

THE THERMODYNAMICS OF ABLATION

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Introduction

The rate of heat transfer between fluids and solid bodies at high temperature and high heat fluxes usually depends not only on the transport properties, heat flux, initial temperature of the system, and flow conditions, but also on any combination of the following processes: sublimation, fusion, vaporization, chemical reactions at the interfaces, decomposition of the solid body below the surface, and the flow behavior of any liquid or glass film which may exist or be formed during the heating process. The prime example illustrating all these processes, and one involving all these factors is that of ablative cooling. This phenomenon will be discussed with the idea of illustrating the type of transport and thermodynamic data required for determining the rate of ablation of a given system as a function of heat flux.

In outlining the problem we will assume that a heat flux is flowing across a gas boundary layer to the surface of the solid body. The origin of this heat flux may be aerodynamic heating as in the case of a nose cone, or it may be due to the presence of a preheated flowing stream as in the case of a rocket nozzle. Figure 1 illustrates the system being considered. This system has been treated in various degrees of generality by Scala (1), Sutton (2), Sutton and Scala (3), Lees (4), Adams and Bethe (5). Our discussion will be limited to a review of their results. The most general problem involves two fluid boundary layers (see figure 1): the gas-solid (or gas-liquid) layer and the liquid-solid layer. The best way to treat the problem is to separate the interaction of the two interfaces. Relations as expressed in equations 1 to 5 are the same for both the gas-solid and the gas-liquid layers and may be applied to either, but for purposes of discussion we will consider them only as they apply to the interaction of the gas-solid interface. The equations are first listed and then a discussion is given of the techniques for evaluating the quantities necessary to solve the problem.

The Gas-Solid Interface

Gas-Solid Interactions

Equation 1 represents the conservation of specie, 1, in a system of n species and for which n-1 such equations are required.

$$\rho u \frac{\partial c_i}{\partial x} + \rho v \frac{\partial c_i}{\partial y} = \frac{\partial}{\partial y} \left(\rho D_{i1} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) + w_i \quad (1)$$

where

- c_i = mass fraction of species.
- ρ = density.
- u = x component of gas velocity (see figure 1).
- v = y component of gas velocity (see figure 1).

$\rho u \frac{\partial c_i}{\partial x}$ = convective concentration change in the x direction.

$\rho v \frac{\partial c_i}{\partial y}$ = convective concentration change in the y direction.

$\frac{\partial}{\partial y} \left(\rho D_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right)$ = concentration changes due to normal and thermal diffusion, respectively.

D_{ij} = binary diffusion coefficient.

D_i^T = thermal diffusion coefficient.

W_i = rate of change of concentration of specie, i, due to chemical reaction.

Mass continuity is expressed by

$$\frac{\partial}{\partial x} (\rho u r_0^n) + \frac{\partial}{\partial y} (\rho v r_0^n) = 0 \quad (2)$$

which states that the total mass is conserved.

Equations 3 and 4 represent the conservation of momentum

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial v}{\partial y} = - \frac{\partial P}{\partial x} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (3)$$

$$\frac{\partial P}{\partial y} = 0 \quad (4)$$

where

$\rho u \frac{\partial u}{\partial x}$ = convective change in momentum in the x direction.

$\rho v \frac{\partial v}{\partial y}$ = convective change in momentum in the y direction.

$\frac{\partial P}{\partial x}$ = pressure gradient in the x direction.

$$\frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) = \text{effect of viscosity on the momentum.}$$

Equation 5 represents the conservation of energy.

