ILINOIS INSTITUTE OF TECHNOLOGY

THERMODYNAMICS OF THE STEADY STATE

BY

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TABLE OF CONTENTS

PREFACE ........................................... Page v
LIST OF TABLES ................................. vii
LIST OF FIGURES .............................. viii

CHAPTER I. INTRODUCTION ................. 1

Background
Statement of the Problem

II. STEADY MASS FLOW ................. 6

Monothermal Processes
General Description
Mathematical Development
Resistance Concept
Forced Vaporization
Process Description
Treatment of Data
Results
Equipment Configuration
Resistance Concept
Dependence of Resistance on Other Quantities
Dimensional Analysis
Diffusion
Process Description
Resistance Concept
Chemical Reactions
Process Description
Simple A = B Reaction
Mathematical Analysis
Results
Resistance Concept
2A = B + B' Reaction

III. STEADY HEAT FLOW ................. 38

Bithermal Processes
General Description
Mathematical Development
Process Function Concept
(continued)
TABLE OF CONTENTS (CONT.)

Other Functions (continued)
Thermal Transpiration
  Process Description
  Static Conditions
  Derivation of Relations
  Knudsen's Equation
Thermal Transpiration
  Argon and Nitrogen Transpiration
  Helium Transpiration
  Empirical Treatment
  Heat of Transport
Thermal Osmosis
  Process Description
  Comparison of Symbolism
Thermal Diffusion
  Process Description
  Comparison of Symbolism

IV. SUMMARY ............................................. 73

General Conclusions
  Monothermal Processes
  Bithermal Processes

APPENDIX ............................................... 78

BIBLIOGRAPHY ......................................... 87

VITA .................................................... 88
Two quantities are introduced on the basis of thermodynamic principles (avoiding the phenomenological approach) to account for a description of the energy transformations that occur in steady-state processes of two types. As a consequence, a thermodynamic language can be developed for nonequilibrium processes.

For monothermal processes, the term $\mathcal{N}$ is defined as the rate of entropy production ($\sigma$) divided by the steady rate of mass flow squared ($\dot{n}^2$). Values of $\mathcal{N}$ calculated from raw experimental data on the process of forced vaporization indicated that it has the significance of a resistance to mass flow. Analytical treatment of the processes of diffusion and chemical reaction yielded similar conclusions.

For bithermal processes, the term $\mathcal{G}$ is defined as the limit of the difference between the reservoir rate of entropy change at a steady rate of mass flow ($\dot{\mathcal{A}}$) and the zero rate of mass flow at vanishing flow. Static equilibrium correlations were made with thermal transpiration data. There were insufficient data available to attach a significance to this quantity. However, the notations of this concept were extended.
to the processes of thermal osmosis and thermal diffusion.

The theoretical concepts in this thesis were outlined by Dr. Ralph J. Tykodi, and the author is grateful for his patient guidance during this research.
LIST OF TABLES

Table

1. Numerical Relationships of Term Groups. 20
2. Values of Heats 69

In the Appendix

3. Summary of Treatment of Alty Data 78
4(A) Term Values for Reaction Type A = B; Based on \( f > 2 > -4 \) 79
4(B) Term Values for Reaction Type A = B; Based on \( 1.25 > f > 0.80 \) 80
4(C) Term Values for \( 2A = B + B' \) Reaction 81
5(A) Thermal Transpiration Data for Argon, \( T_2 = 77^\circ K \) 82
5(B) Thermal Transpiration Data for Argon, \( T_2 = 193.3^\circ K \) 83
5(C) Thermal Transpiration Data for Nitrogen, \( T_2 = 77^\circ K \) 84
5(D) Corresponding Thermal Transpiration Functions For Argon 85
5(E) Thermal Transpiration Data for Helium 86
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Plot of log P as a Function of A for Alty Data</td>
<td>14</td>
</tr>
<tr>
<td>3.</td>
<td>Bar Graph Plot of Resistance-Quantity Ratio for 60, 40, 30, 18°C Water and 1.6°C CCl4 Data</td>
<td>18</td>
</tr>
<tr>
<td>4.</td>
<td>Plot of Equation for Reaction, A = B; Based on -0.4 &lt; f &lt; 1.0 Respectively</td>
<td>30</td>
</tr>
<tr>
<td>5.</td>
<td>Plot of Equation for Reaction, A = B; Based on 1.25 &gt; f &gt; 0.80</td>
<td>31</td>
</tr>
<tr>
<td>6.</td>
<td>Plot of k(a+β) N/2.3R as a Function of the Equilibrium Constant</td>
<td>33</td>
</tr>
<tr>
<td>7.</td>
<td>Plot of Equation for Reaction 2A = B + B'</td>
<td>37</td>
</tr>
<tr>
<td>9.</td>
<td>Thermal Transpiration for Argon</td>
<td>52</td>
</tr>
<tr>
<td>10.</td>
<td>Thermal Transpiration for Nitrogen</td>
<td>53</td>
</tr>
<tr>
<td>11.</td>
<td>Derived Quantity and Function of P1 for Argon</td>
<td>55</td>
</tr>
<tr>
<td>12.</td>
<td>Derived Quantity as a Function of P1 for Nitrogen</td>
<td>56</td>
</tr>
<tr>
<td>13.</td>
<td>Derived Average Quantity as a Function of Corresponding Pressure for Argon</td>
<td>58</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>List of Figures (Cont.)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>14. Plots of Corresponding Quantities for Argon Transpiration Data</td>
<td>59</td>
</tr>
<tr>
<td>15. Thermal Transpiration Data for Helium</td>
<td>61</td>
</tr>
<tr>
<td>16. Derived Quantities as Functions of $P_1$ for Helium</td>
<td>61, 62</td>
</tr>
<tr>
<td>17. Plots of Corresponding Average Quantities for Helium</td>
<td>63</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

Background. The subject of the thermodynamics of the steady state is not new, but treatments are generally based on thermodynamic equations of motion, or phenomenological relations;

\[ J_i = \sum_k L_{ik} X_k, \]  

(I-1)

where the fluxes, \( J_i \), are assumed to be linear functions of the forces, \( X_k \). The principle of microscopic reversibility led Onsager to propose reciprocal relations for the coupled coefficients, \( L_{ik} \), that is,

\[ L_{ik} = L_{ki}. \]  

(I-2)

Although such treatments have proven enlightening, they depart from the basic principle of thermodynamics, which is the definition of functions based on the macroscopic time-invariant properties of a system.

The usual thermodynamic treatment can be identified as equilibrium thermodynamics, since it involves formulations for the energy transformations in reversible processes in which the state of a closed system can be well defined. However, several types of processes can be made to occur wherein the state (or states) of a system open to its environment can be reasonably well defined, even with a dynamic energy

*Numbered references in bibliography.
Steady-state thermodynamics may be identified with the energy transformations incurred by the steady flow of a quantity (s) between two fixed systems which are maintained by external heat and work reservoirs. Impulse thermodynamics may be identified with processes which involve energy transformations that are incurred by single, or repetitive, perturbation of a fixed system. In any event, these processes can be defined so as to fix the time-invariant macroscopic properties of the system. The application of the basic concepts of thermodynamics might then be expected to yield interesting functions that can be developed independently of kinetic concepts (a microscopic basis). The kinetic principles can be utilized for further insight at a later date.

The foundation of thermodynamics is the first law, which simply formulates the conservation of all forms of energy. In equation form, it is

\[ \Delta E = Q - W. \]  

(1-3)

By definition, positive work is done by a system, whereas positive heat is absorbed by a system. The physical definition of work is a force times distance. This concept can be extended so as to represent work as a quantity, or extensive variable (mass, volume, coulombs, etc.), transported through a corresponding
potential, or intensive variable (height, pressure, voltage, etc.). Heat is the passage of a quantity through an arbitrarily defined potential (temperature); it retains a singular role in thermodynamics because of its nebulous character. Heat has been defined in terms of the change in temperature of a given body.

Thus

\[ Q = C \Delta T, \quad (I-4) \]

in which the proportionality constant, \( C \), is a heat capacity characteristic of the body. Because \( C \) is temperature dependent, a quantitative definition of heat depends on the value of \( C \). Therefore specific heat was defined on the basis of the limiting equation

\[ C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}, \quad (I-5) \]

where \( Q \) is measured by defined work equivalents, for example, electrical work.

The concept of a reversible process (such as the limit implied by Eq. I-5) is employed to prove the second law of thermodynamics, namely,

\[ \Delta S = \int \frac{dQ_{\text{reversible}}}{T} \quad (I-6) \]

Thus, if the application of thermodynamics is restricted to reversible processes, it is possible to write Eq. I-3 in the form of an exact differential, as,

\[ dE = \sum_i A_i \, dK_i \quad (I-7) \]
with the symbols \( A_i \) and \( dK_i \) representing elements of potential and quantity, respectively.

In practice, every process for transformation of energy requires a finite rate, and the existence of a rate entails the concept of irreversibility, which is the nemesis of the usual thermodynamics. The inequality,

\[ \Delta S > \int \frac{dQ}{T}, \]  

has been subjected to detailed study by many investigators; e.g., 5, 6, 7 however, the treatment generally assumes kinetic concepts which are incongruous with the usual thermodynamics. From a thermodynamic point of view, a state function (or pseudostate function) to represent the dynamic considerations of energy transformations would be desirable.

**Statement of the Problem.** The purpose of this thesis is to evaluate the possibility of introducing functions which give a thermodynamic "feel" to processes conducted under steady-state conditions. Many processes can be conducted so as to have two well-defined thermodynamic states connected by a gradient region where a "steady state of flow" is maintained. Such a process is irreversible since nonequilibrium conditions are maintained. However, the steady flow of a quantity is obviously determined by a gradient of some suitable thermodynamic potential and a
configuration of the specific equipment.

It is reasonable that a "process function" could be defined which would depend on thermodynamic irreversibility (flow), particularly at conditions near equilibrium. The variation of such a function could be evaluated with respect to (1) the gradient of some suitable thermodynamic potential at a constant experimental configuration and (2) the experimental configuration at a constant gradient of the same potential.

The concepts of the usual equilibrium thermodynamics can be used as primary criteria for such definitions. In addition, because of the singular role of heat, the definitions will depend upon whether the process is conducted at constant temperature or with a temperature gradient.

This thesis will show that, if experimental data to evaluate such functions are obtained, additional scientific evidence can be made available to understand further the concept of irreversibility from a thermodynamic point of view. At the present time, such data are lacking in the scientific literature, the primary emphasis being on the corroboration of kinetic (molecular) concepts and theories.
Monothermal Processes

General Description. This chapter considers some processes which can, in principle, be made to occur under steady-state conditions at constant (external) temperature. Such processes are referred to as monothermal processes. They are generally typified by the schematic diagram in Fig. 1. The system under consideration is bounded by the solid lines in this diagram. It is divided by the two dotted lines, 1' and 2', into three subsystems: states 1 and 2 and a gradient region; states 1 and 2 are well defined to the necessary boundaries of the gradient region, through which a steady mass flow is occurring. External work reservoirs are provided at states 1 and 2, and the system is maintained at the monothermal temperature of the heat reservoir.

The result of these conditions is a steady-rate process in which the gradient of thermodynamic potential between states 1 and 2 causes the flow of mass through the gradient region. In the general case, the ith state is changing mass by the steady mass flow rate, \( \dot{n}_i \). Since nonequilibrium conditions can be maintained by the external heat and work reservoirs, the process is irreversible. However, the system is
FIG. 1 SCHEMATIC DIAGRAM FOR A GENERAL STEADY STATE MASS FLOW AT CONSTANT (EXTERNAL) TEMPERATURE, A MONOTHERMAL PROCESS
typified by the monothermal temperature maintained by the thermal reservoir. It is possible therefore to introduce a "process function" which may define the steady mass flow rate under these conditions.

Mathematical Development. The fundamental inequality of the second law of thermodynamics may be written to maintain an equality similar to other investigators\(^1\),\(^8\) by expressing the entropy production, \(\dot{\sigma}\), as the sum of the rate of entropy change in the reservoir, \(\dot{S}^{(r)}\), and the entropy changes in the subsystems:

\[
\dot{\sigma} = \dot{S}^{(r)} + \sum_i n_i \ddot{S}_i ,
\]

where the dot and bar superscripts refer to the derivative of a quantity with respect to time and moles, respectively. For a steady-rate process, the conservation of mass requires \(\sum_i \dot{n}_i = 0\), that is, \(\dot{n}_1 + \dot{n}_2 = 0\) for the particular case shown in Fig. 1. Therefore \(\sum_i \dot{n}_i \ddot{S}_i\) represents the rate of change of entropy in the system due to the steady flow of mass when each subsystem is well defined. As the rate of entropy change occurring in the system approaches the measurable rate of entropy change occurring in the reservoir, the process becomes reversible and \(\dot{\sigma}\) approaches zero.

