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VAPORIZATION PROCESSES IN THE HYPERSONIC LAMINAR BOUNDARY LAYER*

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Abstract—The net aerodynamic heat transfer into the surface of a vaporizing material depends critically on the blocking action due to the thickening of the boundary layer and on the heat absorbing capacity of the chemical species injected into the boundary layer during the vaporization process.

An analysis of the phenomenon of vaporization is presented for hypersonic flight conditions, and numerical solutions are presented for mass transfer at the stagnation point of an axially-symmetric vehicle. These results were obtained by solving the pertinent boundary layer equations for diffusion, convection and thermal exchange, subject to the appropriate physicochemical constraints arising from the kinetics of vaporization.

In addition, a universal solution is given, in terms of the most significant independent parameters, which defines the flight regimes where the vaporization process is diffusion controlled, kinetically limited, or both.

Utilizing the general correlation formula derived herein, one may estimate the rate of vaporization of an arbitrary material, subject to hypersonic flight conditions, provided only that one has an independent knowledge of certain minimum physicochemical data.

Résumé—Le transfert de chaleur aérodynamique à la surface d'un matériau qui se vaporize dépend principalement de l'action de blocage consécutive à l'épaississement de la couche limite et de la capacité thermique des composés chimiques injectés dans la couche limite pendant la vaporisation.

Une analyse du phénomène de vaporisation dans les conditions du vol hypersonique est présentée et des solutions numériques sont données pour le transport de masse au point d'arrêt d'un obstacle de révolution. Ces résultats ont été obtenus en résolvant les équations de la couche limite pour la diffusion, la convection et l'échange thermique, en tenant compte des conditions physico-chimiques particulières imposées par la cinétique de la vaporisation.

De plus, une solution universelle est donnée en fonction des paramétres indépendants le plus significatifs qui définissent les régimes de vol dans lesquels le processus de vaporisation est commandé par la diffusion, limité par la cinétique, ou les deux ensemble.

En se servant de la formule générale établie ici, on peut calculer la fraction vaporisée d'un matériau arbitraire, soumis aux conditions du vol hypersonique, à condition de disposer seulement de la connaissance d'un minimum de données physico-chimiques.

Zusammenfassung—Die aerodynamische Wärmeübertragung auf die Oberfläche eines verdampfenden Stoffes hängt empfindlich von dem Widerstand der anwachsenden Grenzschicht und der Wärmekapazität des Stoffes ab, der während der Verdampfung in die Grenzschicht gelangt. Für Überschallflug wurde der Verdampfungsvorgang untersucht und für die Stoffübertragung am Staupunkt eines axialsymmetrischen Körpers Lösungen mitgeteilt. Die Ergebnisse wurden erhalten durch die Lösung entsprechender Grenzschichtgleichungen für Diffusion, Konvektion und Wärmeaustausch unter Berücksichtigung des physikochemischen Vorgangs, der von der Kinetik der Verdampfung herrührt. Zusätzlich wurde eine allgemeine Lösung angegeben in Ausdrücken der wichtigsten Parameter, welche die Bereiche definiert, in denen der Verdampfungsvorgang durch die Diffusion oder Kinetik oder durch beides begrenzt ist. Die hier abgeleiteten allgemeinen Beziehungen ermöglichen die Abschätzung der Verdampfungsgeschwindigkeit für einen beliebigen Stoff bei Überschallflug, sofern man eine Mindestkenntnis gewisser physikochemischer Daten besitzt.

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Abstract—Конвективный перенос тепла к поверхности испаряющегося материала характеризуется критической зависимостью интенсивности переноса от тормозного действия, связанного с утолщением пограничного слоя, а также теплопоглощающей способностью химических веществ, вводимых в пограничный слой во время процесса испарения.

Анализ процесса испарения проводится для условий сверхзвукового обтекания. Даны численные решения массопереноса в критической точке осесимметричного тела. Эти результаты получены при решении соответствующих уравнений пограничного слоя для диффузии, конвекции и теплообмена, которые подчиняются соответствующим химико-физическим процессам, обусловленным кинетикой испарения.

Кроме того, даётся общее решение, выраженное через важнейшие параметры. Это решение относится к таким режимам обтекания, в которых процессы испарения определяются или диффузией, или кинетикой, или и тем и другим одновременно.

Используя корреляционную формулу, полученную в данной работе, можно вычислить скорость испарения вещества, подвергающегося сверхзвуковому обтеканию, имея определённый минимум физикохимических данных.

INTRODUCTION

In a paper on heat transfer, which considered mass transfer due to vaporization processes, Nusselt [1] credited Stefan with first having recognized the importance of diffusion in problems involving evaporation. Stefan [2] pioneered in the theory of multicomponent diffusion. Hence, at least several of the aerophysical aspects of evaporation and sublimation have been known for approximately 75 years.

Until recently, the major effort in developing the technology of simultaneous vaporization and diffusion processes has come from chemical engineers [3, 4] engaged in the analysis of mass transfer equipment, and from physicists who have been interested in low density gas dynamics [5–7] and interfacial non-equilibria [8, 9, 10]. In many important practical cases, experimental data have been successfully correlated in the form of equations involving the usual dimensionless groups, such as the Reynolds, Schmidt and Prandtl numbers, so that effective working relationships are now available in standard texts [11].

One of the current major technological problems consists in the development of an efficient thermal shield for hypersonic vehicles. A metallic skin which behaves primarily as a heat sink cannot tolerate high heat fluxes, nor can it absorb sustained hypersonic aerodynamic heating. Hence, interest has focused on other forms of heat absorption schemes involving some form of mass transfer from the surface [12–18].

The analysis presented is a general study in which the physicochemical processes in the gaseous boundary layer are considered in detail, and results having wide utility are presented for the phenomenon of stagnation point vaporization in hypersonic flow.

SYMBOLS

$a_{\text{B.L.}}$ = resistance of boundary layer, reciprocal of the right-hand side of equation (52);
$a_{\text{V.M.}}$ = resistance of vaporizing material, $\sqrt{(2\pi R M_k T_i)}/\alpha P \bar{M}$;
A = number of atoms on surface per square centimeter;
$\bar{c}_p$ = $\sum_n C_n (c_p)_n$, frozen specific heat of the mixture;
$(c_p)_n$ = specific heat of the nth species at constant pressure;
C_n = mass fraction of the nth species;
D_{kn} = diffusion coefficient of the kth species;
D_n^T = thermal diffusion coefficient of the nth species;
E_v = activation energy for removing surface atom from the surface;
f = similarity stream function;
F = partition function for the surface molecule in its normal state for all degrees of freedom;
F^* = partition function of the activated complex in the surface layer, after removing term for motion along reaction coordinate;
h = enthalpy including chemical;
$\boldsymbol{h}$ = Planck's constant;

ΔH_{vap} = enthalpy of vaporization;
$\underset{\rightarrow}{j_i}$ = $\rho_i \underset{\rightarrow}{V_i}$;
k = Boltzmann's constant;
K = frozen coefficient of thermal conductivity;
$\boldsymbol{K}$ = equilibrium constant;
l = $\rho\mu/\rho_i\mu_i$
Le = $\rho\bar{c}_p D_{kn}/K$, Lewis number;
Le^T = $\bar{c}_p D_n^T/K$, thermal Lewis number;
$\bar{M}$ = $\sum_n X_n M_n$, mean molecular weight of gas;
M_n = molecular weight of nth species;
$\dot{m}_i$ = interphase mass transfer rate, $(\rho v)_i$;
Pr = $\bar{c}_p\mu/K$, frozen Prandtl number;
P = pressure;
Q = heat transfer;
r_0 = radius of cross-section of body;
R = universal gas constant;
R_B = nose radius of body;
T = temperature;
u = velocity in x-direction;
v = velocity in y-direction;
$\underset{\rightarrow}{v_n}$ = absolute velocity of nth species;
$\underset{\rightarrow}{V_n}$ = diffusion velocity of nth species;
x = co-ordinate along surface of body;
X_n = mole fraction of species n;
y = co-ordinate normal to surface of body;
Ψ = stream function;
α = vaporization coefficient
α_{vap} = vaporization coefficient defined for non-equilibrium vaporization;
Γ = fraction of ablating material which enters the gas phase;
ϵ = emissivity;
η, ξ = similarity variables;
$\theta = T/T_e$ = non-dimensional temperature;
Θ = $\{\bar{c}_p/(\bar{c}_p)_e\}\theta$;
κ = transmission coefficient;
μ = coefficient of viscosity;
τ = $\mu(\partial u/\partial y)$;
ρ = density;
λ = mean free path;
$(du_e/dx)_s$ = $1/R_B\sqrt{\{2(P_e - P_\infty)/\rho_e\}}$, stagnation point velocity gradient.