$$\begin{aligned} \bar{c}_p \left(\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial y} \right) = & u \frac{\partial P}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 + \frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) \\ & - \sum_i w_i h_i + \sum (c_p)_i \left(\rho D_{i1} \frac{\partial c_i}{\partial y} + D_i^T \frac{\partial T}{\partial y} \right) \frac{\partial T}{\partial y} \quad (5) \end{aligned}$$

where

$$\bar{c}_p = \sum_i c_i (c_p)_i \text{ or the mean heat capacity.}$$

$$(c_p)_i = \left(\frac{\partial h_i}{\partial T} \right)_p \text{ or the heat capacity of specie, } i.$$

$$\bar{c}_p \left(\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial y} \right) = \text{convective heat transfer.}$$

$$h_i = \text{enthalpy of specie, } i.$$

$$u \frac{\partial P}{\partial x} = \text{change in kinetic energy due to pressure gradient.}$$

$$\mu \left(\frac{\partial u}{\partial y} \right)^2 = \text{change in kinetic energy due to viscous loss.}$$

$$\frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) = \text{change in energy due to heat conduction.}$$

$$\sum_i w_i h_i = \text{total heat evolved by chemical reaction.}$$

$$\sum_i (c_p)_i \left(\rho D_{i1} \frac{\partial c_i}{\partial x} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \frac{\partial T}{\partial y} = \text{energy transfer due to both normal and thermal diffusion.}$$

Behavior of the boundary layer is specified by the equation of state, assumed here to be the perfect gas law

$$P = \frac{\rho RT}{\bar{M}} \quad (6)$$

$$\bar{M} = \sum_i x_i M_i \quad (7)$$

where

- P = pressure.
- R = gas constant.
- \bar{M} = mean molecular weight of the boundary layer.
- x_i = mole fraction of specie, i.
- M_i = molecular weight of specie, i.

The Binary Transport Coefficients

Note that the quantities necessary to complete the expression for equation 1 were the rate of reaction, W_i , and the diffusion coefficients, D_{ij} and D_i^T . We shall first discuss the evaluation of D_{ij} from available data. The expression for D_{ij} is given by

$$[D_{ij}]_i = \frac{B \left[\frac{T^3 (M_i + M_j)}{2 M_i M_j} \right]^{1/2}}{P \sigma_{ij}^2 \Omega_{ij}^{(1,1)}(T_{ij}^*)} \quad (8)$$

where

- B = a constant dependent only on force laws assumed.
- $\Omega_{ij}^{(1,1)}$ = a function of collision integrals (tabulated in reference 6) for various potential energy functions.
- $T^* = kT / \epsilon_{ij}$.

σ_{ij} and $\epsilon_{ij}/k = V_{(r)}$ = characteristic constants of the potential energy function,

The potential energy function, $V_{(r)}$, describes the molecular interaction as a function of the distance of separation, r , between two molecules and is most commonly expressed by

$$V_{(r)} = 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (9)$$

where

$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$, and σ_i and σ_j are the cross sections for the molecules, i and j, respectively.

Contrails

$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ and ϵ_i and ϵ_j are the root mean values of the depths of the potential wells for i and j, respectively.

In a multicomponent system containing molecules other than i and j, the binary diffusion coefficient is written as $[D_{ij}]$ and is obtained from D_{ij} as shown in reference 6. Frequently, however, D_{ij} itself, is a good approximation for $[D_{ij}]$ for each pair of molecules. In the absence of the required σ and ϵ , these constants can best be evaluated from the variation of viscosity with temperature or from Joule-Thompson coefficients (6).

Inasmuch as the transport coefficients are interdependent, they will be treated together although they appear scattered through all of the foregoing equations. The binary viscosity coefficient is related to D_{ij} by the following relation:

$$[\mu_{ij}]_i = \frac{5}{3} \left(\frac{M_i M_j}{M_i + M_j} \right) \frac{P [D_{ij}]}{A_{12}^* R T} \quad (10)$$

The binary viscosity coefficient in a multicomponent system, $[\mu_{ij}]$, can be evaluated from μ_{ij} by the method described in reference 6. The coefficient of binary thermal conductivity, $[K_{ij}]$, is approximated by

$$[K_{ij}]_i = \frac{25}{8} P \frac{[D_{ij}]_i}{T A_{12}^*} \quad (11)$$

A^* is approximately unity in both equation 10 and 11. All terms have now been defined.

