) hole has been made in one of the walls to allow molecules to stream out of the system. Suitable means are provided for heating the cell and for accurately measuring its temperature, and the entire assembly is placed in a sealed chamber which may be evacuated to a high degree. The mass flow rate of the molecules is typically measured by detecting via a suitable technique the net accumulation of mass on a target placed in the evacuated chamber

outside the cell in the path of the effusing molecules. Alternatively, the molecular flow rate may be measured by determining the rate of loss of mass of the cell during the course of the experiment with a sensitive balance located within the chamber.

However, it is a particular type of the second category which is the object of the present and all further discussion; this is the torsion effusion cell, originated by Volmer (3). It normally consists of a symmetrical horizontally elongated chamber (e.g. cylinder) with two orifices at opposite ends of the cell and on opposite sides of the vertical central axis from each other. The cell is suspended from a fine elastic wire and, as molecules evaporate from the sample (which has been placed somewhere inside) and issue through the orifices, the reaction forces caused by the momentum of the two molecular beams exert a couple tending to turn the cell about the vertical central axis which coincides with the axis of the wire. At steady state, the cell has turned by a certain angle and is in mechanical equilibrium with the wire, i.e., the reaction couple exerted by the molecular beams is exactly balanced by the elastic torque of the wire. If the wire obeys Hooke's Law for torsion, the angular displacement is a linear function of the reaction couple, and is consequently a measure of the vapor pressure of the sample.

During this and all further discussion it is presumed that the basic mechanism of molecular transport is molecular flow or

Knudsen flow, i.e., we are operating in the realm of extremely low system pressures in which mean free paths are much greater (ten times or more) than a typical cell dimension. Under this circumstance, the effects of intermolecular collisions (or, on a macroscopic scale, viscous effects) can be taken to be negligible. Consequently, collisions of molecules with the walls are the dominant factor in determining the flow behavior of the vapor. This is in contrast to the transport mechanism known as viscous flow in which the higher pressures and consequently shorter mean free paths cause intermolecular collisions to be the overriding consideration in describing flow behavior in a channel or enclosure. Between these regimes lies the transition region in which both intermolecular collisions and molecular collisions on the wall effectively govern the flow characteristics of the vapor. A dimensionless quantity commonly used is an index for describing the type of flow existing in a system is the Knudsen number, denoted here by N_k . This is defined as the ratio of the mean free path of a molecule to a characteristic dimension of the channel or chamber in which a gas is flowing. For example, the Knudsen number for flow in a cylindrical pipe might be based on the diameter of the pipe. For small Knudsen numbers, viscous flow tends to dominate, but as the pressure is lowered, the Knudsen number increases, and molecular flow becomes prevalent. Dushman (4) gives a set of practical limits which demarcate the boundaries of the three flow regimes as follows:

When $N_k < 0.01$, the flow is viscous;
 when $N_k > 1.00$, the flow is molecular;
 when $0.01 < N_k < 1.00$, the flow is in the
 transition range.

Winterbottom (5) points out, however, that molecular flow is not the only transport mechanism for molecules in an effusion cell. Winterbottom and Hirth (6) assert that a molecular wall collision does not consist simply of an impact followed by an immediate re-emission in a random direction, but that there exists the possibility of a molecule becoming temporarily absorbed on the wall surface before it is re-emitted. Winterbottom goes on to state that while the molecule is absorbed it may migrate or diffuse along the surface for some distance before it is emitted. While this surface diffusion theory is not ruled out as a viable transport mechanism in a torsion effusion cell, it has not been included within the scope of this work since the primary intent is to explore the effect of certain cell parameters on cell behavior in light of the consequences of their effect on the molecular flow within the cell. Furthermore, it is a consequence of Winterbottom's theory that the concentration of the absorbed population on the cell walls and hence the re-emission flux (molecules emitted per unit surface area) will tend to be more uniform over the wall surfaces than if surface diffusion did not exist. It will be demonstrated later that strong re-emission flux gradients tend to foster certain nonidealities in the behavior of the particular

torsion effusion cell which has been modelled and will be explained in future discussion. Therefore, it is herewith suggested that the results of the present work will represent a "worst-case" situation insofar as nonidealities caused by flux gradients are concerned.

Although velocities of molecules in the molecular flow range do not experience the Maxwellian randomizing due to intermolecular collisions that they do in the viscous flow range, completely random emission from all surfaces (in both speed and direction) is taken for the norm in this work. It is assumed that either all molecules striking a wall are adsorbed long enough to forget their pasts or else that the surface, while appearing smooth on a macroscopic cell, is rough enough on a microscopic scale to promote diffuse reflections. Although certain evidence (7) exists to support the hypothesis that specular reflection occurs under certain circumstances (e.g. grazing collisions at high velocity), such activity has been excluded from the scope of this discussion, and it is herein assumed that the effect of completely diffuse reflections prevails over that of any specular reflections.

It is this random nature of molecular motion inside an effusion cell which immediately suggests the use of the Monte Carlo method to explore the behavior of the cell over a wide domain in the space of physical cell parameters. Briefly, the Monte Carlo method, in all of its permutations, is a technique for performing integrations by generating a large number of

random variables, each simulating a statistical event, and recording suitable tallies of the outcomes. If the proper tallies are chosen, the ratios of the tallies can be used to estimate the required integrals. One obtains the desired level of accuracy by performing the simulation for a large enough number of events or histories, i.e., one increases the statistical sample size in order to decrease the variances of the estimates.

One elementary application of the Monte Carlo method, shown in Figure 1-1, is to estimate the area which under the curve described by the function $y=f(x)$ over an interval of its domain. One would generate a sequence of ordered pairs (x,y) of uniformly-distributed random numbers from the intervals $0 \leq x \leq a$, $0 \leq y \leq b$; each ordered pair would represent a point in the rectangle. One would simply count the number of randomly selected points lying under the curve by calculating $f(x_1)$ for each x_1 , testing whether the selected y_1 is less than the calculated value of the function, and tallying each positive test. The area under the curve would be approximated by $(N_o/N_t)ab$, where (N_o/N_t) is the fraction of points that fell under the curve. Since reasonable accuracy in results of Monte Carlo calculations can be obtained only with statistical samples containing thousands or even millions of events, its use invariably requires that the simulation be performed by a digital computer.

It will be described later how the flow behavior of molecules in a partial vacuum can be rigorously stated in the form

Figure 1-1. Illustrating the use of the Monte Carlo method to estimate the area under the curve $y = f(x)$ in the interval $0 \leq x \leq a$.

of a set of linear integral equations of the second kind containing terms involving a molecular flux function integrated over the inside surfaces of the enclosure. Unfortunately, the equations present formidable difficulties that preclude any analytic solution for even the simplest geometrical configurations. Consequently, the Monte Carlo method has been adopted as the primary approach to the problem of describing the behavior of a torsion effusion cell. The particular calculation format is as follows: each statistical event is a simulated molecule which is followed from its origin on the surface of the metallic sample to its probabilistically-determined outcome. The molecule will either pass through the orifice and be tallied as part of the effusate or will travel about inside the cell until it is adsorbed on the sample or on a wall surface. Each event is started by selecting a random position on the sample surface and then selecting a random direction of departure from the surface. It is next determined whether the molecule strikes another surface and, if so, the coordinates of the point of impact. It is then decided, according to a probability, whether the molecule will be re-emitted from the surface or will become permanently lost by adsorption. If the molecule is re-emitted, then a random direction of departure is selected and the process repeats until the molecular history is concluded either by adsorption or by escape.

An obvious advantage of the Monte Carlo method for this type of problem is the ease with which virtually any geometrical

configuration may be modelled. Rather than invoke any elegant analytical or numerical techniques, one simply writes the equations which describe the constituent parts of the flow system; the assemblage of these equations together with certain appropriate inequalities constitute a complete geometrical specification of the flow system. Since the molecules are assumed to travel in straight lines, the problem reduces to one of calculating predicted points of intersection of space lines with surfaces, calculating random directions in coordinate systems local to the surfaces, and transforming these directions into directions in the overall coordinate system chosen for the cell. The procedures are simple to derive and are based on a few well known theorems which may be found in any text on elementary calculus and analytic geometry.¹

It is pertinent, however, to mention two important disadvantages. First, whereas the only conceptual requirement for a high degree of accuracy in the results is a willingness to spend a sufficient amount of computer time on the problem, estimated error, i.e., standard deviation, is inversely proportional to the square root of this statistical sample size rather than to its first power. As a result, a point of diminishing returns is reached early in the procedure. Second, as is true with many numerical methods, the result obtained from a calculation is completely inflexible. The result is obtained for a particular setting of the system parameters and is, in general,

¹For example, Goodman (8).

valid for no other. This difficulty may be partially circumvented by presenting the results of a number of calculations made at several points in the parameter space, together with some suitable interpolation scheme. However, this is a stopgap measure and can be cumbersome when the result is a function of a half dozen or more parameters, as is typically the case.

A preferable approach is to perform a seminumerical calculation whenever possible. In other words, as much information as possible about the solution should be extracted by analytical means. This may result in the removal of one or more parameters from the unsolved equation followed by subsequent recombination with the numerical solution to that equation. Incidentally, this is also one of several commonly used Monte Carlo variance reduction techniques (9). In our example of Figure 1-1, if any part of the area under the curve can be subdivided into an irregular region and one or more regions bounded by simple geometrical figures as in Figure 1-2, the area of these regions may be computed exactly from well-known formulas, leaving a smaller irregular area to be calculated numerically. The obvious consequence is that the uncertainty of the area of this region is much smaller than it would be if the total area were computed numerically.

The problem of flow in the torsion effusion cell to be described later has been addressed in this work both numerically and seminumerically. Unfortunately, the seminumerical approach required the use of simplifying assumptions which materially

Figure 1-2. Illustrating a refinement of the Monte Carlo estimate of the area under the curve $y = f(x)$.

The area of the rectangle ABCD would be measured directly between the curve and the line segment DC to be calculated numerically.

detracted from the variance reduction normally realizable in adopting a partly analytical solution. However, a high degree of flexibility was obtained with a solution which could be expressed in the form of an algebraic equation containing one appearance of a common transcendental function.

Both solutions, numerical and seminumerical, are in the form of a set of factors which attempt to relate the behavior of a real torsion effusion cell to that of a so-called "ideal cell", whose behavior can be expressed simply and exactly. The primary quantity is the torsion effusion cell torque correction factor, denoted by ϕ , which is the ratio of actual effusion beam reaction torque to the torque which would appear in an ideal cell. Practical means for calculating ϕ will be set forth later. It will be shown that this factor is proportional to the product of two other dimensionless quantities: the molecular transmission or escape probability, P , and the effusion beam angular distribution factor, ζ . Conceptually, each of these two factors differs from the other in how it affects the behavior of the cell; furthermore, in certain systems, they can be evaluated somewhat independently.

CHAPTER 2.

PREVIOUS WORK

Early attempts to quantify the flow behavior of a highly rarefied gas arose largely during the development of technology for the design of equipment able to attain extremely high degrees of evacuation. On the basis of theoretical considerations followed by experimental verification, Knudsen (10, 11) showed that the flow rate of rarefied gas in a long tube or channel connecting a region of lower pressure, p_1 , with a region of higher pressure, p_2 , is

$$Q = (4/3) c(p_2 - p_1) / \int_0^l \frac{H}{A^2} dl \quad (2-1)$$

where c is the mean molecular speed given by

$$= (8kT/\pi m)^{\frac{1}{2}} \quad (2-2)$$

H is the perimeter, A is the cross sectional area, l is the length along the tube axis, k is Boltzmann's constant, T is the absolute temperature, and m is the molecular mass. Q is a flow rate defined as the product of the volumetric flow rate dV/dt across a plane and the pressure p at the point of measurement. Equation (2-1) is considered to be the molecular flow analogue of the well-known Hagen-Poiseuille equation for laminar viscous flow in a tube. An often-used quantity is the flow conductance¹ defined as

$$F = Q/(p_2 - p_1). \quad (2-3)$$

¹Dushman (4, p. 81).

Incorporating this into equation (2-1), the long-channel conductance is given by

$$F = (4/3) c / \int_0^1 \frac{H}{A^2} dl . \quad (2-4)$$

From this it is seen that molecular flow conductance is independent of pressure considerations and is therefore more useful in the region of molecular flow than is the flow rate.

It can be shown¹ that for an isothermal enclosure containing a small ideal orifice, i.e., one in which the wall thickness is vanishingly small, the molecular conductance is

$$F = cA/4, \quad (2-5)$$

where A is the area of the orifice. Theorizing that a real orifice, i.e., one with a finite wall thickness, is composed of a channel as described by equation (2-4) coupled to an orifice as described by equation (2-5), Dushman (12) obtains the following conductance for a real cylindrical orifice:

$$F = k_c (cA/4), \quad (2-6)$$

where $k_c = (1 + 3/8 l/a)^{-1}$, and l and a are the length and radius, respectively, of the orifice. In comparing this to equation (2-5), one observes that k_c is a factor which corrects for the finite orifice depth. Clausing (13), however, demonstrates that Dushman's formulation of k_c is valid only in the limit as the channel depth, i.e., wall thickness becomes very large, or in other words as $l/a \rightarrow \infty$. From a careful theoretical analysis involving numerical solutions of an integral

¹Dushman (4, p. 90).

equation describing flow in a short channel, Clausing obtains values of an improved factor, k , valid for l/a in the neighborhood of 1.0 and approaching k_c as l/a becomes larger. The factor k , called the Clausing factor, is actually the transmission probability for a short channel, i.e., the fraction of molecules leaving the outlet divided by the number passing through the inlet. This concept, applied to other geometrical configurations, is the object of much future discussion. Consequently, the more general term transmission probability will be preferred in place of the more restrictive term Clausing factor.

DeMarcus (14) generalizes Clausing's one-dimensional integral equation into the form

$$\psi(S) = \psi_o(S) + \int_S K(S', S) \psi(S') dS', \quad (2-7)$$

where $\psi(S)$ is the collision density or flux intensity of molecules per unit area which strike internal surface S , $\psi_o(S)$ is a forcing function based on molecules entering the system, and $K(S', S)$ is a probability kernel which designates the probability density that molecules leaving an element dS' on S will strike another element dS elsewhere on S . Using an elaborate numerical technique, DeMarcus is able to solve equation (2-7) and obtain refined values of k which actually constitute a rigorous upper bound for those Clausing.

In subsequent investigations, Davis (15) has demonstrated the simplicity and versatility of the Monte Carlo method in using it to obtain molecular conductances for pipes of various

shapes. In a somewhat different vein, Sandry and Stevenson (16) have used the Monte Carlo method to calculate transmission probabilities for a pseudo-Langmuir experiment involving vaporization of liquid metal species from menisci at the bottom of an inert crucible.

The first attempt to characterize the effect of the inside of an effusion cell and its interaction with a channel orifice was done by Whitman (17). By considering the numbers of molecules evaporating from the sample and being reflected back and forth across the cell between the sample and the orifice, he arrives at an infinite geometric series representation for the total transport probability out the orifice. His equation is, however, a bit too unwieldy for practical use. In a more simplified analysis, Motzfeldt (18) writes four rate equations which attempt to describe the behavior of a cell with a channel orifice at equilibrium. His solution of the four simultaneous equations which yield a factor relating equilibrium pressure (sample vapor pressure) to the measured vapor pressure, contains only Clausing factors for the orifice and for the cell, the ratio of the two cross-sectional areas, and the condensation coefficient of the sample. The simplicity of Motzfeldt's equation has resulted in its widespread use in later vapor pressure determinations. Unfortunately, both Whitman and Motzfeldt assume (a) that molecular distributions follow the cosine law throughout the system and (b) that pressures are uniform across planes that are perpendicular to the axis of the cell.

It will be seen that these conditions do not always hold. Additionally, both treatments are valid only for an axially-symmetric single orifice effusion cell; consequently, their direct application to a torsion effusion cell is not possible.

More recently, the internal behavior of the axially-symmetric cylindrical cell has been the object of careful and detailed analyses by several investigators, most notably Ward and Mulford (19), Ward et al. (20), Ward (21), Ward and Fraser (22), Ward (23), Ward and Fraser (24), Winterbottom (5), Winterbottom and Hirth (6), and Carlson et al. (25). Ward has hypothesized that departures from ideal operation, i.e., deviations from a cosine effusate distribution and deviations from predicted transmission probabilities, are caused by geometric factors coupled with transport losses on various portions of the inside surfaces of the cell. In particular, he recognizes that a cell with a small orifice behaves as a pinhole camera operating in reverse, i.e., a "pinhole projector", in that the angular distribution function is actually an image of the inside of the cell, with the intensity of the image weighted by the cosine of the angle of departure (measured from the normal to the orifice). Ward's experimental work, followed by Monte Carlo simulations in which transmission probabilities and internal collision densities are measured tend to substantiate his hypothesis. By programming a molecular wall attrition into his simulation, he is able to duplicate the noncosine distributions obtained experimentally.

Consequently, he concludes that deviations in the effusate distributions are actually deficiencies caused by decreased emission rates on surfaces which experience molecular attrition for any reason. This conclusion is of paramount significance to the experimentalist designing or operating an effusion cell since wall losses may occur in several ways. Any irreversible chemical reaction between molecular species and the material composing the wall is likely to cause a net accumulation of mass (attrition) on the wall. Also significant in any high-temperature experiment is the requirement that the cell body be maintained at a uniform temperature; if this is not met, a net migration of material from the sample to cooler surfaces may result. Additionally, the molecular depletion caused by a significantly large orifice will be reflected in a lower wall collision density, and consequently a decreased emission rate.

The surface diffusion theory of Winterbottom and Hirth (6) and its consequences (5) have already been mentioned. Recognizing the importance of a sound mathematical foundation, Carlson et al. (25), derives a rigorous mathematical formulation represented by a set of integral equations which the collision density and transmission probability must satisfy. Carlson does not attempt a rigorous solution of his equation, but does state precisely the simplifying assumptions which will lead one to the equations of Motzfeldt and of Whitman.

Wang and Wahlbeck (7) have investigated angular and velocity distributions experimentally. Their results tend to substantiate the validity of the Maxwellian velocity distribution for near-ideal orifices but show a deviation in the upward direction for channel orifices. They attempt to explain this phenomenon by hypothesizing that specular reflection at grazing angles inside the orifice is preferred by faster molecules. Their work also tends to validate the cosine law assumption for ideal orifices, but places doubt on the Clausing theory applied to circular cylindrical and conical orifices. However, by their own admission, their experimental work was performed with Knudsen numbers in the transition range or very close to it. Consequently, the direct applicability of their results to the present discussion is debatable.

The first attempt to account for the angular distribution of the effusate and the effect of that distribution on experimental results was done by Freeman and Searcy (26). Using Clausing's mathematical analysis of a cylindrical channel, they defined a factor f which is the ratio of the effusion beam reaction force for a channel to the reaction force for an ideal orifice of the same radius, and produced tabular values of f for length-to-radius ratios (l/a) ranging from 0 to 2.0. The correction of Freeman and Searcy has been incorporated directly into the technique of a number of workers, for instance, Pratt and Aldred (27). However, it should be

observed that the validity of f hinges upon the same assumption made by Clausing, namely that molecules enter the passage with cosine-distributed directions and rebound in completely random directions; no account is taken of the effect of internal cell conditions on the distribution of molecules at the entrance to the orifice. It is the problem of extending f to include the effects of cell internals which will occupy all further discussion.

CHAPTER 3.

THEORY

Correction Factors for Torsion Effusion Cells

When a gas is allowed to effuse from an enclosure into a vacuum through an orifice of infinitesimal length (ideal orifice) by molecular flow, it exerts on the cell a reaction force

$$F = pA/2 \quad (3-1)$$

where p is the gas pressure inside the cell in a neighborhood of the orifice and A is the cross-sectional area of the orifice. The factor, f , defined by Freeman and Searcy (26), corrects for the fact that of the molecules entering a channel from the interior of the cell, a fraction of them will be reflected back into the cell, reducing the reaction force. This factor, when multiplied by the ideal reaction force in equation (3-1), yields the reaction force generated by the molecules passing through a channel orifice,

$$F = fpA/2 \quad (3-2)$$

As defined by Freeman and Searcy, f is a function only of the length-to-radius ratio of the channel.

Consider a torsion effusion cell (Figure 3-1) with ideal orifices of areas A_1 and A_2 which are displaced from the pivoted axis by moment arms q_1 and q_2 , respectively. Suppose the cell is operating with no internal losses, i.e., there is no material lost in the walls, and material lost through the orifices is negligible compared to that recondensing on the sample. In this case, the sample is in thermodynamic equilibrium with

its vapor and the pressure of the vapor everywhere inside the cell is essentially the thermodynamic vapor pressure, p_s . This is the defining characteristic of a so-called "ideal cell". The ideal cell torque, γ_{id} , generated by the two effusion beams is obtained by summing moments about the vertical axis, thus

$$\gamma_{id} = p_s (A_1 q_1 + A_2 q_2) / 2. \quad (3-3)$$

The cell is assumed to be suspended at the end of a fine wire with a Hooke's law torsion constant τ . During steady state operation of the cell the enclosure is in mechanical equilibrium with the wire and has twisted it through an angle θ . The torque in the wire is identical to γ_{id} and is equal, by Hooke's law, to $\tau\theta$. Substituting this into equation (3-3) and solving p_s gives

$$p_s = 2\tau\theta / (A_1 q_1 + A_2 q_2). \quad (3-4)$$

In current practice, this equation is corrected (27) for channel orifices by inclusion of the Freeman-Searcy factor, hence the form

$$p_s = 2\tau\theta / (f_1 A_1 q_1 + f_2 A_2 q_2), \quad (3-5)$$

where f_1 and f_2 are the respective correction factors for orifices 1 and 2.

We now generalize f to include effects other than the reflection of molecules back into the enclosure by channel orifices. Consider a general cell which may have orifices of finite length and significant cross-sectional area and in which internal losses may occur on the walls. The wall losses

Figure 3-1. A typical torsion effusion cell.

and the significantly large orifice area will effectively deplete the vapor space of molecules so that thermodynamic equilibrium is no longer maintained and the pressure of the vapor near the orifices is, in general, less than the thermodynamic vapor pressure. The actual torque, γ , exerted by the two effusion beams will consequently differ from the ideal torque, γ_{id} , for a cell possessing the same orifice areas and moment arms. The generalized torque correction factor, denoted by ϕ , is defined by

$$\phi = \gamma/\gamma_{id}, \quad (3-6)$$

and is an extension of Freeman and Searcy's f . For any actual cell with two identifiable orifices it represents the net effect of all phenomena occurring within the cell which contribute to nonideal behavior.

For convenience, we designate separate factors ϕ_1 , and ϕ_2 for each orifice and state that ϕ is their average. Furthermore, we separate the total torque, γ , into the respective contributions of the orifices, namely, γ_1 and γ_2 . Obviously

$$\gamma = \gamma_1 + \gamma_2.$$

Substituting $\tau\theta$ for γ and taking the actual torque contributions γ_1 and γ_2 to be the respective correction factors multiplied by the ideal torque contributions, we have

$$\tau\theta = \phi(A_1 p_s/2)q_1 + \phi_2(A_2 p_s/2)q_2.$$

Solving for p_s , we obtain

$$p_s = 2\tau\theta/(\phi_1 A_1 q_1 + \phi_2 A_2 q_2) \quad (3-7)$$

which is equation (3-5) generalized to account for all nonideal

behavior.