Equation I-7 may be written as

\[
\dot{E} = \sum_i A_i \dot{K}_i .
\]
The potential-quantity concept (viz., TS, PV, etc.) can be utilized with appropriate substitution. On an external (reservoir) basis, the energy passing through the system is

\[ E(s) = -T \dot{s}(r) + \sum_i P_i \dot{v}_i - \sum_j A_j \dot{K}_j \]  

where \( \sum_j A_j \dot{K}_j \) are other possible forms of work, that is, gravitational, electrical, etc. Since the subsystems are assumed to be well defined, the rate of volume transport is simply the ith mass flow times the ith molar volume, and similarly for the rate of energy transport. By introducing the entropy production of a monothermal process from Eq. II-1, the preceding equation can be written on a system basis as

\[ \sum_i \dot{n}_i \bar{E}_i = T \sum_i \dot{n}_i \bar{S}_i - T \sigma - \sum_i \dot{n}_i P_i \bar{v}_i + \sum_j \dot{n}_j A_j \bar{K}_j. \]  

The thermodynamic definition \( G = E + PV - TS \) can be combined into this expression to give

\[ \sum_i \dot{n}_i \bar{G}_i = -T \sigma + \sum_j \dot{n}_j A_j \bar{K}_j. \]  

When Eq. II-5 is then divided by the steady mass flow, \( \dot{n}_i \), the final result in the case of a two-state system can be expressed in terms of the chemical potential, \( \mu \), as
\[ \Delta \mu = -T \sigma / \dot{n}_i + \sum_j A_j \bar{R}_j \dot{n}_j / \dot{n}_i. \] (II-6)

**Resistance Concept.** It is now possible to consider an arbitrary quantity \( N \) as

\[ N = \lim_{\dot{n} \to 0} \frac{\sigma}{\dot{n}^2} = \lim_{\dot{n} \to 0} -\frac{\Delta \mu}{T\dot{n}} + \sum_j A_j \bar{R}_j / \dot{n}. \] (II-7)

As the variable \( \dot{n} \) approaches zero, \( \Delta \mu \) and \( \sigma \) approach zero simultaneously, and there is a possibility of a finite limiting value for \( N \). It then is reasonable to study such a process function over finite ranges of the mass flow where other forms of work are neglected, as defined by the equation

\[ N = -\frac{\Delta \mu}{T\dot{n}} \] (II-8a)

or

\[ -\Delta \mu = \dot{n} (TN). \] (II-8b)

This expression has an analogous form to Ohm's law, which governs the flow of electricity in the steady state \( (E = IR) \). That is, the change in chemical potential \( (-\Delta \mu) \) is equal to a flow \( (\dot{n}) \) times an effective resistance \( (TN) \).

For the sake of completeness in later treatments, Eq. II-8 is factored into several equivalent forms. Thus the gas constant \( R \) can be factored out of \( N \) to result in

\[ -\Delta \mu = \dot{n} (RTN), \] (II-8c)

where \( N = N/R \). Also, since the mass flow in a particular equipment configuration is appropriately
referred to some unit area \( A \)

\[
- \Delta \mu = \hat{\alpha}_a (T_N a),
\]

where \( N_a = N_A \) and \( \hat{\alpha}_a = \hat{\alpha}/A \). The gas constant can be factored into the preceding equation to yield a final form

\[
- \Delta \mu = \hat{\alpha}_a (RT N_a).
\]

Since the chemical potential is in dimensional units of energy, the units for \( N_a \) are time-length\(^2\)/mass, e.g., sec-cm\(^2\)/mole.

The concept of a "resistance" can be evaluated in any of the equivalent forms; \( TN, T_N a, RT N_a, \) and \( RT N_a \). The last \( N_a \), is generally the most convenient.

**Forced Vaporization**

**Process Description.** Forced vaporization is a simple steady-rate process in which mass flow is effected across a liquid-vapor boundary by maintaining a pressure gradient. Alty\(^{10,11} \) performed experiments which closely approximate the idealized conditions described previously (Fig. 1). His initial experiments\(^{10} \) involved measurement of the mass flow that resulted when a fixed pressure was maintained above a tube of water immersed in a constant temperature bath. By pumping on the water through six selected orifices, a steady rate of vaporization was
established at each of three thermostat temperatures and the corresponding pressure was measured. In later work, he performed comparable experiments on water and carbon tetrachloride at one intermediate temperature.

As a consequence, the dynamic change in state can be described as the monothermal vaporization of a liquid under its vapor pressure $P_1$ to a gas at pressure $P_2$. Thus,

$$\tilde{\Delta} A_{\text{liquid, } T, P_1} = \Delta A_{\text{gas, } T, P_2}, \quad (\text{II}-9)$$

where $\Delta$ is used as a symbol for the liquid being vaporized. It is apparent that, if a boundary for the gradient region exists as described in Fig. 1, one can apply Eq. II-8b. Surface cooling effects are ignored and the process is referred to the monothermal temperature.

**Treatment of Data.** The difference in the chemical potential can be expressed in the usual equilibrium manner,

$$-\Delta \mu = -\mu_g + \mu_{\text{liq}} = RT \ln \frac{P_2}{P_1} = \tilde{\Delta}TN. \quad (\text{II}-10)$$

This equation can be put in the following form for a test of Alty's experimental data:

$$\log P_2 = \log P_1 - \tilde{\Delta} N/2.3R. \quad (\text{II}-11)$$
If $N$ is independent of $\hat{n}$, a plot of $\log P_2$ as a function of $\hat{n}$ should be a straight line with a slope of $N/2.3R$ and an intercept of $\log P_1$. Table 3(A) in the appendix lists the pertinent experimental conditions of Alty's investigations. The values for $\hat{n}$ and $P_2$ are not included but were taken directly from his graphs.

**Results.** Alty's data for water and carbon tetrachloride are plotted in the form of Eq. II-11 in Fig. 2. As can be seen from the figure, a straight line represents the data where $P_2$ can be more than five times smaller than $P_1$. For the water data, the slope of each straight line decreases with increasing temperature. The data for carbon tetrachloride are peculiar in that initially (near equilibrium) a relatively higher slope is evident than at higher flow rates (greater than ca. 40 micromoles/sec).

The slopes determined from Fig. 2 are 0.00747, 0.0102, 0.0150, 0.0190, 0.0182 and 0.00489, respectively, for the series 60-40-30-18°C water data and 1.6°C carbon tetrachloride data, near and distant from equilibrium. The surface area for vaporization was estimated from a photograph of the static meniscus. Therefore values of $\mathcal{N}$ and $\mathcal{N}_a$ can be calculated by the relations,

$$\mathcal{N} = 2.3 \text{ (slope)} \quad \text{(II-12)}$$
Fig. 2  Plot of log P as a function of A for Alty's data.
Table 3(B) summarizes values of \( \mathcal{N} \) quantities and functions.

There are several points that can be made about the equipment configuration, the resistance concept, and the dependence of resistance on other tabulated quantities.

**Equipment Configuration.** Several factors affecting the equipment configuration must be considered. In any given bore tube, the actual surface area of the liquid meniscus is influenced by the surface tension, during the process of forced vaporization, because the surface tension depends on temperature. Circumferential effects influence the mass flow rate, that is, as the tube diameter decreases there are relatively more surface molecules adjacent to the wall of the tube (the heat reservoir). The correction for surface area, due to the liquid meniscus, becomes negligible as the bore diameter is increased. Further, thickness certainly influences the mass flow rate.

With such considerations in mind, one effect of the equipment configuration, i.e., the surface area should be correlated on a per-unit-area basis. A different form of Eq. II-13,

\[
\mathcal{N} - \mathcal{N}_a = \mathcal{N} (1 - A)
\]

(II-14)
indicates that the $N - N_a$ difference should become relatively smaller as the surface area approaches one. The relative differences of $N$ and $N_a$ for the 60-40-30-18°C water experiments are 0.0027, 0.0037, 0.0032, and 0.0070, respectively. The difference for the 30°C water experiments with a 0.91 cm$^2$ surface area is smaller than would be expected from the 60-40-18°C experiments with a 0.84 cm$^2$ surface area. Therefore, the per-unit-area basis is considered to be an appropriate means of correlating some effects of equipment configuration.

**Resistance Concept.** If N terms are to be similar to an effective resistance, they should approach zero at the critical temperature of the liquid for this process. Various plots of $N$ ($N_a$) and functions ($TN$, log $N$, log $TN$) were made, but the data were too limited to warrant a display. (A more appropriate treatment of the data is given in the following section.) A straight line could be drawn when the log $TN$ was plotted as a function of viscosity, surface tension, entropy change, and thermal conductivity. The equations for these lines were respectively,

\[
\log TN = 0.607 + 1.4 \quad \text{(II-15a)}
\]
\[
\log TN = 0.052 \tau - 1.8 \quad \text{(II-15b)}
\]
\[
\log TN = 0.062 \Delta S \quad \text{(II-15c)}
\]
\[
\log TN = -8.5 k + 4.8 \quad \text{(II-15d)}
\]
The respective values for N at the critical temperature were extrapolated to 0.04, 2 x 10^{-5}, 1.5 x 10^{-3}, and 0.03. Therefore, it is reasonable to conclude that N approaches a small value at the critical temperature for the process of forced vaporization of water.

**Dependence of Resistance on Other Quantities.**

One may anticipate that a type of corresponding-states argument would be of value for prediction of \( \mathcal{N} \) or \( \mathcal{N}_a \). Values from other quantities to establish a correlation so that \( \mathcal{N} \) or \( \mathcal{N}_a \) could be numerically calculated for other materials. The mass flow rate occurring for conditions of forced vaporization could then be predicted. Such properties as \( \Delta H_v \) (enthalphy change), \( \Delta S_v \) (entropy change), \( \gamma \) (surface tension), and \( 1-T/T_{\text{critical}} \) approach zero as the critical temperature is approached. One may consider any property which can be correlated such as \( k \) (thermal conductivity), \( 1/T \), \( \eta \) (viscosity), \( \rho \) (density), \( T/T_{\text{critical}} \), and others. Collected values for such quantities are included in Table 3(C) in the appendix.

The bar graph plot shown in Fig. 3 can be used to evaluate possible relations of the \( \mathcal{N}_a \) functions with selected quantities. This plot displays the ratio of \( \mathcal{N}_a \), \( T \mathcal{N}_a \), and \( \log T \mathcal{N}_a \) to the indicated quantities, \( Q \), for the 60-40-30-18°C water data and
**FIG. 3** BAR GRAPH OF RESISTANCE-QUANTITY RATIO FOR 60, 40, 30, 16°C WATER AND 1.0°C CC14 DATA RESPECTIVELY.
the 1.6°C carbon tetrachloride data. The ordinate is a relative number scale. This plot indicates that \( \mathcal{N}_a/\eta \) is approximately constant, that is, \( \mathcal{N}_a \) is proportional to the viscosity.

**Dimensional Analysis.** It has been found that \( \mathcal{N}_a \) is approximately proportional to the viscosity. An empirical relation of \( \mathcal{N}_a \) to selected quantities may yield a further understanding of this term. A dimensional analysis can be made of \( \mathcal{N}_a \) as a function of arbitrarily selected quantities which would be expected to affect the mass flow rate in the forced vaporization process.

One may write an empirical equation for \( \mathcal{N}_a \) as a function of powers of the quantities to be considered. For example,

\[
\mathcal{N}_a = F(\eta^a, \Delta S^b, T^c, P^d, k^e, \sigma^f, \rho^g).
\]

(II-16a)

The dimensional units for the quantities were chosen, respectively, as follows:

\[
\frac{\text{sec-cm}^2}{\text{mole}} = F \left( \frac{\text{cal}}{\text{cm}^3} \right)^a \left( \frac{\text{cal}}{\text{deg-mole}} \right)^b \left( \frac{\text{deg}}{\text{cm}} \right)^c \left( \frac{\text{cal}}{\text{cm}^3} \right)^d \\
\left( \frac{\text{cal}}{\text{cm-deg-sec}} \right)^e \left( \frac{\text{cal}}{\text{cm}^2} \right)^f \left( \frac{\text{mole}}{\text{cm}^3} \right)^g.
\]

(II-16b)

A system of five equations can be written for the seven exponents. Assuming that \( a = 1 \) (for viscosity), the solution of all other exponents in terms of \( b \) is:
\[ \mathcal{N}_a = \eta \cdot \Delta S^b \cdot T^{b-1} \cdot P^{b-1} \cdot k^{-1} \cdot \rho^{b-1}. \]  

(II-17a)

Pressure and viscosity have the same units and on the basis of this analysis are completely interchangeable. A general expression can be written by substituting \( X \) for viscosity and pressure,

\[ \mathcal{N}_a = \left[ \frac{T \rho \Delta S}{X} \right]^b \left[ \frac{X}{T \rho} \right] \left[ \frac{X}{X} \right]. \]  

(II-17b)

The symbol \( X \) can be replaced by any combination of pressure and viscosity. The first term is dimensionless and the exponent \( b \) is unknown. The term groupings which maintain the proper dimensional units for \( \mathcal{N}_a \) are: \( \frac{\Delta S \gamma}{k \rho}, \frac{\gamma}{T k \rho}, \frac{\gamma}{T k \rho}, \frac{\gamma}{T k \rho}, \frac{\gamma}{k \rho}, \) and \( \frac{\Delta S \gamma}{k \rho}. \)

The last two indicate the wrong trend and are ignored. Table 1 shows the relative numerical relations of such terms, including the viscosity, with the 60°C water result being used as a reference to evaluate a constant factor for the series.

| System | \( \mathcal{N}_a \) | \( \eta \) | \( \frac{\gamma}{T \rho} \) | \( \frac{\Delta S \gamma}{k \rho} \) | \( \frac{\gamma}{T \rho \gamma} \) | \( \frac{\gamma}{T \rho} \gamma \) | \( \frac{\gamma}{T \rho} \gamma \)
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<thead>
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<td>60°C water</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
</tr>
<tr>
<td>40 water</td>
<td>0.0196</td>
<td>0.0201</td>
<td>0.0169</td>
<td>0.0466</td>
<td>0.063</td>
<td>0.0222</td>
<td></td>
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<tr>
<td>30 water</td>
<td>0.0314</td>
<td>0.0251</td>
<td>0.0182</td>
<td>0.0822</td>
<td>0.148</td>
<td>0.0292</td>
<td></td>
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<tr>
<td>18 water</td>
<td>0.0367</td>
<td>0.0317</td>
<td>0.0201</td>
<td>0.203</td>
<td>0.437</td>
<td>0.0406</td>
<td></td>
</tr>
<tr>
<td>1.6°C CC14</td>
<td>0.0372</td>
<td>0.0399</td>
<td>0.153</td>
<td>0.0923</td>
<td>1.77</td>
<td>0.145</td>
<td></td>
</tr>
</tbody>
</table>
*P - equilibrium vapor pressure of the system at the monothermalt temperature.