Subscripts
A = atoms;
e = outer edge of boundary layer;
i = interface;
M = air molecules;
k = vaporizing species;
n = nth species;
s = stagnation point;
η = denotes differentiation with respect to η;
∞ = infinity, upstream of shock;
0 = sea-level standard.

EXAMINATION OF THE PROBLEM

An analysis of surface melting or sublimation requires a detailed consideration of the vaporization processes at the interface between the condensed and gaseous phases. Because of current technological interest, the following discussion is focused upon a hypersonic environment.

Upon exposure to a hypersonic stream, a surface will at first behave as a heat sink until the surface temperature approaches some critical value. Above this temperature, molecular vibrations will be sufficiently violent to cause a considerable number of particles, at favorable sites, to detach from the surface. During the microscopic collison processes which follow, a number of these particles condense on the surface, while others are transported away by convection and diffusion in the fluid stream. The result is a net interphase mass transfer.

Vaporizing species generally are present in maximum concentration at the surface, which acts as a chemical source. The vaporizing species then diffuse into the gaseous boundary layer and are diluted by the main stream components as they are swept downstream by macroscopic convection. When the diffusion thermo-effect is neglected, the driving force for the diffusion process at any point in a boundary layer is related to the local gradient of the partial pressure of the diffusing species. At the surface, therefore, the driving pressure differential is proportional to $(P_k)_i - (P_k)_e$.

During hypersonic flight, the components of dissociated air which enter the outer edge of the boundary layer are generally not the same species as the gaseous products of vaporization. Hence, the partial pressure of the latter species vanishes asymptotically at some finite distance from the surface, which coincides with the outer edge of the diffusion boundary layer unless dissociation of the injected species occurs. Thus, the driving force for the diffusion of each vaporizing species (other than oxygen or nitrogen) is simply the partial pressure of the vaporizing species at the surface $(P_k)_i$, which is related to the mass fraction $(C_k)_i$ by:

$$(C_k)_i = \frac{(P_k)_i\, M_k}{P_e \bar{M}} \tag{1}$$

It is noted that certain materials yield oxygen or nitrogen as vaporization or pyrolysis products, so that when the behavior of these materials is analyzed, additional compatibility equations must be derived at the surface [19]. When pure sublimation occurs (no liquid phase exists), the mathematical solution to the ablation problem consists of the determination of four unknowns: the interface temperature T_i; the interphase mass transfer $\dot{m}_i$; the interphase energy transfer Q_i; and the mass fraction of vaporizing species at the interface $(C_k)_i$.

There are several additional variables when a two-phase boundary layer forms, that is, when the solid melts to form a liquid phase boundary layer, which flows and vaporizes under the influence of the environmental conditions. Analysis indicates [18] that only two non-trivial unknowns are added to the above four required for the solution to the problem. All other variables of interest are derived quantities. The two additional unknowns are the surface viscous shear stress τ_i and the tangential velocity of the interface u_i.

For the gas phase, the six unknowns may be related functionally through the following equations:

$$\dot{m}_i = \dot{m}_i\, [(C_k)_i,\, T_i] \tag{2}$$

$$Q_i = Q_i(T_i,\, \dot{m}_i,\, u_i) \tag{3}$$

$$\tau_i = \tau_i\, (T_i,\, \dot{m}_i,\, u_i) \tag{4}$$

$$(C_k)_i = (C_k)_i\, (T_i,\, \alpha,\, \dot{m}_i) \tag{5}$$

It is noted that for practical materials u_i is generally so small that it has no influence on the solutions to the gas phase boundary layer equations and is merely determined *a posteriori.*

The functional relationships given in equations (3) and (4) represent the dependence of the heat flux and skin friction on the mass transfer rate. These functions are considered at length in reference [17] and will not be discussed here. Relations (2) and (5) depend critically on the physicochemical properties of the vaporizing species. The relationship given by equation (2) can be obtained directly from boundary layer solutions and is derived later, while equation (5) is a boundary condition which must be obtained from a consideration of the chemical kinetics of the vaporization reaction. In a later section it will be shown that kinetic theory yields as the net interphase mass transfer:

$$\dot{m}_i = \frac{\alpha P \bar{M}}{\sqrt{(2\pi R M_k T_i)}}\, \{(C_k)_{\mathrm{eq}} - C_k\}_i \tag{6}$$

and consequently, $(C_k)_i$ must always be smaller than $(C_k)_{\mathrm{eq},i}$ when a finite mass transfer occurs. It is clear then that equation (6) is the specific representation of the functional relationship given by equation (5). It is only when equations (2) and (6) are equated, that one obtains an *a posteriori* knowledge of the deviation of $(C_k)_i$ from $(C_k)_{\mathrm{eq},i}$. Thus, an *a priori* assumption to the effect that $(C_k)_i = (C_k)_{\mathrm{eq},i}$ violates the microscopic condition represented by equation (6). However, it may be considered as a zeroth order approximation which holds for certain restricted conditions. These conditions will, in fact, be determined in a later section, where it will be shown that $(C_k)_i$ may differ appreciably from $(C_k)_{\mathrm{eq},i}$ during high altitude flight.

BOUNDARY LAYER CONSIDERATIONS

It is assumed here that the gas in the hypersonic laminar boundary layer is a ternary mixture of the products of dissociated air and the vaporizing species. Thus, at any point in the fluid, the mean mass motion depends on the contribution of the air atoms A, the air molecules M, and the vaporizing species k. At the surface of the condensed phase, the interphase mass transfer by convection and diffusion in the gas phase is expressed by:

$$\dot{m}_i = (\sum_n \rho_n \underset{\rightarrow}{v_n})_i = (\rho_A \underset{\rightarrow}{v_A} + \rho_M \underset{\rightarrow}{v_M} + \rho_k \underset{\rightarrow}{v_k})_i \tag{7}$$

When the gas phase atom recombination rates are of the same order of magnitude as the rates of diffusion, heterogeneous atom recombination occurs, and the surface then acts as a sink for atoms and as a source of molecules, which requires the mass balance:

$$(\rho_A \underset{\rightarrow}{v_A})_i = -(\rho_M \underset{\rightarrow}{v_M})_i \qquad (8)$$

Introduction of the latter into equation (7) yields the simple result:

$$\dot{m}_i = (\rho_k \underset{\rightarrow}{v_k})_i \qquad (9)$$

Noting that by definition, the summation of the diffusion fluxes is zero, i.e.

$$\sum_n \underset{\rightarrow}{j_n} = \sum_n \rho_n \underset{\rightarrow}{V_n} = 0 \qquad (10)$$

the introduction of the latter into *either* equation (8) or equation (9) followed by rearrangement, yields the identical constraint:

$$\dot{m}_i = (\underset{\rightarrow}{j_k})_i \{1 - (C_k)_i\}^{-1} \qquad (11)$$

The diffusion flux of a particular species depends rigorously upon the concentration gradients of all the species present in the gas. However, for a good first approximation, the diffusion flux of a species present in moderate amount is given by Fick's law, so that:

$$\underset{\rightarrow}{j_k} = -\rho D_{kn} \frac{\partial C_k}{\partial y} \qquad (12)$$

Thus equation (11) becomes:

$$\dot{m}_i = -\left[\rho D_{kn} \frac{\partial C_k}{\partial y} (1 - C_k)^{-1}\right]_i \qquad (13)$$

This expression relates the interphase mass transfer $\dot{m}_i$ to the concentration gradient $(\partial C_k/\partial y)_i$ which depends strongly on the surface concentration $(C_k)_i$; this relationship can be obtained by solving the boundary layer equations.

Conditions in the gas phase are assumed to be quasi-steady, since a transient response in the overall mass transfer rate is dependent primarily on the temperature response of the condensed phase to a particular heating cycle, and not on gas phase processes. It is also assumed that the third species k has the same transport properties as air molecules. For convenience, it is further assumed that the surface is fully catalytic, while gas phase reactions are frozen. Note that it has been shown [13, 16] that the relationship between heat transfer and mass transfer is virtually the same for frozen and equilibrium stagnation point boundary layers, provided only that the surface is fully catalytic.

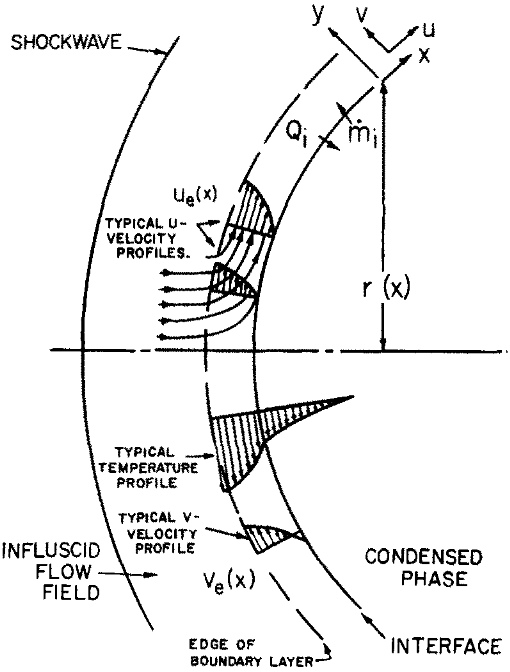

FIG. 1. Co-ordinate system and profiles for vaporizing boundary layer.