The actual torque, γ , may be considered to be the resultant of the contributions of each individual molecule which escapes through an orifice. Each time a molecule collides with a wall and rebounds it undergoes a change in momentum. Since momentum must be conserved, the molecule imparts an equal but opposite change in momentum to the body of the cell. As long as the molecule remains within the cell, molecule and cell constitute a closed system, the changes in momentum of the cell exactly cancel, and there is no net reaction force exerted. However, when a molecule escapes through an orifice, it imparts, at the last point of impact, an impulse to the cell which is not counterbalanced. Consequently, the net torque is the total of the net contributions of impulse to the cell by escaping molecules, determined at their respective last contact points.

Suppose a molecule, after any number of wall collisions, leaves the cell with a vector velocity $\vec{v}$. If $\vec{r}$ is the radius vector extending perpendicularly from the vertical axis to the last point of impact, then the angular momentum vector, $\vec{L}$, of the molecule about the pivotal axis is given by

$$\vec{L} = \vec{r} \times m\vec{v},$$

where m is the molecular mass. The angular impulse imparted to the molecule by the cell, $\vec{G}_m$, is equal to the change in angular momentum of the molecule,

$$\vec{G}_m = \vec{L}_2 - \vec{L}_1,$$

where $\vec{L}_1$ and $\vec{L}_2$ are the angular momenta of the molecule before and after collision with the wall. Assuming the molecule starts from rest, $\vec{L}_1 = 0$ and $\vec{L}_2$ is given by $\vec{r} \times m\vec{v}$. Consequently,

$$\vec{G}_m = \vec{r} \times m\vec{v}.$$

The reaction angular impulse imparted to the cell by the molecule has the same magnitude but opposite direction, or

$$\vec{G} = -\vec{r} \times m\vec{v}.$$

This vector will generally possess a component which is not useful in turning the cell about its axis. Only the vertical component of $\vec{G}$ is useful and its magnitude is the scalar projection of $\vec{G}$ on the vertical axis or

$$\text{proj}_{\hat{u}} \vec{G} = -\vec{r} \times m\vec{v} \cdot \hat{u},$$

where $\hat{u}$ is a unit vector parallel to the vertical axis.

Suppose that, during a time interval Δt , N_1 such molecules escape through orifice 1 and N_2 escape through orifice 2. The average torque exerted by the N_1 molecules is

$$\begin{aligned} \bar{\gamma}_1 &= G_T / \Delta t \\ &= \left| \sum_{i=1}^{N_1} G_{u(i)} \right| / \Delta t, \end{aligned}$$

where $G_{u(i)}$ is the useful torque contribution of the i -th molecule and G_T is the cumulative useful torque of the N_1 molecules. The absolute value is taken to avoid difficulties imposed by coordinate system conventions. (Alternatively, we could choose $\hat{u}$ in the proper direction to make $\bar{\gamma}_1$ positive.) The expression for $\bar{\gamma}_2$ may be written by inspection. During this time interval, suppose that a mass m_s of molecules

evaporates from the sample. Assuming that the vapor pressure of the sample, p_s , is given exactly by the Langmuir equation (1),

$$p_s = (m_s / \alpha_s A_s \Delta t) (2\pi RT/M)^{\frac{1}{2}} \quad (3-8)$$

where α_s is the sample condensation coefficient, A_s the sample surface area, R the universal gas constant, T , the absolute sample temperature, and M the molecular weight, the ideal torque exerted on the cell by the molecules leaving through orifice 1 would be

$$\gamma_{id-1} = \frac{1}{2} A_1 q_1 p_s = \frac{1}{2} A_1 q_1 (m_s / \alpha_s A_s \Delta t) (2\pi RT/M)^{\frac{1}{2}}.$$

Substituting this and the expression for γ_1 into the definition for ϕ_1 gives, after simplification,

$$\phi_1 = \gamma_1 / \gamma_{id-1} = (2\alpha_s A_s G_T / A_1 q m_s) (2\pi RT/M)^{-\frac{1}{2}}. \quad (3-9)$$

To calculate G_T , it is necessary to know the velocities of the molecules as they leave the cell. Since ϕ is a quantity averaged over all molecules exiting through orifice 1, it is appropriate to use an average velocity. It is herein assumed that, for the purpose of predicting velocities of molecules, walls can be modeled as extensions of the vapor phase. If this is valid, then average molecular velocities are predicted by the Maxwell-Boltzmann distribution whether or not intermolecular collisions exist. It can be shown¹ that the average speed of molecules crossing a plane in space (or passing through an orifice) is given by

$$\bar{c}_p = (9\pi RT/8M)^{\frac{1}{2}}. \quad (3-10)$$

¹Appendix A.

Let $\hat{n}_i$ be a unit vector parallel to and codirectional with $\vec{v}_i$. Then, on the average,

$$\vec{v}_i = \hat{n}_i (9\pi RT/8M)^{\frac{1}{2}}.$$

When this expression is used to specify molecular velocities, we have

$$G_T = \left| \sum_{i=1}^{N_1} \vec{r}_i \times m_i [\hat{n}_i (9\pi RT/8M)^{\frac{1}{2}}] \cdot \hat{u} \right|.$$

Substituting this for G_T in equation (3-9) gives, after simplifying,

$$\varphi_1 = (3/2) (\alpha_s A_s / A_1) (1/q_{m_s}) \left| \sum_{i=1}^{N_1} \vec{r}_i \times m_i \hat{n}_i \cdot \hat{u} \right|.$$

Now, represent m_i by the mean molecular mass, $\bar{m}$. The total mass, m_s , leaving the sample is given by $N_s \bar{m}$, where N_s is the total number of molecules leaving the sample in the time interval. Also define a reduced radius vector, $\vec{\rho}_i$, equal to $\vec{r}_i/q$. Substitution of these into the last equation gives

$$\varphi_1 = (3/2) (\alpha_s A_s / A_1) (1/N_s) \left| \sum_{i=1}^{N_1} \vec{\rho}_i \times \hat{n}_i \cdot \hat{u} \right|. \quad (3-11a)$$

By following an identical procedure, we obtain the counterpart for molecules departing through the second orifice:

$$\varphi_2 = (3/2) (\alpha_s A_s / A_2) (1/N_s) \left| \sum_{i=1}^{N_2} \vec{\rho}_i \times \hat{n}_i \cdot \hat{u} \right|. \quad (3-11b)$$

These equations are of extreme significance. A cursory glance at them reveals that all thermodynamic terms have vanished. The cell temperature, for instance, has no effect on the value of φ . It should be recalled, however, that the cell is assumed to operate at a uniform temperature. More generally the expression for φ would contain a temperature-distribution

factor to account for temperature gradients, but such inclusion is beyond the scope of the present treatment. Also, observe that all dimensional quantities have been eliminated, leaving only the ratios of these quantities. Furthermore, $\hat{n}_i$ contains only information relating to the direction of travel of a departing molecule and nothing about its position, mass, or velocity. The spacial relationship of the vectors ρ , $\hat{n}$, and $\hat{u}$ are shown in Figure 3-2. The series quantity will, in general, be heavily dependent upon internal losses and geometry. In other words, the shape of the cell, rather than its size, governs its behavior (provided mean free paths are still large compared to cell dimensions). When equations (3-11a) and (3-11b) are used to calculate correction factors, the two series must be evaluated for quite large values of N_1 , N_2 , and N_g . Consequently, these equations form the basis for the Monte Carlo simulation to be described later.

Considerable insight into the behavior of the cell may be obtained by performing a few more manipulations. In Appendix B it is shown that, for a cosine-distributed effusion beam, the factor $\left| \sum_{i=1}^{N_1} (\vec{\rho}_i \times \hat{n}_i \cdot \hat{u}) \right|$ is equal to $(2/3)N_1$. We now define a quantity ω_1 which is a property of the directional distribution of molecules in the effusion beam from orifice 1 and state that it is equal to $2/3$ for a cosine beam and, in general, other than $2/3$ for any other distribution. Then

$$\left| \sum_{i=1}^{N_1} (\vec{\rho}_i \times \hat{n}_i \cdot \hat{u}) \right| = \omega_1 N_1.$$

The analogous factor ω_2 for orifice 2 is similarly defined.

Figure 3-2. Configuration of the reduced vectors $\vec{\rho}$ and $\hat{\eta}$ with $\hat{u}$ in the proper direction to give a positive reaction.

Substitution of this into equation (3-11a) yields

$$\varphi_1 = (3/2)(\alpha_s A_s / A_1)(\omega_1 N_1 / N_s).$$

We now reduce ω_1 by dividing it by $2/3$, call it the orifice angular distribution factor, and give it the symbol ζ . Also, the fraction N_1/N_s of total molecules which escape through orifice 1 is only the transmission or escape probability for orifice 1, denoted by P_1 . Therefore,

$$\varphi_1 = (\alpha_s A_s / A_1) P_1 \zeta_1. \quad (3-12a)$$

By a similar treatment,

$$\varphi_2 = (\alpha_s A_s / A_2) P_2 \zeta_2. \quad (3-12b)$$

The factors $(\alpha_s A_s / A_1)$ and $(\alpha_s A_s / A_2)$ have special significance other than the fact that they are the only directly measurable quantities appearing in the preceding equations. Since the cell is assumed to be operating at steady state, a mass balance representing numbers of molecules during a time interval can be written as

$$N_1 + N_2 + N_w + N_c = N_s,$$

where $N_{1,2}$ are numbers of molecules lost through the orifices, N_w is the number of molecules (if any) permanently condensing on the walls, N_c is the number of molecules recondensing on the sample, and N_s is the total number of molecules initially evaporating from the sample. With a slight loss in generality, this can also be written

$$2N_o + N_w + N_c = N_s,$$

where N_o is the average of N_1 and N_2 . This form is valid for a symmetrical cell in which $N_1 = N_2$. Dividing by N_o ,

$$2 + (N_w/N_o) + (N_c/N_o) = (N_s/N_o).$$

The number of molecules incident on a surface is equal to the average collision density $\bar{\psi}$ on that surface multiplied by the surface area. On the wall or the sample, this incident flux, when multiplied by the appropriate condensation coefficient α for that surface, gives the number of molecules lost on that surface. Furthermore N_o/N_s is equal to P , the escape or transmission probability for either orifice. Hence,

$$2 + \frac{\bar{\psi}_w \alpha_w A_w}{\bar{\psi}_o A_o} + \frac{\bar{\psi}_s \alpha_s A_s}{\bar{\psi}_o A_o} = \frac{1}{P}$$

Solving for P ,

$$P = [2 + k_w(\alpha_w A_w/A_o) + k_s(\alpha_s A_s/A_o)]^{-1}, \quad (3-13)$$

where $k_w = \bar{\psi}_w/\bar{\psi}_o$ and $k_s = \bar{\psi}_s/\bar{\psi}_o$. Although k_w and k_s cannot in general, be obtained by any simple means, it can be fairly stated that, since it is the tendency of molecules to distribute themselves uniformly throughout an enclosure, these coefficients tend toward 1.0. This is more the case in a cell at equilibrium in which the only molecular sink is the sample. For a first simplification, consider a cell with small orifices and with $\alpha_w = 0$ so there is no permanent adsorption of molecules on the walls. Equation (3-13) simplifies to

$$P = [2 + k_s(\alpha_s A_s/A_o)]^{-1}.$$

In the limit as A_o becomes very small compared to $\alpha_s A_s$, which can be viewed as the effective sample area insofar as adsorption of molecules is concerned, with k_s tending toward 1.0 the first term in the brackets becomes insignificant compared to

the second term. Consequently, $(A_o/\alpha_s A_s)$ can be thought of being the limiting escape probability of the cell, or

$$\lim_{A_o \rightarrow 0} P = (A_o/\alpha_s A_s).$$

Additionally, this quantity can be viewed as a measure of the degree of departure from equilibrium caused by the presence of the orifices, i.e., the equilibrium approximation becomes better as $(A_o/\alpha_s A_s)$ approaches zero. This is not surprising inasmuch as it is generally the goal, when observing any system at equilibrium, to disturb it as little as possible. Applying this result to equations (3-12a) and (3-12b),

$$\varphi_1 \approx \zeta_1,$$

$$\varphi_2 \approx \zeta_2.$$

However, from Appendix C, any cell with uniform internal collision density will emit cosine-law effusion beams. In any cell operating close to equilibrium, this tends to be the case and ζ_1, ζ_2 will each be close to 1. Consequently, for a cell with little or no wall loss and minute orifices,

$$\varphi_1 \approx 1.0,$$

$$\varphi_2 \approx 1.0,$$

with the approximation improving as the cell approaches perfect equilibrium. Somewhat more rigorously, Appendix D shows that, for an ideal cell, φ must indeed be identically equal to 1.

Formulation of Flux Model in Terms of Integral Equations

With the establishment of the cell behavior indices, ϕ , P , ζ , it is now appropriate to set forth a firm mathematical basis for the operation of the cell, from which these outward manifestations may be deduced. Formulated as a set of linear integral equations, the model is a completely rigorous description of steady state operation, but may not be solved generally in closed form. The present development is aligned more closely with the philosophy of Carlson et al. (25), who writes fully rigorous mathematical statements, postponing simplifying assumptions as long as possible, rather than beginning with not wholly justifiable statements as do Whitman (17) and Motzfeldt (18).

We begin by restating and discussing the integral equation of DeMarcus (14),

$$\psi(S) = \psi_0(S) + \int_S K(S', S) \psi(S') dS', \quad (3-14)$$

where $\psi(S)$ is the flux intensity or collision density on surface S in molecules/unit area. The first term on the right side $\psi_0(S)$ is the entrance distribution, i.e., the distribution of molecular flux impinging on S based on molecules first entering the system from the outside, from evaporation, or from any other independent source. The second term describes the distribution of molecular flux based on molecules which have collided with S according to flux distribution $\psi(S)$. The primes are used only to distinguish the dummy variable of integration. The integral is obtained from the differential equation

$$d\psi(S) = K(S', S) \psi(S') dS',$$

which gives the contribution of flux on area element dS by emitting element dS' . The kernel $K(S', S)$ is a symmetrical kernel, obtained from geometrical considerations and based on the cosine law of emission; for points $P(S)$ and $P(S')$, separated by a line segment of length P , the kernel has the value

$$(\cos \theta \cos \theta') / (\pi P^2),$$

where θ and θ' are angles between the line segment and the normals to the surfaces when the two points can "see" each other, and is zero if they are obstructed. Equation (3-14), with its variants, will be employed in the ensuing discussion, but with the inclusion of the coefficient λ , equal to $(1-\alpha)$, to account for permanent condensation of molecules on S , i.e.,

$$\psi(S) = f_0(S) + \lambda \int_{S_1} K(S', S) \psi(S') dS'. \quad (3-15)$$

It should be observed that equation (3-15) is in the classical form of a linear integral equation of the second kind, with a parameter, λ . In general, λ is a function of position, but for the purposes of the following analysis, we assume that λ is constant over large subregions of S .

Let us now specify a particular torsion effusion cell and describe its internal flux distribution in unsolved form with equations derived from equation (3-15). The cell (Figure 3-3) consists of a right circular cylinder, closed at each end by a plane. These elements are collectively denoted as S_2 . The orifices (S_0) are subregions of the cylinder, but are considered distinct from S_2 . The sample is denoted by S_1 and is of arbitrary size, shape, and location. Note that the surface

Figure 3-3. Nomenclature for the various internal surfaces of the cell.

S_0 completely encloses S_1 . Finally, since it is the primary intent to concentrate on the effects of internal cell properties rather than on the effect of the orifice length, the orifices are taken to be of zero length.

With these considerations in mind, we now adapt equation (3-15) to the present model. First, the flux on S_0 is composed of contributions by the sample, S_1 , and the wall, S_2 . Mathematically,

$$\begin{aligned} \psi(S_0) = f(S_0) + \lambda_s \int_{S_1} K(S_1, S_0) \psi(S_1) dS_1 \\ + \lambda_w \int_{S_2} K(S_2, S_0) \psi(S_2) dS_2. \end{aligned}$$

Since S_0 is a perfect sink, it contributes no flux, and no term exists for it. The external function, $f(S_0)$ is caused by molecules initially being evaporated from the sample. Second, the flux on S_1 is composed of contributions by itself and by S_2 . Again, using primes to distinguish the variable of integration,

$$\begin{aligned} \psi(S_1) = f(S_1) + \lambda_s \int_{S_1'} K(S_1', S_1) \psi(S_1') dS_1' \\ + \lambda_w \int_{S_2} K(S_2, S_1) \psi(S_2) dS_2. \end{aligned}$$

Finally, the flux on S_2 is composed of contributions by S_1 and by itself, hence,

$$\begin{aligned} \psi(S_2) = f(S_2) + \lambda_s \int_{S_1} K(S_1, S_2) \psi(S_1) dS_1 \\ + \lambda_w \int_{S_2'} K(S_2', S_2) \psi(S_2') dS_2'. \end{aligned}$$

It is not unrealistic to assume that the sample evaporates molecules at a uniform rate over its entire surface. We denote this rate by n_s which, like ψ , has units of molecules/unit area. Without loss of generality, we may set $n_s \equiv 1$ and redefine

all ψ terms as being normalized flux intensity, i.e., flux obtained for unit sample evaporation intensity. We can therefore represent $f(S)$ as

$$\begin{aligned} f(S_i) &= \int_{S_1} K(S_1, S_i) (1) dS_1 \\ &= \int_{S_1} K(S_1, S_i) dS_1, \end{aligned} \quad (3-16)$$

with $i=1, 2$, or 3 . It is important to note that the integral in equation (3-16) is affected purely by geometrical relationships. This fact will be used later to great advantage. Incorporating this in the model gives us

$$\begin{aligned} \psi(S_o) &= \int_{S_1} K(S_1, S_o) dS_1 + \lambda_s \int_{S_1} K(S_1, S_o) \psi(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2} K(S_2, S_o) \psi(S_2) dS_2, \end{aligned} \quad (3-17a)$$

$$\begin{aligned} \psi(S_1) &= \int_{S_1'} K(S_1', S_1) dS_1 + \lambda_s \int_{S_1'} K(S_1', S_1) \psi(S_1') dS_1' \\ &\quad + \lambda_w \int_{S_2} K(S_2, S_1) \psi(S_2) dS_2, \end{aligned} \quad (3-17b)$$

$$\begin{aligned} \psi(S_2) &= \int_{S_1} K(S_1, S_2) dS_1 + \lambda_s \int_{S_1} K(S_1, S_2) \psi(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2'} K(S_2', S_2) \psi(S_2') dS_2'. \end{aligned} \quad (3-17c)$$

Equations (3-17a), (3-17b), and (3-17c) constitute a completely rigorous mathematical statement of the flux behavior of the model shown graphically in Figure 3-3. Rather than attempting to solve these equations either rigorously or approximately, we add a constraint and a simplifying assumption.

Some measure of complexity may be removed if we limit our discussion to sample surfaces that are everywhere convex, thereby preventing the sample from "seeing" itself. This removes the first and second terms on the right side of equation (3-17b). Physically, this is not unrealistic whenever the sample is in the form of a nonwetting drop on the bottom of

Figure 3-4. Nomenclature for the closed cell.

the cell, or when it is an essentially flat layer of solid on the bottom of the cell. In other cases e.g., turnings or other "hyper-rough" configurations, this will not be strictly valid; however, the net effect of a highly rough surface is to increase the apparent value of α_s , since a molecule striking the sample has a higher probability of capture. Consequently, it often may be possible to make the convex sample assumption, after α_s has been appropriately corrected. Observe that, in the large number of cases in which the true α_s is exactly 1.0, this problem will vanish since contributions by molecules reflected from S_1 will be removed.

The assumption which we now make we attempt to justify by limiting our model to vanishingly small orifices. We simply state, therefore, that the orifices can be represented as two point sinks, i.e., all molecular effusion is taken to be acting at the centroids of the two portions of S_0 . When this assumption is made, the set of equations (3-17a), (3-17b), and (3-17c) may be treated as a perturbed form of the mathematical model we would write if the orifices were replaced by extensions of the surface S_2 .

To aid our discussion, we define the closed-orifice cell shown in Figure 3-4 in which S_0 and S_2 have been replaced by S_3 equal to $S_0 \cup S_2$, thereby completely enclosing the sample, S_1 . The equations which describe this configuration are as follows:

$$\psi_0(S_1) = \lambda_w \int_{S_3} K(S_3, S_1) \psi_0(S_3) dS_3, \quad (3-18a)$$

$$\begin{aligned} \psi_o(S_3) = & \int_{S_1} K(S_1, S_3) dS_3 + \lambda_s \int_{S_1} K(S_1, S_3) \psi_o(S_1) dS_1 \\ & + \lambda_w \int_{S_3'} K(S_3', S_3) \psi_o(S_3') dS_3'. \end{aligned} \quad (3-18b)$$

We complete the description by stating that $\psi_o(S_3) \equiv \psi_o(S_2)$ whenever the point in question, $P(S_3)$, lies on S_2 and $\psi_o(S_3) \equiv \psi_o(S_o)$ whenever $P(S_3)$ lies on S_o .

Since the integral equations used here are linear, we may invoke the principle of superposition. We define a perturbation flux, $\psi_p(S)$ as the difference, point by point, of the solutions of equations (3-17) and equations (3-18), thus

$$\psi_o(S) = \psi_p(S) + \psi(S), \quad (3-19)$$

where S is any surface. If we write two versions of equation (3-18b), one for $\psi_o(S_o)$ and one for $\psi_o(S_2)$, then substitute into each of the three equations for $\psi_o(S_i)$, $i=1, 2$, and 3 , from equation (3-19), we obtain a form from which we may subtract the corresponding parts of equations (3-17). The resulting set of equations is

$$\begin{aligned} \psi_p(S_o) = & \lambda_w \int_{S_o'} K(S_o', S_o) \psi_o(S_o') dS_o' + \\ & \lambda_s \int_{S_1} K(S_1, S_o) \psi_p(S_1) dS_1 + \\ & \lambda_w \int_{S_2} K(S_2, S_o) \psi_p(S_2) dS_2, \\ \psi_p(S_1) = & \lambda_w \int_{S_2} K(S_o, S_1) \psi_o(S_o) dS_o + \\ & \lambda_w \int_{S_2} K(S_2, S_1) \psi_p(S_2) dS_2, \\ \psi_p(S_2) = & \lambda_w \int_{S_o} K(S_o, S_2) \psi_o(S_o) dS_o + \\ & \lambda_s \int_{S_1} K(S_1, S_2) \psi_p(S_1) dS_1 + \\ & \lambda_w \int_{S_2'} K(S_2', S_2) \psi_p(S_2') dS_2'. \end{aligned}$$

Observe that the first term on the right side of each of these equations contains reference only to ψ_o . This means that

these terms are the external or forcing functions and correspond to $f_0(S)$ in equation (3-15). It is now that the assumption of point orifices becomes important. The average $\psi_0(S_0)$ becomes indistinguishable from the values of $\psi_0(S_0)$ evaluated on S_3 at what would be the centroids of the two portions of S_0 . For a symmetrical cell we may denote this by a constant, c_0 . When we substitute this for ψ_0 , we find that we may bring it outside the integrals. The resulting integrals are functions determined purely by geometry. Denoting these by $h(S_i)$, $i=1, 2$, or 3 , we obtain

$$\begin{aligned}\psi_p(S_0) &= c_0 \lambda_w h(S_0) + \lambda_s \int_{S_1} K(S_1, S_0) \psi_p(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2} K(S_2, S_0) \psi_p(S_2) dS_2, \\ \psi_p(S_1) &= c_0 \lambda_w h(S_1) + \lambda_w \int_{S_2} K(S_2, S_1) \psi_p(S_2) dS_2, \\ \psi_p(S_2) &= c_0 \lambda_w h(S_2) + \lambda_s \int_{S_1} K(S_1, S_2) \psi_p(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2'} K(S_2', S_2) \psi_p(S_2') dS_2'\end{aligned}$$

Let $\psi_p^0(S_i)$, $i=1, 2$, or 3 denote the normalized version of $\psi_p(S_i)$, i.e., the solution obtained for $c_0=1$. Then, since these are linear equations, they may be placed in the final form

$$\begin{aligned}\psi_p^0(S_0) &= \lambda_w h(S_0) + \lambda_s \int_{S_1} K(S_1, S_0) \psi_p^0(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2} K(S_2, S_0) \psi_p^0(S_2) dS_2, \quad (3-20a)\end{aligned}$$

$$\psi_p^0(S_1) = \lambda_w h(S_1) + \lambda_w \int_{S_2} K(S_2, S_1) \psi_p^0(S_2) dS_2, \quad (3-20b)$$

$$\begin{aligned}\psi_p^0(S_2) &= \lambda_w h(S_2) + \lambda_s \int_{S_1} K(S_1, S_2) \psi_p^0(S_1) dS_1 \\ &\quad + \lambda_w \int_{S_2'} K(S_2', S_2) \psi_p^0(S_2') dS_2' \quad (3-20c)\end{aligned}$$

where

$$\psi_p(S_i) = c_0 \psi_p^0(S_i), \quad i=1, 2, 3. \quad (3-20d)$$

It should be noted that equations (3-20a) through (3-20c)

constitute an independent set of linear integral equations and are unrelated to the solution of the closed-orifice problem. While symmetry was tacitly assumed for the purpose of simplifying the discussion somewhat, this was by no means essential; for an asymmetric cell, one would simply write two versions of equation (3-20a) and separate $h(S_1)$ and $h(S_2)$ into two parts. Since the present study will later concentrate on symmetrical cells, a more general derivation is not necessary here.