From the above expression we can now evaluate the thermal diffusion coefficient from equations 12 and 13.

$$[d_T]_i = \frac{\rho}{n^2 m_i m_j} \frac{[D_i^T]_i}{[D_{ij}]_i} \quad (12)$$

$$[d_T]_i = \frac{X_i X_j}{6 [K_{ij}]_i} \frac{S_{X_i}^{(i)} - S_{X_j}^{(j)}}{Y_k + X_k} (6 C_{ij}^* - 5) \quad (13)$$

where

- n = number of molecules per cubic centimeter.
- m_i and m_j = mass of molecules, i and j, respectively, in grams per molecule.
- X_i and X_j = mole fractions of i and j, respectively.
- $S_{X_i}^{(i)}$ and $S_{X_j}^{(j)}$ = functions of thermal conductivities and molecular weights.
- C_{ij}^* = ratio of collision integral, which is approximately equal to unity.
- Y_k and X_k = functions of thermal conductivities and mole fractions.

The $[K_{ij}]_i$ is the thermal conductivity to a first degree of approximation as given by Hirschfelder (10).

From the foregoing discussion it is apparent that a knowledge of viscosity coefficients and the potential function for the molecular interaction leads to the evaluation of the

transport properties. Unfortunately, the situation in actual practice is not so simple. Viscosity coefficients have been measured only for readily available compounds and these only at moderate temperatures. For refractory oxides in the gaseous state, the only recourse would be to actual (and difficult!) experimentation or estimation from kinetic hard sphere theory. Even for such simple gases like air, experimental data is lacking.

The Term W_i

The rate of production of specie, i , in any given volume can be generally written as

$$W_i = \sum_{\ell} A_{\ell} e^{-\frac{E_{\ell}}{RT}} \pi [n_j]^m \quad (14)$$

This expression represents the sum total of all the number, ℓ , of reactions which produce and consume the specie, i . The summation is taken over all species, j , partaking in the reactions. The constant, A_{ℓ} , is the Arrhenius factor for the ℓ th reaction.

For a unimolecular decomposition, W_i becomes

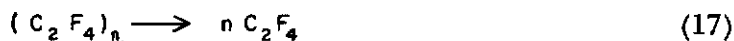
$$W_i = \frac{dn_i}{dt} = A e^{-\frac{E}{RT}} (n_j) \quad (15)$$

E is the energy of activation, and n_j , number of particles of species, i , in a given volume.

If W_i is the result of several reactions, then

$$W_i = \frac{dn_i}{dt} = A_1 e^{-\frac{E_1}{RT}} \pi (n_j)^m + A_2 e^{-\frac{E_2}{RT}} \pi (n_j)^m + \dots + \text{etc.} \quad (16)$$

Of course, W_i involves not only the gas phase reactions, but also the reactions leading to evaporation of species from the solid or liquid surface and subsequent decompositions in the gas phase. For example, if the surface is an organic material such as Teflon, $(C_2F_4)_n$, it has been found necessary to explain the observed W_i by postulating two reactions: first, evaporation of the Teflon; and second, the gas phase reaction with oxygen.



In practice one must make reasonable assumptions about what reactions do take place and the relative contributions of each to the composition of the gas phase and the enthalpy changes in the system. For more complex refractories, this becomes difficult because of the lack of detailed knowledge of the actual species evaporating, the rates of evaporation, and the reaction enthalpies involved. For each given materials system, it is necessary to determine both the species formed and the enthalpy changes.

Conservation of Mass and Momentum

So far, we have confined ourselves to the evaluation of the conservation of species only as given by equation 1. We can now look at the conservation of total mass as expressed by equation 2. In equation 2 the symbols, ρ , u , and v , represent density and the velocity components; r_0 is the cross-sectional radius of the body; and n is a function of the body geometry, being $n = 0$ for a flat plane surface, and $n = 1$ or $n = 2$ for curved surfaces.

Equations 3 and 4, given previously, define the conservation of momentum and introduce no terms not already discussed.