The governing equations may then be written for a body-oriented co-ordinate system (see Fig. 1); conservation of atomic species A:

$$\rho u \frac{\partial C_A}{\partial x} + \rho v \frac{\partial C_A}{\partial y} = \frac{\partial}{\partial y}\left(\rho D_{An} \frac{\partial C_A}{\partial y} + \frac{D_A^T}{T} \frac{\partial T}{\partial y}\right) \qquad (14)$$

Conservation of vaporizing species k:

$$\rho u \frac{\partial C_k}{\partial x} + \rho v \frac{\partial C_k}{\partial y} = \frac{\partial}{\partial y}\left(\rho D_{kn} \frac{\partial C_k}{\partial y} + \frac{D_k^T}{T} \frac{\partial T}{\partial y}\right) \qquad (15)$$

where two diffusion equations are required for a three component gas, since the global conservation of mass replaces the third diffusion equation.

Global continuity:

$$\frac{\partial}{\partial x}(\rho u r_0) + \frac{\partial}{\partial y}(\rho v r_0) = 0 \tag{16}$$

Conservation of momentum:

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{\partial P}{\partial x} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right) \tag{17}$$

$$\frac{\partial P}{\partial y} = 0 \tag{18}$$

Conservation of energy:

$$\rho \bar{c}_p \left(u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y}\right) = u \frac{\partial P}{\partial x} + \mu \left(\frac{\partial u}{\partial y}\right)^2 + \frac{\partial}{\partial y}\left(K \frac{\partial T}{\partial y}\right) + \sum_j \left[(c_p)_j \left(\rho D_{jn} \frac{\partial C_j}{\partial y} + \frac{D_j^T}{T} \frac{\partial T}{\partial y}\right)\right] \frac{\partial T}{\partial y} \tag{19}$$

Equation of state:

$$P = \rho \frac{R}{\bar{M}} T \tag{20}$$

where

$$\bar{M} = \sum_n X_n M_n \tag{21}$$

is the mean molecular weight of the gas.

On introducing the following similarity variables which include the Mangler and Dorodnitsyn transformations [20]:

$$\eta = \frac{\rho_e u_e}{\sqrt{(2\xi)}} \int_0^y \frac{\rho}{\rho_e} r_0 \, dy \tag{22}$$

$$\xi = \int_0^x \rho_i \mu_i u_e r_0^2 dx \tag{23}$$

and defining a stream function:

$$\Psi = (2\xi)^{1/2} f(\eta) \tag{24}$$

such that:

$$\rho u r_0 = \frac{\partial \Psi}{\partial y}, \qquad \rho v r_0 = -\frac{\partial \Psi}{\partial x} \tag{25}$$

the boundary layer equations are reduced to ordinary non-linear differential equations at a stagnation point.

The conservation of atomic species may be written:

$$\left\{\frac{l}{Pr} Le \, (C_A)_\eta\right\}_\eta + f (C_A)_\eta = 0 \tag{26}$$

and the conservation of the *k*th species becomes:

$$\left\{\frac{l}{Pr} Le \, (C_k)_\eta\right\}_\eta + f (C_k)_\eta = 0 \tag{27}$$

which implies that thermal diffusion can be neglected in first approximation. The conservation of momentum becomes:

$$(l f_{\eta\eta})_\eta + f f_{\eta\eta} + \tfrac{1}{2}\left(\frac{\rho_e}{\rho} - f_\eta^2\right) = 0 \tag{28}$$

and the dominant terms in the energy equation are:

$$\left(\frac{l \bar{c}_p}{Pr} \theta_\eta\right)_\eta + f \bar{c}_p \theta_\eta = 0 \tag{29}$$

which implies that the conduction and convection terms are more important than the diffusion terms in the frozen energy equation, when the specific heats of the species in the gas are nearly equal.

These equations constitute a coupled ninth-order system of non-linear ordinary differential equations with split boundary conditions, with a functional behavior shown in Fig. 2. However, since it is assumed that the vaporizing species

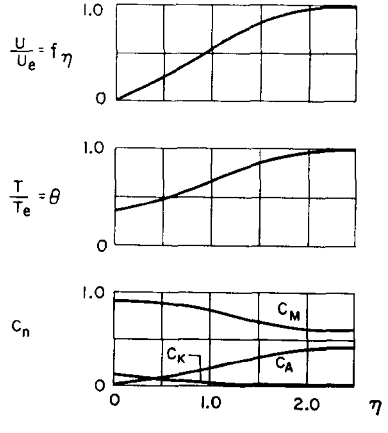

FIG. 2. Gas phase boundary layer profiles.

have the same thermochemical behavior as the air molecules, it is not necessary to consider the diffusion equation for the kth species explicitly during the solution, as demonstrated below. And, it is seen that the system of equations reduces to a set previously solved in a binary mixture analysis [17] (in which the transport and thermodynamic properties of the gas were variable, i.e. they were calculated in terms of the local temperature and composition of the gas).

Before listing the boundary conditions applicable to the analysis of this problem, it will be shown how the dimensionless concentration gradient $(C_k)_{\eta,i}$ may be related to the non-dimensional temperature gradient, $(\theta_\eta)_i$.

Upon defining the function.

$$\Theta = \frac{\bar{c}_p}{(\bar{c}_p)_e}\,\theta \tag{30}$$

and noting that $\bar{c}_p$ is a slowly varying function of η, for moderately high surface temperatures,

$$\Theta_\eta \cong \frac{\bar{c}_p}{(\bar{c}_p)_e}\,\theta\eta \tag{31}$$

and hence equation (29) becomes:

$$\left(\frac{l}{Pr}\,\Theta_\eta\right)_\eta + f\,\Theta_\eta = 0 \tag{32}$$

In order to obtain an equivalent form of the diffusion equation for the kth species, we note that to a very good approximation, the Lewis numbers are nearly unity in which case we may write:

$$\left(\frac{l}{Pr}\,(C_k)_\eta\right)_\eta + f(C_k)_\eta = 0 \tag{33}$$

Since equations (32) and (33) are identical in form, it is only necessary to ensure that they have identical boundary conditions.

At this point, the boundary conditions are:

$$\begin{aligned} \eta = 0:\ C_k(0) &= (C_k)_i \\ \theta(0) &= \theta_i \\ \Theta(0) &= \frac{(\bar{c}_p)_i}{(\bar{c}_p)_e}\,\theta_i = \Theta_i \end{aligned} \tag{34}$$

$$\begin{aligned} \eta = \infty:\ \lim_{\eta\to\infty} C_k &= (C_k)_e \\ \lim_{\eta\to\infty} \theta &= \lim_{\eta\to\infty} \Theta = 1{\cdot}0 \end{aligned} \tag{35}$$

Introducing the new variables:

$$\Theta^* = \Theta - 1 \tag{36}$$

$$C_k = \Theta_i^*\left[1 - \frac{(C_k)_i - C_k}{(C_k)_i - (C_k)_e}\right] \tag{37}$$

we obtain the new boundary conditions:

$$\eta = 0:\quad \Theta^*(0) = \frac{(\bar{c}_p)_i}{(\bar{c}_p)_e}\,\theta_i - 1 = \Theta_i^* \tag{38}$$

$$C_k^*(0) = \Theta_i^*$$

$$\eta = \infty:\quad \lim_{\eta\to\infty} \Theta^* = \lim_{\eta\to\infty} C_k^* = 0 \tag{39}$$

so that the boundary conditions are identical in terms of the new variables, while the differential equations become:

$$\left(\frac{l}{Pr}\,\Theta_\eta^*\right)_\eta + f\,\Theta_\eta^* = 0 \tag{40}$$

$$\left\{\frac{l}{Pr}\,(C_k^*)_\eta\right\}_\eta + f(C_k)_\eta^* = 0 \tag{41}$$

and hence one can now conclude that:

$$\Theta_\eta^* = (C_k)_\eta^* \tag{42}$$

i.e. the two derivatives obey the same equations, and have the same boundary conditions. We are now in a position to determine the eigenvalue $(C_k)_{\eta,i}$ in terms of the temperature gradient $(\theta_\eta)_i$.