It should also be noted that, while the orifices are treated as sinks in earlier discussion, any attempt to solve equations (3-20a) through (3-20c) would necessarily treat the orifices as point sources since they supply the molecular collisions which occur in the closed-orifice model but not in the original (open-cell) model. However, we do not address the problem of calculating the perturbation flux, since emphasis will rather be placed on the asymptotic solution resulting from vanishingly small orifices.

An Approximate Solution to the Closed-Cell Equations

Since the integral equation model is of little practical use in unsolved form, we now address the problem of obtaining an approximate closed-form solution of the equations. We make the following assumptions about the cell:

1. The orifices possess vanishingly small apertures.
2. The sample cannot "see" itself.
3. The orifices are ideal, i.e., of infinitesimal length.

4. Molecules tend to disperse uniformly throughout the enclosure.

The first three assumptions necessarily cause us to adopt the form in equations (3-18a) and (3-18b). The first two assumptions were explicitly made in their development, but the third was implicit since no account was taken of reflection of molecules back into the cell by channel orifices. Such account would be negligible since, in general, the orifices affect the behavior of the cell only to a minute degree. The fourth assumption is primarily a consequence of the form of the kernel of integration defined for equation (3-14), but the surface diffusion phenomenon, if present to any significant degree, would also contribute. This important assumption will be considered more fully later.

Equations (3-18a) and (3-18b) are a coupled set of linear equations and may be uncoupled, in this case, simply by substituting (3-18a) into (3-18b) for $\psi_0(S_1)$:

$$\begin{aligned}\psi_0(S_3) = & \int_{S_1} K(S_1, S_3) dS_3 \\ & + \lambda_s \int_{S_1} K(S_1, S_3) \lambda_w \int_{S_3'} K(S_3', S_1) \psi_0(S_3') dS_3' dS_1 \\ & + \lambda_w \int_{S_3'} K(S_3', S_3) \psi_0(S_3') dS_3',\end{aligned}$$

with primes added to avoid confusion of the variables of integration. This may be rearranged into the form

$$\begin{aligned}\psi_0(S_3) = & \int_{S_1} K(S_1, S_3) dS_3 \\ & + \lambda_s \lambda_w \int_{S_1} \int_{S_3'} K(S_1, S_3) K(S_3', S_1) \psi_0(S_3') dS_3' dS_1 \\ & + \lambda_w \int_{S_3'} K(S_3', S_3) \psi_0(S_3') dS_3' .\end{aligned}$$

Interchanging the order of integration and recalling that

$\psi_0(S_3')$ is independent of the differential area dS_1 , we obtain

$$\begin{aligned}\psi_0(S_3) &= \int_{S_1} K(S_1, S_3) dS_3 \\ &+ \lambda_s \lambda_w \int_{S_3'} \left[\int_{S_1} K(S_1, S_3) K(S_3', S_1) dS_1 \right] \psi_0(S_3') dS_3' \\ &+ \lambda_w \int_{S_3'} K(S_3', S_3) \psi_0(S_3') dS_3' .\end{aligned}$$

The integration indicated by the quantity in brackets may, in principle, be performed beforehand; since S_1 is a parameter of integration, the result is a function or compound kernel depending only on S_3' and S_3 , and will be denoted by $K'(S_3', S_3)$. We may combine the last two terms to obtain

$$\begin{aligned}\psi_0(S_3) &= \int_{S_1} K(S_1, S_3) dS_3 \\ &+ \lambda_w \int_{S_3'} [K(S_3', S_3) + \lambda_s K'(S_3', S_3)] \psi_0(S_3') dS_3' .\end{aligned}\tag{3-21}$$

By inspection, we see that equation (3-21) is a linear integral equation of the second kind and may solve it by classical techniques. We stress that this simple form could not be obtained without the second simplifying assumption, i.e., that the sample cannot "see" itself.

The bracketed quantity in equation (3-21) is the kernel of integration. The fact that it consists of two terms has the following physical significance: any molecule emitted from surface S_3 will either strike S_3 at another point or will strike the sample, S_1 . Any molecule striking the sample has the probability λ_s of being re-emitted. Since the sample cannot "see" itself, the molecule must proceed to a collision on S_3 . The term $K(S_3', S_3)$ represents those molecules leaving dS_3' and proceeding directly to dS_3 ; $\lambda_s K'(S_3', S_3)$ represents those molecules reaching dS_3 via S_1 .

The classical form for the solution of a linear integral equation of the second kind such as

$$g(x) = g_0(x) + \lambda \int_D k(x', x) g(x') dx', \quad (3-22)$$

where D is the domain of x , is an infinite series¹,

$$g(x) = g_0(x) + \lambda g_1(x) + \lambda^2 g_2(x) + \dots \quad (3-23a)$$

The coefficient functions $g_1(x)$, $g_2(x)$ are defined by

$$g_{i+1}(x) = \int_D k(x', x) g_i(x') dx', \quad i=0,1,\dots \quad (3-23b)$$

In this manner, the solution of equation (3-21) may be represented by

$$\psi_0(S_3) = f_0(S_3) + \lambda_w f_1(S_3) + \lambda_w^2 f_2(S_3) + \dots \quad (3-24a)$$

where

$$f_0(S_3) = \int_{S_1} K(S_1, S_3) dS_1 \quad (3-24b)$$

and

$$f_{i+1}(S_3) = \int_{S_3} [K(S_3', S_3) + \lambda_s K'(S_3', S_3)] f_i(S_3') dS_3'. \quad (3-24c)$$

The solution (3-24) has the following physical significance: the total collision density, $\psi_0(S_3)$ may be considered to be composed of the contributions of many repeated collision of individual molecules on the wall. Molecules first entering the vapor phase, specifically through initial evaporation from S_1 , strike the wall with collision density $f_0(S_3)$. Of these molecules, a fraction λ_w will be re-emitted. Some of these molecules will proceed directly to the second encounter with S_3 ; all others will strike S_1 , with a fraction λ_s being re-emitted. All molecules re-emitted from S_1 must immediately encounter S_3 ;

¹Courant and Hilbert (28, pp. 140-141).

these molecules, along with those which did not strike S_1 collectively form the second coefficient function, $f_1(S_3)$. Of these molecules, a fraction λ_w will be emitted, ultimately to form $f_2(S_3)$, and so on.

It is appropriate at this point to make a few remarks about the convergence of the series in equation (3-24a), although it is not the present intent to set forth a completely rigorous specification of the criteria for convergence.

First, it should be recalled that equations (3-24) are an attempt to describe a system at steady state. The sample is continually producing molecules which must be removed or "sunk" somewhere. Since the orifices are effectively absent, there must be condensation either on the wall, or on the sample, or both in order for the model to be self-consistent. Bearing this in mind, we may reason that λ_s and λ_w may not simultaneously be 1. This is not obvious from direct examination of (3-24a); however, let us integrate both sides over S_3 to obtain

$$\int_{S_3} \psi_0(S_3) dS_3 = \int_{S_3} f_0(S_3) dS_3 + \lambda_w \int_{S_3} f_1(S_3) dS_3 + \dots$$

The first term on the right is the total number of molecules first striking S_3 , and is also equal to the total number of molecules initially leaving the sample,

$$\int_{S_1} n dS_1 = \int_{S_1} (1) dS_1 = A_{S1}.$$

With no loss on the sample, mass balances show that each of the subsequent integrals on the right side is also. Thus,

$$\begin{aligned} \int_{S_3} \psi(S_3) dS_3 &= A_{S1} + \lambda_w A_{S1} + \lambda_w^2 A_{S1} + \dots \\ &= A_{S1} (1 + \lambda_w + \lambda_w^2 + \dots), \end{aligned}$$

and it is well known that the convergence interval for the power series in parentheses is $-1 < \lambda_w < 1$. Since negative λ_w is meaningless here, our criterion is simply $0 \leq \lambda_w < 1$.

The foregoing analysis, while physically quite meaningful, is not sufficiently restrictive to gauge the convergence of equation (3-24a) since it merely requires that the integral of a function be bounded, a condition which is satisfied by many unbounded functions. A more discriminating test for integral equations in functions of a single variable is known¹ and may easily be adapted to this problem. Let us hypothesize

$$|K_c(S_3', S_3)| \leq M$$

$$|f_0(S_3)| \leq N,$$

where M and N are constants and $K_c(S_3', S_3)$ is the combined kernel

$$K(S_3', S_3) + \lambda_s K'(S_3', S_3).$$

By equation (3-42c),

$$|f_1(S_3)| \leq \int_{S_3'} MN \, dS_3' = NMA_{S_3}$$

Similarly,

$$|f_2(S_3)| \leq \int_{S_3'} M(NMA_{S_3}) \, dS_3' = N(MA_{S_3})^2,$$

and so on. Then, by equation (3-24a)

$$|\psi_0(S_3)| \leq N + \lambda_w N(MA_{S_3}) + \lambda_w^2 N(MA_{S_3})^2 + \dots$$

or

$$|\psi_0(S_3)| \leq N[1 + (\lambda_w MA_{S_3}) + (\lambda_w MA_{S_3})^2 + \dots].$$

¹Lovitt (29, p. 11).

The geometric series in brackets will converge only if

$$\lambda_w M A_{S_3} < 1,$$

or

$$M < (\lambda_w A_{S_3})^{-1} \quad (3-25)$$

In order for this inequality to be satisfied, some upper bound, M , must exist for $K_c(S_3', S_3)$; failure for M to exist does not guarantee failure of the solution to converge but indicates a potential source of difficulty. Since this kernel is composed of the kernels $K(S_3', S_3)$ and $K'(S_3', S_3)$, it is appropriate to consider the boundedness of each one separately. Suppose

$$|K(S_3', S_3)| \leq M_1, \quad (3-26a)$$

$$|\lambda_s K'(S_3', S_3)| \leq M_2. \quad (3-26b)$$

By the Triangle Inequality,

$$|K(S_3', S_3) + \lambda_s K'(S_3', S_3)| \leq |K(S_3', S_3)| + |\lambda_s K'(S_3', S_3)|,$$

and, by the inequalities (3-26a) and (3-26b),

$$|K(S_3', S_3) + \lambda_s K'(S_3', S_3)| \leq M_1 + M_2.$$

The sum $M_1 + M_2$ may be taken for a possible bound M for

$|K_c(S_3', S_3)|$, although it may not, in general, be the least upper bound.

As discussed in Appendix D, the tendency of the kernel $K(S_3', S_3)$ to become unbounded is due to the appearance of the square of the distance separating the points P on S_3 and P' on S_3' in the denominator. As this distance approaches zero, the kernel will become infinite if the numerator is not identically

zero. This condition is met when the points lie on the same plane surface, but is not met when P and P' lie on adjacent surfaces in the region of a sharp corner. Consequently, $|K(S_3', S_3)|$ cannot be expected to possess an upper bound in a corner region.

Turning now to the compound kernel

$$K'(S_3', S_3) = \int_{S_1} K(S_3', S_1) K(S_1, S_3) dS_1,$$

we see that, since $K(S_3', S_1)$ and $K(S_1, S_3)$ involve points on S_1 and S_3 which are separated by a distance possessing a lower bound, these kernels do possess an upper bound, M_3 . Thus,

$$K(S_3', S_3) \leq \int_{S_1} M_3 M_3 dS_1 = M_3^2 A_{S_1}.$$

Therefore, we conclude that any tendency for $K_c(S_3', S_3)$ to be unbounded is related to a so-called "corner effect" involving the simple kernel $K(S_3', S_3)$. While this is of no great concern in a theoretical sense, it is a potential source of two practical difficulties when numerical solutions of the flux equation are contemplated. First is the most obvious problem of overflow in a finite-difference, integration, when one attempts to compute the molecular flux at a point far within a corner region. Second, and somewhat more subtle is a problem frequently encountered in a Monte Carlo flux calculation. Molecules entering a corner region sometimes get "stuck", i.e., they may experience a great many collisions before they leave the corner region. During a molecule's transit in this region, direction-calculating procedures will typically involve extremely small distances in the denominators of some terms, and

computed results may vary over an extremely wide range. The result is either overflow or, more commonly, accumulated roundoff error in which positional coordinates eventually may erroneously indicate that the molecule has somehow "penetrated" the wall. In either case, the problem is basically one of numerical instability. One way to circumvent the problem in the first case is to choose an increment large enough that the average values of the kernel and flux terms in a corner are small enough for a computer to handle. Attempts to circumvent instability in the Monte Carlo calculation usually involve some stopgap tactic such as testing molecular coordinates and discarding molecules which get "stuck".

The solution given by equations (3-24) is still not in a particularly tractable form; however, we now invoke the fourth assumption, namely, that molecules tend to disperse uniformly throughout the enclosure. This is equivalent to saying that the coefficient functions, f_i , in (3-24a) tend to become constant or uniform over all points on S_3 . We now hypothesize that, although f_0 and the first few f_i following f_0 in the series may contain strong gradients, at some point, i.e., at the k -th term in the series, the flux terms become effectively uniform. In other words, f_i is uniform for $i=k, k+1, k+2, \dots$. Applying this to equation (3-24c),

$$f_{k+1}(S_3) = \int_{S_3} [K(S_3', S_3) + \lambda_S K'(S_3', S_3)] f_k(S_3') dS_3',$$

but, by hypothesis, $f_k(S_3)$ and $f_{k+1}(S_3)$ are uniform with constant values for f_k and f_{k+1} . Consequently,

$$f_{k+1} = f_k \int_{S_3} [K(S_3', S_3) + \lambda_s K'(S_3', S_3)] dS_3'.$$

Integrating both sides over S_3 gives a mass balance,

$$\int_{S_3} f_{k+1} dS_3 = \int_{S_3} f_k \int_{S_3} [K(S_3', S_3) + \lambda_s K'(S_3', S_3)] dS_3' dS_3,$$

or

$$f_{k+1} A_{S_3} = f_k \left[\int_{S_3} \int_{S_3} K(S_3', S_3) dS_3' dS_3 + \lambda_s \int_{S_3} \int_{S_3} K'(S_3', S_3) dS_3' dS_3 \right],$$

and, dividing by A_{S_3} ,

$$f_{k+1} = f_k \left[A_{S_3}^{-1} \int_{S_3} \int_{S_3} K(S_3', S_3) dS_3' dS_3 + \lambda_s A_{S_3}^{-1} \int_{S_3} \int_{S_3} K'(S_3', S_3) dS_3' dS_3 \right].$$

The first term in brackets is the view factor,¹ $F_{S_3-S_3}$, or that fraction of molecules leaving S_3 and immediately striking S_3 . Since all molecules which do not fall into this category must strike S_1 with exactly λ_s of them returning directly to S_3 , the second term in brackets must be the view factor $F_{S_3-S_1}$. Consequently,

$$f_{k+1} = f_k [F_{S_3-S_3} + \lambda_s F_{S_3-S_1}].$$

We do not know $F_{S_3-S_3}$ but we can readily obtain $F_{S_3-S_1}$ and, since the sum of the two factors must be 1, we may write

$$f_{k+1} = f_k [(1 - F_{S_3-S_1}) + \lambda_s F_{S_3-S_1}].$$

It is property of view factors that

$$A_{S_1} F_{S_1-S_3} = A_{S_3} F_{S_3-S_1};$$

since all molecules leaving S_1 must strike S_3 , $F_{S_1-S_3} = 1$,

and we have

¹ For a detailed discussion of view factors, see Hottel (30, p. 65) or any treatise on radiative heat transfer such as Hottel and Sarofim (31, p. 25) et seq.

$$F_{S3-S1} = A_{S1}/A_{S3}.$$

Making this substitution,

$$f_{k+1} = f_k [1 - (1 - \lambda_s) A_{S1}/A_{S3}].$$

With $\lambda_s = 1 - \alpha_s$, we have, finally,

$$f_{k+1} = f_k [1 - (\alpha_s A_{S1}/A_{S3})].$$

An identical application to the next pair of terms in the series gives

$$\begin{aligned} f_{k+2} &= f_{k+1} [1 - (\alpha_s A_{S1}/A_{S3})] \\ &= f_k [1 - (\alpha_s A_{S1}/A_{S3})]^2, \end{aligned}$$

and so on. We may now apply this to the series solution to give

$$\begin{aligned} \psi_0(S_3) &= f_0(S_3) + \lambda_w f_1(S_3) + \lambda_w^2 f_2(S_3) + \dots \\ &\quad + \lambda_w^k [f_k + \lambda_w f_{k+1} + \lambda_w^2 f_{k+2} + \dots] \\ &= f_0(S_3) + \lambda_w f_1(S_3) + \lambda_w^2 f_2(S_3) + \dots \\ &\quad + \lambda_w^k f_k [1 + \lambda_w (1 - \alpha_s A_{S1}/A_{S3}) + \dots]. \end{aligned}$$

Finally, replacing the geometric series in brackets with its equivalent,

$$\begin{aligned} \psi_0(S_3) &= f_0(S_3) + \lambda_w f_1(S_3) + \lambda_w^2 f_2(S_3) + \dots \\ &\quad + \lambda_w^k f_k [1 - \lambda_w (1 - \alpha_s A_{S1}/A_{S3})]^{-1}. \end{aligned} \quad (3-27)$$

Equation (3-27) states, in essence, that the total flux, $\psi_0(S_3)$, in the enclosure consists of two parts: a gradiential or entrance solution denoted by $\sum_{i=0}^{k-1} f_i(S_3)$ and a diffuse uniform background denoted by $\lambda_w^k f_k [1 - \lambda_w (1 - \alpha_s A_{S1}/A_{S3})]^{-1}$. We may symbolize this by writing

$$\psi_0(S_3) = \Phi_g(S_3; k) + \Phi_d(S_3; k),$$

where $\Phi_g(S_3; k)$ is the portion of the solution to which all

flux gradients are attributed and $\Phi_d(S_3; k)$ is the diffuse background.

It should now be noted that the selection of k is rather arbitrary and that no particular value is necessarily the "best" value to use in all situations. On the basis of preliminary Monte Carlo "experiments", to be described later, it is observed that most of the flux gradients in the sum of the first twenty coefficients are due to strong trends in $f_0(S_3)$ and that all further coefficients are highly uniform in comparison. Consequently, for the level of accuracy to be attained in this approach, it is not unreasonable to attribute all significant gradients to $f_0(S_3)$, i.e., to set $k=1$. This is rather fortunate, since, although $f_0(S_3)$ is readily obtained, it is extremely difficult to predict (without recourse to a computer) a reasonable value of f_k for $k > 1$. Thus, we dictate, for our present purposes, that

$$\psi_0(S_3) = f_0(S_3) + \lambda_w f_1 [1 - \lambda_w (1 - \alpha_s A_{S1}/A_{S3})]^{-1} \quad (3-28a)$$

or

$$\psi_0(S_3) = \Phi_g(S_3; 1) + \Phi_d(S_3; 1), \quad (3-28b)$$

and set about to develop a means of calculating $f_0(S_3)$ and f_1 .

In order to do this, we must now make our most restrictive assumption, namely, that the sample surface, S_1 , not only is everywhere convex, but is perfectly spherical and is situated in the exact center of the cell. Unfortunately, this model is not particularly realistic, since it is not feasible, in practice, to suspend a molten drop in the middle of the cell,

but it is desirable from a mathematical standpoint by the symmetry of the system. Furthermore, we speculate that this model will tend to represent the effect of lumping the sample at the center of the cell instead of distributing it uniformly on the cell floor. The latter configuration could be treated as another limiting case, but obviously loses the advantage of axial symmetry.

In Appendix E the following expression is derived for the normalized flux from a uniformly-emitting sphere:

$$\psi = (R_s/D)^2 \cos \beta, \quad (3-29)$$

where R_s is the sphere radius, D is the distance from the center of the sphere to the point on the surface where ψ is measured, and β is the angle from the normal to the surface to the line joining the point on the surface to the center of the sphere. Applying this to our configuration as shown in Figure 3-5, we have, on the cylinder,

$$\cos \beta = R/(R^2 + l^2)^{\frac{1}{2}}$$

and

$$D = (R^2 + l^2)^{-1},$$

and, on each of the end plates,

$$\cos \beta = L/(r^2 + L^2)^{\frac{1}{2}}$$

and

$$D = (r^2 + L^2)^{-1}.$$

Substituting these into equation (3-29) gives an exact analytical specification of $f_0(S_3)$ on the cylinder and endplates, namely,

$$f_0(l) = R_s^2 R (R^2 + l^2)^{-3/2}$$

on the cylinder and

$$f_o(r) = R_s^2 L (r^2 + L^2)^{-3/2}$$

on an end plate. These may further be manipulated into forms involving dimensionless parameters, namely,

$$f_o(1/L) = (b^2/a^3) [(1/L)^2 + (1/a)^2]^{-3/2} \quad (3-30a)$$

and

$$f_o(r/R) = (ab^2) [(r/R)^2 + a^2]^{-3/2} \quad (3-30b)$$

on the cylinder and end plates, respectively. The dimensionless parameters are defined by

$$a = L/R$$

$$b = R_s/R.$$

Equations (3-30a) and (3-30b) depend only on the relative sizes of the cell dimension.

We must now develop a method for obtaining f_1 . Our reasoning is as follows: $f_o(S_3)$ is the distribution in molecules per unit area striking S_3 the first time; the integral $\int_{S_3} f_o(S_3) dS_3$ must therefore be the total number of molecules striking S_3 the first time. Since the molecules were evaporated from the sample immediately before, this number is also given by

$$\int_{S_1} (1) dS_1 = A_{S1}.$$

A quantity $\lambda_w A_{S1}$ will be re-emitted from this first wall collision, and of this, some fraction will be reabsorbed by the sample, this fraction depending on λ_s and on geometry. The remainder will be distributed, supposedly uniformly, on S_3 and will, after division by A_{S3} , be equal to f_1 . However, since

Figure 3-5. The relationship of the surface two-dimensional coordinate systems to the cell three-dimensional coordinate system.

$f_0(S_3)$ is nonuniform, we are prohibited from using view factors to calculate the attrition of molecules from the first wall by collision on the sample.