This tabulation shows little improvement over the unique correlation of \( \mathcal{N}_a \) to viscosity (viz. \( \mathcal{N}_a = 0.031 \gamma \)). Considerably more data are necessary before \( \mathcal{N}_a \) values can become reliable indices of the process of forced vaporization. There are many experimental difficulties in performing the experiments to meet the conditions described previously.

**Diffusion**

**Process Description.** The diffusion of a component (A) through another component (B) can be set up as a steady-rate process wherein a steady mass flow of component A is effected across a mixture (A + B) by maintaining a pressure gradient. The flow of a gas through a metal membrane is an excellent example, e.g., the permeability of hydrogen through platinum foil. The principle of such a process satisfies the steady-state monothermalt conditions described previously (Fig. 1). In such cases, it is necessary to assume that the boundaries of the subsystems are permeable to component A, that is, they must be semi-permeable membranes or solution interfaces. A steady flow, \( \dot{n}_A \), is established across the mixture region by the gradient of a thermodynamic potential between
states 1 and 2.

With these considerations, the change in state can be represented in a dynamic fashion entirely similar to forced vaporization,

$$\mathbf{n}_A \mathbf{A}(\text{gas}, T, P_1) \rightarrow \mathbf{n}_A \mathbf{A}(\text{gas}, T, P_2). \quad (\text{II-18})$$

It is necessary to assume that the difference in chemical potential across the boundaries of the gradient region ($1'$ and $2'$) is approximately zero. The difference in chemical potential between states 1 and 2 can then be written

$$\mu_A^{(2)} - \mu_A^{(1)} = \mu_A^{(2')} - \mu_A^{(1')}$$

where the subscripts $A$ and $A'$ refer to pure component $A$ and the $A$ in the mixture respectively, while the superscripts refer to the identified states. The approximation of the preceding equation can be applied directly to Eq. II-8,

$$-\Delta \mu = -\mu_A^{(2)} + \mu_A^{(1)} =$$

$$\mathbf{n}_A (\text{TN}). \quad (\text{II-20})$$

Diffusion data are reported on a per-unit-area basis; the results are expressed in terms of a diffusion coefficient, $D$, which is defined as the amount of material diffusing across a plane of 1 -cm$^2$ area in unit time under a concentration gradient.

**Resistance Concept.** There is little to be gained
by computing new numerical values of $N$ from numerical diffusion coefficient values. It can be shown analytically that $N$ can be related to $D$ in a fashion that supports the notion that $N$ is a "resistance" to the steady-mass-flow rate of a diffusion process.

Fick's law of diffusion can be written as

$$ \Delta_A = -D^c \left( \frac{dc}{dx} \right) \quad (\text{II-21}) $$

or in an equivalent form which is of more direct use,

$$ \Delta_A = -D^{\mu} \left( \frac{d\mu}{dx} \right) \quad (\text{II-22}) $$

where $D^c$ and $D^{\mu}$ are diffusion coefficients based on the concentration gradient $(dc/dx)$ and the chemical potential gradient $(d\mu/dx)$. The combination of Eq. II-20 and Eq. II-22 expressed per unit area for mass transfer results in

$$ D^{\mu} \left( \frac{d\mu}{dx} \right) = \frac{\Delta \mu}{TN_a} \quad (\text{II-23}) $$

or, when $\Delta \mu$ is approximately equal to $(d\mu/dx) \cdot \Delta x$,

$$ D^{\mu} = \frac{\Delta x}{TN_a} = \frac{\Delta x}{(TN)_A} \quad (\text{II-24}) $$

The right side of the equation is completely analogous to the electrical resistivity equation in which resistivity ($\rho$), resistance ($R$), cross section ($A$), and conductor length ($L$) are related by

$$ \rho = RA/L. \quad (\text{II-25}) $$

The effect of increasing diffusion "resistivity" ($TN_A/\Delta x$) is to decrease the diffusion coefficient,
as would be expected if this term is to have the significance of resistivity. Correspondingly, the equivalent terms TN and $RTN$ also have the significance of resistance.

**Chemical Kinetics**

**Process Description.** A chemical reaction is a complicated process which in principle can be treated as a sequence of steady-states. Such a process does not meet the general considerations described previously (Fig. 1), since three processes are occurring: (1) diffusion of reactants into the reaction zone, (2) the chemical reaction, and (3) diffusion of the products out of the reaction zone. However, one may naively treat a chemical reaction as a quasi-steady process in which a mass flow is effected by maintaining the reaction rate. Thus, the gradient region can be considered to be a well-stirred reaction zone where reactants are admitted and products are removed at a rate determined by the rate of the chemical reaction. Subsystems 1 and 2 can be assumed to be fixed states corresponding to the reactants and products.

At constant temperature, this process can almost be treated in the manner of forced vaporization and diffusion. It must be assumed that the change in free energy for the chemical reaction is an appropriate gradient of chemical potential for a steady
mass transfer rate of reactants to products. The rate of reaction can be referred to the concentration change of one species in the reaction. That is, the rate of steady mass flow through the well-stirred reaction zone can be expressed on the basis of species A. The simple \( A = B \) reaction is considered in the following section, and the \( 2A = B + B' \) reaction is mentioned.

**Simple \( A = B \) Reaction.** The moles of product formed are equal to the moles of reactant depleted in the simple chemical reaction which can be represented as

\[
\dot{n} A(T, (A)) \xrightarrow{k \rightarrow k'} \dot{n} B(T, (B)), \tag{II-26}
\]

where \( k \) and \( k' \) refer to the forward and backward kinetic rate constants and \( (A) \) and \( (B) \) refer to the concentrations of A and B, respectively. This change in state is entirely similar to the case of forced vaporization and diffusion.

A general rate of change of free energy with respect to time for this reaction can be expressed as

\[
\frac{d}{dt} (\Delta G(a)) = \dot{n}(a) (\mu_b - \mu_a), \tag{II-27}
\]

where the \( (a) \) subscript is used to refer to the basis of species A which is necessary in more complicated reactions.

The chemical potential of the \( i \)th component is generally represented in terms of the activity and a
standard state as

\[ \mathcal{M}_i (T,P) = RT \ln \text{activity} + \mathcal{M}_i(T,P) \cdot \]  

(II-28)

The rate of change of free energy for a reaction taking place under nonequilibrium conditions can be written as

\[ \frac{d (\Delta G_{(a)})}{dt} = \tilde{A}_{(a)} RT (\ln Q - \ln K), \]  

(II-29a)

or

\[ \Delta \mathcal{M}_{(a)} = RT (\ln Q - \ln K), \]  

(II-29b)

where Q and K, respectively, refer to the usual nonequilibrium and equilibrium activity (concentration) ratios of products to reactants.

The net reaction rate for a chemical reaction, \( \dot{\varepsilon} \), is equal to the forward minus the backward rate of reaction. It can be represented in terms of the rate of change of concentration of a particular species with respect to time. By expressing the concentration \( C \) as mass per unit volume, a quantity \( \mathcal{N}_v \) based on volume may be introduced

\[ \mathcal{N}_v = - \frac{\Delta \mathcal{M}_{(a)}}{RT \dot{\varepsilon}_{(a)}}, \]  

(II-30)

where the subscript \( (a) \) identifies, as before, the particular species that is being considered. Thus, \( \mathcal{N}_v \) is defined on the basis of the equivalents (referred to one mole of species A) of reaction per unit volume.
The rate of quasi-steady mass flow through a well-stirred reaction zone is determined by the rate of reaction, and Eq. II-29b can be combined with Eq. II-30 to result in an equation similar to forced vaporization,

$$\ln Q - \ln K = \xi(a) \mathcal{N}_v,$$  \hspace{1cm} (II-31)

where the potential \(\ln Q - \ln K\) represents the rate-controlling potential for the chemical reaction.

The reaction rate data for simple reactions, such as optical rotation of sugars in solution, ortho-para hydrogen conversion, etc., could be analyzed on the basis of this equation. However, chemical reaction rate data are usually expressed with mechanisms and such quantities as forward and backward rate constants, activation energies, frequency factors, and the like. One may just as well employ the concepts of the chemical kineticist to determine how \(\mathcal{N}_v\) is related to nonequilibrium conditions on the basis of equilibrium and rate constants.

**Mathematical Analysis.** A general solution for the evaluation of \(\mathcal{N}_v\) is proposed in terms of (1) a "parameter", \(f\), for the reaction and (2) a dimensionless "rate" of reaction which is abbreviated \(\bar{Q}\). The definition of these symbols and others that will be used are as follows:

\[ x - \text{concentration of A at time } t \]
\( x_e \) — concentration of A at chemical equilibrium

\( a \) — initial concentration of A

\( b \) — initial concentration of B

\( f = \frac{x}{x_e} \) (defined)

\( \frac{a}{K + 1} = f(a + b) \) (defined)

In addition, the value of \( K \) is the usual \( k/k' \) ratio. Thus, the following relations are made available for algebraic manipulations;

\[
K = \frac{k}{k'} = \frac{a + b - x_e}{x_e}, \tag{II-32}
\]

\[
x_e = \frac{a + b}{K + 1}, \tag{II-33}
\]

\[
x = fx_e = \frac{f(a + b)}{K + 1}. \tag{II-34}
\]

The usual expression for \( Q \),

\[
Q = \frac{(a + b) - x}{x}, \tag{II-35a}
\]

can be transformed to a functional dependency on \( K \) and \( f \) by substituting Eq. II-34 for \( a + b \), thus,

\[
Q = (K + 1 - f)/f. \tag{II-35b}
\]

In a similar fashion, the usual expression for \( \dot{z} \),

\[
\dot{z} = -\dot{x} = k(x) - k' \left[ (a + b) - x \right], \tag{II-36a}
\]

can be transformed to a dependency on \( K \), \( f \), and \( a \) by utilizing Eq. II-34 and Eq. II-32 for \( x' \),

\[
z = k(a + b) \left[ (f - 1)/K \right], \tag{II-36b}
\]

\[
z = k(a + b) \frac{\bar{z}}{K}. \tag{II-36c}
\]

Equations II-35b and II-36c can be substituted into Eq. II-31 and rearranging in an analogous fashion.
to the forced vaporization treatment,

$$\log \left[ \frac{(K + 1 - f)/f}{1 - f} \right] = \log K - \frac{k(a + b)}{2.3} \mathcal{N}_v(\bar{Z}).$$

(II-37)

If $\mathcal{N}_v$ is independent of $\bar{Z}$ a plot of $\log Q$ as a function of $\bar{Z}$ should be a straight line with an intercept of $\log K$ and a slope of $k(a + b) \mathcal{N}_v/2.3$.

Results. This method of presentation allows one to evaluate $\mathcal{N}_v$ for such a chemical reaction having an equilibrium constant $K$; a forward rate constant $k$; and initial concentrations of components $A$ and $B$, $a$ and $b$. As mentioned previously, one may consider the "parameter" of reaction, $f$, or the dimensionless "rate" of reaction, $\bar{Z} = (f - 1)/K$, as a basis for such plots. Figures 4 and 5 display the result of plotting $\log Q$ as a function of $\bar{Z}$ for seven $K$ values over the range $+1 > \bar{Z} > -0.6$ and over the range $1.25 > f > 0.30$, respectively. As a consequence, Fig. 4 gives a broader picture of the dependency of $k(a + b) \mathcal{N}_v/2.3$ (the slope) than Fig. 5 which limits the comparison to conditions near equilibrium. The equilibrium condition is represented by $\bar{Z} = 0$ (no reaction) and/or $f = 1.0 \ (x = x_e)$. Table 4A and 4B in the appendix tabulates the numerical values for these plots. Fig. 5 indicates that $\mathcal{N}_v$ is constant for a region of $\bar{Z}$, very near equilibrium.
Fig. 4  PLOT OF EQUATION FOR REACTION A=B: BASED ON 
-0.4 < \( \frac{2}{\sqrt{2}} \frac{(f - 1)}{K} \) < 1.0
Fig. 5  Plot of Equation for Reaction A=B: Based on 1.25 > f > 0.80
However, the broad picture (Fig. 4) shows an appreciable dependency on the variable, \( \theta \), except for an equilibrium constant near one, or less.