Differentiating equation (37) and introducing equation (36) we obtain:

$$(C_k)_\eta^* = \frac{\Theta_i^*}{(C_k)_i - (C_k)_e}\,(C_k)_\eta = \Theta_\eta^* = \Theta_\eta \tag{43}$$

and upon introducing equations (30) and (31) and rearranging equation (43) we find the general relationship between the dimensionless temperature and concentration gradient:

$$(C_k)_\eta = \frac{(C_k)_i - (C_k)_e}{\{\bar{c}_p/(\bar{c}_p)_e\}\,\theta - 1}\,\frac{\bar{c}_p}{(\bar{c}_p)_e}\,\theta_\eta \tag{44}$$

Since the mass fraction of the vaporizing species other than oxygen or nitrogen vanishes at the outer edge of the boundary layer, then by definition $(C_k)_e = 0$, and thus at the wall one obtains for vaporizing species (other than oxygen or nitrogen):

$$(C_k)_{\eta,i} = \frac{(C_k)_i\,(\theta_\eta)_i}{\theta_i - (\bar{c}_p)_e/(\bar{c}_p)_i} \tag{45}$$

Thus, solving the binary mixture equations (26), (28), (29) and obtaining the eigenvalue $(\theta_\eta)_i$ as a function of the flight conditions, the dimensionless wall temperature θ_i, and the dimensionless mass transfer rate $-f_i$, also solves equation (27) implicitly by means of the relationship given in equation (45).

The results obtained are now combined with equation (13). The similarity transformation requires:

$$\left(\frac{\partial}{\partial y}\right)_i = \sqrt{\left\{2\,\frac{\rho_i}{\mu_i}\left(\frac{du_e}{dx}\right)_s\right\}}\left(\frac{\partial}{\partial \eta}\right)_i \tag{46}$$

and equation (13) becomes:

$$\dot{m}_i = -\frac{\sqrt{\{2(\rho_i/\mu_i)(du_e/dx)_s\}}\,\rho_i(D_{kn})_i(C_k)_{\eta,i}}{\{1-(C_k)_i\}} \tag{47}$$

Since $$D_{kn} = \frac{\mu}{\rho}\,\frac{Le}{Pr}$$

equation (47) also may be written:

$$\dot{m}_i = -\sqrt{\left\{2\rho_i\mu_i\left(\frac{du_e}{dx}\right)_s\left(\frac{Le}{Pr}\right)_i\right\}}\,\frac{(C_k)_{\eta,i}}{\{1-(C_k)_i\}} \tag{48}$$

and since the mass transfer rate also may be written in terms of the non-dimensional stream function:

$$\dot{m}_i = -\sqrt{\left\{2\,\rho_i\mu_i\left(\frac{du_e}{dx}\right)_s\right\}}f_i \tag{49}$$

the compatibility condition becomes:

$$\frac{\dot{m}_i}{\sqrt{\{2\,\rho_i\mu_i(du_e/dx)_s\}}} = -f_i = -\frac{(Le/Pr)_i(C_k)_{\eta,i}}{1-(C_k)_i} \tag{50}$$

where $(C_k)_{\eta,i}$ is given by equation (45).

When the correlated eigenvalues and properties [17] are substituted into equation (50) one obtains the typical results shown in Fig. 3.

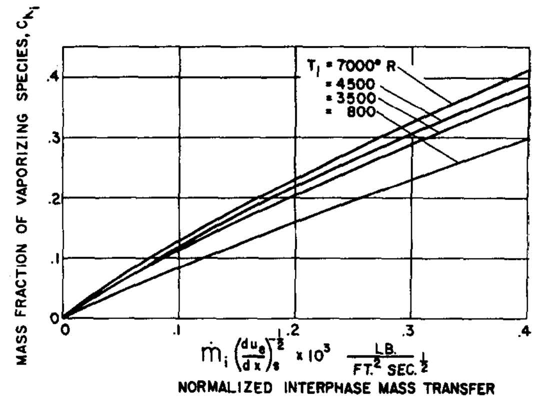

FIG. 3. Mass transfer of vaporizing species at 100,000 ft altitude and Mach No. 20.

Since the normalized interphase mass transfer

$$\dot{m}_i \Big/ \sqrt{\left\{\left(\frac{du_e}{dx}\right)_s\right\}}$$

appears to be almost a linear function of the mass fraction of vaporizing species at the interface, $(C_k)_i$, and since du_e/dx is inversely proportional to the nose radius R_B, this suggests that a useful form for representing all of the data, for the full range of hypersonic flight conditions, is the function $\dot{m}_i\sqrt{(R_B)}/(C_k)_i$.

Results are shown in Fig. 4 for the evaluation of the function $\dot{m}_i\sqrt{(R_B)}/(C_k)_i$ for various flight speeds, altitudes and surface temperatures at a value of $(C_k)_i = 0{\cdot}4$. It is seen that the interphase mass transfer function correlates directly with the boundary layer density. That is, a decrease in altitude (an increase in free stream density), causes a logarithmic increase in $\dot{m}_i\sqrt{(R_B)}/(C_k)_i$. Either an increase in flight speed, or a decrease in wall temperature acts to increase the mass transfer function since the density of the boundary layer rises for each of these effects.

When the results of a large number of individual calculations at various flight speeds, altitudes and wall temperatures are correlated, the result is:

$$\frac{\dot{m}_i}{(C_k)_i}\left[\frac{R_B}{P_\infty/P_0}\right]^{1/2} = 0{\cdot}40 + 0{\cdot}115 \times 10^{-3}(h_e - h_i) \tag{51}$$

when the enthalpies h_e and h_i are expressed in British thermal units per pound, R_B in feet and

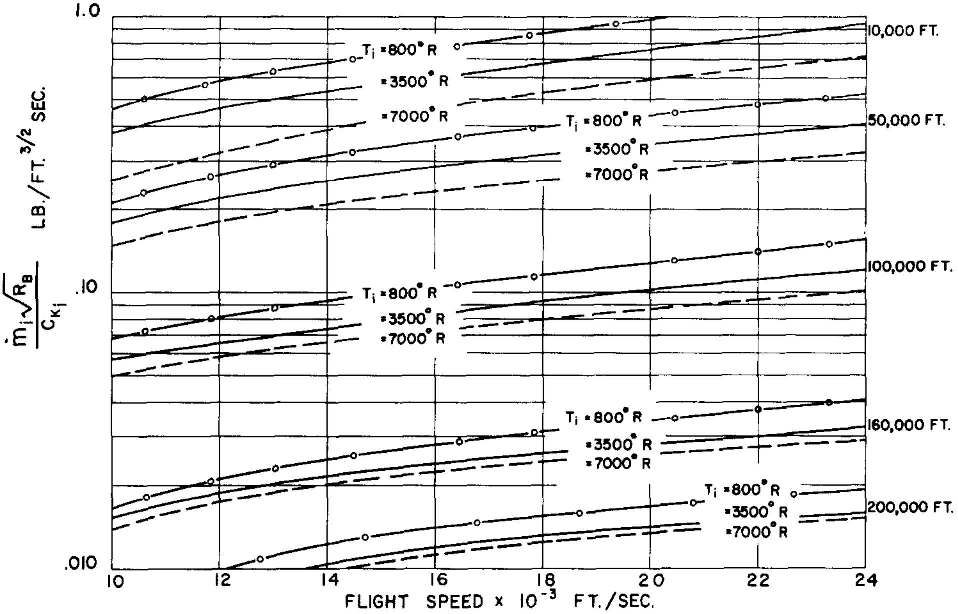

FIG. 4. Mass transfer rate vs. flight speed.

$\dot{m}_i$ in pounds per square feet seconds. Equation (51) represents all of the data within 25 per cent error.

For routine calculation, it is convenient to express the interphase mass transfer function in terms of altitude, flight speed and surface temperature. An equation which represents all of the data within a 15 per cent error may be written as the product of three factors.

$$\frac{\dot{m}_i\sqrt{R_B}}{(C_k)_i} = [1{\cdot}2333 - 6{\cdot}6667 \times 10^{-5}T_i] \times$$
$$\times\ [10^{-(4\cdot3243\ +\ 3\cdot9668\ \times\ 10^{-6}\ \mathrm{Alt.})}] \times \quad (52)$$
$$\times\ [V_\infty{}^{(0\cdot9976\ -\ 1\cdot201\ \times\ 10^{-6}\ \mathrm{Alt.})}]$$

Here T_i is expressed in degrees Rankine, the altitude in feet, the flight speed V_∞ in feet per second and the other symbols have the same dimensions as in equation (51).

Obviously, for best results, the data appearing in Fig. 4 should be used directly.

ANALYSIS OF THE VAPORIZATION PROCESS

A. *Vaporization in equilibrium systems*

1. *General considerations.* In an equilibrium system, the net rate of vaporization is identically zero, and the condensation rate and the forward rate of vaporization must be equal. Furthermore, from statistical theory it may be shown [21], that in a system in chemical equilibrium,

$$\underset{\rightarrow}{(\dot{m}_k)_i} = \underset{\leftarrow}{(\dot{m}_k)_i} = \alpha\,(P_k)_{\mathrm{eq}}\sqrt{\left(\frac{M_k}{2\pi R T_i}\right)} \quad (53)$$

Thus, the forward rate of evaporation for an equilibrium system may be calculated precisely if each quantity appearing in the right-hand side of equation (53) is known.