We are, however, able to calculate this loss by integration of a loss function over the entire surface S_3 . The following expression for the loss or absorption of molecules emitted with intensity n_e from a surface by sphere is derived in Appendix F:

$$d = \alpha_s n_e \cos \beta (R_s/D)^2, \quad (3-31)$$

where β , R_s , and D have the same meanings as before. The emission intensity n_e is necessarily equal to $\lambda_w f_0(S_3)$; substituting for $f_0(S_3)$ from equation (3-29) and combining with equation (3-31) gives

$$d = \alpha_s \lambda_w (R_s/D)^4 \cos^2 \beta.$$

This is to be integrated over S_3 in two steps: The cylinder, and the end plates.

For the cylinder we express D and $\cos \beta$ in terms of R and l , obtaining

$$d = \alpha_s \lambda_w R_s^4 R^2 (R^2 + l^2)^{-3}.$$

The total loss on S_1 from the cylinder (S_{3a}) is

$$\begin{aligned} L_1 &= \int_{S_{3a}} d \, dA \\ &= \int_{-L}^L d / (2\pi R dl) = 2 \int_0^L d \, (2\pi R dl) \\ &= 2 \int_0^L \alpha_s \lambda_w R_s^4 R^2 (R^2 + l^2)^{-3} (2\pi R dl) \\ &= \pi R_s^4 \alpha_s \lambda_w \left[\frac{3}{2R^2} \tan^{-1}(L/R) + (5L/2R) (R^2 + L^2)^{-1} \right. \\ &\quad \left. - (L^3/R) (R^2 + L^2)^{-2} \right]. \end{aligned} \quad (3-32)$$

In like manner we express D and $\cos \beta$ on the end plates in terms of r and L , obtaining

$$d = \alpha_s \lambda_w R_s^4 L^2 (r^2 + L^2)^{-3}.$$

Integrating over the end plates (S_3b) gives their contribution to the loss on S_1 ,

$$\begin{aligned} L_2 &= \int_{S_3b} h dA = 2 \int_0^R h (2\pi r dr) \\ &= 2 \int_0^R \alpha_s \lambda_w R_s^4 L^2 (r^2 + L^2)^{-3} (2\pi r dr) \\ &= \pi \alpha_s \lambda_w R_s^4 [L^{-2} - L^2 / (R^2 + L^2)^2]. \end{aligned} \quad (3-33)$$

The total loss is obtained by adding L_1 and L_2 from equations (3-32) and (3-33) to give, after considerable algebraic manipulation,

$$L = \alpha_s \lambda_w A_{S1} (R_s/R)^2 M(L/R), \quad (3-34)$$

where $A_{S1} = 4\pi R_s^2$ is the area of S_1 and M is an intricate function of the cell length-to-radius ratio and is defined by

$$M(x) = [(3/2)\tan^{-1}x + (x^{-2} + 2 + (5/2)x + (3/2)x^3)/(1 + x^2)^2]/4.$$

We are now able to predict f_1 ; the total number of molecules striking S_3 on the second collision is equal to the integral of the second term in the series solution, and this is in turn equal to the difference between the emission from the first collision and the loss. Mathematically,

$$\int_{S_3} (f_1 \lambda_w) dS_3 = \lambda_w A_{S1} - L$$

or

$$f_1 \lambda_w A_{S3} = \lambda_w A_{S1} - \alpha_s \lambda_w A_{S1} (R_s/R)^2 M(L/R),$$

which simplifies to

$$f_1 = (A_{S1}/A_{S3}) [1 - \alpha_s (R_s/R)^2 M(L/R)]. \quad (3-35)$$

With total flux on the cylinder known from equations (3-28a), (3-30a), and (3-35), we are now able to calculate the transmission or escape probability. It is simply the ratio of the total number of molecules on S_0 divided by the total number leaving the sample or

$$P = \int_{S_0} \psi_0(S_0) dS_0 / \int_{S_1} (1) dS_1 \\ = (A_{S0}/A_{S1}) \overline{\psi_0(S_0)},$$

where A_{S0} is the area of an orifice and $\overline{\psi_0(S_0)}$ is the average flux evaluated at the orifice.

Equations (3-12a) and (3-12b), adapted for a symmetrical cell, become

$$\varphi = (\alpha_s A_{S1}/A_{S0}) P \zeta, \quad (3-36)$$

and, substituting for P ,

$$\varphi = \alpha_s \overline{\psi_0(S_0)} \zeta, \quad (3-37)$$

since the area ratios cancel.

Unfortunately, the calculation of the effusion beam angular distribution factor, ζ , is not a simple matter; it requires integration of a geometrical quantity, weighted by emission intensity, over those portions of the cell interior which are visible from the outside. The calculation is discussed in Appendix G, but requires the use of a digital computer when applied to the configuration presently under consideration since the cell contains an internal obstruction, the sample.

It will be pointed out later that Monte Carlo results indicate that, in the range of greatest interest, i.e., the

"near-ideal" region, λ_w is normally not far removed from 1 and, consequently, the total flux inside the cell is very nearly uniform. As shown in Appendix C, in such a situation the angular distribution of the effusate is approximately cosine, and ζ will be close to 1. Therefore, a not unreasonable value of φ may be obtained by setting $\zeta=1$, giving simply,

$$\varphi = \alpha_s \sqrt{\psi_0(S_0)}. \quad (3-38)$$

CHAPTER 4.

THE MONTE CARLO SIMULATION

Most of the theoretical formulations derived earlier are valid for a wide variety of possible geometrical configurations. Before obtaining an approximate solution to the flux equations, Chapter 3, placed no restrictions on the cell other than that the orifices be very small and (later) that the sample be convex. In order to obtain a practical solution, it was maintained, one must make the assumptions appropriate for the configuration of interest and thereby take advantage of what simplifications they may engender. The approximate solution in the last section of Chapter 3 is an illustration of this principle.

The remainder of this exposition describes an actual Monte Carlo simulation of the configuration used in the example: this chapter describes the mathematical construction of the model, and the next chapter compares the results of the simulation with the corresponding behavior predicted by the approximate solution.

For the purposes of the simulation, the configuration and dimensional terminology shown in Figure 4-1 were adopted. The cell consisted of a thin-walled right circular cylinder of radius A and length $2B$ and was closed at both ends by planes. The spherical sample, of radius R , is situated with its center at the origin, the center of the cell. The orifices, each of

Figure 4-1. Dimensional terminology for the Monte Carlo simulation

diameter D and moment arm q , are of infinitesimal length.

Figure 4-1 shows that the Cartesian coordinates x , y , and z are used to indicate spacial positions within the cell; however, several other coordinate systems, local to certain events (collision, evaporation, etc.), will be used in this chapter to facilitate the formulation of mathematical models of these events. The former will hereinafter be known as the cell or global coordinate system, and any specific instance of the latter will be called a local coordinate system. It is apparent that transformation equations must also be supplied with the local systems in order to identify points in these systems with coordinates in the global system; these will be devised when appropriate.

A flow chart of the algorithm used to simulate molecular histories is given in Appendix H; a listing of one version of the FORTRAN program which implements the algorithm is given in Appendix I. Each molecular history starts with an evaporation at the sample. Using a local spherical coordinate system whose origin coincides with the center of the sample, the program chooses a random location on the sample surface. Then, using a spherical system local to this random location, the program randomly chooses a set of direction cosines which are converted, via a set of transformation equations, to a set of direction cosines in the global system. The space line possessing these direction cosines may, in general, intersect several surfaces which comprise the cell. In order to determine

which intersection is the correct impact point for the molecule just emitted, the program eliminates those points which lie in the direction opposite from that in which the molecule is traveling and selects from those remaining the one lying closest to the point of emission (i.e., the one which offers the minimum transit distance). The present position of the molecule is updated to indicate the selected point of impact. The next action depends on whether the surface is a wall or is that part of the cylinder which comprises one of the orifices. If it is the latter, effusion statistics are taken and the program recycles, initiating a new molecular history. If the surface is a wall, the program uses the appropriate condensation coefficient (α_w for the wall and α_s for the sample) to determine (probabilistically) if the molecule should condense. If it condenses, the program starts a new molecular history; otherwise the program uses a local coordinate system to choose a random direction of departure, and the process repeats.

The Spherical Sample

We begin discussion by devising a detailed mathematical model for the events that occur at the sample:

1. Selection of a random point of evaporation on the surface of the sample.
2. Departure of the molecule in a random direction.
3. Collision of a molecule with the sample.

In order to treat the first process, we define the

two-dimensional set of local coordinates depicted in Figure 4-2 to specify points on the sample. The local coordinates of points on the sphere may be converted to coordinates in the global system by the transformation

$$\begin{aligned}x &= R_s \sin \eta \cos \theta \\y &= R_s \sin \eta \sin \theta \\z &= R_s \cos \eta.\end{aligned}\tag{4-1}$$

We see that the problem of choosing a random point on the sphere is tantamount to choosing a random ordered pair (η, θ) . Howell and Perlmutter (32), who present a technique for choosing points on a hemisphere weighted by the cosine distribution, demonstrate that η and θ may be selected independently. In this case we desire to select evenly-weighted points, but the method may be adapted immediately; furthermore, η and θ may still be chosen independently. The probability frequency distribution of uniformly distributed molecules on element dS of the sphere is

$$dS/(4\pi) = (\sin \eta \, d\eta \, d\theta)/(4\pi).$$

The right member may be split into the independent distributions

$$\sin \eta \, d\eta/2, \quad d\theta/2\pi$$

It may be verified that these are the correct (normalized) forms by integrating them over $0 \leq \eta \leq \pi$ and $0 \leq \theta \leq 2\pi$ to obtain 1 in each case. The cumulative distributions are

$$\int_0^\eta (\sin \eta^* \, d\eta^*)/2 = (1 - \cos \eta)/2,$$

$$\int_0^\theta d\theta^*/2\pi = \theta/2\pi.$$

Figure 4-2. Local coordinate system for points on the surface of the spherical sample. Point O is also the origin of the global system, and the z -axis is the pivotal axis of the cell.

To obtain correctly weighted values of η and θ , it is necessary merely to select random numbers R_1 and R_2 from a uniform distribution in the interval (0,1) and solve the equations

$$(1 - \cos \eta)/2 = R_1$$

$$\theta/2\pi = R_2$$

for η and θ . The coordinates (η , θ) are converted to coordinates (x, y, z) in the global system via the transformation (4-1).

The second process, selection of the direction of departures, is similarly handled. Recalling that the directions of evaporating molecules follow a cosine distribution, we use the original forms given by Howell and Perlmutter, namely,

$$\cos^2 \eta = R_1$$

$$\theta/2\pi = R_2$$

where R_1 and R_2 are random drawings from the uniform distribution on the interval (0, 1). This selection of η and θ in the system local to the surface of the sample implies a local set of direction cosines given by

$$a' = \sin \eta' \cos \theta'$$

$$b' = \sin \eta' \sin \theta'$$

$$c' = \cos \eta',$$

where the primes denote quantities defined for the local system. As shown in Appendix J, these may be transformed into the global system by the equations.

$$a = (a' \cos \eta + c' \sin \eta) \cos \theta - b' \sin \theta,$$

$$b = (a' \cos \eta + c' \sin \eta) \sin \theta + b' \cos \theta,$$

$$c = c' \cos \eta - a' \sin \eta.$$

Consequently, the molecule departs the sample in the direction of the vector

$$a\hat{i} + b\hat{j} + c\hat{k}.$$

The problem of collision with the sample of a molecule emitted from another surface is equivalent to a problem of answering the following questions:

1. Does the molecule collide?
2. If so, where?
3. What is the distance from the point of emission to the point of collision?

The first two questions are answered most completely by solving an intersection problem involving the sample and the line of action of the departure vector. The third question must be included since this line may, in general, intersect more than one surface; the correctly-chosen surface is the one offering the shortest transit distance.

Let $P_1 (x_1, y_1, z_1)$ be the point of departure of a molecule (on a surface other than the sample) in the direction of the vector

$$a\hat{i} + b\hat{j} + c\hat{k}$$

where a , b , and c are direction cosines. The equation describing the sample (a sphere situated on the origin) may be written

$$x^2 + y^2 + z^2 = R_s^2,$$

and the equation describing the line of action of the vector is

$$\frac{x - x_1}{a} = \frac{y - y_1}{b} = \frac{z - z_1}{c}$$

Assuming an intersection occurs at a point $P_2(x_2, y_2, z_2)$, we may write a set of three independent equations:

$$x_2^2 + y_2^2 + z_2^2 = R_s^2$$

$$y_2 = y_1 - (b/a)(x_1 - x_2)$$

$$z_2 = z_1 - (c/a)(x_1 - x_2).$$

Substituting the second and third equations into the first, we obtain, after some manipulation,

$$x_2^2 + (bx_2/a - \alpha)^2 + (cx_2/a - \beta)^2 = R_s^2$$

where

$$\alpha = (b/a) x_1 - y_1$$

and

$$\beta = (c/a) x_1 - z_1$$

This may then be arranged into the general quadratic form,

$$A'x_2^2 + B'x_2 + C' = 0$$

where

$$A' = (a^2 + b^2 + c^2)/a^2,$$

$$B' = -(2/a)(\alpha b + \beta c),$$

$$C' = \alpha^2 + \beta^2 - R_s^2.$$

Consequently, x_2 is given by the general quadratic solution,

$$x_2 = [-B' \pm (B'^2 - 4A'C')^{\frac{1}{2}}]/2A',$$

and y_2 and z_2 may be obtained from the equation of the line.

The three possible types of solutions are:

1. $B'^2 - 4A'C' < 0$, indicating two complex values of x_2 ; no intersection.

2. $B'^2 - 4A'C' = 0$, indicating x_2 is a double root; a grazing collision.
3. $B'^2 - 4A'C' > 0$, indicating two real distinct values of x_2 .

Although the second question is entirely answered by solving for x_2 , y_2 , and z_2 , the first question is only partially so; if the molecule is traveling directly away from a collision with the sample (not possible in this configuration, but definitely possible in some), $B'^2 - 4A'C'$ will still be nonnegative. Such situations may immediately be discarded by testing a coordinate difference with its corresponding direction cosine (e.g. $x_2 - x_1$ with a); if both possess the same sign then the molecule is traveling toward the sample. If both are zero then the test is inconclusive and another difference must be tested. In any one instance at least one of the three possible tests will be conclusive. If a collision occurs, the third question is answered conclusively by means of the Pythagorean theorem:

$$d = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{\frac{1}{2}},$$

where d is the transit distance.

The last problem associated with modelling the sample regards determining whether the molecule striking the sample condenses or is re-emitted. The probability of condensation is (also) the sample accommodation or condensation coefficient (α_s), a number between 0 and 1. Each time a molecule encounters the sample surface a random number, R_1 is taken from the uniform distribution on the interval (0,1). The molecule condenses if $R_1 < \alpha_s$.

The Cylindrical Wall

The two processes controlling molecular encounters on the cylindrical wall are

1. Re-emission of a molecule from the surface in a random direction.
2. Collision with the cylinder of a molecule originating either on the cylinder or on another surface.

As with the earlier treatment of the problem of emission from the sample, we define a local coordinate system for a point on the cylinder. Note, however, that molecules are never initially evaporated from the cylinder; consequently it is not necessary to select random points on the cylinder. The configuration is shown in Figure 4-3. With $x, y,$ and z denoting coordinates in the global system and $x', y',$ and z' denoting coordinates in the local system, elementary equations expressing rotation and translation of axes¹ yield the following relations:

$$x = x_0 - x' \sin \nu - z' \cos \nu,$$

$$y = y_0 + y',$$

$$z = z_0 + x' \cos \nu - z' \sin \nu,$$

where $P_0(x_0, y_0, z_0)$ is the global position of the local system origin and ν is the angle of rotation shown in Figure 4-3. Since

$$\cos \nu = x_0/A,$$

$$\sin \nu = z_0/A,$$

¹See any elementary calculus textbook such as Goodman (8).

Figure 4-3. Local-to-global coordinate transformation for the cylindrical surface.

where A is the cylinder radius and the global direction numbers are given by

$$a = x - x_0,$$

$$b = y - y_0,$$

$$c = z - z_0,$$

we may write

$$a = -x'(z_0/a) - z'(x_0/a),$$

$$b = y',$$

$$c = x'(x_0/a) - z'(z_0/a).$$

Observe that if we choose x' , y' , and z' such that

$$x' = \sin \eta' \cos \theta',$$

$$y' = \sin \eta' \sin \theta',$$

$$z' = \cos \eta',$$

with η' and θ' weighted according to the cosine distribution (by the random number technique described earlier), then x' , y' , and z' will actually be direction cosines in the local system. Since x' , y' , and z' are the lengths of the components of position vector $\overrightarrow{P_0' P_1'}$, and since a space vector has the same magnitude in any coordinate system, the direction numbers a , b , and c are direction cosines in the global system.

The problem of collision of a molecule with the cylindrical wall is concerned with answering the same questions as in collision with the sample. For a molecule emitted from another surface (or at another part of the cylinder) at point P_1 (x_1 , y_1 , z_1) with direction cosines a , b , and c , we assume that the line of action of the vector $\hat{a}i + \hat{b}j + \hat{c}k$ intersects the

cylinder at a point $P_2(x_2, y_2, z_2)$. The coordinates of P_2 must simultaneously satisfy the defining equations of the cylinder and the line. Thus

$$x_2^2 + z_2^2 = A^2,$$

$$\frac{x_2 - x_1}{a} = \frac{y_2 - y_1}{b} = \frac{z_2 - z_1}{c}$$

The solution of this set of independent equations is

$$z_2 = [-B' \pm (B'^2 - 4A'C')^{\frac{1}{2}}]/2A',$$

$$x_2 = x_1 + (a/c)(z_2 - z_1),$$

$$y_2 = y_1 + (b/c)(z_2 - z_1),$$

where

$$A' = (a/c)^2 + 1$$

$$B' = -2\alpha(a/c),$$

$$C' = \alpha^2 - R^2,$$

$$\alpha = (a/c)z_1 - x_1.$$

If $B'^2 - 4A'C' < 0$, the intersection does not exist and if $B'^2 - 4A'C' = 0$, the intersection is a grazing collision by a molecule originating outside the cylinder. Since neither of these events is possible for molecules in our system (molecules are always inside the cylinder throughout their histories, we discard such happenings beforehand. Consequently, $B'^2 - 4A'C'$ is always greater than zero and the line of action must intersect the cylinder at exactly two points. Our strategy for selecting the appropriate point is: if P_1 lies on the cylinder, then one solution for P_2 will be identical to P_1 and one will be distinct from it. We accept the latter

solution and discard the former. If P_1 does not lie on the cylinder, we use the value of z_2 such that

$$(z_2 - z_1)/c > 0;$$

in other words, we take the point P_2 that lies in the direction of travel of the molecule. The first two questions have been answered. The third question is answered as previously; the transit distance is

$$d = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{\frac{1}{2}}$$

The problem of condensation of the molecule on the cylindrical wall is handled in the same way as with the sample, except α_w is used instead of α_s .

The Planar End Surfaces

The planar end surfaces are treated in the same manner as the cylindrical surface, except the local-to-global transformations are simpler. The two surfaces are given by

$$y = B,$$

$$y = -B,$$

with local-to-global transformations

$$x_1 = x_0 - y',$$

$$y_1 = B - z',$$

$$z_1 = z_0 - x'$$

for the surface $y = B$ and

$$x_1 = x_0 + y',$$

$$y_1 = -B + z',$$

$$z_1 = z_0 + x'$$

for the surface $y = -B$.

Using the same technique as before to choose random direction cosines we obtain

$$a = -\sin \eta \sin \theta,$$

$$b = -\cos \eta,$$

$$c = -\sin \eta \cos \theta$$

for the first surface and

$$a = \sin \eta \sin \theta,$$

$$b = \cos \eta,$$

$$c = \sin \eta$$

for the second surface.

For the collision problem, we specify a molecule at point $P_1(x_1, y_1, z_1)$ with direction cosines a , b , and c , and postulate an intersection $P_2(x_2, B, z_2)$ of the associated space line

$$\frac{x - x_1}{a} = \frac{y - y_1}{b} = \frac{z - z_1}{c}$$

with the plane $y = B$. The coordinates of such a point must simultaneously satisfy the equation of the line and of the plane; the solution is

$$x_2 = x_1 + (a/b)(B - y_1);$$

$$y_2 = B;$$

$$z_2 = z_1 + (c/b)(B - y_1).$$

No intersection exists if $y_1 \neq B$ and $b = 0$. The quantity $(B - y_1)/b$ is positive if the molecule travels toward the intersection and negative if it travels away from the intersection. The transit distance is calculated in the same manner as for

collisions on the sample or the cylinder.

The plane $y = -B$ is treated in an analogous manner; the coordinates of the intersection are

$$x_2 = x_1 - (a/b)(B + y_1),$$

$$y_2 = -B,$$

$$z_2 = z_1 - (c/b)(B + y_1).$$

The collision does not exist if $b = 0$ or if $(B + y_1)b > 0$, and the transit distance is identically calculated.

The problem of effusion is treated by the routine simulating intersections with the cylinder. Whenever a collision on the cylinder is accepted effusion through orifice 1 occurs if

$$(y_2 - q)^2 + z_2^2 = (D/2)^2$$

and effusion through orifice 2 occurs if

$$(y_2 + q)^2 + z_2^2 = (D/2)^2,$$

where y_2 and z_2 are coordinates calculated for the impact point on the cylinder. Every effusion requires that either N_1 or N_2 be incremented; the tallied value of $\vec{\rho} \times \hat{\eta} \cdot \hat{u}$ may be computed from the expression $(x_2b - y_2a)/q$.

It was the primary object of the Monte Carlo simulation program to tally torque contributions $(\vec{\rho} \times \hat{\eta} \cdot \hat{u})$ so that values of ϕ could be calculated. It has already been stated, however, that it became expedient to obtain wall flux distributions from actual Monte Carlo simulations.

This was done in two stages. In the first, the program was modified by dividing the cylindrical wall into 40 adjacent rings or bins of equal area. Since the cell was symmetric with

respect to the plane $y = 0$, the bins for positive and negative y were combined, and each collision on the cylindrical wall resulted in a bin tally being incremented, the bin number (1 - 20) depending on the distance $|y|$ from the plane $y = 0$. The end surfaces were similarly treated; each was divided into 20 bins of equal width and tallied depending upon the value of r (radial distance from cell axis). Because of symmetry, the bin tallies of the two end surfaces were lumped together. Since simulation of a cell with vanishingly-small orifices was contemplated, the program was run with orifice diameter (D) set to zero. Large numbers of molecules were observed from their origins at the sample to their condensation on one of the surfaces, and one bin tally was taken for each wall collision, regardless of the age of the molecule at impact. Consequently, flux distributions obtained from these tallies represented the total flux intensity (or total gas pressure) as a function of position.

It was noted that some insight into the behavior of an effusion cell could be gained by maintaining a number of different sets of bin tallies on each surface, with the appropriately-tallied set depending on the number of previous collisions experienced by the molecule (the "collision age" of the molecule). Flux distributions calculated from each of these sets of tallies would represent coefficients of the series in equations (3-24a). The first twenty of these terms was calculated in this manner.

CHAPTER 5.

RESULTS OF THE SIMULATION

The experimental program was divided into three sections or phases. Phase I was concerned with evaluating the effect of cell parameters on the magnitude and distribution of molecular flux on the cell walls. In an attempt to gain insight into the effects observed in Phase I, Phase II was designed to investigate the influence of cell parameters on the individual flux terms of the infinite series solution, equation (3-24a). Phase III was a complete simulation used to determine the effect of cell parameters on ϕ , ζ , and P , in light of the findings of Phases I and II.