The measured slopes from Fig. 5 (conditions near equilibrium) are plotted as a function of the equilibrium constant in Fig. 6. The \( \mathcal{N}_v \) term is always positive because \( \theta \) changes sign with \( \log Q/K \). In the positive \( \theta \) direction, \( k(a + b) \mathcal{N}_v/2.3 \) increases with increasing \( K \). In the negative \( \theta \) direction, \( k(a + b) \mathcal{N}_v/2.3 \) increases less markedly with increasing \( K \). That is, the slopes \( m_{\theta^+} \) and \( m_{\theta^-} \) diverge with increasing equilibrium constant.

**Correlation of the Resistance Term.** The plot shown in Fig. 6 is approximately represented by the linear equation,

\[
k(a + b) \mathcal{N}_v/2.3 = 0.45 K + 0.30, \quad \text{(II-38a)}
\]

which can be rearranged to

\[
(a + b) \mathcal{N}_v/2.3 = 1/k (0.45 K + 0.30).
\]

\[
\text{(II-38b)}
\]

For different chemical reactions having the same equilibrium constant but a different forward rate constant, the \( \mathcal{N}_v \) term varies inversely as the forward rate constant. That is, the notion of \( \mathcal{N}_v \) as a resistance term is still maintained since higher forward rate constants will result in a smaller \( \mathcal{N}_v \) term.

The equilibrium and rate constants can be
FIG. 6  PLOT OF $k(a+b) \frac{N_c}{2.3 R}$ AS A FUNCTION OF THE EQUILIBRIUM CONSTANT
represented by equations of the form,

\[
K = K^0 e^{-\frac{\Delta H}{RT}},
\]

(II-39)

\[
k = k^0 e^{-\frac{\Delta E}{RT}},
\]

(II-40)

where \( K^0 \) and \( k^0 \) refer to the integration constants and \( \Delta H \) and \( \Delta E \) refer to the heat of reaction and the activation energy, respectively. The substitution of these equations into Eq. II-38 results in

\[
(a + b) \mathcal{N}_v / 2.3 = 0.45 \frac{K^0}{k^0} e^{-\frac{(\Delta H - \Delta E)}{RT}} + \frac{0.3 \Delta E}{k^0} e^{\frac{RT}{RT}}. \tag{II-41}
\]

For the sake of an argument, one may suppose that \( \Delta H = \Delta E \). Then, for a specific chemical reaction \( \mathcal{N}_v \) increases as (1) the activation energy is increased and (2) the temperature is lowered. Both cases are explanations for slower rates of reaction and the notion of a resistance is maintained.

Finally, for reactions having the same forward rate constant but different equilibrium constants, the \( \mathcal{N}_v \) term varies directly as the equilibrium constant. Thus, increasing the equilibrium constant results in increasing \( \mathcal{N}_v \). But the equilibrium constant is expressed as the ratio of the forward to backward rate constants. A larger equilibrium constant at constant forward rate constant
implies a smaller backward rate constant. Thus \( \mathcal{N}_v \) varies as the inverse sum of the forward and backward rate constants. The slope term is sensitive to conditions away from equilibrium, particularly where the equilibrium constants is much different than one.

2 \( \text{A} = \text{B} + \text{B}' \) Reaction. A similar treatment can be made for the reaction,

\[
2 \text{A} \xrightleftharpoons[k_1/k_2]{k} \text{B} + \text{B}',
\]

where the same symbols will be used as defined before, except that:

- \( \text{b} \) - concentration of \( \text{B} \) initially equal to concentration of \( \text{B}' \) initially

\[
Q = \frac{2k(f^2 - 1) - (f-1)^2}{4k(2\sqrt{k} + 1)} \quad \text{(defined)}
\]

The following relations are then made available for algebraic manipulations,

\[
K = \frac{k}{k'} = \left[ \frac{(a+2b) - x}{a} \right]^2 / x_e^2,
\]

\[
x_e = \frac{a + 2b}{2 \sqrt{k} + 1},
\]

\[
x = f x_e = \frac{f(a + 2b)}{2 \sqrt{k} + 1}.
\]

The positive square root is chosen for the quadratic solution of Eq. II-43 (Eq. II-44). The usual expression for \( Q \),

\[
Q = \frac{(a + 2b - x)^2}{4x_e^2}, \quad \text{(II-46a)}
\]

can be transformed into

\[
Q = \left[ \frac{2 \sqrt{k} + 1 - f}{2f} \right]^2. \quad \text{(II-46b)}
\]
Likewise, the usual expression for \( \hat{z}_a \),

\[
\hat{z}_a = - \lambda = kx^2 - k' \left[ \frac{a + 2b - x}{2} \right]^2, \tag{II-47a}
\]
can be transformed to

\[
\hat{z}_a = k(a+2b)^2 \left[ \frac{2 \sqrt{K} (r^2-1) - (r-1)^2}{4k(2 \sqrt{K} + 1)} \right], \tag{II-47b}
\]

\[
\hat{z}_a = k(a+2b)^2 \frac{a}{2}. \tag{II-47c}
\]

The relations, Eq. II-46b and Eq. II-47c can be substituted into Eq. II-31, obtaining the analogous form;

\[
\log \left[ \frac{2 - \sqrt{K} + 1 - r}{2r} \right]^2 = \log K - \left[ \frac{k(a+2b)^2 N_v}{2.3} \right] \frac{a}{2}. \tag{II-48}
\]

The plot of this equation for three \( K \) values is shown in Fig. 7. Table 4C in the appendix tabulates the numerical values from which this plot was made. The difference between this reaction and the previous reaction is that the slope terms are more sensitive. That is, the \( N_v \) term could only be considered as relatively constant very near equilibrium.
FIG. 7  PLOT OF EQUATION FOR REACTION 2A=B + B'
Bithermal Processes

General Description. This chapter considers some processes which can, in principle, be well defined under steady state conditions with a temperature gradient. Such processes may be generally typified by the schematic diagram in Fig. 8. The system under consideration is bounded by the solid lines of this diagram. The system, as pictured, is composed of three elements; that is, state 1, state 2, and a gradient region containing the link. Heat, $\dot{q}$, flows into the system from the reservoir at the constant higher temperature, $T_1$, and out of the system into the reservoir at the constant lower temperature, $T_2$. It is tacitly assumed that the link can be adiabatically insulated so that the loss of heat, $\dot{q}'$, from the link is zero. In the general case, states $i$ are changing mass by the steady mass flow rate, $\dot{n}_i$. The steady rate of mass flow involves work at the constant $i$th pressure, that is, the pistons $P_1$ and $P_2$. It is also presumed that the thermal reservoir boundaries can be established ($1'$ and $2'$) so as to effect a gradient region in and near the link such that states 1 and 2 are well defined. Then the energy and mass transport can be considered to be
FIG. 8 SCHEMATIC DIAGRAM FOR A GENERAL STEADY STATE PROCESS INVOLVING THERMAL MIGRATION PHENOMENA, A BITHERMAL PROCESS
occurring across such a gradient region (link), whether it be a capillary, membrane, mixture, etc.

The establishment of a thermal gradient through the connecting link by maintaining the isothermal reservoirs, results in thermal migration phenomena such as transpiration, osmosis, diffusion, etc. Further, such phenomena may be considered to be the result of a bithermal process. At the limit of zero mass flow, heat is still able to flow under a steady state condition. As a consequence, a different approach is required to define a function that possesses a dynamic aspect from a thermodynamic point of view. It is possible to measure the heat flow through the system by utilizing the entropy loss or gain, $S(r)$, of the external heat reservoirs both with and without mass flow. It then becomes possible to define a new function that may approach a finite limit at the limit of zero mass flow. A general treatment for bithermal processes is developed as follows.

**Mathematical Development.** A bithermal process may be considered first to be conducted under the condition that no mass flow is effected across the link. No net P-V work is done, and neglecting other forms of work, the change of energy of the system with respect to time is zero, if the rate of the specific reservoir entropy change at zero mass flow is used as
a measure. Thus, 

$$\sum_i E_i^{(0)} = - \sum_i T_i S_i^{(0)} = 0,$$  

(III-1)

where the subscript, i, refers to the respective heat and/or work reservoir and the superscript, (o), refers to the condition of zero mass flow.

Secondly, this process may be considered to be conducted with a steady rate of mass flow, $\dot{\lambda}_i$. As in the case of the monothermal treatment, the subsystems are assumed to be well defined. Then the rate of change of energy through the system with respect to time can be expressed as the ith mass flow times the ith molar energy, and similarly for the volume transport. The thermal portion of the energy must be represented in terms of the rate of the specific reservoir entropy loss or gain. In equation form,

$$\sum_i E_i^{(\dot{\lambda})} = \sum_i \dot{\lambda}_i E_i = \sum_i T_i S_i^{(\dot{\lambda})} - \sum_i \dot{\lambda}_i P_i \dot{V}_i,$$  

(III-2a)

where the $(\dot{\lambda})$ superscript refers to the condition of a steady mass flow. The thermodynamic definition, $H = E + PV$, can be introduced into the preceding equation for those parts which refer to the system to obtain,

$$\sum_i n_i \dot{w}_i = - \sum_i T_i \dot{S}_i^{(\dot{\lambda})}.$$  

(III-2b)

The summation terms of reservoir entropy at the condition of zero mass flow, Eq. III-1, are equivalent to zero and may be subtracted from the right
side of the preceding equation without disturbing the equality, thus,

$$\sum_i a_i \dot{H}_i = -\sum_i T_i \dot{s}_i^{(A)} + \sum_i T_i \dot{s}_i^{(0)}.$$  

(III-3)

Rearrangement of this equation for a particular system such as was described in Fig. 8 results in

$$\ddot{H}_1 - \ddot{H}_2 = -T_1 \left[ \frac{\dot{s}_1^{(A)} - \dot{s}_1^{(0)}}{a_1} \right] +$$

$$T_2 \left[ \frac{\dot{s}_2^{(A)} - \dot{s}_2^{(0)}}{a_2} \right].$$  

(III-4)

**Process Function Concept.** The entropy difference of the reservoir measured with respect to time at a steady mass flow ($\dot{A}$) and zero mass flow ($\dot{0}$) respectively, can be used to define a new process function as the mass flow approaches zero. In symbolic terms,

$$-(\ddot{s}_i - G_i) = \lim_{\dot{A} \to 0} \left[ \frac{\dot{s}_i^{(A)} - \dot{s}_i^{(0)}}{\dot{A}} \right].$$

(III-5)

The substitution of this definition into Eq. III-4 results in

$$\ddot{H}_1 - \ddot{H}_2 = T_1(\ddot{s}_1 - G_1) -$$

$$T_2(\ddot{s}_2 - G_2).$$  

(III-6)

A generally applicable form of Eq. III-6, using the thermodynamic definition, $\mu = \ddot{H} - T\ddot{S}$, may be
written,

$$\Delta \mu = \mu_1 - \mu_2 = T_2 G_2 -$$

$$T_1 G_1 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (\text{III}-7)$$

This equation applies for a bithermal process such as thermal migration phenomena, where states 1 and 2 are well defined.

The significance of Eq. III-7 lies in the fact that the quantity, $G$, has the appearance of a state property. This equation can be put in many forms for the presentation of experimental data. It is difficult to predict a useful form of presentation without having some knowledge about the dependency of $G$ on state variables and equipment configuration. Most measurements of thermal migration phenomena (as will be discussed later) are restricted to a static, or equilibrium condition with respect to mass transfer. As a consequence, the variation of a specific $G$ term cannot be ascertained with the available data. Experiments could be performed to measure the quotient, as defined by Eq. III-5 in terms of the isothermal reservoir entropy changes, as the mass flow approaches zero. This would resolve the question concerning the value and the variation of a specific $G$ term. Investigators do not report the necessary data and it is only possible to make guesses in an effort to gain more insight. One can show that
functional dependencies are obtained with the available experimental data.

This can be accomplished by defining some type of average of the individual $\mathcal{G}_1$ and $\mathcal{G}_2$ terms, such as

$$\mathcal{G}_{12} = \frac{T_1 \mathcal{G}_1 - T_2 \mathcal{G}_2}{T_1 - T_2}. \quad (\text{III-8})$$

Employing this concept of an "average", Eq. III-7 can be put in a differential form as

$$d(\Delta \mathcal{M}) = d(\mathcal{M}_1 - \mathcal{M}_2)$$
$$= (T_2 - T_1) d \mathcal{G}_{12} + \mathcal{G}_{12} dT_2 - \mathcal{G}_{12} dT_1. \quad (\text{III-9})$$

This equation can be employed as a basic equation for deriving functional dependencies of various "average" $\mathcal{G}$ terms on state variables.