Most refractory substances yield several different gaseous molecules during vaporization. Carbon, for example, produces the following equally important species [22]:

$$\mathrm{C(s)} \rightleftharpoons \mathrm{C(g)} \quad (54a)$$

$$\mathrm{2C(s)} \rightleftharpoons \mathrm{C_2(g)} \quad (54b)$$

$$\mathrm{3C(s)} \rightleftharpoons \mathrm{C_3(g)} \quad (54c)$$

Different values of M_k, α and $(P_k)_{\mathrm{eq}}$ will be associated with each reaction, so that a different equation (53) must be written for each. In most cases an increase in temperature leads to a more extensive polymerization of the equilibrium vapor [23]. Particular care must be taken therefore in extrapolating low temperature vapor pressure data, because other more complex molecular species, whose presence is not suspected, may become the major constituents of the equilibrium vapor at high surface temperatures.

Let us discuss in greater detail the above three quantities which appear on the right-hand side of equation (53). It is clear that once the vaporizing species has been identified, its molecular weight M_k is immediately known, and hence the molecular weight requires no further discussion.

2. *The evaporation or condensation coefficient.* The evaporation or condensation coefficient α is defined here for an equilibrium system as the fraction of gaseous molecules of species k which condenses on collision with the surface. Obviously α cannot be greater than unity. No general theory has been developed for obtaining the quantity α from fundamental molecular data, and relatively little reliable experimental data have been obtained even for vaporization reactions of the simple type illustrated by equation (55) below.

It might be expected that α is a function of the temperature of the system, of the crystallographic face under consideration, and of its previous history, as well as the vaporization reaction under investigation. In general, however, in many simple vaporizations the average effective value of α lies between 0·1 and 1, and is not affected appreciably by the temperature. Values of α less than 0·1 are observed when considerable molecular rearrangement occurs during the vaporization process. Detailed discussions of the dependence of the α of individual substances on temperature and on the crystallographic face can be found in the literature [24–31].

Finally, it must be pointed out that contamination of the surface, caused either by the presence of impurities within the material or by reaction products from the gas phase, may lead to large decreases in the rate of vaporization [32] and thus to smaller effective values of α.

3. *Simple vaporization reactions.* The simplest class of vaporization reactions is represented by:

$$a\,A\ (\text{condensed}) \rightleftharpoons A_a\ (\text{g}) \qquad (55)$$

where A_a may be any gaseous atomic or molecular species having the same empirical formula as the condensed phase. The reactions given in equations (54) are typical.

For vaporization reactions of the type shown in equation (55), the vapor pressure $(P_k)_{\text{eq}}$ is identical with the equilibrium constant $\boldsymbol{K}$, and $\boldsymbol{K}$ can be calculated directly from fundamental thermodynamic quantities which are generally available.

Familiar substances which boil at moderate temperatures, such as water, nitrogen or mercury, have a $(P_k)_{\text{eq}}$ which is known precisely at all temperatures up to the critical point. On the other hand, the vapor pressure of substances which boil at temperatures higher than 2000°C is subject to uncertainty, particularly if several complex molecular species are important components of the equilibrium vapor as in the case of graphite. For such materials, the probable error in $(P_k)_{\text{eq}}$ is generally no smaller than $\pm$ 20 per cent and may become as great as a factor of 10 [33].

4. *Complex vaporization reactions.* In more complex types of vaporization reactions, the empirical formula of the vapor molecules differs from that of the condensed phase, and a new condensed phase may appear at the interface. In such cases the choice of an appropriate value of $(P_k)_{\text{eq}}$ and of α presents greater difficulties. Two examples of such types of reaction are discussed briefly here.

The first example is characterized by an equation of the form:

$$XY(\text{s}) \rightleftharpoons X(\text{g}) + Y(\text{s}) \cdot \qquad (56)$$

In this type of reaction the equilibrium vapor pressure P_X is again identical with the equilibrium constant $\boldsymbol{K}$, which is again only a function of the temperature. During the course of the vaporization process, however, a layer of Y builds up at the interface, and eventually the net rate of vaporization may become controlled by the rate of diffusion of gaseous X through condensed Y. Great care must be exercised therefore in choosing the value of α, since α will depend on the thickness of the layer of Y and on the diffusion coefficient of X(g) in Y. Illustrative of this type of vaporization reaction are:

$$\mathrm{SiC(s)} \rightleftharpoons \mathrm{C(s)} + \mathrm{Si(g)} \tag{57}$$

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)} \tag{58}$$

The second example is characterized by:

$$XY\mathrm{(s)} \rightleftharpoons X\mathrm{(g)} + Y\mathrm{(g)} \tag{59}$$

which is another commonly encountered type of vaporization reaction. In such cases the equilibrium condition is:

$$P_X P_Y = \boldsymbol{K} \tag{60}$$

If no excess X or Y are present from other sources in the equilibrium gas, then $P_X = P_Y$ and

$$(P_X)_{\mathrm{eq}} = (P_Y)_{\mathrm{eq}} = \sqrt{\boldsymbol{K}} \tag{61}$$

In the more general case, when excess X or Y are present, equation (60) must be utilized since the simplification to (61) does not apply.

In such a case severe difficulties are encountered in determining α. Even when the macroscopic forward rates of vaporization of X and Y are equal, so that no buildup of a new phase is encountered, it is probable that the stoichiometric composition of the surface layer is not identical with the composition of the bulk condensed phase. Thus, the extent and nature of the chemisorbed layer of X and of Y may affect greatly the value of α.

As apparent from equation (60), although the product of $(P_X)_{\mathrm{eq}}$ and $(P_Y)_{\mathrm{eq}}$ is well defined, the individual values of $(P_X)_{\mathrm{eq}}$ and $(P_Y)_{\mathrm{eq}}$ are not, so that equilibrium vapor at any given temperature does not have a definite composition.

The composition of the chemisorbed layer will vary as the ratio of the pressure of X(g) to Y(g) varies from zero to infinity. Therefore, the values of α at any given temperature will vary also with the gas phase composition, and X(g) and Y(g) must have different values of α. In such cases the vaporization coefficient becomes an indeterminate quantity, and this approach is not applicable. A more fruitful approach in this instance is to rely on reaction rate theory, or perhaps use the concept of α which will be introduced as α_{vap}. An example of such a reaction is:

$$\mathrm{MgO(s)} \rightleftharpoons \mathrm{Mg(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \tag{62}$$

B. *Vaporization in non-equilibrium systems*

1. *General considerations.* In general, the net rate of a vaporization reaction is the difference between the rates of the forward and reverse reactions:

$$(\dot{m}_k)_i = \underset{\rightarrow}{(\dot{m}_k)_i} - \underset{\leftarrow}{(\dot{m}_k)_i} \tag{63}$$

The system cannot truly be in equilibrium when net vaporization takes place and thus the rate equations discussed in Section A are not necessarily applicable. Two major assumptions must be made in order to obtain a rate equation during non-equilibrium vaporization:

(a) Not only is the forward rate of vaporization assumed to be independent of the partial pressure of foreign gases, it is also assumed to be independent of the partial pressure of the vaporizing species.

(b) The fraction of incident molecules which condense on colliding with the surface is independent of the partial pressure of foreign components and of the vaporizing species.

As a consequence of assumption (a), the forward rate of vaporization is exactly the same as that obtained during equilibrium vaporization.

$$\underset{\rightarrow}{(\dot{m}_k)_i} = \alpha\,(P_k)_{\mathrm{eq}} \sqrt{\left\{\frac{M_k}{2\pi R T_i}\right\}} \tag{64}$$

where the α appearing in equation (64) is the equilibrium condensation coefficient. In general, the rate of condensation is given by:

$$\underset{\leftarrow}{(\dot{m}_k)_i} = \alpha\,(P_k)_i \sqrt{\left(\frac{M_k}{2\pi R T_i}\right)} \tag{65}$$

where α is the fraction of sticky collisons, and $(P_k)_i$ is evaluated one mean free path from the surface and is not necessarily the equilibrium vapor pressure appearing in equation (53). As a consequence of assumption (b), the α appearing in equation (65) is equal to the equilibrium condensation coefficient, and hence, on substituting equations (64) and (65) into equation (63), the net rate of vaporization is obtained:

$$(\dot{m}_k)_i = \alpha \sqrt{\left(\frac{M_k}{2\pi R T_i}\right)}\,\{(P_k)_{\mathrm{eq}} - P_k\}_i \tag{66}$$

2. *The evaporation or condensation coefficient.* Before proceeding with a discussion of equation

(66), one should consider the errors introduced in the calculated rates of vaporization of non-equilibrium systems by the assumptions that the rate of vaporization and the condensation coefficient α are independent of the gas phase composition.