Heat Capacity

The only term remaining to be discussed is the heat capacity, which appears in equation 5. When molecular data is available, heat capacities for gases are readily estimated. For example, if the vibrational frequencies of a molecule are known, the heat capacity is given by

$$c_p = A + R \sum_i \left(\frac{h_c}{kT} \right)^2 \frac{d_i \omega_i^2 e^{-\frac{\omega_i h_c}{kT}}}{1 - e^{-\frac{\omega_i h_c}{kT}}} \quad (19)$$

where

- A = 3.5R for diatomic and linear molecules and 4R for nonlinear molecules.
- R = gas constant.
- h = Planck's constant.
- k = Boltzmann's constant.
- d_i = degeneracy of the i th mode.
- c = speed of light.
- ω_i = vibrational frequency of i th mode in cm^{-1} , and summation is carried out over all vibrations of the molecule.

Unfortunately, the equation has shortcomings: first, usually there is little information about the molecules formed in a complex evaporation; and second, heat capacity cannot be represented by an assembly of simple harmonic oscillators at high temperatures. Under such conditions, once again recourse lies only in experimental observations.

In principle, we have demonstrated how all coefficients may be evaluated for all the foregoing equations. We must emphasize, however, that supporting data for the materials of interest in the re-entry problem are largely not available. Such data, which include the rates and types of species evaporating from a given surface, the heats of vaporization and reaction, and molecular properties of the various species, must be determined experimentally.

Correlation

Since the complexity of the equations which have been written is manifoldly increased by the necessity of solving them for a multicomponent system rather than for a simple binary system, it becomes obvious that solution of the gas-solid (or gas-liquid) interaction for real materials requires some simplifying assumptions.

Two assumptions that can be made are:

1. Thermal diffusion is negligible for many cases.
2. The composition of the boundary layer at any given point is that which corresponds to the equilibrium composition at a steady-state temperature at that point; or equilibrium is established at the gas-solid interface and the species are assumed to diffuse without further reaction into the boundary layer.

These assumptions eliminate the need for specific knowledge of reaction rates, but require knowledge of the equilibrium constants. Of course, neither aspect of assumption 2 is valid if evaporation is accompanied by decomposition of the solid. In some instances, we can assume that the change of solid to gas is irreversible but that shifting equilibrium is maintained in the gas phase. This is certainly true in the case of decomposing organic solids in an air stream.

Still further simplifications can be made for most real cases. The ablation of Teflon by interaction with an air boundary layer, for example, can be treated by assuming that the dominant chemical reactions are as expressed previously in equations 17 and 18 and that equation 17 is the rate controlling reaction at the surface. The linear recession rate for the solid can be obtained from the energy balance and the integrated mass production rate expressed for equation 17. Imposing the condition that $T = T_w$ at the surface and $T = T_o$ inside the solid. The energy balance can be expressed as

$$\frac{d}{dY} \left(K \frac{\partial T}{\partial Y} \right) + \rho \dot{Y} c_s \frac{dT}{dY} = \rho A (h_m - h_p) e^{-\frac{E}{RT}} \quad (20)$$

where

- K = thermal conductivity of the gas phase.
- c_s = specific heat of the solid phase.
- E = activation energy for equation 17.
- A = Arrhenius factor.
- $(h_m - h_p)$ = enthalpy of depolymerization.

Scala (1) found that the linear rate of ablation can then be expressed as:

$$\dot{Y}^2 = \frac{K_s A e^{-\frac{E}{RT}}}{\frac{E}{RT_w} \left[1 - \frac{T_o + \delta}{T_w} + \frac{E \delta}{RT_w^2} \left(1 - \frac{T_o}{T_w} \right) \right]} \quad (21)$$

where

$$\delta = \frac{h_m - h_p}{c_s \frac{E}{RT_w} \left(1 - \frac{T_o}{T_w} \right)}$$

- K_s = thermal diffusivity of Teflon.
- T_o = bulk temperature of the solid.
- T_w = wall temperature of the solid.