Phase I simulated a cell with closed orifices and concentrated on the effect of the variables B/A , R_s/A , α_s , and α_w . Each was permitted two possible values, and one computer calculation was made for each of the sixteen possible combinations. The twenty bin tallies for the cylinder and end planes were converted to reduced flux by the formula

$$\psi(S) = (N_i/N_s)/(\Delta A_i/A_s), \quad (5-1)$$

where N_i is the i -th bin tally, N_s the total number of molecular histories, ΔA_i the surface area of the i -th bin, and A_s is the sample surface area. This definition is consistent with the earlier usage of the concept of normalized flux. The results are shown graphically in Appendix K, Figures K-1 through K-16 as reduced flux versus a dimensionless length along the cylinder (l/D) or a dimensionless radius on an end

plane (r/A). In each figure, the theoretical prediction is shown for comparison.

A few conclusions may immediately be drawn from the findings of Phase I. First and most important, the shape and magnitude of the flux curve is highly dependent on the value of α_w . For values of α_w near zero, wall loss is slight, and the flux curve is fairly uniform, its magnitude being not far removed from the value of $1/\alpha_s$. For values of α_w closer to one, wall loss is more significant. Strong flux gradients appear, and the overall magnitude is less, often by several orders of magnitude. The effects of α_s , R_s/A , and B/A are much more obscure than that of α_w and tend to depend on the value of α_w .

Phase II also simulated a cell with closed orifices and studied the variables B/A , R_s/A , and α_s . Since α_w appears explicitly in equation (3-24a) but is known not to affect the flux coefficients, it was immediately eliminated from consideration. The other three variables assumed essentially the same values they had in Phase I, resulting in a total of eight combinations. Tallies for the first twenty wall reflections were kept and converted to reduced flux via equation (5-1). The first five of these functions, and the averages of all twenty, are plotted for each of the eight cases in Figures K-17 through K-32. The theoretical averages of the second through the twentieth flux coefficients are also shown for comparison. These were based on the previously discussed iteration

$$f_{i+1} = f_i(1 - \alpha_s A_s/A),$$

where f_i is the theoretical average of the i -th flux coefficient and A is the total surface area of the inside of the enclosure, exclusive of the sample. From this, it follows that

$$f_i = f_1(1 - \alpha_s A_s/A)^{i-1} \quad (5-3)$$

where f_1 is the average of the second flux term. Taking the logarithms of both sides,

$$\log f_i = \log f_1 + (i-1) \log(1 - \alpha_s A_s/A), \quad (5-3)$$

which is the equation of a straight line. Consequently, a semi-logarithmic plot of f_i versus i is a straight line.

Although only the first five flux terms of each case are shown in Appendix K, it was noted in the study the shapes of the curves become essentially constant after about the fifth term. High-order curves in Cases 1 and 3 contained significant trends (low at the left, high at the right), while all other cases did not. Table K-3 demonstrates this fact for two representative examples: Cases 1 and 2.

Of the conclusions that may be drawn from the findings of Phase II, the most notable is that flux gradients are caused by strong trends in about the first five flux coefficients. Gradients in the total flux plots of Phase I occur when α_w is close to one (λ_w close to zero), causing the more diffuse higher terms to become less significant. In other words, the existence of a wall loss does not cause a gradient, but merely makes apparent an already existing gradient. The considerable attenuation in the magnitude of the total flux curves observed

in Phase I for high wall loss is directly attributable to the greatly attenuated contributions of the higher order flux coefficients.

Inasmuch as the gradient in the first term is considerably more prominent than the gradient of any of the higher terms, support is given to the assertion made in the development of the theoretical model that a good first approximation may be made by attributing all of the flux gradients in the Phase I curves to the respective first flux coefficients of Phase II. It was found that the measured values of $f_0(1/B)$ agree closely with the theoretical values predicted by equation (3-30a). Although significant point-by-point deviations of the higher terms exist about their respective means, these means are predicted well by the theoretical equations (3-35) and (5-2), especially for terms of order five or higher.

With considerable knowledge having been gained from Phases I and II about the properties of the molecular flux function, Phase III attempted to observe the consequences of these properties in a cell with open orifices. The cell ϕ , ζ , and P were calculated for eight settings of the cell parameters B/A , R_s/A , D , Q , α_s , and α_w . Insofar as possible, the parameter settings were based on those used in Phases I and II except when computational difficulties forced changing the values of R_s and α_w . The parameter settings and results are shown in Tables K-4 through K-6. The corresponding theoretically predicted values of P are included for comparison.

In comparing these values, it can be seen that in all cases but two the deviation of theoretical P from simulation P was commensurate with the standard deviation of the simulation values. The two exceptions are Case 5 and Case 8. Case 10 of Phase I contains the appropriate closed-cell flux plot for the parameter settings of Phase III, Case 8; the large deviation between the two curves at $1/B = 0.8$ explains the over 100% deviation between theoretical P and simulation P . Although no corresponding Phase I case exists for Phase III, Case 5, Phase I, Case 5 comes close; it predicts a deviation of about 12.5%. Despite these two anomalies, the theoretical model shows good agreement with the simulation, considering the resolutions limitations of the Monte Carlo technique, over a range of values of P of some two and one half orders of magnitude.

The results of Phase II show that ζ is highly sensitive to the value of α_w , and depends primarily upon it. The results tend to confirm the prediction of Appendices B and C that $\zeta = 1$ for uniform internal flux. Unfortunately, the value of ϕ estimated from theory will be seriously in error if ζ is assumed to be 1 when α_w is significantly removed from zero.

It is appropriate at this point to consider the causes of the shortcomings of the theoretical model. In the results of Phase II, the model was generally able to predict the mean values of the high order flux coefficients with good accuracy, but was unable to account for any gradients in these coefficients. Moreover, there generally were significant departures

in the lower order coefficients (the second through about the fifth). However, the first term was predictable with a high degree of accuracy.

These facts tend to explain deviations observed in the results of Phase I. At low wall depletion, deviations were predominantly caused by cumulative error in an infinite number of high order terms. However, with high wall depletion, departures were caused by the error in assuming that all of the gradient in the total flux function was attributable to the first term; the Monte Carlo curves virtually always had higher peaks and lower valleys than did the theoretical curves. High order terms, forced into insignificance, contributed negligible error.

Deviations evident in the results of Phases I and II contributed to errors in the results of Phase III. However, additional error was undoubtedly due to the finite orifice widths used in the full simulation, i.e., to the failure to correct for the perturbation flux. Such error is not discernible since the theoretical deviation was generally comparable to the Monte Carlo random error. In other words, the Monte Carlo method is not sufficiently sensitive to detect directly the effect of an orifice depletion if the orifice area is small.

Considerable error may be imparted by improper choice of the value of q/B since the theoretical deviation of the local flux intensity is strongly dependent on this quantity.

However, no attempt has been made to find a criterion for a priori selection of the optimum value of q/B .

CHAPTER 6.

RECOMMENDATIONS FOR FUTURE STUDIES

The theoretical model derived in Chapter 3 admittedly contains several key assumptions that are difficult to justify. Moreover, the requirement that the sample be perfectly spherical and suspended in the exact center of the cell makes the model hardly ready for immediate application to experimental work. Obviously, some refinements are needed.

One of the foremost areas open for refinement is the sample configuration. The original reason for modelling a suspended spherical sample was purely mathematical: the cell was symmetrical in several respects and analysis was greatly simplified since certain dimensional variables could be eliminated. The attempt was made to evaluate primary effects when the sample was lumped at the center rather than evenly distributed; the configuration used was merely the simplest possibility. Three likely aspects of the problem of evaluating secondary effects are:

1. moving the sample to an off-axis location;
2. making the sample nonspherical;
3. considering a sample with extended area.

The first two aspects would immediately arise in the realistic case of a molten meniscus resting on the floor of the cell. A means of correcting for this situation would likely be devised by adding to the model adjustable parameters whose values would

be determined by empirical means. The third aspect would arise when the sample exhibited porosity or extreme surface roughness. Examples of these would be samples consisting of powder, grains, or turnings. Observe that for some considerations and over a limited range of sizes, the quantity $\alpha_s A_s$ may be viewed as an effective sample area. One possibility for a means of correcting for the third aspect would be to devise an empirical correction for $\alpha_s A_s$. All of these considerations still apply to a lumped-sample configuration; the alternative will be described shortly.

Among the findings of Phase II were the facts that the first flux coefficient, $f_0(1/B)$, was well described by a simple algebraic expression and that the high order coefficients (about f_{10} and higher) were essentially uniform and well described by the geometrical progression predicted by theory. No simple statement could be made about the intermediate terms; they contained significant gradients and their shapes depended on geometry in a complex way. The assumptions that all gradients were in the first term and that intermediate terms behaved as higher terms allowed the model to predict primary effects, but significant error was introduced.

A better functional form must be found for the intermediate terms. If properly done, this will tend to alleviate both of these difficulties. Gradients would be more accurately described as would the higher terms, whose magnitudes depend on the intermediate terms.

The theoretical solutions presented in Chapter 5 never took account of the perturbation flux caused by the finite areas of the orifices. The Monte Carlo solutions were not sufficiently sensitive to ascertain the need for such a correction. Consequently, the magnitude of this error should be estimated and, if significant, a suitable correction scheme should be devised.

It was pointed out in Chapter 5 that severe error may be introduced by assuming $\zeta = 1$ if significant wall loss exists. A little reflection shows that for a lumped sample at the center of the cell, $\zeta < 1$ whenever there is wall loss because of the effect of the wall loss on the flux distribution. Appendix G outlines that calculation of ζ from the flux distribution. Unfortunately, the required integrations would be cumbersome, and an obstruction such as the sample would make them prohibitively difficult. For an obstructing sample configuration at least two possible avenues are open. The factor ζ can be determined by a Monte Carlo integration for isolated instances (as was done in Phase III). The disadvantage is that the results are inflexible and must be interpolated for intermediate points. Alternatively, the theoretical flux could be used in a scheme which analytically integrates the flux distribution function over as much of the internal surface area as possible before encountering discontinuities caused by an obstructing sample. This approach would likely yield a more flexible analytical correction, but would be only an approximation.

No attempt was made in this study to examine the effect of varying the thickness of the cell wall. The effect of the wall thickness is manifest in the behavior of the orifices since, in this case, it is identical to the length of the orifice channels. The results of Clausing (13) and of Freeman and Searcy (26) make certain qualitative facts evident. Since a finite channel length results in the reflection of some entering molecules back into the enclosure, one effect will be to decrease P , the total effusion probability. If it can be demonstrated that the orifice entrance distribution is diffuse (Maxwellian), then it is likely true that the overall escape probability can be approximated by the product of the orifice Clausing factor and the corresponding escape probability for a knife-edge orifice. This would not be exact because the reflected molecules would distort the internal wall flux distribution somewhat (but the tendency would be toward the already-studied closed-orifice cell). If the inside surface of the orifice channel possessed uniform characteristics (i.e., α_w) and exhibited diffuse reflection the effect would be to make the effusate more diffuse and cause ζ to approach one. Since P and ζ would tend in opposite directions the effect on ϕ is uncertain. The problem may be solvable by a Monte Carlo integration (a finite difference integration would be unworkable), but it should be observed that the decreased P means fewer escaping molecules, and variance reduction would be more difficult. Therefore, the approach must be modified from the one

used in Phase III. As stated earlier, a flat sample uniformly distributed on the cell floor is the other major possibility for a sample configuration. Although this problem would be asymmetrical, so would a practical lumped-sample problem. It is speculated that the cell would be essentially devoid of longitudinal flux gradients and would essentially eliminate the problems associated with ζ . The problem of determining ϕ would be equal to the problem of determining P .

The overriding advantage is that the absence of the obstruction caused by a lumped sample makes finite difference techniques feasible. Such techniques would probably involve the establishment of a two dimensional grid or grids on each of the inside surfaces of the enclosure and an appropriate iteration formula devised to cause the values of the points in the grid to approach an appropriate flux distribution function.

Two possible approaches are immediately evident for solving the integral equations appropriate for the configuration. One is the method of successive substitutions. This is actually the infinite series solution discussed in Chapter 3 since solving an integral equation such as equation (3-22) by recursively substituting $g(x)$ for itself in the integral results in a solution of the form of equation (3-23a). The scheme would establish the entrance distribution $f_0(S)$ from the sample and then obtain $f_1(S)$ as from the sample and then obtain $f_1(S)$ as

$$\int_S K(S', S) f_0(S') dS',$$

by stepping through each point in the grids. The next term

would be obtained by an identical process and so on. Assuming that higher order terms are approximately described by the iterative formula

$$f_{i+1} = f_i(1 - \alpha_s A_s/A),$$

it may easily be shown that for the worst case of $\alpha_w = 0$, the sum of the first i terms converges to within ϵ of the limit of the infinite series when

$$i \geq \log \epsilon / \log (1 - \alpha_s A_s/A). \quad (6-1)$$

By way of comparison, Phase III, Cases 1 and 3 had $\alpha_s A_s/A$ values of 0.1 and 0.01, and required 301,000 and 37,000 molecular histories. Processor time requirements were 79.9 minutes and 89.5 minutes, and standard deviations of around 5% were achieved in each case. Use of equation (6-1) shows that in a finite difference integration, 5% error for $\alpha_s A_s/A$ of 0.1 and 0.01 will be obtained for i equal to 29 and 298. Although molecular histories in a Monte Carlo integration cannot be precisely related to iterations in a finite difference integration, it is doubtful that 298 iterations would take more than a minute or two of processor time, even for a finely divided grid.

The limitation on how small $\alpha_s A_s/A$ can be made depends on how many iterations one is willing to make; consequently no upper bound on iterations can be set for a particular ϵ . However, it is easily shown that the least upper bound of $\alpha_s A_s/A$ is $2/\pi$. For an accuracy level of 1% ($\epsilon = 0.01$), this corresponds to a greatest lower bound of 4.55 for i . Thus, at least

five iterations would always be required to obtain 1% accuracy for a flat sample configuration.

The other approach is the method of successive approximations¹ in which an arbitrary starting distribution is integrated to produce a better approximation to the solution. This new distribution is similarly integrated and so on. As in the method of successive substitutions, a grid would be established on each surface, and the process would be essentially a relaxation technique. Its rate of convergence depends on numerical considerations which will not be discussed here. The latter method might conceivably converge more rapidly than the former, but the former has the advantage that the individual flux terms can be itemized, as they were in Phase II.

In either case, the procedure is self-correcting provided the iteration is stable, and error is eliminated rapidly. Contrariwise, each Monte Carlo event tends to contribute to the variance of the result as well as the result itself.

Several other miscellaneous considerations are also open to investigation. At the end of his Monte Carlo study of a pseudo-Langmuir vaporization crucible, Sandry (33) recommends that future investigators examine the effect of intermolecular collisions. In light of some of the conclusions of Wang and Wahlbeck (7), such effort would also be appropriate to

¹Lovitt (29, p. 15).

studies on the torsion effusion cell after more important work already described had been adequately covered.

APPENDIX A .

MOLECULAR AVERAGE VELOCITIES

In this work the ability to calculate molecular average velocities becomes important in two respects: it is necessary to know the velocities of molecules emitted from surfaces, either by evaporation or by rebound; it is necessary to know the velocities of molecules passing through orifices. Assuming that the distribution of speeds of rebounding molecules is independent of direction, a little reflection will show that the same distribution must also apply to molecules passing through an orifice. We further assume that, in the absence of the randomizing effect of intermolecular collisions, velocity averages are satisfactorily predicted by the Maxwell-Boltzmann distribution, although the exact velocity distributions may not be. If velocity distributions are independent of direction then it is necessary to consider only molecular speeds; with this in mind, we proceed to obtain the appropriate average speed by considering the Maxwell-Boltzmann distribution of molecular speeds in free space, namely,

$$dN_c = 4\pi N(m/2\pi kT)^{3/2} \exp(-mc^2/2kT)c^2 dc, \quad (A-1)$$

where

dN_c = the number of molecules per unit volume with speeds between c and $c + dc$,

N = the number of molecules/unit volume,

m = the molecular mass,

k = Boltzmann's constant,

T = the absolute temperature,
with arithmetic mean and root-mean-square given respectively
by

$$\bar{c} = (8kT/\pi m)^{\frac{1}{2}} \quad (A-2)$$

and

$$\bar{u} = (3kT/\pi m)^{\frac{1}{2}}. \quad (A-3)$$

The first mean is found by taking the ratio of the first moment of the distribution to the zero-th moment; the second mean is the square root of the ratio of the second moment to the zero-th moment.

Loeb¹ points out that in an effusion process, faster molecules stand a greater chance of exiting than do slower molecules. In other words, it is by reason of their speeds that molecules effuse and the distribution of speeds of effusing molecules is actually that given by equation (A-1), weighted by a factor c . Consequently, Loeb's calculation of the root-mean-square speed of effusing molecules is

$$\bar{u}_c = (4kT/\pi m)^{\frac{1}{2}}, \quad (A-4)$$

and is, in fact, the square root of the ratio of the third moment of (A-1) to its first moment. By this reasoning, we would surmise that the corresponding arithmetic mean would be the ratio of the second moment to the first moment which is

$$\bar{c}_e = (9\pi kT/8m)^{\frac{1}{2}}, \quad (A-5)$$

and which can also be expressed as

¹Loeb (34, pp. 114-116).

$$\bar{c}_e = (9\pi RT/8M)^{\frac{1}{2}}.$$

Some of the guesswork may be removed by proceeding with a somewhat more definite analysis, based on the conservation of linear momentum. Suppose N_0 molecules effuse through an orifice into a vacuum from inside an enclosure containing a Maxwellian gas, i.e., one whose molecular velocities are predicted by the Maxwell-Boltzmann distribution. The angular distribution of the effusion beam is necessarily cosine¹ and, from Appendix B, the magnitude of the momentum vector of the beam is

$$(2/3)m\bar{c}_e N_0.$$

Let p be the gas pressure inside the cell. The force required to impart this momentum to the effusing molecules is $pA/2$, where A is the area of the orifice. By Newton's second law, this force is equal to the time rate of change of momentum of the effusing molecules. Thus,

$$(2/3)m\bar{c}_e (N_0/\Delta t) = pA/2,$$

where Δt is the time required to effuse N_0 molecules. From kinetic gas theory² the number of molecules striking a surface per unit area is

$$N\bar{c}/4.$$

Consequently, at the orifice,

$$(2/3)m\bar{c}_e (N\bar{c}/4) = p/2,$$

¹Loeb (34, pp. 308-309).

²Loeb (34, p. 105).

or

$$\bar{c}_e \bar{c} (mN)/3 = p.$$

The quantity mN is the density of the gas and, by the ideal gas law,

$$mN = Mp/RT = Mp/kT.$$

Substituting p/kT for N and solving for $\bar{c}_e$,

$$\bar{c}_e = 3kT/m\bar{c}.$$

Finally, substituting for $\bar{c}$ from equation (A-2) and simplifying,

$$\bar{c}_e = (9\pi kT/8m)^{\frac{1}{2}}. \quad (A-5)$$

In still another vein, equation (A-5) may be obtained by calculating the mean of Kennard's¹ distribution function for Maxwellian molecules crossing a plane in free space. However, this is not surprising since that function is proportional to (A-1), weighted by a factor c .

¹Kennard (35, p. 62).

APPENDIX B.

MOMENTUM OF A COSINE-DISTRIBUTED EFFUSION BEAM

It should be noted that, for molecules emitted from an element of area δA , which may be an orifice, part of a wall surface, or an element of a plane in free space, the cosine law distribution, when applicable, is symmetrical with respect to the normal to the surface at which δA is defined. Let us define a coordinate system as shown in Figure B-1. Molecules emitted from δA possess a linear momentum $m\vec{v}$, where m is the molecular mass and $\vec{v}$ is its velocity; the magnitude of this momentum is mc , where c is the molecular speed. Each molecular momentum may be resolved into a normal component and a lateral component, i.e., a component perpendicular to δA and a component tangent to the surface on which δA is situated. However, since the distribution is symmetrical, i.e., all values of β have equal probability of occurring, the lateral components will cancel, leaving only the sum of the normal components. The present task is to evaluate this sum.

For N molecules leaving δA , cosine-distributed molecules will, by definition, obey the equation

$$dN = (N/\pi) \cos \alpha \, d\Omega, \quad (\text{B-1})$$

where dN is the number of molecules leaving in solid angle $d\Omega$.

That N/π is the correct coefficient for the weighting factor $\cos \alpha$ may be proved by evaluating the integral

$$\int_0^{2\pi} \int_0^{\pi/2} (N/\pi) \cos \alpha \, d\Omega = \int_0^{2\pi} \int_0^{\pi/2} (N/\pi) \cos \alpha (\sin \alpha \, d\alpha \, d\beta)$$

Figure B-1. Coordinate geometry for an effusion beam.

to yield N .

The magnitude of the total momentum of the effusion beam may be obtained by summing the normal components of the momenta of molecules leaving δA in each solid angle $d\Omega$. The magnitude of the momentum of each element is

$$m\bar{c}(N/\pi) \cos \alpha d\Omega,$$

where $\bar{c}$ is the mean molecular speed (assumed constant for all α, β), and the magnitude of the normal component, which is the cosine of the total magnitude, is

$$m\bar{c}(N/\pi) \cos^2 \alpha d\Omega.$$

Replacing $d\Omega$ by $\sin \alpha d\alpha d\beta$, we obtain the magnitude of the effusion beam by integrating, thus

$$\int_0^{2\pi} \int_0^{\pi/2} m\bar{c}(N/\pi) \cos^2 \alpha \sin \alpha d\alpha d\beta = (2/3)m\bar{c}N. \quad (\text{B-2})$$

In Chapter 3 it was shown that the angular momentum of a molecular beam from a torsion effusion cell about the pivotal axis could be expressed as

$$\sum_{i=1}^{N_0} \vec{r}_i \times \vec{m}\vec{v}_i \cdot \hat{u} \quad (\text{B-3})$$

where N_0 is the number of molecules exiting, $\vec{r}_i$ is a radius vector drawn perpendicularly from the pivotal axis to the last point of wall contact of the i -th exiting molecule. $\bar{m}$ is the mean molecular mass, $\vec{v}_i$ is the velocity of the i -th molecule, and $\hat{u}$ is a unit vector parallel to the pivotal axis. We now set about to calculate this quantity for a cosine-distributed effusion beam.

In the present discussion all references to the cosine

distribution have tacitly assumed that the emitting element is virtually a point. Applied to a torsion effusion cell, this infers that the orifices behave as point emitters of molecules into the vacuum surrounding the cell. Consequently, considerable simplification may be realized since each term in the series (B-3) may be evaluated at a single point, namely, the orifice; in other words, $\vec{r}_i$ is a constant, $\vec{r}$.

Referring to Figure B-2, we observe that $\vec{r}$ is composed of components $\vec{r}_1$ and $\vec{r}_2$, which are perpendicular to, and parallel to the longitudinal axis of the cell. Consequently, an equivalent representation of (B-3) is

$$\bar{m} \sum_{i=1}^{N_0} [\vec{r}_1 \times \vec{v}_i \cdot \hat{u} + \vec{r}_2 \times \vec{v}_i \cdot \hat{u}]$$

or

$$\bar{m} \left[\sum_{i=1}^{N_0} \vec{r}_1 \times \vec{v}_i \cdot \hat{u} + \sum_{i=1}^{N_0} \vec{r}_2 \times \vec{v}_i \cdot \hat{u} \right]$$

Examining the first term in brackets, we see that when we resolve $\vec{v}_i$ into a normal component ($\vec{v}_{i,n}$) and a tangential component ($\vec{v}_{i,T}$), this term becomes

$$\sum_{i=1}^{N_0} \vec{r}_1 \times \vec{v}_{i,n} \cdot \hat{u} + \vec{r}_1 \times \left(\sum_{i=1}^{N_0} \vec{v}_{i,T} \right) \cdot \hat{u}.$$

But $\vec{r}_1 \times \vec{v}_{i,n} = 0$ by definition by the cross product and

$\sum_{i=1}^{N_0} \vec{v}_{i,T} = 0$ by the symmetry of the cosine distribution. Consequently, that first term is identically zero and the angular

momentum is simply

$$\bar{m} \sum_{i=1}^{N_0} \vec{r}_2 \times \vec{v}_i \cdot \hat{u}.$$

Figure B-2. Geometrical arrangement for passage of the i -th molecule in an effusion beam.