Attempts have been made in recent years to develop a theory which relates the forward rate of vaporization to the partial pressure of the vapor. This was done by relating the concentration of active sites for the vaporization process to the rate of diffusion of molecules on a surface [34, 35]. Difficulties are encountered in giving an adequate physical description of even an idealized surface, and these theories are still qualitative in nature. For some types of cubic crystals, it has been estimated, for example, that the forward rate of vaporization may vary by a factor of 3 as the partial pressure is varied from zero to the equilibrium pressure [34]. The best experimental work on this subject has been done by Hock and Neumann [26], on single crystals of potassium. In this case a definite dependence on partial pressure has been obtained for both the rate of vaporization and the condensation coefficient. The observed total variation in the rate of vaporization was approximately a factor of 2. No such variation was observed for molten potassium [27]. Less precise experiments indicate that the vaporization rate of other metals has a dependence upon partial pressure which is no larger than that found for potassium. Thus, the errors introduced by the assumptions that the effective condensation coefficient and the rate of vaporization are independent of the partial pressure, are of the same magnitude as those which enter into the determination of α under equilibrium conditions.

In some cases it has been found that the presence of small amounts of some foreign molecular species can lead to a large change in the rate of vaporization, by acting as a catalyst for the vaporization process. This situation is most likely encountered in vaporizations having a low value of α, where there is an appreciable excess activation energy of vaporization so that catalytic effects can become most important. The best known example of this type is the increased rate of vaporization of ammonium chloride in the presence of moisture [36].

3. *Vaporization into a vacuum.* The experimental determination of the net rate of vaporization is generally carried out in a vacuum. Therefore, some authors have found it convenient to define the evaporation coefficient, as the ratio of the experimentally determined net rate of vaporization to the Langmuir expression for the forward rate of vaporization

$$\alpha_{\text{vap}} = \frac{(\dot{m}_k)_i \text{ (vacuum)}}{(P_k)_{\text{eq}} \sqrt{\{M_k/2\pi RT_i\}}} \tag{67}$$

Thus, α_{vap} is intended as a measure of the error in the Langmuir expression

$$(\dot{m}_k)_i = (P_k)_{\text{eq}} \sqrt{\left\{\frac{M_k}{2\pi RT_i}\right\}} \tag{68}$$

Note the tacit assumption by these authors that the forward rate of vaporization and the net rate of vaporization are identical, if the material vaporizes into a vacuum. It is clear that at high rates of vaporization, the vacuum is partially destroyed in the immediate vicinity of the surface so that care must be exercised in the use of equation (67). That is, the reverse reaction (condensation) may not necessarily be negligible.

The subscript "vap" has been added to α in equation (67) to emphasize that this definition of the vaporization coefficient is not necessarily equivalent to the equilibrium condensation coefficient α. It is considered that the use of α, which is rigorously defined for equilibrium vaporization, is preferable to the use of α_{vap} defined for non-equilibrium vaporization, since only for equilibrium vaporization systems is the forward rate of vaporization related unambiguously to the rate of condensation through the equilibrium constant. When α is defined by means of equilibrium vaporization processes, it has physical meaning in that it is the "sticking coefficient" of the equilibrium vapor, whereas α_{vap} is merely a measure of the error in the Langmuir expression and cannot be directly related to the fraction of sticky collisions during non-equilibrium vaporization. While α must lie between zero and unity, α_{vap} can exceed unity. Under the special conditions when the forward rate of vaporization is independent of the partial pressure of the foreign and vaporizing species, α_{vap} and α are identical.

In view of the discussion presented in Section B(1), one may, within the framework of assumptions (a) and (b), use α_{vap} and α interchangeably, although it is clear that both α_{vap} and the "sticking fraction" will actually have some dependence on P_k.

4. *Complex vaporization into a boundary layer.* For net vaporization into a boundary layer, as will be discussed in the following section, the partial pressure P_k, evaluated at one mean free path from the surface, depends partially on the rate of convection and diffusion into the boundary layer.

For simple vaporization reactions no added complications are anticipated. As an example of what may occur in a complex (but not overcomplicated) vaporization reaction, consider equation (59). In the simplest case, already discussed, where no chemical reactions take place to remove either species X or Y from the gas phase and where no X or Y is normally present in the boundary layer, under equilibrium conditions, equation (61) still applies.

If a chemical reaction occurs which consumes either X or Y, or if species X or Y are components of the free stream which enter the boundary layer, the quasi-equilibrium gas composition may exist nevertheless. Hence, equation (60) still is valid, but in such a case $P_X \neq P_Y$ since P_X and P_Y are affected by the presence of the free stream components and the products of reaction. A further relationship between P_X and P_Y can be established by introducing the equilibrium constant of the chemical reaction.

If preferential diffusion occurs due to unequal diffusion coefficients or due to unequal concentration gradients, but if a quasi-equilibrium vaporization process is still assumed, again equation (60) applies while (61) does not. Now, in addition to the equilibrium constants, an added relationship between P_X and P_Y must be sought in the conservation of mass at the interface (chemical source–sink considerations) [19].

Finally, for a non-equilibrium vaporization process, one must have a precise knowledge of the forward rate of vaporization since the process is no longer diffusion controlled.

C. *Summary of available experimental data*

Experimentally determined values of α and α_{vap} are given in Tables 1 and 2 for a number of materials. Since data on the rate of vaporization

Table 1

Substance	Gaseous molecule	α_{vap}	Temperature (°C)	Reference
White phosphorus	P_4	~ 1		[23]
Red phosphorus	P_4	10^{-6}		[23]
Arsenic	As_4	5×10^{-4}		[23]
Iodine	I_2	0·037–0·005	−56–35	[30]
Rhombic sulfur	S_8	0·7	16–32	[24, 25]
Potassium (liquid)	K	1	67–119	[27]
Potassium (solid)	K	1·7–0·9	50–63	[26]
Many metals, solid and liquid	atoms	~ 1		[32, 43]
Graphite	C	0·4	2400	[22]
	C_2	0·3	2400	[22]
	C_3	0·1	2400	[22]
	C_5	$\leqslant 10^{-3}$	2400	[22]
Arsenolite	As_4O_6	~ 1		[46]
Claudetite	As_4O_6	10^{-6}		[46]
Water and ice	H_2O	~ 1		[47]
Potassium chloride	KCl	0·72	407–469	[29]
Potassium perrhenate	$KReO_4$	0·7	780–853	[48]
Many organic acids alcohols and hydrocarbons		0·36–1		[31, 47, 49, 50]

are available only for a limited number of substances (most of which appear in the tables) no effort has been made to select materials of interest for hypersonic flight, and further, no distinction is made between α and α_{vap} in these tables.

Table 2

Substance	Products of vaporization	α_{vap}	T (°C)	Reference
Na_2CO_3	$Na(g) + O_2(g) + CO_2(g) + Na_2O(g)$	0·02	881–1107	[51]
BN	$B(s) + N_2(g)$	$\sim 10^{-4}$		[52]
AlN	$Al(g) + N_2(g)$	$\sim 10^{-4}$		[52]
Mg_3N_2	$Mg(g) + N_2(g)$	"very low"		[53]
NH_4Cl	$NH_3(g) + HCl(g)$	0·003–0·0004	118–221	[28] [54]
TaC	$Ta(l) + C(g)$	~ 1		[54]
WC	$W(l) + C(g)$	~ 1		

The rates of vaporization from which the value of the vaporization coefficient was computed were usually obtained under vacuum conditions, and so are generally α_{vap} for which no attempt has been made to determine the effect of the partial pressure of the vaporizing species. Since α is temperature dependent, the temperature at which the experiments were conducted is listed for most of the substances.

Table 1 lists values of α for simple vaporization reactions of the type illustrated by equation (55). Table 2 deals with complex reactions which are listed individually in the table.

It should be apparent from the scarcity of data that much remains to be done in this field.

D. *Vaporization kinetics*

When adequate data are not available for $(P_k)_{\text{eq}}$ and for α, it becomes necessary to obtain the forward rate of vaporization $\dot{m}_k$ from kinetic expressions containing other molecular parameters. A large number of general expressions have been proposed which require more or less detailed data about the system in question, and which are only partially successful in predicting the few accurately known rates of vaporization. Only the most widely used expressions are given here. The following three equations:

$$(\underset{\rightarrow}{\dot{m}_k})_i = AM_k\nu \exp\left(-\frac{E_v}{RT}\right) \text{ [37, 38]} \quad (69)$$

$$(\underset{\rightarrow}{\dot{m}_k})_i = 2\,AM_k\nu \frac{E_v}{RT} \exp\left(-\frac{E_v}{RT}\right) \text{ [39]} \quad (70)$$

$$(\underset{\rightarrow}{\dot{m}_k})_i = AM_k\kappa \frac{kT}{h} \frac{F^*}{F} \exp\left(-\frac{E_v}{RT}\right) \text{ [40, 41, 42]} \quad (71)$$

all rest on three basic assumptions:

(a) Each molecule at a surface is exactly equivalent to every other, so that any molecule will have an equal probability of vaporizing.