Note that reaction 18 affects the ablation rate only to the extent to which it determines T_w since the availability of oxygen at the Teflon surface is negligible. The oxygen is consumed in boundary layer, only a negligible amount being available at the surface.

Another characteristic quantity which can be calculated from the solution to equation 21 is

$$Q^* = \frac{\text{heat transfer to a nonablating surface at } T_w}{\text{mass ablating from the surface at } T_w} \quad (22)$$

This definition gives a convenient measure for the heat of ablation

$$Q^* = \left[\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w + (h_w - h_s) \right] \quad (23)$$

where

\dot{m} = rate of mass ablation

\bar{Q} = heat transfer to the actual solid across the interface.

h_w = enthalpy of the gas phase at the wall.

h_s = enthalpy of the solid at the wall.

To evaluate h_w properly, the gas composition must be known which, in turn, requires a knowledge of the surface temperature and \bar{Q}_s at the interface, which can be determined for the quasi-steady state condition by numerical techniques. In principle, then, we have a method for evaluating Q^* , $\Delta \dot{m}$, and T_w .

As noted before, all these quantities depend critically on the knowledge of high temperature thermodynamic and transport properties. Moreover, a knowledge of the kinetics of "evaporation" or gasification must also be known if correct use is to be made of the thermodynamic properties. The problem of calculating Q^* , of course, in turn involves evaluating the effects of aerothermodynamic parameters such as stagnation enthalpy, pressure, and the composition of the boundary layer.

Experimentally, Q^* is determined by measuring the rate of mass loss, \dot{m} , at a given surface temperature and stagnation enthalpy, and measuring the heat transfer rate to a copper calorimeter from a boundary layer at the same stagnation enthalpy and wall temperature.

$$Q^* = \frac{\dot{Q}_{col}}{\dot{m}} \quad (24)$$

The Liquid-Solid Interface

All the foregoing discussion has been limited to determining the change in the heat transfer rate due to mass transfer into the boundary layer from a vaporizing surface.

In the general case of ablation the effect of the liquid-solid boundary layer should also be considered (see figure 1). A set of equations for the liquid-solid boundary similar to equations 1 to 5 can be written and solved. This discussion will be restricted to stating the effect of ablative melting on Q^* .

The expression for Q^* , when ablative melting is considered, can be written as

$$Q^* = \frac{\dot{Q}_{cal}}{\dot{m}_{total}} = f \left[\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w + (h_w - h_s) + \frac{(1-f)}{f} (h_l - h_{so}) \right] \quad (25)$$

where

- f = fractional loss of material from a given surface due to gasification and vaporization.
- h_{so} = enthalpy of the cold solid (interior).
- h_l = average enthalpy of the liquid (which for thin layers may be taken as equal to the enthalpy of the liquid at the gas-liquid interface).
- h_w = enthalpy of the gas at the gas-liquid interface.
- $\Delta \dot{m}$ = mass ablation rate at the gas-liquid interface.
- $\Delta \bar{Q}$ = heat transfer rate to the liquid at the gas-liquid interface.

In the above expression, $\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w$ and $(h_w - h_s)$ contribute only a fraction, f , to Q^* , while $(h_l - h_s)$, which represents the heat carried away by the flow of the liquid layer, contributes the remainder.

The problem reduces itself to the determination of the flow behavior of the liquid, which is governed by its viscosity under a given set of stagnation conditions, including the shear stress on the liquid layer. For a viscous liquid, the last term of equation 25 may be a steep function of temperature since viscosity varies exponentially with temperature. The variation of f with surface conditions for a number of systems, such as silica, has already been calculated (5,6) and found to be determined in most cases by the values for $\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w$ and $(h_w - h_s)$.