By the well known identity¹ involving the triple scalar product of three vectors, the angular momentum may also be expressed as

$$\bar{m} \sum_{i=1}^{N_0} \hat{u} \times \vec{r}_2 \cdot \vec{v}_i.$$

But $\hat{u} \times \vec{r}_2$ is a vector normal to the orifice with the same magnitude as $\vec{r}_2$; this magnitude is defined in Chapter 3 as q , the orifice moment arm. Consequently

$$\hat{u} \times \vec{r}_2 = q\hat{n}$$

where $\hat{n}$ is a unit normal vector and the momentum becomes

$$\bar{m} \sum_{i=1}^{N_0} (q\hat{n}) \cdot \vec{v}_i$$

or

$$\bar{m}q\bar{c} \sum_{i=1}^{N_0} \hat{n} \cdot \hat{\eta}$$

where $\hat{\eta}$ is the unit velocity vector. Finally, we may use the definition of the dot product of $\hat{n}$ and $\hat{\eta}$ to write

$$\bar{m}q\bar{c} \sum_{i=1}^{N_0} \cos \alpha_i$$

where α_i is the angle of $\hat{\eta}$ from the normal. By an integration essentially identical to the one performed earlier, we see $\cos \alpha_i$, when weighted by the cosine distribution (i.e. $\cos \alpha_i$ and summed over N_0 is simply $(2/3)N_0$. Thus, the angular momentum of the cosine-distributed effusion beam is

$$(2/3)\bar{m}q\bar{c}N_0. \quad (B-4)$$

Note that this expression differs from the expression for linear momentum (B-2) by the inclusion of the moment arm q . We might have inferred (B-4) from (B-3) by applying the

¹ $\vec{A} \cdot \vec{B} \times \vec{C} = \vec{A} \times \vec{B} \cdot \vec{C}$ and $\vec{A} \cdot \vec{B} \times \vec{C} = \vec{C} \cdot \vec{A} \times \vec{B} = \vec{B} \cdot \vec{C} \times \vec{A}.$

definition of angular momentum to the resultant of the individual molecular momenta. However, the procedure used is preferable since it is slightly more rigorous and because it provides some insight into the nature of the term $\vec{p} \times \hat{\eta} \cdot \hat{u}$, as used in Chapter 3. We re-emphasize that the use of the attribute $\cos \alpha_1$ of an effusing molecule requires that the orifice be regarded as a point; for real situations both the normal to the orifice and α must be redefined for every molecule. In such a case it is much simpler to use $\vec{p} \times \hat{\eta} \cdot \hat{u}$.

APPENDIX C.

THE ANGULAR DISTRIBUTION OF MOLECULES

EFFUSING FROM AN IDEAL ORIFICE

It will be shown that a simple relationship exists relating the flux intensity inside a cell to the angular distribution of the effusate. As in Appendix B, discussion is limited to extremely small orifices, thus permitting angular measurements to be made at a single point. Furthermore, we specify the orifices to be ideal, i.e., of infinitesimal width.

We begin by considering the contribution of molecular flux at a point P on a surface S from a differential element dS' on emitting surface S' (see Figure C-1). Point P is connected to dS' by a line segment of length ρ at an angle θ' from the normal to dS' . Surface S' is emitting with an intensity of n_e molecules per unit area. The solid angle subtended by dS' at P is

$$d\Omega' = dS' \cos \theta' / \rho^2.$$

By DeMarcus' differential equation¹, the flux contributed to S at P by dS' is

$$d\psi = n_e dS' \cos \theta \cos \theta' / \pi \rho^2,$$

where θ is the angle of incidence of molecules on S at P.

But in this instance, $\theta = 0$ and

$$d\psi = n_e dS' \cos \theta' / \pi \rho^2.$$

Substituting $d\Omega'$ for its equivalent,

¹DeMarcus (14, Part I, p. 13).

Figure C-1. Molecular flux on point P by element dS' .

Figure C-2. Molecular flux on point P by element dS' through an element of orifice.

$$d\psi = n_e d\Omega' / \pi. \quad (C-1)$$

Let us now imagine the situation depicted by Figure C-2 in which S is a hemisphere of radius r centered over a differential orifice element, dA. S' is some internal surface of the enclosure. We specify dS' to be that portion of S' visible at P; in other words, dS' and dA both subtend solid angle dΩ' at P. Expressing this solid angle in terms of dA,

$$d\Omega' = dA \cos \alpha / r^2,$$

and, combining this with equation (C-1),

$$d\psi = n_e dA \cos \alpha / \pi r^2.$$

For a sufficiently small orifice we may integrate at constant $n_e \cos \alpha / \pi r^2$ to give

$$\psi = n_e A \cos \alpha / \pi r^2,$$

where A is the area of the orifice. The total number of molecules striking surface element dS is

$$dN = \psi dS = n_e A \cos \alpha dS / \pi r^2.$$

But dS/r^2 is dΩ, the solid angle subtended by dS at the orifice. Consequently,

$$dN = (n_e A / \pi) \cos \alpha d\Omega. \quad (C-2)$$

Comparing this with the cosine distribution defined by equation (B-1), we see that (C-2) fits the distribution only if $n_e A = N$, the total number of molecules transmitted through the orifice. But both A and N are constant and we immediately conclude that the sole criterion for a point orifice to emit molecules in a cosine distribution is that all points on the

interior surfaces of the cell that are visible from the outside be emitting uniformly.

APPENDIX D.

BOUNDEDNESS OF THE KERNEL $K(S', S)$

In Chapter 3 it was noted that the convergence of the series solution of the molecular flux equation (3-15) is intimately related to whether or not the kernel

$$K(S', S) = \cos \theta \cos \theta' / \pi \rho^2 \quad (D-1)$$

is bounded over its domain. We emphasize that any failure of $K(S', S)$ to be bounded does not ensure that the solution will fail to converge but note that such failure will be a potential pitfall in practical attempts to solve the flux equation.

To begin, we consider a point P on surface S separated from point P' on surface S' by a distance ρ . The kernel $K(S', S)$, which is a function of the positions of P and P', tends (generally) to diverge as ρ approaches zero. However, $K(S', S)$ also depends upon the orientations of S and S' relative to each other; if $\cos \theta \cos \theta'$ also approaches zero as ρ approaches zero then we have the indeterminate form 0/0. We see that, in order to decide whether $K(S', S)$ is bounded or unbounded, it is necessary to express it in terms of actual coordinates and study the effect of those variables.

Before doing that, however, we may immediately observe that if S and S' are the same surface, then $\theta = \theta' = \pi/2$, and $\cos \theta \cos \theta' = 0$. Since the numerator in (D-1) is always zero for all $\rho > 0$ then

$$\lim_{\rho \rightarrow 0} K = 0.$$

Now let us consider the case in which S and S' are two

intersecting planes with P and P' near the intersection (refer to Figure D-1). Surfaces S and S' are described, respectively, by the equations

$$F(y, z) = (\tan \beta)y + z = 0$$

$$G(z) = z = 0$$

With no loss in generality, we may keep P' on the y axis and specify the relative positions of P and P' by only three variables: a, b, and c. In order to determine $\cos \theta$ and $\cos \theta'$ it is convenient to specify normal vectors $\vec{n}$ and $\vec{n}'$ and distance vector $\vec{\rho}$ whose tail is at P and head at P' and use the definition of the dot product. In particular,

$$\vec{n} = \vec{\nabla} F = (\tan \beta)\hat{j} + \hat{k};$$

$$\vec{n}' = \vec{\nabla} G = \hat{k};$$

$$\vec{\rho} = -a\hat{i} + (c + b \cos \beta)\hat{j} - b \sin \beta \hat{k}.$$

From this

$$\cos \theta = \frac{\vec{n} \cdot \vec{\rho}}{|\vec{n}| |\vec{\rho}|} = \frac{c \sin \beta}{\rho},$$

$$\cos \theta' = \frac{-\vec{n}' \cdot \vec{\rho}}{|\vec{n}'| |\vec{\rho}|} = \frac{b \sin \beta}{\rho},$$

and

$$K(S', S) = \frac{\cos \theta \cos \theta'}{\pi \rho^2} = \frac{bc \sin^2 \beta}{[a^2 + b^2 + bc \cos \beta + c^2]}. \quad (D-2)$$

The limit of this expression as a, b, and c approach zero is, in general, path-dependent; that is, the limit depends upon the relative rates at which the variables approach zero.

Figure D-1. Proximate points on two intersecting planes.

For example, if $a = b = c$, then

$$\begin{aligned} K(S', S) &= \frac{a^2 \sin^2 \beta}{\pi[a^2 + a^2 + a^2 \cos \beta + a^2]} \\ &= \frac{\sin^2 \beta}{\pi[3 + \cos \beta]^2} \frac{1}{a^2}, \end{aligned}$$

which increases without bound as a approaches zero. In contrast, if a , b , and c approach zero such $a = b$ and $c = a^3$, then

$$\begin{aligned} K(S', S) &= \frac{a \cdot a^3 \sin^2 \beta}{\pi[a^2 + a^2 + a \cdot a^3 \cos \beta + a^6]^2} \\ &= \frac{\sin^2 \beta}{\pi[2 + a^2 \cos \beta + a^4]^2}, \end{aligned}$$

which obviously has $\sin^2 \beta / 4\pi$ as its limit.

One other case deserves attention; in the present study one surface is a circular cylinder. We can apply for the formulation of the kernel for two intersecting planes by treating them as tangent to the cylinder as in Figure D-2. We immediately note that β is no longer constant, but is related to the separation of the two points. In particular,

$$\tan(\beta/2) = b/R = c/R$$

where R is the radius of the cylinder. By the identity

$$\tan(\beta/2) = (1 - \cos \beta) / \sin \beta$$

we have

$$\sin^2 \beta = (b/R)^2 (1 + \cos \beta)^2.$$

Substituting this and $b = c$ into (D-2),

Figure D-2. Proximate points on a cylinder.

$$K(S', S) = \frac{1}{\pi R^2} \frac{(1 + \cos \beta)^2}{[(a/b)^2 + (2 + \cos \beta)]^2}.$$

We immediately see that, although the limit is path-dependent, the denominator can never be zero and $K(S', S)$ is bounded.

In fact, although

$$0 \leq \lim_{\substack{a \rightarrow 0 \\ b \rightarrow 0}} a^2/b^2 < \infty,$$

the range of the limit of the kernel is only

$$0 \leq \lim_{\substack{a \rightarrow 0 \\ b \rightarrow 0}} K(S', S) \leq 1/4\pi R^2.$$

Although these cases are not all inclusive, we may generalize by saying that the tendency for $K(S', S)$ to be unbounded occurs in the corner regions of an enclosure. Our initial alarm at observing that the limit of the kernel is path-dependent subsides when it is recalled that we are actually concerned with the value of the kernel for two points near the corner. In a numerical calculation we are perfectly content to leave undefined the value of molecular flux precisely at the corner and instead simply be prepared for numerical instabilities which might arise naturally in attempting to evaluate an improper integral, for this is exactly what we are doing.

APPENDIX E.

FLUX INTENSITY FROM A UNIFORMLY
EMITTING SPHERE

DeMarcus' differential flux equation may be applied to a number of simple configurations; when applied to a sphere and integrated, as shall be done presently, the result is almost disarmingly simple. The differential flux equation may be written

$$d\psi = \psi' K(S', S) dA', \quad (E-1)$$

where $d\psi$ is the flux contribution on surface S by element dA' on surface S' on which is impinging flux intensity ψ' . This form presumes, of course, that all impinging flux is re-emitted. In Chapter 3 interest was placed on finding the contribution to the flux intensity on the inside of the cell (S) by uniform initial emission (evaporation) by a spherical sample (S'). In this case, it is more appropriate to write

$$d\psi = n_g K(S', S) dA',$$

or, if ψ is normalized by treating $n_g = 1$, then

$$d\psi = K(S', S) dA'. \quad (E-2)$$

In Chapter 3, the integral of this was used as the entrance or forcing function

$$f_0(S_3) = \int_{S_1} K(S_1, S_3) dS_1.$$

In Figure E-1 we see a representation of the problem. Since element dA can "see" somewhat less than one half of the entire surface area of S' at any time, it is appropriate to consider only a hemisphere. We first establish a coordinate

system on the hemisphere by transformation

$$\begin{aligned}x' &= R_s \cos \eta \sin \xi \\y' &= R_s \sin \eta \sin \xi \\z' &= R_s \cos \xi\end{aligned}\tag{E-3}$$

and define the surface by

$$F(x, y, z) = x'^2 + y'^2 + z'^2 - R_s^2 = 0.$$

A normal vector on S' at point $P'(x', y', z')$ is

$$\vec{\nabla} F = 2x' \hat{i} + 2y' \hat{j} + 2z' \hat{k} = \vec{n}.$$

Located a distance D away from the center of the base of the hemisphere is element dA on S tilted on angle β from a plane parallel to the base of the hemisphere. Surface S can be expressed by the equation

$$G(y, z) = (\tan \beta)y - z + D = 0$$

a normal vector (the one in which we are interested) is

$$\vec{\nabla} G = (\tan \beta)\hat{j} - \hat{k} = \vec{n}.$$

The cosines of the angles of departure (θ') and incidence (θ) are found by forming the normalized dot products

$$\begin{aligned}\cos \theta &= \frac{\vec{\rho} \cdot \vec{n}}{|\vec{\rho}| |\vec{n}|} \\ \cos \theta' &= \frac{\vec{\rho}' \cdot \vec{n}'}{|\vec{\rho}'| |\vec{n}'|}\end{aligned}$$

where $\vec{\rho} = -\vec{\rho}'$ is the vector with its tail at dA and its head at dA' . With $\rho = x + y' + (z' - D)$, we obtain, after simplification,

$$\cos \theta = [y' \sin \beta + (D + z') \cos \beta] / \rho$$

$$\cos \theta' = (Dz' - R_s^2) / \rho R_s.$$

The complete kernel is

$$\begin{aligned} K(S', S) &= \cos \theta \cos \theta' / \pi \rho^2 \\ &= [y' \sin \beta + (D - z') \cos \beta] (Dz' - R_s^2) / \pi R_s \rho^4 \\ &= [y' \sin \beta + (D - z') \cos \beta] (Dz' - R_s^2) / \pi R_s (R_s^2 + D^2 + 2Dz')^2. \end{aligned}$$

Substituting the transformations (E-3), we obtain, after some manipulation,

$$K(S', S) = \frac{\cos \beta}{4\pi R_s D} = \frac{(\sin \eta \sin \xi \tan \beta + 1/m - \cos \xi)(\cos \xi - m)}{[m/2 + 1/2m + \cos \xi]^2}$$

where $m = R_s/D$. The element of area on S' is

$$dA' = R_s^2 \sin \xi \, d\xi \, d\eta$$

so that

$$d\psi = \frac{\cos \beta}{4\pi R_s D} \frac{(\sin \eta \sin \xi \tan \beta + 1/m - \cos \xi)(\cos \xi - m)}{[m/2 + 1/2m + \cos \xi]^2}$$

$$\cdot R_s^2 \sin \xi \, d\xi \, d\eta.$$

The total contribution on dA is found by integrating $d\psi$ over all positions of S' visible to dA . Thus

$$\begin{aligned} \psi &= \frac{m \cos \beta}{4\pi} \\ &\int_0^{2\pi} \int_0^{\frac{\pi}{2} - \alpha} \frac{(\cos \xi - m)(\sin \eta \sin \xi \tan \beta - \cos \xi + 1/m) \sin \xi \, d\xi \, d\eta}{(m/2 + 1/2m - \cos \xi)^2} \end{aligned}$$

For convenience, we divide the integration into two parts I_1 and I_2 such that

$$\psi = \frac{m \cos \beta}{4\pi} (I_1 + I_2).$$

The first part is

$$\begin{aligned} I_1 &= \int_0^{2\pi} \int_0^{\frac{\pi}{2} - \alpha} \frac{(\cos \xi - m)(1/m - \cos \xi) \sin \xi \, d\xi \, d\eta}{(m/2 + 1/2m - \cos \xi)^2} \\ &= 2\pi \int_0^{\frac{\pi}{2} - \alpha} \frac{(\cos \xi - m)(1/m - \cos \xi) \sin \xi \, d\xi}{(m/2 + 1/2m - \cos \xi)^2} \end{aligned}$$

Let $A = m/2 + 1/2m$. Then

$$I_1 = -2\pi \int_0^{\frac{\pi}{2} - \alpha} \frac{1 - 2A \cos \xi + \cos^2 \xi}{(A - \cos \xi)^2} \sin \xi \, d\xi.$$

Completing the square in the numerator and dividing,

$$\begin{aligned} I_1 &= -2\pi(1 - A^2) \int_0^{\frac{\pi}{2} - \alpha} \frac{\sin \xi \, d\xi}{(A - \cos \xi)^2} \\ &\quad - 2\pi \int_0^{\frac{\pi}{2} - \alpha} \sin \xi \, d\xi, \end{aligned}$$

and we observe that both integrals are elementary forms. Performing the integrations and simplifying,

$$I_1 = 4\pi m(1 - \sin^2 \alpha)/(1 - 2m \sin \alpha + m^2).$$

The second part is

$$I_2 = \tan \beta \int_0^{2\pi} \int_0^{\frac{\pi}{2} - \alpha} \frac{(\cos \xi - m) \sin^2 \xi \sin \eta \, d\xi \, d\eta}{(m/2 + 1/2m - \cos \xi)^2}.$$

But

$$\int_0^{2\pi} \sin \eta \, d\eta = -\cos 2\pi + \cos 0 = 0.$$

Therefore

$$I_2 = 0$$

and

$$\begin{aligned} \psi &= \frac{m \cos \beta}{4\pi} \left[\frac{4\pi m(1 - \sin^2 \alpha)}{1 - 2m \sin \alpha + m^2} \right] + 0 \\ &= m^2 \cos \beta (1 - \sin^2 \alpha) / (1 - 2m \sin \alpha + m^2). \end{aligned}$$

From Figure E-1 we see that $\sin \alpha$ is equal to R_s/D . Substituting this for $\sin \alpha$ and for m , we obtain after simplifying,

$$\psi = (R_s/D)^2 \cos \beta. \quad (E-4)$$

APPENDIX F.

ATTRITION OF ENTRANCE FUNCTION

MOLECULES BY THE SAMPLE

In Chapter 3 one stage of the development of the flux model required some means of relating successive flux coefficients to each other. The starting point was the iterative equation

$$f_{i+1}(S_3) = \int_{S_3} [K(S_3', S_3) + \lambda_s K'(S_3', S_3)] f_i(S_3') dS_3'. \quad (F-1)$$

Rather than confront the formidable difficulties of attempting to obtain functions $f_i(S_3)$ by repeated integrations starting with the entrance function $f_0(S_3)$, we first noticed that if we treated f_i and f_{i+1} as uniform over S_3 then they would be related by view factors which were expressible in terms of the readily-obtainable surface areas of the sample and of the enclosure. This procedure was reasonable for relating $f_1(S_3)$ to $f_2(S_3)$ and all higher terms, but was unsatisfactory for obtaining $f_1(S_3)$ from the entrance function $f_0(S_3)$ since the latter is highly nonuniform.

In order to overcome this difficulty we attempt a compromise: we perform part of the integration in equation (F-1) to determine the exact quantity of material rebounding from its first encounter with the wall and use a mass balance to calculate the remainder. The rest of the compromise is that we assume $f_1(S_3)$ to be uniform and simply distribute uncaptured molecules evenly over the wall with the intensity f_1 . Consequently, the

present task is to derive an expression for the quantity of molecules which strike the sample after their first encounters with the wall.

The problem is primarily a geometrical one; $f_0(S_3)$ is determined entirely by geometrical considerations, and the number of rebounding molecules which strike the sample is determined by the size and position of the sample relative to the enclosure. In our procedure we will first represent the spherical sample as an apparent disk and then derive a function expressing the number of molecules emitted by an element dA ; which are intercepted by the disk. After this the disk will be replaced by the sphere, the function $f_0(S_3)$ will be used to specify the emission rate for dA' , and the differential expression will be integrated to obtain the total loss function.

In Figure F-1 we see that, to an observer at P the sphere with radius R situated with its center a distance D from P would appear as a disk with radius R' and situated a distance D' from P. Since $\sin a = R_s/D$, we may write

$$\begin{aligned} R' &= R_s \cos a \\ &= R_s [1 - \sin^2 a]^{\frac{1}{2}} \\ &= R_s [1 - (R_s/D)^2]^{\frac{1}{2}}. \end{aligned} \tag{F-2}$$

Also, since $A = D \cos a$,

$$\begin{aligned} D' &= A \cos a = D \cos^2 a \\ &= D [1 - \sin^2 a] \\ &= D [1 - (R_s/D)^2]^{\frac{1}{2}} \end{aligned} \tag{F-3}$$

Figure F-1. Relationship of a sphere to its apparent disk.

Figure F-2. Configuration for an element dA' transmitting molecules to a disk.

Turning to the problem of absorption by a disk we see, from Figure F-2, that emitting surface S' is specified by the equation

$$F(y, z) = (\tan \beta)y - z + D = 0,$$

from which

$$\vec{n} = \vec{\nabla} F = (\tan \beta)\hat{j} - \hat{k}.$$

The cosine of the angle of departure from dA' follows by forming the dot product

$$\cos \theta' = \frac{\vec{\rho}}{|\vec{\rho}|} \cdot \frac{\vec{n}'}{|\vec{n}'|}$$

which becomes

$$\cos \theta' = \cos \beta \frac{r \sin \xi \tan \beta + D}{(r^2 + D^2)^{\frac{1}{2}}}$$

The cosine law emission function, namely,

$$(n_e/\pi) \cos \theta' d\Omega$$

gives the distribution of molecules leaving dA' per unit area of surface, emitting with intensity n_e . In this case

$$d\Omega = dA \cos \theta / \rho^2.$$

From Figure F-2, $\cos \theta = D/(r^2 + D^2)^{\frac{1}{2}}$ and $dA = r dr d\xi$. Consequently the emission function becomes

$$\frac{n_e}{\pi} \frac{(r \sin \xi \tan \beta + D) D r dr d\xi}{(r^2 + D^2)^2}.$$

This expression, when integrated over S (the limits of r and ξ are $0, R$ and $0, 2\pi$, respectively), gives the number of molecules leaving dA' per unit area of emitting surface that strike the

disk. Multiplying that result by α_s gives the absorption function, namely

$$d = \alpha_s \psi \cos \beta [R^2 / (R^2 + D^2)].$$

Using equations (F-2) and (F-3), which relate a sphere to its apparent disk, the absorption function becomes

$$d = \alpha_s n_e \cos \beta (R_s / D)^2. \quad (F-4)$$

APPENDIX G.

CALCULATION OF THE ANGULAR DISTRIBUTION FACTOR

While we do not attempt to perform a detailed investigation of the variation of the orifice angular distribution factor (ζ) with cell parameters, a few experimental values, which were obtained for selected parameter settings, have been disclosed. We now present a formal description of the identity of ζ in terms of integrals involving cell flux intensity.