(b) The activation energy of vaporization is equal to the enthalpy of vaporization.

(c) The vaporization reaction is a kinetically simple one-stage reaction.

The first two equations contain other added assumptions and may be considered as special cases of the third one, but they contain fewer parameters and are relatively easy to apply. Generally, they cannot be expected to yield anything more than an estimate of the order of magnitude.

The last expression, given in equation (71), has been used with considerable success to calculate the rate of vaporization of potassium chloride, benzene and sulfur. It is difficult to apply, however, since the partition functions F are sensitive functions of many uncertain parameters. Furthermore, it is difficult to estimate the reliability of the three assumptions mentioned above.

As a consequence of the first assumption all of these equations predict that the forward rate of vaporization is independent of the partial pressure of the foreign components of the vaporizing species. Attempts [34] to refine these models in order to make them consistent with known behavior of surfaces have not yielded any quantitative results as yet.

E. *Conclusions*

It is concluded that the value of the vaporization coefficient may vary over very wide limits, and that it is unsafe to assume that it is close to unity for refractory substances except when dealing with a highly restricted group of substances. In most cases the rate of vaporization may be predicted to within one order of magnitude only when detailed knowledge of the mechanism and the rate of the evaporization process are available.

The following factors tend to favor a large value of α, ($\alpha > 0{\cdot}1$):

(a) The presence of a liquid rather than solid phase.
(b) The necessity of little molecular rearrangement during vaporization.
(c) The absence of impurities at the vaporizing surface.

THE RATE-DETERMINING STEP CONTROLLING MASS TRANSFER

The curves shown in Fig. 5 are helpful in visualizing the effects considered in the preceeding sections. Kinetic theory (equation (6)), predicts that the interphase mass transfer is a decreasing function of the mass fraction of vaporizing species $(C_k)_i$ (evaluated at one mean free path from the surface). Thus, when $(C_k)_i$, is identically equal to $(C_k)_{\text{eq},i}$ the gas is in equilibrium with the surface and the net interphase mass transfer is zero. This is shown in Fig. 5 by the curves labelled "kinetic theory".

Boundary layer theory, equation (51), or equation (52) predicts that the interphase mass transfer is an increasing function of the vaporizing species $(C_k)_i$, which is evaluated at one mean free path from the surface. This result also is shown in Fig. 5 by the curves labelled "boundary layer theory".

In the steady state, the vaporized gas is transported away from the interface by convection and diffusion at a rate equal to the net rate of vaporization. Thus, the intersections of the curves shown in Fig. 5(a) and 5(b) represent the condition of microscopic compatability between kinetic theory and boundary layer theory.

In Fig. 5(a) it is seen that for a given material, at a given surface temperature, the vaporization process will be either diffusion controlled, rate controlled, or in the transition regime between the two, depending upon the slope of the boundary layer theory solution which is a unique function of environmental conditions. In Fig. 5(b), it is seen that, for given conditions, the vaporization process will be again either diffusion controlled, rate controlled, or in the transition regime depending on the slope of the kinetic theory expression, which depends primarily on the magnitude of α.

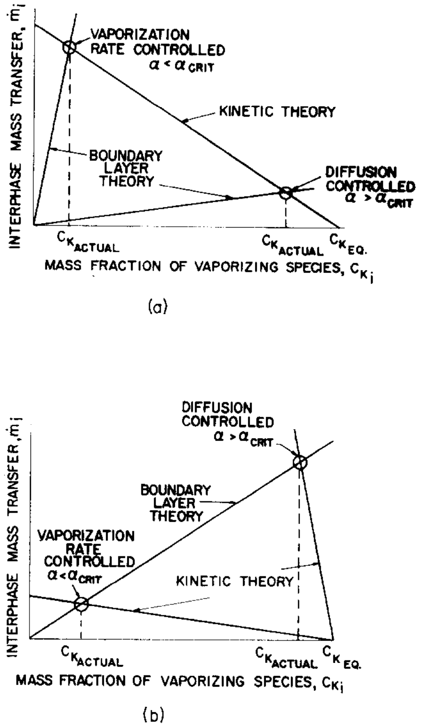

FIG. 5. Relationship between interphase mass transfer and equilibrium mass fraction.
(a) Effect of environment on net rate of vaporization.
(b) Effect of vaporization coefficient on net rate of vaporization.

In either case the magnitude of $(C_k)_i$ obtained at the point of intersection determines whether the slowest, and hence the rate-determining, step of the vaporization process is diffusion or the vaporization rate.

It is perhaps interesting to draw an analogy between the mass transfer process and ohmic flow. One may write the boundary layer solution in the form:

$$(C_k)_i = a_{\text{B.L.}}\, \dot{m}_i \sqrt{R_B} \tag{72}$$

where $a_{\text{B.L.}}$ represents the resistance of the boundary layer to the diffusion and convection of the vaporizing species. Similarly, the kinetic theory expression may be written:

$$(C_k)_i = (C_k)_{\mathrm{eq},i} - a_{\mathrm{V.M.}}\,\dot{m}_i \tag{73}$$

where $a_{\mathrm{V.M.}}$ represents the resistance of the material to the vaporization process. Upon eliminating $(C_k)_i$ between equations (72) and (73), one obtains:

$$(C_k)_{\mathrm{eq},i} = \dot{m}_i\,(a_{\mathrm{B.L.}}\,\sqrt{R_B} + a_{\mathrm{V.M.}}) \tag{74}$$

Equation (74) shows that the boundary layer diffusion and convection process, and the vaporization process may be thought of as two resistances in series. The interphase mass transfer $\dot{m}_i$ is analogous to the current and the equilibrium mass fraction $(C_k)_{\mathrm{eq},i}$ is analogous to the driving force. Then $(C_k)_i$ is the voltage drop due to the boundary layer resistance, and the total resistance is the sum of the two resistances $a_{\mathrm{B.L.}}\sqrt{R_B}$ and $a_{\mathrm{V.M.}}$ The boundary layer resistance, $a_{\mathrm{B.L.}}\sqrt{R_B}$, appears as an increasing function of body size, while the resistance of the material to vaporization, is independent of body size. It is seen also that since the magnitude of $a_{\mathrm{V.M.}}$ is inversely proportional to the vaporization coefficient, the two limiting values of the interphase mass transfer are:

$$\lim_{\alpha \to \infty} \dot{m}_i = \frac{(C_k)_{\mathrm{eq},i}}{a_{\mathrm{B.L.}}\sqrt{R_B}} \tag{75}$$

$$\lim_{\alpha \to 0} \dot{m}_i = \frac{(C_k)_{\mathrm{eq},i}}{a_{\mathrm{V.M.}}} \tag{76}$$

That is, as α approaches infinity, the rate-determining step of the vaporization process is diffusion and convection in the boundary layer. As α approaches zero, the vaporization process becomes kinetically controlled. For intermediate values of α, the overall process is governed by the kinetics of the vaporization process and the resistance of the boundary layer.

The parameter α has been singled out for special attention in equations (75) and (76) because, as shown previously, the vaporization coefficient is generally the most difficult physical quantity to evaluate with sufficient accuracy. While equations (75) and (76) are mathematically correct, it is not necessary to go to the limits zero and infinity, since the process becomes practically diffusion controlled or kinetically controlled for finite values of α. The problem consists of the determination of the conditions which define the two limiting regimes and the transition regime. Therefore, two critical values of α can be defined, one at each end of the transition regime. However, the larger of these is of greater practical interest and will be defined here by the following expression:

$$\begin{cases} \alpha = \alpha_{\mathrm{crit}} \\ (C_k)_i = 0{\cdot}9\,(C_k)_{\mathrm{eq},i} \end{cases} \tag{77}$$

α_{crit} is therefore the value of α for which the resistance of the vaporization process $a_{\mathrm{V.M.}}$ is 10 per cent of the total resistance

$$a_{\mathrm{V.M.}} + a_{\mathrm{B.L.}}\sqrt{R_B}.$$

When $\alpha = \alpha_{\mathrm{crit}}$ it may be assumed that

$$(C_k)_i = (C_k)_{\mathrm{eq},i}$$

without introducing an error greater than 10 per cent in the calculated value of $\dot{m}_i$, and the vaporization process is an "equilibrium" process. For higher values of α, the "equilibrium" assumption will lead to errors smaller than 10 per cent and so if this accuracy is sufficient, the quantity α need not be used for determining the net interphase mass transfer, since equation (52) suffices.