Other Functions. For the sake of completeness, another definition can be introduced at this point, that is

$$-\mathcal{G}^a = \left(\frac{\partial \mathcal{M}_1}{\partial T_1}\right)_2, \quad (\text{III-10a})$$

where the intensive variables at state 2 (or 1) are held constant e.g. $P_2$, $T_2$ (or $P_1$, $T_1$) are constant. Thus,

$$\mathcal{G}^a = \frac{\partial}{\partial T_1} \left[ T_1 \mathcal{G}_1 - T_2 \mathcal{G}_2 \right]$$
$$= \mathcal{G}_1 + T_1 \left( \frac{\partial \mathcal{G}_1}{\partial T_1} \right)_2 - T_2 \left( \frac{\partial \mathcal{G}_2}{\partial T_1} \right)_2. \quad (\text{III-10b})$$
Or, using the average quantity, from Eq. III-8, one obtains,

\[ \mathcal{G}_1^3 = \mathcal{G}_{12} + (T_1 - T_2) \left( \frac{\partial \mathcal{G}_{12}}{\partial T_1} \right)_2 \cdot \]

(III-10c)

The bithermal process function, \( \mathcal{G} \), has the dimensions of entropy. A number of process properties can be deduced on the basis of usual thermodynamic manipulations. Heat capacities and a heat could thus be represented by equations of the sort:

\[ C_{11} = T_1 \left( \frac{\partial \mathcal{G}_1}{\partial T_1} \right)_2 \cdot \]

(III-11)

\[ C_{12} = T_1 \left( \frac{\partial \mathcal{G}_1}{\partial T_2} \right)_1 \cdot \]

(III-12)

\[ Q_1 = T_1 (S_1 - \mathcal{G}_1) \cdot \]

(III-13)

One may operate on the derivative quantity, \( \mathcal{G}^3 \), introduced in Eq. III-10a obtaining the corresponding partial quantities as,

\[ C_{11}^3 = T_1 \left( \frac{\partial \mathcal{G}_1^3}{\partial T_1} \right)_2 \cdot \]

(III-14)

\[ C_{12}^3 = T_1 \left( \frac{\partial \mathcal{G}_1^3}{\partial T_2} \right)_1 \cdot \]

(III-15)

\[ Q_1^3 = T_1 (S_1 - \mathcal{G}_1^3) \cdot \]

(III-16)

Two functions that can be evaluated with some present experimental data are \( \mathcal{G}_1^3 \) and \( \left( \frac{\partial \mathcal{G}_{12}}{\partial T_1} \right)_2 \).

**Thermal Transpiration**

**Process Description.** Thermal transpiration is a bithermal process wherein a steady mass flow could be effected across a capillary connecting link by maintaining the two inter-connected systems (in
different monothermal heat reservoirs) with external work reservoirs (pistons). Typical experimental data are reported on the basis of the static pressure difference that results when two constant volume systems at different temperatures are connected by a small diameter capillary. That is, the static pressure difference (identified as a bitherm) is measured as a function of (1) the absolute pressure of one of the systems, usually that one at the higher temperature and/or (2) the equipment configuration details of the connecting link, such as diameter, type of material, etc. The general character of the result is that the higher temperature, \( T_1 \), system exhibits a higher pressure, \( P_1 \). At low pressures, or where the mean free path of the molecules as predicted by the kinetic theory is large compared to the diameter of the capillary, the measured pressures approach those predicted by the Knudsen equation,

\[
\frac{P_1}{P_2} = \left( \frac{T_1}{T_2} \right)^{1/2}.
\tag{III-17}
\]

As the absolute pressure of the system is increased, this ratio departs from \( \left( \frac{T_1}{T_2} \right)^{1/2} \), until at higher pressures \( \frac{P_1}{P_2} \) is approximately one.

The change in state under consideration for such conditions can be identified as follows, for any gas, \( A \);

\[
A(g, T_1, P_1) \overset{\text{II}}{\rightleftharpoons} A(g, T_2, P_2). \tag{III-18}
\]
Static Conditions. The change in state shown by Eq. III-18 is represented as static equilibrium. It appears that there are no dynamic data available in the literature involving a controlled mass flow. Thus, no attempts can be made to estimate the magnitude and variation of the specific \( G \) quantities as defined by Eq. III-5. It is necessary to apply the lesser approach, that is, calculating some functional dependencies of the "average" quantities as described previously.

Certain conditions can be imposed on the process to provide a basis for preliminary calculations of this sort, such as (A) fixing the temperatures of the subsystems at each end of the capillary, i.e., \( dT_1 = dT_2 = 0 \), (B) fixing the state of one subsystem at either end of the capillary, i.e., \( dT_1 = dP_1 = 0 \) or \( dT_2 = dP_2 = 0 \), and even (C) fixing the temperature and pressure of the subsystems at opposite ends of the capillary, i.e., \( dT_1 = dP_2 = 0 \) or \( dT_2 = dP_1 = 0 \). Conditions (A) and (B) are amenable to the proposed type of analysis. Case (C) is foreign and does not lend itself to interpretation with ordinary data. Therefore it will not be discussed further.

The relation between temperature and pressure that is imposed by Knudsen's equation, Eq. III-17, can be used as a preliminary basis for predicting limiting
values for the $G$ quantities that will be derived in the following section. These results can be compared with the results of such calculations from some available experimental data in the literature. An empirical equation will also be used to explain one anomaly between the treatment of raw data and that predicted by the Knudsen equation. Finally, the heat of transport, $Q^*$, defined by other investigators\textsuperscript{1}, \textsuperscript{21} as,

$$Q^* = q_h - q_1$$

or

$$Q^* = Q - \bar{H}$$

will be expressed in terms of the symbols employed herein.

**Derivation of Relations.** The restriction of condition (A), $dt_1 = dT_2 = 0$, can be imposed on

$$d(M_1 - M_2) = (T_2 - T_1) dG_{12} +$$

$$G_{12}dT_2 - G_{12}dT_1,$$

and differentiation with respect to $P_1$ results in

$$\left(\frac{\partial G_{12}}{\partial P_1}\right)_{T_1, T_2} = \left[\frac{1}{T_2 - T_1}\right]$$

$$\left[\bar{v}_1 - \bar{v}_2 \left(\frac{\partial P_2}{\partial P_1}\right)\right].$$

(III-21a)

Now $\Delta P = P_1 - P_2$, which upon differentiation and rearrangement results in $(\partial P_2/\partial P_1) = 1 - (\partial \Delta P/\partial P_1)$. Substituting this relation into Eq. III-21a gives

$$\left[\frac{\partial G_{12}}{\partial P_1}\right]_{T_1, T_2} = \left[\frac{1}{T_2 - T_1}\right] \left[\bar{v}_{11} - \bar{v}_2 +$$
\[
\bar{v}_2 \left( \frac{\partial \Delta P}{\partial P_1} \right) \] .
\quad (III-21b)

Assuming the ideal gas law, this equation can be re-arranged to:

\[
\frac{1}{R} \left[ \frac{\partial \mathcal{G}_{12}}{\partial P_1} \right]_{T_1, T_2} = \left[ \frac{T_2}{P_2(T_1 - T_2)} \right] \left[ 1 - \frac{T_1 P_2}{T_2 P_1} - \left( \frac{\partial \Delta P}{\partial P_1} \right) \right] .
\quad (III-21c)
\]

The \( \mathcal{G}_{12} \) term can be referred to the entropy change by subtracting the entropy change with respect to \( P_1 \) from the left side of Eq. III-21c and adding \( R/P_1 \) to the right. That is, the equivalent Maxwell's expression, \( (\partial S_1/\partial P_1) = -(\partial v_1/\partial T_1) \), resulting in

\[
\frac{1}{R} \left[ \frac{\partial \left( \mathcal{G}_{12} - S_1 \right)}{\partial P_1} \right]_{T_1, T_2} = \left[ \frac{T_2}{P_2(T_1 - T_2)} \right] \\
\left[ 1 - \frac{P_2}{P_1} - \frac{\partial \Delta P}{\partial P_1} \right] .
\quad (III-21d)
\]

Because thermal transpiration data is found to be most easily presented (in complete form) on a semi-logarithmic plot, this is transformed to

\[
\frac{1}{R} \left[ \frac{\partial \left( \mathcal{G}_{12} - S_1 \right)}{\partial P_1} \right]_{T_1, T_2} = \left[ \frac{T_2}{P_1 P_2(T_1 - T_2)} \right] \\
\left[ \Delta P - \left( \frac{\partial \Delta P}{\partial \ln P_1} \right) \right]_{T_1, T_2} .
\quad (III-21e)
\]

The restriction of condition (B), \( dT_2 = dP_2 = 0 \), can be imposed upon the definition,
It can also be shown that when the Knudsen pressures where $A P$ approaches zero.

One obtains directly, upon rearrangement

$$\ddot{V}_1 \left( \frac{\partial P_1}{\partial T_1} \right)_T = \ddot{S}_1 - G^\delta_1.$$  \hfill (III-22a)

Substituting the ideal gas law relationship for $\ddot{V}_1$ gives

$$\left( \frac{d \ln P_1}{d \ln T_1} \right)_T = \frac{(\ddot{S}_1 - G^\delta_1)}{R}. \hfill (III-22b)$$

The quantities, \( \frac{1}{R} \left[ \frac{\partial}{\partial P_1} \left( G^\delta_1 - S_1 \right) \right] T_1, T_2 \) and \((\ddot{S}_1 - G^\delta_1)^2/R\) may be evaluated under conditions where the Knudsen equation is applicable and at higher pressures where $\Delta P$ approaches zero.

**Knudsen Equation.** It can be shown from the Knudsen equation, Eq. III-1, that

$$\left( \frac{\partial \Delta P}{\partial \ln P_1} \right) = P_1 \left[ 1 - (T_2/T_1)^{1/2} \right] = \Delta P .$$  \hfill (III-23)

Thus, the quantity in Eq. III-21c, $\Delta P = (\partial \Delta P/\partial \ln P_1)$, approaches zero at low pressures where the Knudsen equation holds. The increase of pressure results in a condition where $\Delta P$ and $\partial \Delta P/\partial \ln P_1$ approach zero. Therefore, the function that was determined under condition (A), \( \frac{1}{R} \left[ \frac{\partial}{\partial P_1} \left( G^\delta - S_1 \right) \right] T_1, T_2 \), must approach zero when the Knudsen equation is mathematically exact (at low pressures) and also approach zero at some higher pressure.

It can also be shown that when the Knudsen
The Knudsen equation is applicable, that
\[
\left( \partial \ln \frac{P_1}{\partial \ln T_1} \right)_j = \left( \partial \ln \frac{P_2}{T_2} \right) = 0.5.
\] (III-24)
Since the result of increasing pressure causes \( P_1 \rightarrow P_2 \), this relation approaches zero at higher pressures.

Thus, the relation determined under condition (B), \( (\bar{S}_1 - \rho \gamma_1)/R \) is 0.5 when the Knudsen equation is applicable (at lower pressures) and approaches zero at higher pressures. The limiting values of Eq. III-21e and Eq. III-22b have been established in terms of the Knudsen equation so as to provide a basis for the calculations of the same quantities from some experimental data.

**Argon and Nitrogen Transpiration.** The raw data of Los and Ferguson\(^{14}\) for the thermal transpiration of argon and nitrogen is tabulated on Table 5(A-D) in the appendix. Their measurements of \( P_1 / P_2 \) and \( P_1 \) were made at a constant higher temperature of about 300°K and two lower temperatures of 77.3°K and 193.3°K. Four different capillaries were used simultaneously in the measurements; 0.1065 cm Pyrex, 0.1018 cm Tru Bore, 0.0510 cm Tru Bore, and 0.0487 cm Cu-Ni alloy; designated as \( R_1, R_2, R_3, \) and \( R_4 \) respectively. Their data are shown in Fig. 9 (for argon) and Fig. 10 (for nitrogen). The Knudsen line is indicated as a dotted line on the figures to indicate the departure
(A) $T_1 = 301.2^\circ K, T_2 = 77.3^\circ K$

(B) $T_1 = 300.2^\circ K, T_2 = 193.3^\circ K$

FIG. 9 THERMAL TRANSPIRATION FOR ARGON
(A) $T_1 = 302.4^\circ K$, $T_2 = 77.3^\circ K$

(B) $T_1 = 302.4^\circ K$, $T_2 = 193.3^\circ K$

---

**Fig. 10** THERMAL TRANSPIRATION FOR NITROGEN
from ideality. No measurements of the pressure difference are made below a pressure of about 35 microns. As can be seen in the plot, the departure from the Knudsen equation in this region is small, for all the cases. At about 150 microns, the pressure difference decreases with increasing pressure. Only three pressure differences were reported for the nitrogen transpiration at $T_2 = 193.3^\circ K$.

Also tabulated in Table 5(A-D) in the appendix are the calculated values for the functions,

$$\frac{1}{R} \left[ \delta \left( \bar{G}_{12} - \bar{S}_1 \right)/\delta P_1 \right] \frac{1}{T_1, T_2} \quad \text{and} \quad \left( \bar{S}_1 - \bar{G}_1 \right)/R$$

resulting from the conditions (A) and (B) described previously. The calculation of the former function, involved the measurement of the slope, $\delta \Delta P/\delta \Delta P_1$, directly from Fig. 9 and 10. These slopes were determined at $P_1$ pressures to about 1000 microns and are also included in the tables of the appendix. The result of plotting this function as a function of the higher pressure, $P_1$, is shown in Fig. 11 and 12. At the higher pressures this quantity approaches zero as was anticipated. As the pressure decreases to where the Knudsen equation should be more applicable, there is little tendency for this quantity to approach zero. One concludes that the Knudsen equation is only a limiting case that is never mathematically exact. This will be discussed further in a later section with the
(A) \( T_1 = 301.2^\circ K, T_2 = 77.3^\circ K \)

(B) \( T_1 = 300.2^\circ K, T_2 = 193.3^\circ K \)

FIG. 11 DERIVED QUANTITY AS A FUNCTION OF \( P_1 \) FOR ARGON
\[ T_1 = 302.4^\circ K, \quad T_2 = 77.3^\circ K \]

**Fig. 12** DERIVED QUANTITY AS A FUNCTION OF P₁ FOR NITROGEN

\[ 40 \times \left[ \frac{T}{1_d e/(1 + 2 \cdot C e)} \right] ^{3/4} \]
aid of an empirical equation.