In Chapter 3 was derived the following defining equation for the cell correction factor:

$$\varphi = (3/2)(\alpha_s A_s / A_o) \frac{1}{N_s} \sum_{i=1}^{N_o} (\vec{\rho} \times \hat{\eta} \cdot \hat{u}),$$

which is equivalent to

$$\varphi = (3/2)(\alpha_s A_s / A_o) \frac{N_o}{N_s} \frac{1}{N_o} \sum_{i=1}^{N_o} (\vec{\rho} \times \hat{\eta} \cdot \hat{u})$$

or

$$\varphi = (3/2)(\alpha_s A_s / A_o) P \frac{1}{N_o} \sum_{i=1}^{N_o} (\vec{\rho} \times \hat{\eta} \cdot \hat{u}).$$

Consequently

$$\zeta = \frac{3}{2} \frac{1}{N_o} \sum_{i=1}^{N_o} (\vec{\rho} \times \hat{\eta} \cdot \hat{u}). \quad (G-1)$$

For local emission rate n_e the cosine law of emission, namely

$$(n_e / \pi) \cos \theta' d\Omega,$$

gives the number of molecules per unit area leaving emitting element dA' in solid angle $d\Omega$. If dA is an element of area on the orifice then the number of molecules leaving dA' and passing through dA is

$$(n_e dA' / \pi) \cos \theta' (\cos \theta dA / \rho^2).$$

For any particular setting of dA' and dA the dimensionless

momentum $(\vec{\rho} \times \hat{\eta} \cdot \hat{u})$ may be regarded as constant. Therefore the contribution of dA' and dA to the series in (G-1) is

$$(\vec{\rho} \times \hat{\eta} \cdot \hat{u})(n_e dA'/\pi) \cos \theta' (\cos \theta dA/\rho^2)$$

or

$$n_e (\vec{\rho} \times \hat{\eta} \cdot \hat{u}) K(S, S_0) dA dA'.$$

where S is the interior of the enclosure and S_0 is the plane of the orifice. The complete sum is the integral

$$\int_S \int_{S_0} n_e (\vec{\rho} \times \hat{\eta} \cdot \hat{u}) K(S, S_0) dA dA'.$$

The total number of escaping molecules is

$$N_0 = \int_S \int_{S_0} n_e K(S, S_0) dA dA'.$$

Therefore

$$\zeta = \frac{3}{2} \frac{\int_S \int_{S_0} n_e (\vec{\rho} \times \hat{\eta} \cdot \hat{u}) K(S, S_0) dA dA'}{\int_S \int_{S_0} n_e K(S, S_0) dA dA'} \quad (G-2)$$

If the orifice area is sufficiently small, both integrals may be regarded as being constant and

$$\zeta = \frac{3}{2} \frac{A_0 \int_S n_e (\vec{\rho} \times \hat{\eta} \cdot \hat{u}) K(S, S_0) dA}{A_0 \int_S n_e K(S, S_0) dA}$$

Since the integral in the denominator is simply the average flux at the orifice, $\overline{\Psi(S_0)}$ we are left with

$$= (3/2) \overline{\Psi(S_0)} \int_S n_e (\vec{\rho} \times \hat{\eta} \cdot \hat{u}) K(S, S_0) dA. \quad (G-3)$$

The difficulty with evaluating this last integral in general terms is that, although $(\vec{\rho} \times \hat{\eta} \cdot \hat{u})$ and $K(S, S_0)$ are both functions only of geometry, the local emission rate, n_e , must come from the local flux intensity, ψ , which is not known generally.

APPENDIX H.

FLOW DIAGRAM

Figures H-1 through H-13 show a computational and logic flow diagram of the basic Monte Carlo program used in Phase III. The main program and its five subroutines are included. The important variable identifiers are summarized in Appendix I, which also shows a listing of the program.

Figure H-1. Main program.

Figure H-2. Main program

Figure H-3. Main program

Figure H-4. Main program

Figure H-5. Main program

Figure H-6. Main program

Figure H-7. Main program

Figure H-8. Main program

Figure H-9. Subroutine SURF1.

Figure H-10. Subroutine SURF2.

Figure H-11. Subroutine SURF2A.

Figure H-12. Subroutine SURF3.

Figure H-13. Subroutine SURF4.

APPENDIX I.

PROGRAM LISTING

A listing of the basic Monte Carlo program used in Phase III is herein presented and is the realization of the algorithm diagrammed in Appendix H. It is coded in the FORTRAN IV language and is intended to be used with the IBM OS/360 FORTRAN H compiler. Table I-1 gives a list of the important identifiers, with their purposes and corresponding symbols used in the text, if any.

Table I-1. Definitions of identifiers used in the program.

Identifier	Definition	Symbol in text
SURF1	Subroutine to determine impact coordinates of a molecule on the sample surface (S).	
SURF2	Subroutine to determine impact coordinate on the cylinder (S_2) of a molecule not beginning its transit on the cylinder.	
SURF2A	Modified version of SURF2 for a molecule beginning its transit on the cylinder.	
SURF3	Subroutine to determine impact coordinates of a molecule on the end of plane S_3 .	
SURF4	Same as SURF3 except for end plane S_4 .	

Table I-1 (continued).

Identifier	Definition	Symbol in text
NPARM	Input parameter whose value is 1 for the first run in a chain of continued runs and 2 for any of the continuation runs.	
A	Cell radius.	A
B	Cell half length.	B
D	Orifice diameter.	D
Q	Orifice moment arm.	q
R	Sample radius.	R, R _s
ALPHA	Sample condensation coefficient.	α_s
WL	Wall loss or wall condensation coefficient.	α_w
NMAX	Maximum number of molecular histories for this run.	
NRAND	A random integer used with subroutine RANDU. As input, it is the seed for the random number sequence.	
RAND	A random real number generated by RANDU from the uniform distribution on (0,1).	R ₁ , R ₂
SUM1, SUM2	Summations of torque contributions of molecules effusing through orifices 1 and 2, respectively.	$\Sigma(\vec{\rho} \times \hat{\eta} \cdot \hat{u})_1,$ $\Sigma(\vec{\rho} \times \hat{\eta} \cdot \hat{u})_2$
SSQ1, SSQ2	Summations of the squares of the torque contributions for orifices 1 and 2, respectively	

Table I-1 (Continued).

Identifier	Definition	Symbol in text
N1, N2	Counters of molecules effusing through orifices 1 and 2, respectively.	N_1, N_2
NS	Counter of evaporated molecules.	N_s
DS(4)	An array, one of whose elements contains the square of distance to collision upon return from one of the subroutines SURF1 - SURF4.	
X,Y,Z	Present global coordinates of a molecule.	x_1, y_1, z_1
TORQ	Torque contribution of an effusing molecule.	$\vec{p} \times \hat{\eta} \cdot \hat{u}$
PHI1, PHI2	Calculated values of cell correction factors for orifices 1 and 2, respectively.	φ_1, φ_2
VAR1, VAR 2	Statistical variances of φ_1 and φ_2 .	
X2(4), Y2(4), Z2(4)	Coordinate arrays, One member of each contains predicted collision coordinates upon return from one of the subroutines SURF1 - SURF4.	x_2, y_2, z_2
AP, BP, CP	Present global direction cosines of an emitted molecule.	a, b, c

```

COMMON A,B,D,Q,R,AP,EP,CP,X,Y,Z,X2,Y2,Z2,CS
DIMENSION X2(4),Y2(4),Z2(4),DS(4)
REAL*8 SUM1,SUM2,SSQ1,SSQ2
DIMENSION LABEL1(20),LABEL2(20)
DATA LABEL2/20 * ' '/
DATA N1,N2,NS/0,0,0/
DATA SUM1,SUM2,SSQ1,SSQ2/0.0,0.0,0.0,0.0/
READ (5,50) LABEL1
50  FORMAT (20A4)
    READ (5,51) NPARM
51  FORMAT (I1)
    READ (5,52) A,B,D,Q,R
52  FORMAT (5E10.0)
    READ (5,53) ALPHA,WL
53  FORMAT (2F10.0)
    READ (5,54) NMAX,NRAND
54  FORMAT (I10)
    GO TO (55,56),NPARM
56  READ (4,57) LABEL2,SUM1,SUM2,SSQ1,SSQ2,N1,N2,NS,NRAND
57  FORMAT (20A4/4Z16/4I10)
    REWIND 4
55  CONTINUE
    DD2S = (D/2.C)**2
    WRITE (6,800) NRAND,A,B,D,Q,R
800  FORMAT (1H1,80(14-))/' INPUT'//
    1 10X,'STARTING RANDOM NUMBER',T42,I10/
    2 10X,'A - DIMENSION',T41,1PE11.4/
    3 10X,'B - DIMENSION',T41,1PE11.4/
    4 10X,'ORIFICE DIAMETER',T41,1PE11.4/
    5 10X,'ORIFICE MOMENT ARM',T41,1PE11.4/
    6 10X,'SAMPLE RADIUS',T41,1PE11.4/
    WRITE (6,801) ALPHA,WL,NMAX
801  FORMAT (10X,'CONDENSATION COEFFICIENT',T41,1PE11.4/
    1 10X,'WALL LOSS PROBABILITY',T41,1PE11.4/
    2 10X,'MAXIMUM HISTORIES',T42,I10)

```

```

      WRITE (6,802) SUM1,SUM2,SSQ1,SSQ2,N1,N2,NS
802  FORMAT (10X,'SUMMATION (1)',T41,1PE11.4/
1    10X,'SUMMATION (2)',T41,1PE11.4/
2    10X,'SSQ (1)',T41,1PE11.4/
3    10X,'SSQ (2)',T41,1PE11.4/
4    10X,'N1',T42,I10/
5    10X,'N2',T42,I10/
6    10X,'NS',T42,I10////)
      NMAX = NS + NMAX

C
C      VAPORIZE A MOLECULE.
C
C      CHOOSE RANDOM POSITION AND DIRECTION OF
C      EMISSION.  INTERMEDIATE VARIABLES ARE
C
C      T1      COS (ETA)
C      T2      SIN (ETA)
C      T3      THETA
C      T4      CCS (THETA)
C      T5      SIN (THETA)
C      T6      CCS (ETA PRIME)
C      T7      SIN (ETA PRIME)
C      T8      THETA PRIME)
C      T9      COS (THETA PRIME)
C      T10     SIN (THETA PRIME)
C      T11     X PRIME
C      T12     Y PRIME
C
1    CONTINUE
      NS = NS + 1
      IF (NS .GT. NMAX) GO TO 700
      CALL RANDU (NRAND,NRAND,RAND)
      T1 = 1.0 - 2.0 * RAND
      T2 = SIN (ARCCS (T1))
      CALL RANDU (NRAND,NRAND,RAND)

```



```

T3 = 6.28318 * RAND
T4 = COS (T3)
T5 = SIN (T3)
X = R * T2 * T4
Y = R * T2 * T5
Z = R * T1
CALL RANDU (NRAND,NRAND,RAND)
T6 = SQRT (RAND)
T7 = SIN (ARCOS (T6))
CALL RANDU (NRAND,NRAND,RAND)
T8 = 6.28318 * RAND
T9 = COS (T8)
T10 = SIN (T8)
T11 = T7 * T9
T12 = T7 * T10
T15 = T11 * T1 + T6 * T2
AP = T15 * T4 - T12 * T5
BP = T15 * T5 + T12 * T4
CP = T6 * T1 - T11 * T2
DETERMINE DISTANCES TO SURFACES.

C
C
3 CALL SURF2
  CALL SURF3
  CALL SURF4
  DO 2 I = 2,4
    IF (DS(I) .NE. AMIN1 (DS(2),DS(3),DS(4)) )
1 GO TO 2
  GO TO (100,200,300,400) , I
2 CONTINUE
  GO TO 1

C
C ROUTINES TO SERVICE SELECTED SURFACE
C
C SURFACE S1

```

```

100  X = X2(1)
      Y = Y2(1)
      Z = Z2(1)

C
C   TEST FOR ABSORPTION
C
      CALL RANDU (NRAND,NRAND,RAND)
      IF (RAND .GT. ALPHA) GO TO 101
      GO TO 1

C
C   CALCULATE RANDOM DIRECTION OF EMISSION
C   FROM SURFACE S1
C
101  T13 = SQRT (X**2 + Y**2)
      T14 = SQRT (X**2 + Y**2 + Z**2)
      T1 = Z/T14
      T2 = T13/T14
      T4 = X/T13
      T5 = Y/T13
      CALL RANDU (NRAND,NRAND,RAND)
      T6 = SQRT (RAND)
      T7 = SIN (ARCOS(T6))
      CALL RANDU(NRAND,NRAND,RAND)
      T8 = 6.28318 * RAND
      T9 = COS (T8)
      T10 = SIN (T8)
      T11 = T7 * T9
      T12 = T7 * T10
      T15 = T11 * T1 + T6 * T2
      AP = T15 * T4 - T12 * T5
      BP = T15 * T5 + T12 * T4
      CP = T6 * T1 - T11 * T2

C
C   DETERMINE DISTANCES TO SURFACES
C

```

```

      GO TO 3
C
C   SURFACE S2
C
200  X = X2(2)
      Y = Y2(2)
      Z = Z2(2)
C
C   TEST FOR REFLECTION
C
      IF ((Y-C)**2 + Z**2 .LE. DC2S.AND.
1  X .GT. 0.0) GO TO 500
      IF ((Y+C)**2 + Z**2 .LE. DC2S.AND.
1  X .LT. 0.0) GO TO 600
C
C   TEST FOR ABSORPTION
C
      CALL RANDU (NRAND,NRAND,RAND)
      IF (RAND .GT. WL) GO TO 201
      GO TO 1
201  CALL RANDU (NRAND,NRAND,RAND)
      T1 = SQRT (RAND)
      CALL RANDU (NRAND,NRAND,RAND)
      T2 = 6.28318 * RAND
      T3 = SIN (ARCCOS(T1))
      T4 = COS (T2)
      AP = -T3 * T4 * (Z/A) - T1 * (X/A)
      BP = T3 * SIN (T2)
      CP = T3 * T4 * (X/A) - T1 * (Z/A)
C
C   DETERMINE DISTANCES TO SURFACES
C
      CALL SURF1
      CALL SURF2A
      CALL SURF3

```

```

CALL SURF4
BMIN = AMIN1(DS(1),DS(2),DS(3),DS(4))
IF (DS(1) .EQ. BMIN) GO TO 100
IF (DS(2) .EQ. BMIN) GO TO 200
IF (DS(3) .EQ. BMIN) GO TO 300
IF (DS(4) .EQ. BMIN) GO TO 400
GO TO 1

C
C   SURFACE S3
C
300  X = X2(3)
      Y = Y2(3)
      Z = Z2(3)

C
C   TEST FOR ABSORPTION
C
      CALL RANDU(NRAND,NRAND,RAND)
      IF (RAND .GT. WL) GO TO 301
      GO TO 1
301  CALL RANDU (NRAND,NRAND,RAND)
      T1 = 6.28318 * RAND
      CALL RANDU (NRAND,NRAND,RAND)
      BP = -SQRT(RAND)
      T2 = SIN (ARCCOS (-BP))
      AP = -T2 * SIN (T1)
      CP = -T2 * COS (T1)

C
C   DETERMINE DISTANCES TO SURFACES
C
      CALL SURF1
      CALL SURF2
      CALL SURF4
      BMIN = AMIN1 (DS(1),DS(2),DS(4))
      IF (DS(1) .EQ. BMIN) GO TO 100
      IF (DS(2) .EQ. BMIN) GO TO 200

```

```

      IF (DS(4) .EQ. BMIN) GO TO 400
      GO TO 1
C
C      SURFACE S4
C
400    X = X2(4)
      Y = Y2(4)
      Z = Z2(4)
C
C      TEST FOR ABSORPTION
      CALL RANDU ( NRAND,NRAND,RAND)
      IF (RAND .GT. WL) GO TO 401
      GO TO 1
401    CALL RANDU (NRAND,NRAND,RAND)
      T1 = 6.28318 * RAND
      CALL RANDU ( NRAND,NRAND,RAND)
      BP = SORT (RAND)
      T2 = SIN (ARCCOS(BP))
      AP = T2 * SIN (T1)
      CP = T2 * COS (T1)
C
C      DETERMINE DISTANCES TO SURFACES
C
      CALL SURF1
      CALL SURF2
      CALL SURF3
      BMIN = AMIN1 (DS(1),DS(2),DS(3))
      IF (DS(1) .EQ. BMIN) GO TO 100
      IF (DS(2) .EQ. BMIN) GO TO 200
      IF (DS(3) .EQ. BMIN) GO TO 300
      GO TO 1
C
C      BRANCH HERE ON EFFUSION THROUGH ORIFICE 1.
C
500    TORC=(X*BP - Y*AP)/Q

```

```

      N1 = N1 + 1
      SUM1 = SUM1 + TORQ
      SSG1 = SSG1 + TORQ**2
      GO TO 1

C
C      BRANCH HERE ON EFFUSION THROUGH ORIFICE 2
C
600   TORQ = (X*BF - Y*AP) / Q
      N2 = N2 + 1
      SUM2 = SUM2 + TORQ
      SSG2 = SSG2 + TORQ**2
      GO TO 1

700   NS = NS - 1
      RNS = FLOAT(NS)
      RSUM1 = SUM1
      RSUM2 = SUM2
      COEFF = 24.0 * ALPHA * (R/D)**2
      PHI1 = COEFF * (ABS(RSUM1)/RNS)
      PHI2 = COEFF * (ABS(RSUM2)/RNS)
      VAR1 = (COEFF**2)*(SSG1 - SUM1**2/RNS)/(RNS**2)
      VAR2 = (COEFF**2)*(SSG2 - SUM2**2/RNS)/(RNS**2)
      WRITE (6,701) PHI1,PHI2,VAR1,VAR2
701   FORMAT (1X,80(1H-))/' CUTPUT'//
      1 10X,'PHI (1)',T41,1PE11.4/
      2 10X,'PHI (2)',T41,1PE11.4/
      3 10X,'VAR ( PHI (1) )',T41,1PE11.4/
      4 10X,'VAR ( PHI (2) )',T41,1PE11.4/
      WRITE (6,702) SUM1,SUM2,SSG1,SSG2
702   FORMAT (10X,'SUMMATION (1)',T41,1PE11.4/
      1 10X,'SUMMATION (2)',T41,1PE11.4/
      2 10X,'SSQ (1)',T41,1PE11.4/
      3 10X,'SSQ (2)',T41,1PE11.4/
      WRITE (6,703) N1,N2,NS,NRAND
703   FORMAT (10X,'N1',T42,I10/
      1 10X,'N2',T42,I10/

```

```

2  10X,'NS',T42,I10/
2  10X,'LAST RANDOM NUMBER',T42,I10)
  WRITE (6,704) LABEL1,LABEL2
704  FORMAT (1//2X,'RLN INFCRMATICN--',2(//10X,20A4))
  WRITE (7,705) LABEL1,SUM1,SUM2,SSQ1,SSQ2,N1,N2,NS,NRAND
705  FORMAT (20A4/4Z16/4I10)
  STCP
  END

```

SUBROUTINE SURF1

C
C
C
C
C
C
C

LOCATES THE INTERSECTION OF A SPECIFIED
SPACE LINE WITH THE SAMPLE, DETERMINES
IF INDICATED INTERSECTION IS VALID, AND
CALCULATES DISTANCE.

```

COMMON A,B,C,Q,R,AP,BP,CP,X,Y,Z,X2,Y2,Z2,DS2
DIMENSION X2(4),Y2(4),Z2(4),DS2(4)
ALPHA = ((BP/AP)*X - Y)
BETA = ((CP/AP)*X - Z)
AA = (1.0 + (BP/AP)**2 + (CP/AP)**2)
BB = -2.0*((BP/AP) * ALPHA + (CP/AP) * BETA)
CC = (ALPHA**2 + BETA**2 - R**2)
T1 = BB**2 - 4.0*AA*CC
IF (T1 .GE. 0.0) GO TO 1
DS2(1) = 1.0E50
RETURN

```

1

```

T1 = SQRT(T1)
XX1 = (-BB + T1)/(2.0 * AA)
XX2 = (-BB - T1)/(2.0 * AA)

```

```

      IF (ABS (XX1 - X) .LT. ABS (XX2 - X)) GO TO 2
      X2(1) = XX2
      GO TO 3
2     X2(1) = XX1
3     DELTX = X2(1) - X
      DELTXA = DELTX/AP
      IF (DELTXA .GE. 0.0) GO TO 4
      DS2(1) = 1.0E50
      RETURN
4     DELTY = -BP * DELTXA
      Y2(1) = Y - DELTY
      DELTZ = -CP * DELTXA
      Z2(1) = Z - DELTZ
      CS2(1) = DELTX **2 + DELTY**2 + DELTZ**2
      RETURN
      END

```

SUBROUTINE SURF2

```

C
C LOCATES PREDICTED INTERSECTION OF
C MOLECULAR TRAJECTORY WITH THE
C CYLINDER S2. THE ROUTINE PRESUMES THAT THE
C MOLECULE DOES NOT ALREADY LIE ON S2
C

```

```

COMMON A,B,C,Q,R,AP,BP,CP,X,Y,Z,X2,Y2,Z2,DS
DIMENSION X2(4),Y2(4),Z2(4),DS(4)
IF (ABS(CP) .LT. 0.09) GO TO 2
ALPHA = (AP/CP) * Z - X
AA = (AP/CP)**2 + 1.0
BB = -2.0 * (AP/CP) * ALPHA
CC = ALPHA**2 - A**2

```



```

T1 = SQRT (EE**2 - 4.0 * AA * CC)
Z2(2) = (-BB + T1)/(2.0*AA)
IF ((Z2(2) - Z)/CP .LT. 0.0) GO TO 1
X2(2) = X + (AP/CP) * (Z2(2) - Z)
Y2(2) = Y + (BP/CP) * (Z2(2) - Z)
DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
RETURN
1  Z2(2) = (-BB - T1)/(2.0*AA)
   X2(2) = X + (AP/CP) * (Z2(2) - Z)
   Y2(2) = Y + (BP/CP) * (Z2(2) - Z)
   DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
   RETURN
2  ALPHA = (CP/AP) * X - Z
   AA = (CP/AP)**2 + 1.0
   BB = -2.0 * (CP/AP) * ALPHA
   CC = ALPHA**2 - AA**2
   T1 = SQRT (EE**2 - 4.0 * AA * CC)
   X2(2) = (-BB + T1)/(2.0 * AA)
   IF ((X2(2) - X)/AP .LT. 0.0) GO TO 3
   Z2(2) = Z + (CP/AP) * (X2(2) - X)
   Y2(2) = Y + (BP/AP) * (X2(2) - X)
   DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
   RETURN
3  X2(2) = (-BB - T1)/(2.0 * AA)
   Z2(2) = Z + (CP/AP) * (X2(2) - X)
   Y2(2) = Y + (BP/AP) * (X2(2) - X)
   DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
   RETURN
END

```

SUBROUTINE SURF2A

C
C
C
C
C

PERFORMS SAME FUNCTION AS SURF2
EXCEPT CALCULATION PRESUMES THAT
THE MOLECULE ORIGINATES ON S2

```
COMMON A,B,C,Q,R,AP,BP,CP,X,Y,Z,X2,Y2,Z2,DS
DIMENSION X2(4),Y2(4),Z2(4),DS(4)
IF (ABS(CP) .LT. 0.09) GO TO 2
ALPHA = (AP/CP) * Z - X
AA = (AP/CP)**2 + 1.0
BB = -2.0 * (AP/CP) * ALPHA
CC = ALPHA**2 - A**2
T1 = SQRT(BB**2 - 4.0 * AA * CC)
Z2P = (-BB + T1)/(2.0 * AA)
Z2M = (-BB - T1)/(2.0 * AA)
IF (ABS(Z2M - Z) .GT. ABS(Z2P - Z)) GO TO 1
X2(2) = X + (AP/CP) * (Z2P - Z)
Y2(2) = Y + (BP/CP) * (Z2P - Z)
Z2(2) = Z2P
DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
RETURN
1 X2(2) = X + (AP/CP) * (Z2M - Z)
Y2(2) = Y + (BP/CP) * (Z2M - Z)
Z2(2) = Z2M
DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
RETURN
2 ALPHA = (CP/AP) * X - Z
AA = (CP/AP)**2 + 1.0
BB = -2.0 * (CP/AP) * ALPHA
CC = ALPHA**2 - A**2
T1 = SQRT(BB**2 - 4.0 * AA * CC)
X2P = (-BB + T1)/(2.0 * AA)
X2M = (-BB - T1)/(2.0 * AA)
IF (ABS(X2M - X) .GT. ABS(X2P - X)) GO TO 3
Z2(2) = Z + (CP/AP) * (X2P - X)
```

```

Y2(2) = Y + (BP/AP) * (X2P - X)
X2(2) = X2P
DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
RETURN
3  Z2(2) = Z + (CP/AP) * (X2M - X)
Y2(2) = Y + (BP/AP) * (X2M - X)
X2(2) = X2M
DS(2) = (X2(2) - X)**2 + (Y2(2) - Y)**2 + (Z2(2) - Z)**2
RETURN
END

```

```

SUBROUTINE SURF3
COMMON A,B,C,Q,R,AP,BP,CP,X,Y,Z,X2,Y2,Z2,DS
DIMENSION X2(4),Y2(4),Z2(4),DS(4)
DELTY = B - Y
IF (BP .EQ. 0.0 .OR. DELTY*BP .LT. 0.0) GO TO 1
DELTX = (AP/BP) * DELTY
X2(3) = X + DELTX
DELTZ = (CP/BP) * DELTY
Z2(3) = Z + DELTZ
Y2(3) = B
DS(3) = DELTX**2 + DELTY**2 + DELTZ**2
RETURN
1 DS(3) = 1.0E50
RETURN
END

```

```

SUBROUTINE SURF4
COMMON A,B,D,Q,R,AP,BP,CP,X,Y,Z,X2,Y2,Z2,DS
DIMENSION X2(4),Y2(4),Z2(4),DS(4)
DELTY = -(B + Y)
IF (EP .EQ. 0.0 .OR. DELTY*BP .LT. 0.0) GO TO 1
DELT X = (AP/BP) * DELTY
X2(4) = X + DELT X
DELT Z = (CP/BP) * DELTY
Z2(4) = Z + DELT Z
Y2(4) = -B
DS(4) = DELT X**2 + DELTY**2 + DELT Z**2
RETURN
1 DS(4) = 1.0E50
RETURN
END

```

APPENDIX J.