The value of α_{crit} is, of course, a function of the other parameters, which are the precise environmental conditions, the molecular weight of the vaporizing species M_k, the surface temperature T_i, the mean molecular weight of the gas at the surface $\bar{M}_i$ and the geometric scale factor $\sqrt{R_B}$.

It is therefore of considerable interest to determine the value of α_{crit} for various flight conditions as a function of these other parameters. This is done by introducing the relation given in equation (1) into equation (6) and obtaining

$$\dot{m}_i\sqrt{(R_B)} = \left[\frac{\alpha\sqrt{R_B}}{\sqrt{(2\pi R)}}\,\frac{P\bar{M}}{\sqrt{(M_k T)}}\,\{(C_k)_{\mathrm{eq}} - C_k\}\right]_i \tag{78}$$

On letting $\{C_k/(C_k)_{\text{eq}}\}_i = 0{\cdot}9$ and rearranging equation (78), one obtains:

$$(\alpha\sqrt{R_B})_{\text{crit}} = 9\left(\frac{\dot{m}_i\sqrt{(R_B)}}{(C_k)_i}\right)\sqrt{(2\pi R)}\,\frac{\sqrt{(M_kT_i)}}{Pe\bar{M}_i} \quad (79)$$

which is a completely general equation.

If one now selects a particular altitude and flight speed, the value of the stagnation pressure P_e is obtained from normal shock tables for dissociated air, and the value of

$$\{\dot{m}_i\sqrt{(R_B)}/(C_k)_i\}$$

is known from the boundary layer solution presented previously. Thus, a general relationship between $(\alpha\sqrt{R_B})_{\text{crit}}$ and the environmental conditions (altitude and flight speed) can be obtained for any specified value of the mean molecular weight $\bar{M}_i$ and of M_kT_i.

Notice that the value of $\{\dot{m}_i\sqrt{(R_B)}/(C_k)_i\}$ calculated earlier does depend somewhat on $(C_k)_i$ and T_i. This dependence appears to be small, however (see Fig. 3), and is neglected here.

Fig. 6 shows this general relationship graphically, and is a plot of $(\alpha\sqrt{R_B})_{\text{crit}}$ vs. flight altitude. The effect of varying the average molecular weight $\bar{M}_i$, $23 \leqslant \bar{M}_i \leqslant 33$ is shown approximately by the width of the bands shown in Fig. 5. Separate bands are drawn for each of three different values of M_kT_i; these three values were chosen to cover the region of greatest interest where the values of particular interest are usually $5 \leqslant M_k \leqslant 100$, and

$$1000° \leqslant T_i \leqslant 5000°\text{R}.$$

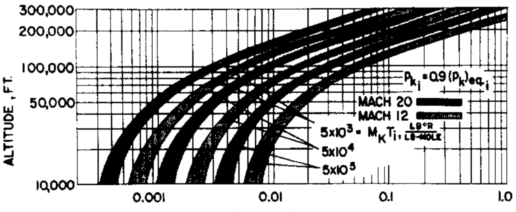

FIG. 6. Critical limit of vaporization coefficient.

Finally, the effect of flight velocity is shown by plotting two bands for each of the three values of M_kT_i, one band being for a Mach number of 12, and the other for a Mach number of 20.

The curves have been plotted for constant M_kT_i and Mach number as a matter of convenience. In considering the behavior of a particular material during the flight of a hypersonic vehicle along a given trajectory, the value of T_i, M_k, $\bar{M}_i$ and the velocity will change with altitude. The time dependent behavior of a single material on a particular flight path will cut across the curves of Fig. 6. These curves show the value of $(\alpha\sqrt{R_B})_{\text{crit}}$ defined by $\{C_k/(C_k)_{\text{eq}}\}_i = 0{\cdot}9$ for the full range of hypersonic flight conditions.

When $\alpha > \alpha_{\text{crit}}$, $\{C_k/(C_k)_{\text{eq}}\}_i > 0{\cdot}9$, and the vaporization may be considered to be "equilibrium" vaporization since the process is diffusion controlled. When $0{\cdot}012\ \alpha_{\text{crit}} < \alpha < 0{\cdot}9\ \alpha_{\text{crit}}$, then $0{\cdot}1 < \{C_k/(C_k)_{\text{eq}}\}_i < 0{\cdot}9$, and the net rate of vaporization is determined both by diffusion and by the kinetics of the vaporization process, and the value of α must appear explicity in the equations.

When $\alpha < 0{\cdot}012\ \alpha_{\text{crit}}$, then

$$\{C_k/(C_k)_{\text{eq}}\}_i < 0{\cdot}1$$

and the boundary layer resistance can be neglected with respect to the material resistance and the net rate of vaporization may be considered equal to the forward rate of vaporization:

$$\dot{m}_i = \frac{\alpha p\bar{M}}{\sqrt{(2\pi RM_kT_i)}}(C_k)_{\text{eq},i} \quad (80)$$

An approximate formal expression for the curves shown in Fig. 6 is obtained as follows:

The introduction of equation (48), followed by some dimensional analysis shows that $(\alpha\sqrt{R_B})_{\text{crit}}$ varies inversely as the Schmidt number, inversely as the square root of the stagnation pressure, directly as the square root of M_kT_i, and directly as the fourth root of the stagnation temperature,

$$(\alpha\sqrt{R_B})_{\text{crit}} \sim \left(\frac{Le}{Pr}\right)_i\sqrt{\left(\frac{M_kT_i}{P_e}\right)}\,(T_e)^{1/4} \quad (81)$$

One can anticipate, as verified by the results shown in Fig. 6 that the region is which $(C_k)_i$ deviates from $(C_k)_{\text{eq},i}$ is one in which the stagnation pressure is low and the product

M_kT_i is large. Thus, at low altitudes—10,000 ft or less—for instance, the ratio $\{C_k/(C_k)_{eq}\}_i$ deviates from unity only for very low flight speeds and very large values of M_kT_i. At higher altitudes, this ratio may deviate from unity even at higher flight speeds (Mach number ~ 20). Notice that if the nose radius is small, this also will increase the tendency for the ratio $\{C_k/(C_k)_{eq}\}_i$ to deviate from unity. The ratio $(Le/Pr)_i$ has been evaluated as a function of flight conditions, using the properties of dissociated air, for which the ratio is of the order of 2. Actually, this ratio depends critically on the molecular weight of the injected species. For light particles, i.e. $M_k \sim 5$, the ratio $(Le_k/Pr)_i$ can exceed 5: however, this effect is minimized by the reduction in M_kT_i. Since the curves shown in Fig. 4 were determined using the transport properties of dissociated air, which ignores the effect of foreign gases, an additional correction for extremely light or heavy gases would involve multiplying α_{crit} obtained from Fig. 6 by the ratio $(Le_k/Le_{\text{air}})_i$.

An analysis has recently been performed in which the relationship between the interphase mass transfer and the vaporization coefficient has been established for the non-equilibrium vaporization of a refractory oxide at high altitude [55]. The dependence of the effective mass fraction at the surface upon $\alpha\sqrt{R_B}$ is shown in Fig. 7. Note that three vaporization regimes are clearly demarcated, which are the specific representation of Fig. 5(b).

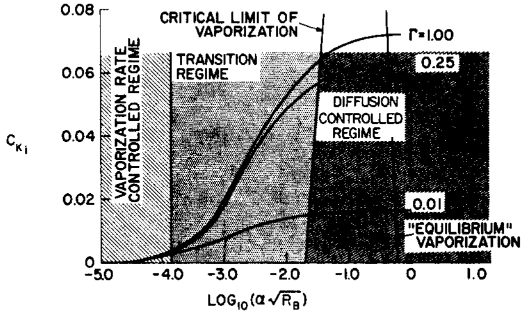

FIG. 7. Dependence of the non-equilibrium mass fraction of injected species upon the vaporization coefficient.

Altitude = 200,000 ft $P_e/P_0 = 0{\cdot}192$

V_∞ = 23,600 ft/sec $\epsilon_i/R_B = 0{\cdot}50\ \text{ft}^{1/2}$

CONCLUSIONS

When a material is subjected to severe heating conditions, the net rate of interphase mass transfer during vaporization may be diffusion controlled, kinetically limited or both, depending on the magnitude of the vaporization coefficient α.

The flight regimes where the vaporization process is diffusion controlled, kinetically limited or both, are defined by a universal solution, utilizing the most significant independent parameters.

One may estimate the rate of vaporization of an arbitrary material, subject to hypersonic flight conditions, utilizing the numerical solutions or the general correlation formula derived herein (provided only that one has an independent knowledge of certain minimum physicochemical data).

In addition, an extensive summary is given of the available experimental data regarding forward rates of vaporization.

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