In the calculation of the latter quantity, it was necessary to pick arbitrary $P_{300}$ pressures and determine the corresponding $P_{77}$ and $P_{193}$. This assumes that the $P_{193}-P_{77}$ static equilibrium, if it were measured, would be identical to that determined from $P_{300}-P_{77}$ and $P_{300}-P_{193}$ static equilibrium where $P_{300}$ is the same for the latter determinations. (The subscripts refer to the temperatures of the subsystem).

Fig. 13 displays the result of plotting this quantity as a function of its corresponding pressure. This quantity varies from 0.5 (Knudsen line) to 0 as the pressure reaches about 1000 microns.

The consistency of the corresponding "average" $(\tilde{S}_1 - G_1^3)/R$ quantity is tested by plotting their values against each other as shown in Fig. 14. The character of this plot indicates that the lower temperature $(\tilde{S}_{77} - G_{77}^3)/R$ decreases more rapidly relative to the higher temperature $(\tilde{S}_{300} - G_{300}^3)/R$ as the corresponding pressure is decreased.

**Helium Transpiration.** In Keesom's book$^{15}$, there are published similar thermal transpiration data for helium at a constant higher temperature of 273.1°K and three lower temperatures of 4, 20, and 90°K respectively. A table in his book tabulates $P_1/P_2$ at selected $P_1$ pressures and constant $T_1$.
FIG. 13 DERIVED AVERAGE QUANTITY AS FUNCTION OF CORRESPONDING PRESSURE
FIG. 14

PLOTS OF CORRESPONDING QUANTITIES FOR ARGON
temperature for the three lower temperatures. Table 5(E) in the appendix tabulates his numerical values for a capillary diameter of unity. This data are plotted in Fig. 15 for the three temperatures involved indicating the Knudsen lines as before. The data are similar to the Los and Ferguson data, however, at \( P_1 = 10,000 \) microns the pressure difference was assumed to be exactly zero. Keesom has correlated his data with the aid of an empirical equation over this range.

The quantities,
\[
\frac{1}{R} \left[ \frac{\partial}{\partial (G_{12}-S_1)/P_1} \right] T_1, T_2
\]
and \((S_1 - G_1^3)/R\) were calculated in the fashion as described previously for the Los and Ferguson data. The numerical values of these quantities are tabulated in the table in the appendix. They are plotted in Fig. 16 as a function of the \( P_1 \) pressure. The plots are similar in character to the Los and Ferguson treatment. Fig. 17 displays the corresponding values of the average \((S_1 - G_1^3)/R\) quantities.

**Empirical Treatment.** It is appropriate to indicate limiting values for such quantities on the basis of an empirical equation. An empirical equation for the relation of the \( P_2/P_1 \) pressure ratio of any gas as a function of all the possible variables has been suggested as

\[
\bar{\frac{S_1 - G_1^3}{R}} = \text{function of all variables}
\]
$T_1 = 273.1^oK$

*FIG. 15 THERMAL TRANSPERSION DATA FOR HELIUM*
FIG. 16 DERIVED QUANTITIES AS FUNCTIONS OF $P_1$ FOR HELIUM
FIG. 17 PLOTS OF CORRESPONDING AVERAGE QUANTITIES FOR HELIUM
For the function of Eq. 111-21e:

\[
\frac{P_2}{P_1} = \frac{\alpha_{He}(f \Phi_g X)^2 + \beta_{He}(f \Phi_g X) + \left[\frac{T_2}{T_1}\right]}{\alpha_{He}(f \Phi_g X)^2 + \beta_{He}(f \Phi_g X) + 1} \quad (III-25)
\]

where:

\[
\alpha_{He} = 3.70 \left[1.70 - 2.6 \times 10^{-3}(T_1 - T_2)\right]^{-2}
\]

\[
\beta_{He} = 7.88 \left[1 - (T_2/T_1)^{1/2}\right]
\]

\[
f = 1 \quad (\text{for } < 1 \text{ cm i.d. capillary})
\]

\[
f = 1.22 \quad (\text{for } > 1 \text{ cm i.d. capillary})
\]

\[
X = P_1 d \quad (P_1 \text{ in mm Hg and } d \text{ in mm})
\]

\[
\Phi_g = \text{characteristic constant of any gas referred to helium, } \Phi = 1.00, \text{ as follows,}
\]

\[
\begin{align*}
\text{Ne} & = 1.30 & \text{O}_2 & = 2.87 & \text{Kr} & = 3.90 \\
\text{H}_2 & = 1.44 & \text{CO} & = 3.31 & \text{CO}_2 & = 4.52 \\
\text{A} & = 2.70 & \text{N}_2 & = 3.53 & \text{Xe} & = 6.41
\end{align*}
\]

When the capillary diameter, the particular gas and both temperatures are fixed, this equation reduces to

\[
\frac{P_2}{P_1} = \frac{\alpha P_1^2 + \beta P_1 + (T_2/T_1)^{1/2}}{\alpha P_1^2 + \beta P_1 + 1} \quad (III-26)
\]

where \(\alpha\) and \(\beta\) are new constants as can be seen by the mentioned considerations. With the upper and lower temperature, this is equivalent to condition (A), from which one can derive the following equation for the function of Eq. III-21e:

\[
\frac{1}{R} \left[\frac{-\partial(S_1 - S_{12})}{\partial P_1}\right] = \frac{T_2}{T_1 - T_2} \left[1 - \left(\frac{T_2}{T_1}\right)^{1/2}\right]
\]
As \( P_1 \) approaches zero (or considered negligible with respect to other variables) this equation reduces to

\[
\frac{1}{\mathcal{R}} \left[ \frac{\partial \left( \frac{G}{P_1} \right)}{\partial P_1} \right]_{T_1, T_2} \approx 7.88 \left[ \frac{T_2}{T_1 - T_2} \right]
\]

\[
\left[ 1 - \left( \frac{T_2}{T_1} \right)^{1/2} \right]^2 \left[ \frac{T_2}{T_1} \right]^{1/2}
\]

Thus, this function varies inversely as the cube of the higher pressures.
attempts to derive a similar evaluation for \((\bar{S}_1 - \mathcal{G}^\partial_1)/R\). This quantity appears to be reasonably predictable from the Knudsen equation.

**Heat of Transport.** Finally, it is desired to express the heat of transport, \(Q^*\), as defined by other investigators in terms of the thermodynamic symbols that are employed herein. The manner in which \(Q^*\) is experimentally determined is by the equation

\[
{dP}/{dT} = -\frac{Q^*}{VT} \quad \text{(III-30)}
\]

It was shown previously that the restriction of

\[
dT_2 = dP_2 = 0 \quad \text{upon the definition,}
\]

\[
-\mathcal{G}^\partial_1 = \left(\partial \mu_1 / \partial T_1\right)_2 \quad \text{(III-10a)}
\]

results in

\[
\bar{v}_1 \left(\partial P_1 / \partial T_1\right)_2 = \bar{S}_1 - \mathcal{G}^\partial_1 \quad \text{(III-22a)}
\]

This equation can be rearranged in the following form,

\[
\left(\partial P_1 / \partial T_1\right)_2 = T_1 \left(\bar{S}_1 - \mathcal{G}^\partial_1 \right) / \bar{v}_1 T_1 \quad \text{(III-31)}
\]

Equating the numerators of the right sides of the equivalent expressions, Eq. III-30 and Eq. III-31, the expression of \(Q^*\) in terms of the symbols employed herein is,

\[
Q^* = T_1 \left(\mathcal{G}^\partial_1 - \bar{S}_1 \right) \quad \text{(III-32)}
\]

One can alternately compare Eq. III-19, Eq. III-20 and Eq. III-13,

\[
Q^* = q_{h} - q_{l} \quad \text{(III-19)}
\]

\[
Q^* = Q - \bar{H} \quad \text{(III-20)}
\]
\[ Q^d = T_1 (\bar{S}_1 - G^d_1) \]  

(III-13)

In either case, one concludes that when a heat of transport is zero, the value of \( \bar{S}_1 \) is equal to the value of \( G^d_1 \). It can also be noted that state quantities are implied by the symbols proposed herein.

**Thermal Osmosis**

**Process Description.** Thermal osmosis is a process that is similar to thermal transpiration except that the connecting link is a permeable membrane (Fig. 8). Experiments\(^{18,19,20}\) have been performed wherein the conditions described previously are approximately satisfied. A rubber membrane is usually used as a connecting link and the pressure difference that develops in a constant volume system between states 1 and 2 is measured. The passage of gas is said to take place by the process of solution, and while thermal transpiration generally results in the condition that the higher temperature subsystem exhibits the higher pressure, thermal osmosis exhibits higher pressures at either temperature depending upon the particular gas and membrane that are employed. The investigators interpret their results in terms of a "heat of solution" similar to the "heat of transport" in thermal transpiration. In fact the data are usually represented by an equation of the form\(^{19,20}\),
\[ \ln \frac{P_2}{P_1} = -\frac{Q^*}{RT_1(T_1-1/T_2)}, \quad (\text{III-33}) \]

where \[ Q^* = \Delta H + Q_m^*. \quad (\text{III-34}) \]

The \( Q^* \) is said to be the sum of \( \Delta H \) (heat of solution) and \( Q_m^* \) (heat of transport). Equation III-33 does represent the results over appreciable ranges of temperature and pressure.

The data are not amenable to the type of analysis that was employed for thermal transpiration because of the limited amount of data on pressure bitherms. The data are simply summarized in terms of the "heats".

**Comparison of Symbolism.** The definition of Eq. III-10a

\[ -\mathcal{G}_1^\delta = (\partial \mu / \partial T_1)_2 \quad (\text{III-10a}) \]

can be rearranged to

\[ d \ln P_1 = \frac{T_1 (\bar{S}_1 - \mathcal{G}_1^\delta) \, dT_1}{R T_1^2} = \]

\[ \frac{T_1 (\bar{S}_1 - \mathcal{G}_1^\delta)}{d(1/T_1)}. \quad (\text{III-35}) \]

Comparison of Eq. III-33 and Eq. III-35 show that

\[ Q^* = \Delta H + Q_m^* = < T_x^\delta (\mathcal{G}_x^\delta - \bar{S}_x^\delta) > _{x}, \quad (\text{III-36}) \]

where the subscript \( x \) implies some kind of average value. As before, one concludes that when \( Q^* = 0, \bar{S} = \mathcal{G}^\delta \). The solution of Eq. III-36 for \( \mathcal{G}_x^\delta \) can be expressed
In Table 2.

This process must be treated as a bithermal process similar to that of osmosis and transpiration. This process must be treated as a series of quasi-steady states wherein the conditions or processes are maintained for a sufficiently long time.

\[
\mathcal{G}^d_{Av} = \frac{\mathcal{Q}^*}{T_{Av}} + \overline{S}_{Av},
\]

\[
= \ln \left( \frac{P_2}{P_1} \right) + \overline{S}_{Av}, \quad (III-37a)
\]

or

\[
\mathcal{G}^d_{Av} = \overline{S}_{Av} + \frac{\Delta H}{T_{Av}} + \frac{\mathcal{Q}^*_m}{T_{Av}}. \quad (III-37b)
\]

Some values reported for \( \Delta H, \mathcal{Q}^* \), and \( \mathcal{Q}^*_m \) are shown in Table 2.

**Table 2 - Values of Heats**

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \Delta H )</th>
<th>( \mathcal{Q}^* )</th>
<th>( \mathcal{Q}^*_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-2800</td>
<td>-1800</td>
<td>1000</td>
</tr>
<tr>
<td>N₂</td>
<td>100</td>
<td>-260</td>
<td>-360</td>
</tr>
<tr>
<td>H₂</td>
<td>800</td>
<td>100</td>
<td>-700</td>
</tr>
<tr>
<td>H₂O</td>
<td>-4200</td>
<td>-3400</td>
<td>800</td>
</tr>
</tbody>
</table>

At any given temperature (assuming that the values in Table 2 are accurate indices) it is concluded that the \( \mathcal{G}^d_{Av} - \overline{S}_{Av} \) quantity decreases with respect to increasing molecular complexity and increasing boiling (or melting) points as indicated by the series \( H_2 - N_2 - CO_2 - H_2O \).