SPHERICAL-TO-SPHERICAL TRANSFORMATION

In Chapter 4 the requirement arose for a method to transform direction cosines defined in a local spherical coordinate system which was situated at an arbitrary point on the sample surface into direction cosines defined in the cell or global system. The problem is portrayed in Figure J-1. The global system, denoted by unprimed axes, has its origin at point $(0, 0, 0)$. The local system, denoted by primed axes, has its origin at P_1 , with coordinates $(0, 0, 0)$ in the local system, but coordinates (x_1, y_1, z_1) in the global system. Point P_2 has coordinates (x_2, y_2, z_2) in the global system and coordinates (x_2', y_2', z_2') in the local system. Vector $\overrightarrow{P_1P_2}$ is a position vector in the local system and possesses direction cosines a', b', c' in the local system; we wish to express these as direction cosines a, b, c in the global system.

To facilitate the development, we show the two systems as projections: onto the $x - y$ plane in Figure J-2 and onto the plane in which the x' and z' axes lie in Figure J-3. In Figure J-2, the visible projections of the x_2' , y_2' , and z_2' vectors are $x_2' \cos \eta$, y_2' , and $z_2' \sin \eta$, respectively. The first and the third component combine to give a vector of length $x_2' \cos \eta + z_2' \sin \eta$; from this it may be deduced that

$$\begin{aligned} x_2 - x_1 &= (x_2' \cos \eta + z_2' \sin \eta) \cos \theta - y_2' \sin \theta, \\ y_2 - y_1 &= (x_2' \cos \eta + z_2' \sin \eta) \sin \theta + y_2' \cos \theta. \end{aligned}$$

Figure J-1. Spherical-to-spherical transformation.

Figure J-2: Projection onto the x - y plane.

Figure J-3. Projection onto the x' - z' plane.

In Figure J-3, it is apparent that

$$z_2 - z_1 = z_2' \cos \eta - x_2' \sin \eta.$$

If the vector $\overrightarrow{P_1P_2}$ is of unit length, then x_2' , y_2' , and z_2' are identical to the local direction cosines a' , b' , and c' , respectively. Since a vector has the same length in any coordinate system, the components $(x_2 - x_1)$, $(y_2 - y_1)$, and $(z_2 - z_1)$ must be identical to the global direction cosines a , b , and c , respectively. Consequently,

$$a = (a' \cos \eta + c' \sin \eta) \cos \theta - b' \sin \theta,$$

$$b = (a' \cos \eta + c' \sin \eta) \sin \theta + b' \cos \theta,$$

$$c = c' \cos \eta - a' \sin \eta.$$

With these equations it may easily be verified by forming the sum of the squares of a , b , and c that

$$a^2 + b^2 + c^2 = a'^2 + b'^2 + c'^2.$$

APPENDIX K.

ENUMERATION OF RESULTS

Following is a disclosure of the results of the Monte Carlo simulation, Phases I, II, and III. Figures K-1 through K-16 are computer-drawn plots of reduced flux data from Phase I. Table K-1 gives parameter settings for all sixteen cases. Table K-2 gives the parameter settings of the eight cases of Phase II. In Figures K-17 through K-32 are plotted for each case the first five of twenty flux terms followed by the means of all twenty curves. Table K-3 gives the standard deviations about the means of the curves of Cases 1 and 2. Case 1 is a representative example of a situation in which high order curves contain substantial deviations due to gradients, while Case 2 is an example of a situation in which they do not. The results of Phase III are presented in Tables K-4 through K-6. The first two of these contain cell parameter settings, sample sizes, and measured values of φ and ζ , with estimated standard deviations of φ and ζ . The last table presents the measured values of P with the corresponding theoretical values; the standard deviation and the departure of theoretical P are included for comparison.

Table K-1. Phase I: parameter settings and sample sizes for the sixteen cases.

Case	B/A	R_s/A	α_s	α_w	N_s
1	2.0	0.5	1.0	0.0	101,000
2	2.0	0.5	1.0	0.5	201,000
3	2.0	0.5	0.1	0.0	11,000
4	2.0	0.5	0.1	0.5	201,000
5	2.0	0.05	1.0	0.0	1,050
6	2.0	0.05	1.0	0.5	201,000
7	2.0	0.05	0.1	0.0	110
8	2.0	0.05	0.1	0.5	201,000
9	5.0	0.5	1.0	0.0	101,000
10	5.0	0.5	1.0	0.5	251,000
11	5.0	0.5	0.1	0.0	10,100
12	5.0	0.5	0.1	0.5	251,000
13	5.0	0.05	1.0	0.0	1,050
14	5.0	0.05	1.0	0.5	501,000
15	5.0	0.05	0.1	0.0	110
16	5.0	0.05	0.1	0.5	501,000

Figure K-1. Phase I, Case 1.

Figure K-2. Phase I, Case 2.

Figure K-3. Phase I, Case 3.

Figure K-4. Phase I, Case 4.

Figure K-5. Phase I, Case 5.

Figure K-6. Phase I, Case 6.

Figure K-7. Phase I, Case 7.

Figure K-8. Phase I, Case 8.

Figure K-9. Phase I, Case 9.

Figure K-10. Phase I, Case 10.

Figure K-11. Phase I, Case 11.

Figure K-12. Phase I, Case 12.

Figure K-13. Phase I, Case 13.

Figure K-14. Phase I, Case 14.

Figure K-15. Phase I, Case 15.

Figure K-16. Phase I, Case 16.

Table K-2. Phase II: parameter settings and sample sizes for the eight cases.

Case	R_s/A	B/A	α_s	N_s
1	0.5	2.0	1.0	201,000
2	0.5	2.0	0.0	101,000
3	0.5	5.0	1.0	201,000
4	0.5	5.0	0.0	101,000
5	0.05	2.0	1.0	101,000
6	0.05	2.0	0.0	101,000
7	0.05	5.0	1.0	101,000
8	0.05	5.0	0.0	101,000

Figure K-17. Phase II, Case 1.

Figure K-18. Phase II, Case 1.

Figure K-19. Phase II, Case 2.

Figure K-20. Phase II, Case 2.

Figure K-21. Phase II, Case 3.

Figure K-22. Phase II, Case 3.

Figure K-23. Phase II, Case 4.

Figure K-24. Phase II, Case 4.

Figure K-25. Phase II, Case 5.

Figure K-26. Phase II, Case 5.

Figure K-27. Phase II, Case 6.

Figure K-28. Phase II, Case 6.

Figure K-29. Phase II, Case 7.

Figure K-30. Phase II, Case 7.

Figure K-31. Phase II, Case 8.

Figure K-32. Phase II, Case 8.

Table K-3. Phase II: standard deviation about the mean for each flux curve, Cases 1 and 2.

Flux term number	$\sigma_M(\%)$, Case 1 ^a	$\sigma_M(\%)$, Case 2 ^a
0	68.1	68.3
1	14.4	24.6
2	5.29	8.63
3	8.85	3.92
4	11.1	2.39
5	12.0	1.81
6	12.3	1.85
7	11.5	1.82
8	12.7	1.23
9	12.4	1.48
10	13.3	1.52
11	12.2	1.52
12	12.1	1.34
13	12.6	1.54
14	11.5	1.65

^a σ_M is equal to the sum of squares of the measured flux values about the curve mean divided by 20, the number of measured points on each curve, and expressed as a percent of the curve mean.

Table K-3. (continued)

Flux term number	$\sigma_M(\%)$, Case 1	$\sigma_M(\%)$, Case 2
15	12.5	1.59
16	12.5	1.76
17	12.3	1.26
18	12.3	1.81
19	11.7	1.23

Table K-4. Phase III: parameter settings and sample sizes for the eight cases.^a

Case	B	D	Q	R _s	α_s	α_w	$\frac{\alpha_s A_s}{A_o}$	N _s
1	2.0	0.1	1.0	0.5	1.0	0.0	400.	301,000
2	2.0	0.1	1.0	0.5	1.0	0.5	400.	1,801,000
3	2.0	0.1	1.0	0.5	0.1	0.0	40.	37,000
4	2.0	0.1	1.0	0.5	0.1	0.5	40.	1,501,000
5	2.0	0.2	1.0	0.16	1.0	0.0	10.24	41,000
6	5.0	0.1	1.0	0.5	1.0	0.0	400.	101,000
7	5.0	0.1	4.0	0.5	1.0	0.0	400.	101,000
8	5.0	0.2	4.0	0.5	1.0	0.5	100.	1,001,000

^aIn all cases A = 1.

Table K-5. Phase III: output data.^a

Case	N ₀	SUM ^b	SSQ ^c	φ	$\sigma_{\varphi}(\%)$	ζ	$\sigma_{\zeta}(\%)$
1	750.5	496.43	559.80	.9896	4.76	.9922	3.06
2	769.0	229.26	247.22	7.638×10^{-2}	6.86	.4472	5.83
3	852.5	555.16	635.24	.9003	4.51	.9768	2.98
4	735.5	215.49	238.08	8.614×10^{-3}	7.16	.4395	6.14
5	3350.5	2237.14	2513.5	.8382	2.19	1.002	1.43
6	245.5	162.81	183.38	.9672	8.31	.9948	5.33
7	245.0	160.10	123.55	.9511	6.94	.9802	2.72
8	194.5	85.165	62.425	1.276×10^{-2}	9.28	.6568	5.89

^aResults in this table and in Table K-5 are averages for the two orifices.

^bSUM is the average summation of torque contributions of the two orifices.

^cSSQ is the average sum of squares of the torque contributions of the two orifices.

Table K-6. Phase III: comparison of theoretical escape probability, P_{th} , with that calculated by the simulation.

Case	$P_{M.C.}$	P_{th}	σ_P (Monte Carlo)	$\frac{P_{th} - P_{M.C.}}{P_{M.C.}}$
1	2.493×10^{-3}	2.341×10^{-3}	3.65	-6.10
2	4.270×10^{-4}	4.137×10^{-4}	3.61	-3.11
3	2.304×10^{-2}	2.484×10^{-2}	3.39	7.81
4	4.900×10^{-4}	4.647×10^{-4}	3.69	-5.16
5	8.172×10^{-2}	9.702×10^{-2}	1.66	18.7
6	2.431×10^{-3}	2.352×10^{-3}	6.37	-3.22
7	2.426×10^{-3}	2.140×10^{-3}	6.38	11.77
8	1.943×10^{-4}	4.064×10^{-4}	7.17	109.1

APPENDIX L.

ERROR ANALYSIS: VARIANCES OF φ , P , and ζ

The techniques developed for estimating the variances of the statistics from the Monte Carlo simulation are now disclosed. Recall the basic torque factor formula

$$\varphi = (3/2)(\alpha_s A_s / A_o) N_s^{-1} \sum_{i=1}^{N_o} (\vec{p} \times \hat{\eta} \cdot \hat{u}), \quad (L-1)$$

in which, for convenience, A_o is the average area of both orifices and N_o is the average effusate. No error is introduced by averaging when the cell is symmetrical, as it was in Phase III. Again for convenience, we rewrite equation (L-1) as

$$\varphi = (3/2)(\alpha_s A_s / A_o) N_s^{-1} \sum_{i=1}^{N_o} T_i, \quad (L-2)$$

where T_i is the torque contribution of the i -th molecule. In Chapter 3 it was shown that this equation could be expressed as

$$\varphi = (3/2)(\alpha_s A_s / A_o) P, \quad (L-3)$$

where P is the escape probability for the orifices combined.

To begin, we derive an estimate for the variance of P .

Let

$$\sum_{i=1}^{N_o} T_i = \sum_{i=1}^{N_o} I_j X_j$$

where I_j is an identifier equal to 1 if the molecule effuses and 0 if it does not. We assume

1. X_j is a random drawing from the T population;
2. I_j, X_j are all statistically independent.

Moreover,

1. $P(I_j = 1) = p,$
 $P(I_j = 0) = 1 - p = q,$
2. $T_i = X_j.$

Because of the statistical independence of all $I_j, X_j,$

$$V[\sum_{j=1}^{N_s} I_j X_j] = \sum_{j=1}^{N_s} V[I_j X_j],$$

and

$$\begin{aligned} V[I_j X_j] &= E[(I_j X_j)^2] - E^2[I_j X_j], \\ &= E[I_j X_j^2] - E^2[I_j X_j]. \end{aligned}$$

Now

$$\begin{aligned} E[I_j X_j^2] &= E[I_j X_j^2 | I_j = 1] \cdot P(I_j = 1) \\ &= +E[I_j X_j^2 | I_j = 0] \cdot P(I_j = 0) \\ &= E[X_j^2 | I_j = 1] \cdot P(I_j = 1) \\ &= E[X_j^2] p. \end{aligned}$$

Also

$$E[I_j X_j] = E[X_j] p.$$

Therefore

$$V[I_j X_j] = E[X_j^2] p - E^2[X_j] p^2$$

and

$$V[\sum_{j=1}^{N_s} I_j X_j] = N_s (E[X_j^2] p - E^2[X_j] p^2).$$

Consequently,

$$V \frac{[\sum_{j=1}^{N_s} I_j X_j]}{N_s} = \frac{1}{N_s^2} N_s (E[X_j^2] p - E^2[X_j] p^2),$$

which may be manipulated to the form

$$V \frac{\sum_{j=1}^{N_s} I_j X_j}{N_s} = \frac{V[T]p + E^2[T]pq}{N_s}. \quad (L-4)$$

By means of the approximations

$$V[T] \cong \frac{1}{N_0} \sum_{i=1}^{N_0} (T_i - \bar{T})^2,$$

$$E[T] \cong \frac{1}{N_0} \sum_{i=1}^{N_0} T_i,$$

and

$$p \cong N_0/N_s,$$

we obtain, upon substitution into equation (L-4) and simplification,

$$V \frac{1}{N_s} \sum_{i=1}^{N_0} T_i \cong \frac{1}{N_s^2} \sum_{i=1}^{N_1} T_i^2 - \frac{1}{N_s^3} \left(\sum_{i=1}^{N_1} T_i \right)^2, \quad (L-5)$$

and this is equal to $V[P\omega]$

We may estimate the variance of ϕ and ω by the well-known propagation of error theorem¹ which states that the expected value of a function of n variables,

$$f = f(x_1, x_2, \dots, x_n)$$

is given by

$$\bar{f} = f(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n),$$

and its variance by

$$V[f] = \sum_{k=1}^n \left(\partial f / \partial x_k \right)^2 V[x_k].$$

Thus,

$$V[P\omega] = P^2 V[\omega] + \omega^2 V[P].$$

Since P is a function of a binomial distribution, its variance is

¹For example, see Mickley, Sherwood, and Reed (36, p. 63).

$$V[\omega] = \frac{P(1 - P)}{N_s}$$

$$= \frac{N_o N_s - N_o^2}{N_s^3}$$

Substituting into equation (L-6) for $V[P\omega]$ and $V[P]$ and solving for $V[\omega]$, we obtain, after considerable manipulation,

$$V[\omega] = \frac{1}{N_o^2} \sum_{i=1}^{N_o} T_i^2 - \frac{1}{N_o^3} (\sum_{i=1}^{N_o} T_i)^2. \quad (L-7)$$

Since $\zeta = 3/2 \omega$, further application of the propagation of error theorem yields

$$V[\zeta] = \frac{9}{4} V[\omega];$$

$$V[P\zeta] = \frac{9}{4} V[P\omega]. \quad (L-8)$$

Finally, since equation (L-3) may be put in the form

$$\varphi = (\alpha_s A_s / A_o) P\zeta,$$

the variance of φ is

$$V[\varphi] = (\alpha_s A_s / A_o)^2 V[P\zeta]. \quad (L-9)$$

BIBLIOGRAPHY

1. Langmuir, I. Vapor pressure of metallic tungsten. Physical Review 2: 329. 1913.
2. Knudsen, M. Experimentelle Bestimmung des Druckes gesättigter Quecksilberdämpfe bei 0° und höheren Temperaturen. Annalen der Physik 29: 197. 1909.
3. Volmer, M. Molargewichtsbestimmung im Gaszustand bei sehr niedrigen Drucken. Zeitschrift für Physikalische Chemie Bodenstein-Festband Abt. A: 863. 1931.
4. Dushman, S. Scientific foundations of vacuum technique. 2nd ed. John Wiley and Sons, Inc., New York, N.Y. 1963.
5. Winterbottom, W. L. Vapor-solid interactions and the effusion oven. I. The total effusion current through a cylindrical orifice. The Journal of Chemical Physics 47: 3456. 1967.
6. Winterbottom, W. L. and Hirth, J. P. Diffusional contribution to the total flow from a Knudsen cell. The Journal of Chemical Physics 37: 784. 1962.
7. Wang, K. C. and Wahlbeck, P. G. Effusion. VI. Velocity distributions of gaseous CsCl from near-ideal and right-circular cylindrical orifices. The Journal of Chemical Physics 53: 2896. 1970.
8. Goodman, A. W. Analytic geometry and the calculus. The Macmillan Company, New York, N.Y. 1963.
9. Shreider, Yu. A. The Monte Carlo method. Pergamon Press, New York, N.Y. 1966.
10. Knudsen, M. Die Gesetze der Molekularströmung und der Gase durch Röhren. Annalen der Physik 28: 75. 1909.
11. Knudsen, M. Molekularströmung des Wasserstoffs durch Röhren und das Hitzdrahtmanometer. Annalen der Physik 35: 389. 1911.
12. Dushman, S. The production and measurement of high vacuum. The General Electric Review, Schenectady, N.Y. 1922.

13. Clausing, P. Über die stromung sehr verdünnter Gase durch Röhren von beliebiger Länge. *Annalen der Physik* 12: 96. 1932.
14. DeMarcus, W. C. The problem of Knudsen flow. U.S. Atomic Energy Commission Report K-1302 (Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee). 1957.
15. Davis, D. H. Monte Carlo calculation of molecular flow rates through a cylindrical elbow and pipes of other shapes. *Journal of Applied Physics* 31: 1169. 1960.
16. Sandry, T. D. and Stevenson, F.D. Molecular conductance from a curved surface through a cylindrical hole by Monte Carlo methods. *The Journal of Chemical Physics* 31: 1169. 1960.
17. Whitman, C. I. On the measurement of vapor pressures by effusion. *The Journal of Chemical Physics* 20: 161. 1952.
18. Motzfeldt, K. The thermal decomposition of sodium carbonate by the effusion method. *Journal of Physical Chemistry* 59: 139. 1955.
19. Ward, J. W. and Mulford, R. N. R. Study of some of the parameters affecting Knudsen effusion. I. *The Journal of Chemical Physics* 47: 1710. 1967.
20. Ward, J. W., Mulford, R. N. R., and Bivens, R. L. Study of some of the parameters affecting Knudsen effusion. II. *The Journal of the Chemical Physics* 47: 1718. 1967.
21. Ward, J. W. Study of some of the parameters affecting Knudsen effusion. III. *The Journal of Chemical Physics* 47: 4030. 1967.
22. Ward, J. W. and Fraser, M. V. Some of the parameters affecting Knudsen effusion. IV. *The Journal of Chemical Physics* 49: 3743. 1968.
23. Ward, J. W. Study of some of the parameters affecting Knudsen effusion. V. *The Journal of Chemical Physics* 49: 5129. 1968.
24. Ward, J. W. and Fraser, M. V. Study of some of the parameters affecting Knudsen effusion. VI. *The Journal of Chemical Physics* 50: 1877. 1969.

25. Carlson, K. D. Gilles, P. W., and Thorn, R. J. Analysis of molecular flow in an isothermal enclosure. The Journal of Chemical Physics 38: 2064. 1963.
26. Freeman, R. W. and Searcy, A. W. The effect of channel holes on the force exerted by effusing vapors. The Journal of Chemical Physics 22: 762. 1954.
27. Pratt, J. N. and Aldred, A. T. Torsion-effusion apparatus for the study of vapour pressures of alloys. Journal of Scientific Instruments 36: 465. 1959.
28. Courant, R. and Hilbert, D. Methods of mathematical physics. Volume I. Interscience Publishers, Inc., New York, N.Y. 1953.
29. Lovitt, W. V. Linear integral equations. Dover Publications, Inc., New York, N.Y. 1950.
30. Hottel, H. C. Radiant heat transmission. In W. H. McAdams. Heat Transmission. 3rd ed. Pages 55-125. McGraw-Hill Book Company, New York, N.Y. 1967.
31. Hottel, H. C. and Sarofim, A. F. Radiative transfer. McGraw-Hill Book Company, New York, N.Y. 1967.
32. Howell, J. R. and Perlmutter, M. Monte Carlo solution of thermal transfer through radiants media between gray walls. Transactions of the ASME, Journal of Heat Transfer 86: 116. 1964.
33. Sandry, T. D. Molecular conductances from a curved surface through a cylindrical hole. Unpublished M.S. thesis. Iowa State University, Ames, Iowa 1969.
34. Loeb, L. B. The kinetic theory of gases. 3rd ed. Dover Publications, Inc., New York, N.Y. 1961.
35. Kennard, E. H. Kinetic theory of gases. McGraw-Hill Book Company, Inc., New York, N.Y. 1938.
36. Mickley, H. S. Sherwood, T. K. and Reed, C. E. Applied mathematics in chemical engineering. 2nd. ed. McGraw-Hill Book Company, Inc., New York, N.Y. 1957.