Conclusion

We emphasize, in conclusion, that if evaporation is at high temperature, a knowledge of thermodynamics, transport properties, and kinetics would greatly aid in calculating the value of Q^* . Such information is at present required for many systems now being considered, i.e., organic solids and refractory materials. The only type of information now available, to a limited extent, for refractory materials are heat capacities, heats of formation, and heats of evaporation. Unfortunately, enthalpies and heat capacities of solids at high temperatures can best be obtained by direct measurements. In contrast, transport properties of gases at high temperatures, can probably best be determined from some measurements of molecular interactions, which can be suitably translated into transport properties.

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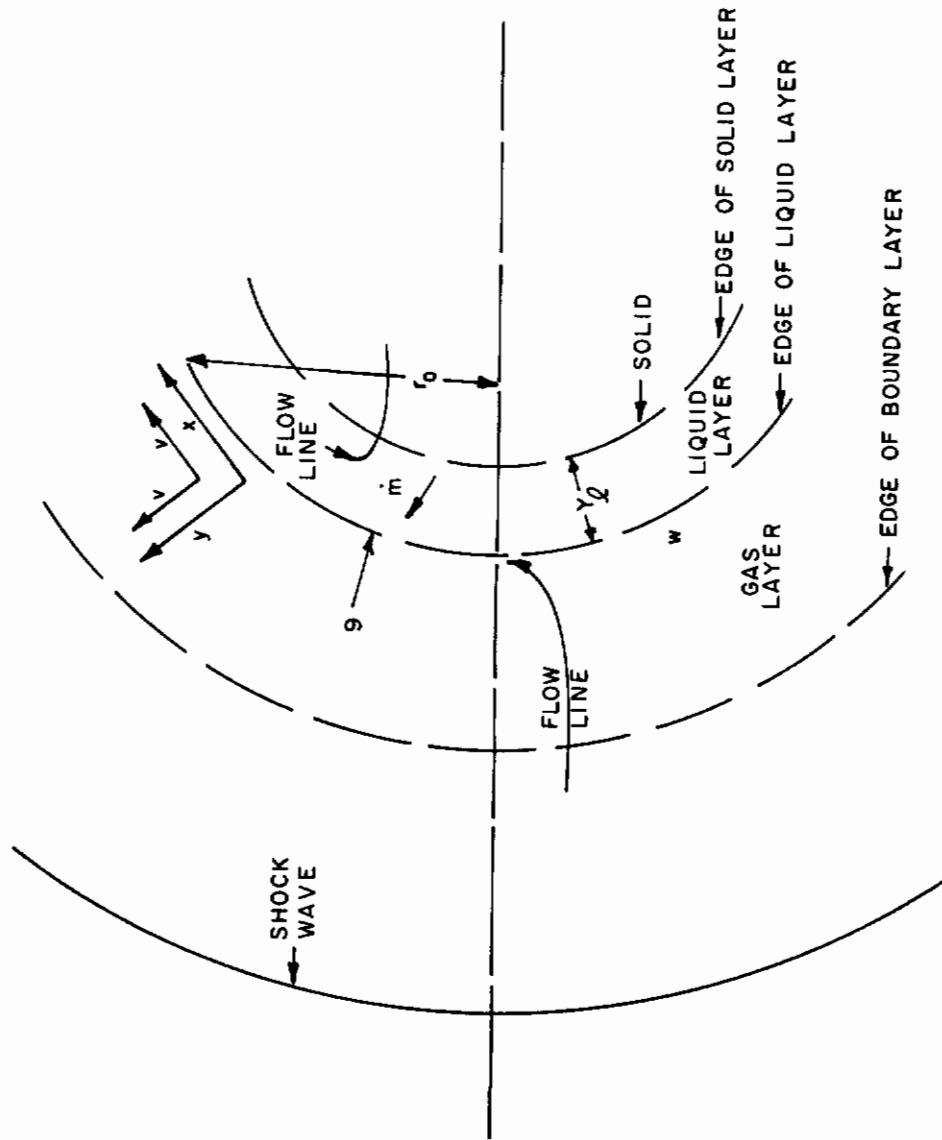


Figure 1. System of Gas Solid Interface