**Thermal Diffusion**

**Process Description.** Thermal diffusion is a bithermal process similar to that of osmosis and transpiration. This process must be treated as a series of quasi-steady states wherein the conditions...
of a bithermal process (Fig. 8) are approximately satisfied. The experimental data\textsuperscript{4,22} that are reported consist of the measurement of the concentration gradient that develops in a two component system because of a temperature gradient. In a binary system, the results are reported on the relative separation of the two components in terms of the Soret coefficient which is defined as\textsuperscript{1}

\[ s = -\frac{\partial \log x_1/x_2}{\partial T} = \frac{(Q_1^* - Q_2^*)}{RT^2}, \]

(Ill-38)

where \( x \) refers to the mole fraction and the subscripts refer to each component. The heats of transport, \( Q_i^* \), have been defined by Wirtz\textsuperscript{21,22} as

\[ Q_i^* = q_h - q_l, \]

(Ill-19)

so that a kinetic interpretation of the heat of transport is obtained thusly: a molecule which makes an activated jump between two points in the material require an energy, \( q_l \), for the elongation of its thermal vibration together with an energy, \( q_h \), required for the creation of a "hole". Since the molecule and the "hole" exchange positions at two different temperatures the result is Eq. Ill-19 for the transport heat. Such discussions are apart from thermodynamics. It is to be simply shown that \( Q_i^* \) (whatever it may be) retains its consistency in terms of the symbols employed herein.
Comparison of Symbolism. A general form for the definition made previously, Eq. III-10a may be written,

\[- \mathcal{G}^\delta_i = (\partial \mu_i / \partial T_i)_j. \quad \text{(III-10a)}\]

The problem then involves an appropriate expression for the chemical potential of the ith component where state j is fixed such that differentiation with respect to \( T_i \) can be performed. For an ideal system, the chemical potential of a component i can be written,

\[\mu_i(T,P) = \mu_i^0(T,P) + kT \ln x_i \quad \text{(III-39)}\]

The substitution of Eq. III-39 into Eq. III-10a above, results in the following upon partial differentiation:

\[- \mathcal{G}^\delta_i = R \ln x_i + RT \left( \partial \ln x_i / \partial T_i \right)_j + \]

\[S^0(T, P, x = 1), \quad \text{(III-40a)}\]

which can be arranged in the following form:

\[\left( \partial \ln x_i / \partial T_i \right)_j = - T_i (\mathcal{G}^\delta_i + \]

\[S^0(T, P, x = 1) + R \ln x_i) / RT_i^2. \quad \text{(III-40b)}\]

The latter equation is evidently,

\[\left( \partial \ln x_i / \partial T_i \right)_j = T_i \left( \bar{S}_i - \mathcal{G}^\delta_i \right) / RT_i^2. \quad \text{(III-40c)}\]

Thus, it is seen that the heat of transport, \( Q_i^* \), is related in terms of the symbols employed herein
in the same fashion as that obtained in thermal transpiration and thermal osmosis, that is,

\[ Q_i^* = T_i \left( G_i^\delta - S_i \right) \]  

(III-36)
CHAPTER IV
SUMMARY

General Conclusions. This thesis has shown that quantities can be defined that have a thermodynamic "feel" to processes that are conducted under steady state conditions. These quantities are defined on the time invariant macroscopic properties of a defined system and further, they refer to particular states in a fashion similar to thermodynamic quantities. They may be identified as "process functions" since they relate a process rate to a gradient of thermodynamic potential under the configuration of the specific equipment.

For the monothermal processes (forced vaporization, diffusion and chemical kinetics), a quantity, \( \mathcal{N} \), was developed which has the analogous feel of a resistance to the steady rate of mass flow. Thus, the flow of mass in a steady rate process becomes fixed by an equation of the form,

\[
- \Delta \mu = \mathfrak{M} \left( RT \mathcal{N} \right),
\]

where the gradient of chemical potential, \( -\Delta \mu \), is equal to a steady rate of mass flow, \( \mathfrak{M} \), times a resistance term, \( RT \mathcal{N} \). There is insufficient raw experimental data reported for the rigorous evaluation of such a treatment.

For the bithermal processes (thermal trans-
Monothermal Processes. In the case of forced vaporization, Alty's data were selected as having
suitable experimental conditions for an evaluation of such a treatment. It is found that the $N$ functions decreased with respect to increasing temperature for the water data. This fact supports the notion of resistance, since as the critical temperature is approached there should be no resistance to vaporization. The calculated $N_a$ for the forced vaporization of water in the range of 18-60°C varied from 0.04 to 0.01 sec-cm² per micromole. The value of $N_a$ was correlated to the viscosity ($N_a = 0.031\gamma$) and a dimensional analysis indicated that $N_a$ should be predicted from a combination of variables such as $\gamma/T_k\rho$. These results are inconclusive because of the narrow temperature range for the water experiments.

The carbon tetrachloride data are peculiar, in that through a relatively narrow range of mass flow the calculated $N$ decreased by a factor of about 3. Only one temperature was reported for the forced vaporization of carbon tetrachloride. No combination of thermodynamic or physical properties was found that correlated $N$ values between water and carbon tetrachloride better than viscosity. It is suggested that further study of the process of forced vaporization over a wider range of temperature and closer control of the variables is necessary for
a rigorous evaluation of $\mathcal{N}$ and its associated dependencies.

In the case of diffusion, an analytical correlation between $\mathcal{N}_a$ values and the ordinary diffusion coefficient showed that higher $\mathcal{N}$ values resulted in lower diffusion coefficients, supporting the resistance notion. Furthermore, on a per unit area basis a completely analogous situation to electrical resistivity was identified.

The treatment of chemical reactions as quasi-steady processes required that $\mathcal{N}$ be fixed on the basis of volumetric units since chemical reaction rate is expressed on the basis of the rate of change of concentration. A general solution for $\mathcal{N}_v$ was proposed so that $\mathcal{N}_v$ at equilibrium could be evaluated for any reaction having an equilibrium constant, $K$; a forward kinetic rate constant, $k$; and initial concentrations of reactants and products, $a$ and $b$ respectively. The $\mathcal{N}_v$ term is found to be unique for a reaction and constant very near equilibrium. This term is inversely proportional to the rate constants, thus supporting the notion of a resistance to mass flow. It is extremely sensitive to simple complications in the reactions, such as going from an $A = B$ reaction to a $2A = B + B'$ reaction.

**Bithermal Processes.** It was necessary to
The necessity for a reference state is evident in static equilibrium conditions. Two functions were derived,

\[ \frac{1}{R} \left[ \frac{\partial (\mathcal{G}_{12} - \bar{\mathcal{S}}_1)}{\partial} \right] \frac{T_1 - T_2}{R} \]

thermal transpiration data for helium, nitrogen and argon were used to determine their values. The value of the former quantity was found to increase from zero (at very high pressures) to about 0.003 microns \(^{-1}\) at low pressures. On the basis of the Knudsen equation it should approach the value of zero at low pressure. An empirical equation was used to show it has a limit of about 1 at very low pressures. The latter quantity varies from 0.5 to zero as the pressure is increased as is predicted from the Knudsen equation.

For thermal osmosis and diffusion, no numerical calculations were made. All thermal migration phenomena are interpreted on the basis of heats of transport which are shown to be related to the symbols defined by the equation,

\[ \mathcal{Q}^* = T_i \left( \mathcal{G}_{ij} - \bar{\mathcal{S}}_i \right) \]

The necessity for a reference state is evident in the consideration of such state quantities.
APPENDIX

Table 3 - Summary of Treatment of Alty Data

<table>
<thead>
<tr>
<th>A. Experimental Conditions</th>
<th>Water</th>
<th>Water</th>
<th>Water</th>
<th>Water</th>
<th>near</th>
<th>distant</th>
</tr>
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<td>30</td>
<td>18</td>
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<td>1.6</td>
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<tr>
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<td>313</td>
<td>303</td>
<td>291</td>
<td>275</td>
<td>275</td>
</tr>
<tr>
<td>3. P_l</td>
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<td>31.82</td>
<td>15.48</td>
<td>35.6</td>
<td>35.6</td>
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<td>1.552</td>
<td>1.552</td>
</tr>
<tr>
<td>5. A</td>
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<td>0.84</td>
<td>0.91</td>
<td>0.84</td>
<td>0.89</td>
<td>0.89</td>
</tr>
</tbody>
</table>

B. "Resistance" Treatment

| 1. m                        | 0.00747| 0.01015| 0.01502| 0.0190| 0.0182| 0.00489 |
| 2. N                        | 0.143  | 0.195  | 0.288  | 0.365 | 0.349 | 0.094   |
| 3. \( \mathcal{N} \)        | 0.0172 | 0.0233 | 0.0346 | 0.0437| 0.0418| 0.0112  |
| 4. \( \mathcal{N}_a \)      | 0.0145 | 0.0196 | 0.0314 | 0.0367| 0.0372| 0.0100  |
| 5. T \( \mathcal{N}_a \)     | 4.83   | 6.14   | 9.51   | 11.0  | 10.2  | 2.75    |
| 6. log T \( \mathcal{N}_a \) | 0.685  | 0.790  | 0.979  | 1.04  | 1.01  | 0.44    |

C. Collected Quantities*

| 1. \( \Delta H \)           | 10.14  | 10.34  | 10.43  | 10.55 | 8.01  |
| 2. \( \Delta S \)           | 30.4   | 33.0   | 34.4   | 36.2  | 29.2  |
| 3. T/T_c                    | 0.514  | 0.483  | 0.468  | 0.450 | 0.494 |
| 4. \( \gamma \)             | 66.18  | 69.56  | 71.18  | 73.05 | 29.2  |
| 5. \( \gamma \)             | 0.47   | 0.65   | 0.81   | 1.05  | 1.29  |
| 6. k                        | 0.378  | 0.364  | 0.355  | 0.343 | 0.106 |
| 7. 1/T                       | 0.0030 | 0.0032 | 0.0033 | 0.0034| 0.00364|
| 8. 1/\( \rho \)             | 0.0547 | 0.0552 | 0.0554 | 0.0555| 0.0100|
| 9. \( d \rho /dT \)         | 0.175  | 0.164  | 0.160  | 0.145 | -     |
| 10. 1-(T/T_c)               | 0.486  | 0.517  | 0.532  | 0.550 | 0.506 |

* From: Langes Handbook of Chemistry and Perrys Chemical Engineers Handbook.

** From equilibrium.
Table 4(A) - Term Values For Reaction Type A = B: Based on $1 > 2 > -1$

<table>
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<tr>
<th>$q$</th>
<th>$K = 10$</th>
<th>$K = 3.0$</th>
<th>$K = 1.0$</th>
<th>$K = 0.33$</th>
<th>$K = 0.10$</th>
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<td>(-)</td>
<td>(+)</td>
<td>(-)</td>
<td>(+)</td>
</tr>
<tr>
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<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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Table 4(B) - Term Values For Reaction Type A = B: Based on 1.25 > f > 0.80

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<tr>
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<td>10.55</td>
<td>10.30</td>
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<td>9.46</td>
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<td>1.023</td>
<td>1.013</td>
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<td>0.892</td>
</tr>
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<td>-0.005</td>
<td>-0.0027</td>
<td>0.0027</td>
<td>0.0052</td>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>Q</td>
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<td>1.050</td>
<td>0.946</td>
<td>0.902</td>
<td>0.809</td>
<td>0.600</td>
</tr>
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<td>0.0434</td>
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</tr>
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</tr>
<tr>
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</tr>
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<td>-</td>
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Table 4(C) - Term Values For $2A = B + B'$ Reaction

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<th>log Q</th>
<th>( \bar{Q} )</th>
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Table 5(A) - Thermal Transpiration Data For Argon\(^{14}\), \(T_1 = 301.2^\circ K\), \(T_2 = 77.3^\circ K\)

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<th>(P_{AV}) microns</th>
<th>29.5</th>
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<th>87.3</th>
<th>106.7</th>
<th>161.2</th>
<th>219.6</th>
<th>349.5</th>
<th>602.3</th>
<th>884.1</th>
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<td>12.9</td>
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<td>113.2</td>
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<td>605.2</td>
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<td>886.9</td>
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<tr>
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<td>25.7</td>
<td>27.0</td>
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<tr>
<td>(R_4 = 0.0487) cm</td>
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<td>20.3</td>
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* times 10\(^4\)
Table 5(B) – Thermal Transpiration Data For Argon\(^{14}\), \(T_1 = 300.2^0\text{K}\), \(T_2 = 193.3^0\text{K}\)

<table>
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<th>82.9</th>
<th>138.1</th>
<th>170.1</th>
<th>256.9</th>
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<th>428.2</th>
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<td>1. (\Delta P_1), microns</td>
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<td>6.7</td>
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<td>7.0</td>
<td>6.3</td>
<td>5.8</td>
<td>4.9</td>
<td>3.4</td>
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<td>86.3</td>
<td>141.6</td>
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<td>334.2</td>
<td>430.6</td>
<td>767.7</td>
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<td>79.6</td>
<td>134.6</td>
<td>166.6</td>
<td>253.7</td>
<td>328.4</td>
<td>425.7</td>
<td>764.3</td>
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<td>-</td>
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<td>887.0</td>
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<td>79.4</td>
<td>-</td>
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<td>328.2</td>
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<td>-2.4</td>
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<tr>
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<td>-</td>
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<td>1.4</td>
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<td>9.6</td>
<td>11.4</td>
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<td>-</td>
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<td>14.0</td>
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<td>88.6</td>
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<td>435.2</td>
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<td>162.9</td>
<td>-</td>
<td>323.8</td>
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<td>18</td>
<td>10.5</td>
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<td>4.2</td>
<td>3.2</td>
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</table>

* times 10\(^4\)
Table 5(C) - Thermal Transpiration Data For Nitrogen\textsuperscript{14}, $T_1 = 302.3^\circ K$, $T_2 = 77.3^\circ K$

<table>
<thead>
<tr>
<th>$P_{Av}$, microns</th>
<th>(31.9)</th>
<th>(64.2)</th>
<th>(100.1)</th>
<th>(130.5)</th>
<th>(170.3)</th>
<th>(226.7)</th>
<th>(455.0)</th>
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<th>(1146.5)</th>
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<td>9.6</td>
<td>11.3</td>
<td>11.3</td>
<td>10.9</td>
<td>10.0</td>
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<td>6.1</td>
<td>4.6</td>
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<td>69.8</td>
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<td>135.9</td>
<td>175.3</td>
<td>233.2</td>
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<td>224.2</td>
<td>452.0</td>
<td>651.8</td>
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<td>-2.7</td>
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<td>1.6</td>
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<td>0.17</td>
<td>0.066</td>
<td>0.016</td>
</tr>
<tr>
<td>$R_2 = 0.1018$ cm</td>
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</tr>
<tr>
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<td>9.7</td>
<td>11.6</td>
<td>11.7</td>
<td>11.2</td>
<td>10.6</td>
<td>9.7</td>
<td>6.6</td>
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<tr>
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<td>70.0</td>
<td>106.0</td>
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<td>458.3</td>
<td>657.2</td>
<td>1148</td>
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<tr>
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<td>94.3</td>
<td>124.9</td>
<td>165.0</td>
<td>221.9</td>
<td>451.7</td>
<td>652.0</td>
<td>1145</td>
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<td>1.8</td>
<td>-1.0</td>
<td>-2.6</td>
<td>-3.3</td>
<td>-4.0</td>
<td>-4.3</td>
<td>-3.3</td>
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</tr>
<tr>
<td>5. Eq. III-21e</td>
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<td>8.3</td>
<td>4.4</td>
<td>2.8</td>
<td>1.7</td>
<td>0.92</td>
<td>0.18</td>
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<td>0.016</td>
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<td>$R_3 = 0.0510$ cm</td>
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<tr>
<td>1. $\Delta P$, microns</td>
<td>14.7</td>
<td>19.8</td>
<td>22.7</td>
<td>23.8</td>
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<td>23.1</td>
<td>19.2</td>
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<td>39.3</td>
<td>74.2</td>
<td>111.5</td>
<td>142.4</td>
<td>182.4</td>
<td>238.1</td>
<td>464.6</td>
<td>662.1</td>
<td>1152</td>
</tr>
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<td>24.6</td>
<td>54.4</td>
<td>88.8</td>
<td>118.6</td>
<td>158.2</td>
<td>215.0</td>
<td>445.4</td>
<td>646.0</td>
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<td>8.3</td>
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<td>3.6</td>
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<td>-4.7</td>
<td>-8.5</td>
<td>-9.7</td>
<td>-8.0</td>
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<td>9.8</td>
<td>6.8</td>
<td>4.1</td>
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<td>1.9</td>
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<td>26.7</td>
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<td>21.3</td>
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<td>11.6</td>
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<td>75.0</td>
<td>112.5</td>
<td>144.4</td>
<td>183.7</td>
<td>239.9</td>
<td>465.3</td>
<td>662.6</td>
<td>1152</td>
</tr>
<tr>
<td>3. $P_2$, microns</td>
<td>24.3</td>
<td>53.4</td>
<td>87.6</td>
<td>117.6</td>
<td>157.0</td>
<td>213.6</td>
<td>444.0</td>
<td>645.0</td>
<td>1140</td>
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<td>4.0</td>
<td>0</td>
<td>-4.3</td>
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<td>-11.0</td>
<td>-8.8</td>
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<tr>
<td>5. Eq. III-21e</td>
<td>22.0</td>
<td>10.0</td>
<td>5.7</td>
<td>4.4</td>
<td>3.2</td>
<td>2.1</td>
<td>0.53</td>
<td>0.23</td>
<td>0.054</td>
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</table>

*times \(10^4\)
### Table 5(D) Corresponding Thermal Transpiration Functions For Argon

<table>
<thead>
<tr>
<th>( P_{300} ), microns</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>600</th>
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<tbody>
<tr>
<td>( R_1 = 0.1065 ) cm</td>
<td></td>
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</tr>
<tr>
<td>1. ( P_{193} ), microns</td>
<td>4.00</td>
<td>8.05</td>
<td>16.7</td>
<td>34.9</td>
<td>53.9</td>
<td>93.0</td>
<td>193.0</td>
<td>395.0</td>
<td>596.0</td>
</tr>
<tr>
<td>2. ( P_{77} ), microns</td>
<td>2.53</td>
<td>5.15</td>
<td>12.9</td>
<td>29.6</td>
<td>48.0</td>
<td>87.0</td>
<td>189.0</td>
<td>393.0</td>
<td>594.0</td>
</tr>
<tr>
<td>3. ( \frac{(\mathcal{G}_{\alpha} - S)}{R} )</td>
<td>0.50</td>
<td>0.49</td>
<td>0.41</td>
<td>0.31</td>
<td>0.24</td>
<td>0.15</td>
<td>0.080</td>
<td>0.026</td>
<td>0.016</td>
</tr>
<tr>
<td>4. ( \frac{(\mathcal{G}_{77} - S)}{R} )</td>
<td>0.50</td>
<td>0.48</td>
<td>0.28</td>
<td>0.18</td>
<td>0.13</td>
<td>0.073</td>
<td>0.023</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>( R_2 = 0.1018 ) cm</td>
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<td></td>
</tr>
<tr>
<td>1. ( P_{193} ), microns</td>
<td>4.00</td>
<td>8.05</td>
<td>16.5</td>
<td>34.7</td>
<td>53.8</td>
<td>92.8</td>
<td>193.0</td>
<td>395.0</td>
<td>595.0</td>
</tr>
<tr>
<td>2. ( P_{77} ), microns</td>
<td>2.53</td>
<td>5.15</td>
<td>12.6</td>
<td>29.3</td>
<td>47.7</td>
<td>86.6</td>
<td>188.0</td>
<td>392.0</td>
<td>594.0</td>
</tr>
<tr>
<td>3. ( \frac{(\mathcal{G}_{\alpha} - S)}{R} )</td>
<td>0.50</td>
<td>0.49</td>
<td>0.43</td>
<td>0.32</td>
<td>0.24</td>
<td>0.17</td>
<td>0.080</td>
<td>0.026</td>
<td>0.020</td>
</tr>
<tr>
<td>4. ( \frac{(\mathcal{G}_{77} - S)}{R} )</td>
<td>0.50</td>
<td>0.48</td>
<td>0.29</td>
<td>0.18</td>
<td>0.13</td>
<td>0.076</td>
<td>0.027</td>
<td>0.008</td>
<td>0.003</td>
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<tr>
<td>( R_3 = 0.0510 ) cm</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. ( P_{193} ), microns</td>
<td>4.00</td>
<td>8.05</td>
<td>16.1</td>
<td>33.0</td>
<td>50.7</td>
<td>87.8</td>
<td>185.0</td>
<td>386.0</td>
<td>588.0</td>
</tr>
<tr>
<td>2. ( P_{77} ), microns</td>
<td>2.53</td>
<td>5.15</td>
<td>11.0</td>
<td>25.0</td>
<td>40.8</td>
<td>75.8</td>
<td>173.0</td>
<td>376.0</td>
<td>580.0</td>
</tr>
<tr>
<td>3. ( \frac{(\mathcal{G}_{\alpha} - S)}{R} )</td>
<td>0.50</td>
<td>0.49</td>
<td>0.49</td>
<td>0.44</td>
<td>0.38</td>
<td>0.29</td>
<td>0.18</td>
<td>0.078</td>
<td>0.054</td>
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<tr>
<td>4. ( \frac{(\mathcal{G}_{77} - S)}{R} )</td>
<td>0.50</td>
<td>0.48</td>
<td>0.41</td>
<td>0.30</td>
<td>0.23</td>
<td>0.16</td>
<td>0.074</td>
<td>0.030</td>
<td>0.011</td>
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<tr>
<td>( R_4 = 0.0487 ) cm</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. ( P_{193} ), microns</td>
<td>4.00</td>
<td>8.05</td>
<td>16.1</td>
<td>33.2</td>
<td>49.5</td>
<td>86.5</td>
<td>184.0</td>
<td>384.0</td>
<td>586.0</td>
</tr>
<tr>
<td>2. ( P_{77} ), microns</td>
<td>2.53</td>
<td>5.15</td>
<td>10.4</td>
<td>24.2</td>
<td>39.5</td>
<td>74.4</td>
<td>171.0</td>
<td>374.0</td>
<td>579.0</td>
</tr>
<tr>
<td>3. ( \frac{(\mathcal{G}_{\alpha} - S)}{R} )</td>
<td>0.50</td>
<td>0.49</td>
<td>0.49</td>
<td>0.43</td>
<td>0.43</td>
<td>0.33</td>
<td>0.19</td>
<td>0.093</td>
<td>0.060</td>
</tr>
<tr>
<td>4. ( \frac{(\mathcal{G}_{77} - S)}{R} )</td>
<td>0.50</td>
<td>0.48</td>
<td>0.48</td>
<td>0.34</td>
<td>0.24</td>
<td>0.16</td>
<td>0.082</td>
<td>0.030</td>
<td>0.013</td>
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</table>
Table 5(E) - Summary of Thermal Transpiration For Helium\textsuperscript{15}, $T_1 = 273.1^\circ$K, $R = 1$

<table>
<thead>
<tr>
<th>$P_1$, microns</th>
<th>1.0</th>
<th>10</th>
<th>30</th>
<th>100</th>
<th>300</th>
<th>1000</th>
<th>10,000</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Data:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>A. $T_2 = 4^\circ$K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. $P_1/P_2$</td>
<td>7.587</td>
<td>4.805</td>
<td>2.688</td>
<td>1.710</td>
<td>1.232</td>
<td>1.040</td>
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<tr>
<td>2. $\Delta P$, microns</td>
<td>0.8682</td>
<td>7.902</td>
<td>19.612</td>
<td>41.521</td>
<td>56.15</td>
<td>38.47</td>
<td>0</td>
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<tr>
<td>3. $P_2$, microns</td>
<td>0.1318</td>
<td>2.098</td>
<td>10.388</td>
<td>58.48</td>
<td>243.85</td>
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<tr>
<td>B. $T_2' = 20^\circ$K</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1. $P_1/P_2$</td>
<td>3.596</td>
<td>3.008</td>
<td>2.383</td>
<td>1.637</td>
<td>1.220</td>
<td>1.040</td>
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<td>2. $\Delta P$, microns</td>
<td>0.7219</td>
<td>6.676</td>
<td>17.411</td>
<td>38.913</td>
<td>54.20</td>
<td>38.460</td>
<td>0</td>
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<tr>
<td>3. $P_2$, microns</td>
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<td>3.324</td>
<td>12.589</td>
<td>61.087</td>
<td>246.80</td>
<td>961.54</td>
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<tr>
<td>C. $T_2'' = 90^\circ$K</td>
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<td></td>
</tr>
<tr>
<td>1. $P_1/P_2$</td>
<td>1.730</td>
<td>1.677</td>
<td>1.538</td>
<td>1.340</td>
<td>1.153</td>
<td>1.036</td>
<td>1.000</td>
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<td>0.4220</td>
<td>4.037</td>
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<td>25.373</td>
<td>40.00</td>
<td>34.75</td>
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<td>0.5780</td>
<td>5.963</td>
<td>19.506</td>
<td>74.627</td>
<td>260.0</td>
<td>965.25</td>
<td>10,000</td>
</tr>
</tbody>
</table>

**II. Derived Functions:**

A. Eq. III-21e

| 1. $<A_v>$ | 273:4 | 0.031 | 0.00035 | 0.00034 | 0.41 | 0.412 | 0.693 | 0 |
| 2. $<A_v>$ | 273:20 | 0.047 | 0.0020 | 0.0013 | 0.00025 | 0.460 | 0.550 | 0 |
| 3. $<A_v>$ | 273:90 | -0.047 | -0.0033 | 0.000065 | 0.00022 | 0.430 | 0 |

B. Eq. III-22b

| 1. $(S-\hat{G})/R_{273:90}$ | 0.495 | 0.463 | 0.390 | 0.264 | 0.129 | 0.027 | 0 |
| 2. $(S-\hat{G})/R_{273:20}$ | 0.489 | 0.422 | 0.332 | 0.189 | 0.076 | 0.015 | 0 |
| 3. $(S-\hat{G})/R_{20:4}$ | 0.463 | 0.292 | 0.118 | 0.026 | 0.0074 | 0 | 0 |
| 4. $(S-\hat{G})/R_{90:4}$ | 0.474 | 0.338 | 0.202 | 0.079 | 0.022 | 0.010 | 0 |
| 5. $(S-\hat{G})/R_{90:20}$ | 0.487 | 0.387 | 0.292 | 0.132 | 0.038 | 0.020 | 0 |
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13. Hartley, Trans Far Soc, 27, 10 (1931); 42B, 7 (1946); Phil Mag 12, 473 (1931); Trans Far Soc, 45, 801 (1949).


VITA

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During his undergraduate study at IIT, Mr. Erikson was employed half time as a water chemist at P. E. Madden and Company and later as a plating chemist at the Lake Shore Electrographic Corporation. For the past seven years, he has been employed at the Armour Research Foundation as a Chemical Engineer in the Propellant Section. Much of his work is concerned with the initiation-deflagration-detonation transitions in unstable systems.

Mr. Erikson has published three papers. He is a member of the American Institute of Chemical Engineers, the American Rocket Society and the Alpha Chi Sigma professional fraternity.

Mr. Erikson has been married for 10 years and he is the father of a nine-year-old girl and a five-year-old boy.