symmetric case when $L = 5$ and $w = 0.5$. The value of the symmetric case Biot number is the average of the Biot numbers in the asymmetric case. As expected, the temperature ratio along the fin length is the lowest at $y = 1$, $z = 0.5$ and is the highest at $y = -1$, $z = -0.5$.

The relationships between L and Biot number ratio Bi_2/Bi_1 for equal amounts of heat loss based on $Bi_1 = Bi_3 = Bi_5 = 0.01$ and $w = 0.5$ are shown in Fig. 5. The trends of L with Biot number ratio Bi_2/Bi_1 have negative slopes for the three cases of Biot number ratio Bi_4/Bi_3 illustrated. Furthermore, Fig. 5 shows that the slope becomes more negative as the Biot number ratio of Bi_4/Bi_3 decreases. Figure 6 presents the relationships between the w and Biot number ratio Bi_2/Bi_1 for equal amounts of heat loss based on $Bi_1 = Bi_3 = Bi_5 = 0.01$ and $L = 5$. The value of w decreases as Biot number ratio Bi_2/Bi_1 increases. When Fig. 6 is compared to Fig. 5, the slope of Fig. 6 becomes more negative as Biot number ratio Bi_4/Bi_3 decreases but the difference between both values, that is, $Bi_4/Bi_3 = 5$ and 1, are relatively small.

IV. Conclusions

The following conclusions can be drawn from these results.

1) Heat loss increases nonlinearly as fin length increases, whereas it increases linearly as fin width increases.

2) When the average of the Biot number ratios Bi_2/Bi_1 and Bi_4/Bi_3 are the same, there is more heat loss in the case of asymmetric top to bottom and symmetric right to left than vice versa when w is small, and this relationship reverses as w increases. The crossover point appears to be approximately $w = 1$, which represents the dimensionally invariant point $w' = l$.

3) The fin length and width must decrease as Biot number ratio Bi_2/Bi_1 increases to produce equal amount of heat loss and the slope increases as Biot number ratio Bi_4/Bi_3 decreases.

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Demythicizing the Gibbs Potential for Determination of Chemical Equilibrium Conditions

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Introduction

It is well known that the chemical equilibrium of a multicomponent system is characterized by the minimization of thermodynamic functions such as internal energy U, enthalpy H, Helmholtz potential F, and Gibbs potential G

$$(\mathrm{d}U)_{S,V} = (\mathrm{d}H)_{S,p} = (\mathrm{d}F)_{T,V} = (\mathrm{d}G)_{T,p} = \sum_{i}^{n} \mu_i \, \mathrm{d}N_i = 0 \tag{1}$$

where μ_i is the molar chemical potential defined as

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,p,N_{j\neq i}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} \tag{2}$$

The same characterization can be achieved by resorting to the maximization of the entropy and the relative entropic potentials.[1] The equivalence of the different formulations should appear clear from Eq. (1). Nevertheless, some misunderstandings appear in the literature because the thermodynamic constraints [subscripts in Eq. (1)] are most often considered a consequence of the physical transformation followed by the system toward the finale state of equilibrium, rather than a virtual mathematical procedure. In this regard, the chemist favors the minimization of the Gibbs potential whereas the physicist is more used to minimizing the Helmholtz potential, without fully perceiving that, within a specific equilibrium problem, both criteria yield the same equilibrium conditions. On the other hand, thermodynamics textbooks also show that the gas-phase equilibrium constants K_p, K_c, $\ldots$, are connected by simple relations such as

$$K_p = \exp(-\Delta\mu^\circ/RT) = K_c \cdot (RT)^{\Delta\nu} = \cdots \tag{3}$$

In Eq. (3), K_p and K_c are the equilibrium constants in terms of partial pressures and concentrations, $\Delta\mu^\circ$ is the reaction standard free energy, and $\Delta\nu$ is the difference between the sums of the stoichiometric coefficients of the products and the reactants, respectively. Researchers, therefore, use either K_p or K_c, regardless of the transformation that the system undergoes; as a matter of fact, they use the minimization of any one of the thermodynamic functions appearing in Eq. (1), in flagrant contradiction with the textbooks that stress the importance of using the different constants according to the particular transformation that the system experiences. In particular,

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chemical thermodynamics textbooks[2,3] favor Gibbs and Helmholtz potentials by supplying data to obtain $\Delta\mu^\circ$ and induce researchers to believe that only these two functions can be used. Such a choice is commonly justified by the corresponding constraints involving state parameters $[(T, p)$ or $(T, V)]$ that lend themselves to easy measurement and control.

In the following section, we present an alternative way to obtain the same chemical-equilibrium conditions enforced by Eq. (1) by resorting to two uncommon criteria, whose corresponding thermodynamic constraints can be hardly interpreted as representative of a real-world transformation of the system.

Two Uncommon Criteria of Chemical Equilibrium

To emphasize the contradiction introduced by the association of physical transformations with states of equilibrium and, hopefully, to clarify misunderstandings, we select two, rather uncommon, thermodynamic functions[4,5] that turn out to be equivalent to those appearing in Eq. (1) for the purpose of defining the conditions of chemical equilibrium. These are the fundamental relations

$$p = p(G, T, N_1, N_2, \ldots) \tag{4}$$

$$V = V(F, T, N_1, N_2, \ldots) \tag{5}$$

The corresponding equilibrium criteria are readily obtained from the differential expressions

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i^n \mu_i\,\mathrm{d}N_i \tag{6}$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i^n \mu_i\,\mathrm{d}N_i \tag{7}$$

which, after proper rearrangement and after Eq. (1) is taken into account, yield, respectively,

$$(\mathrm{d}p)_{G,T} = -\frac{1}{V}\sum_i^n \mu_i\,\mathrm{d}N_i = 0 \tag{8}$$

$$(\mathrm{d}V)_{F,T} = \frac{1}{p}\sum_i^n \mu_i\,\mathrm{d}N_i = 0 \tag{9}$$

The maximization of p [minus sign in Eq. (8)] and the minimization of V with the prescription of the appropriate state parameters [subscripts on the left-hand sides of Eq. (8) and (9)] will lead to the same equilibrium conditions provided by the minimization of the functions appearing in Eq. (1).

A practical application adapted from an example in Ref. 6 will provide a more explicit understanding of this point. Consider the dissociation experienced by two moles of N_2O_4, in a volume V at temperature T and pressure p, according to the reaction

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{10}$$

If x is the degree of advancement of the reaction $(0 \le x \le 2)$, the expressions of the Gibbs and Helmholtz potentials of the perfect gas mixture $[p = (2+x)RT/V]$ read, respectively,

$$G(T, p, x) = (2-x)\left\{\mu_a^\circ + RT\ln\left[\frac{(2-x)p}{(2+x)}\right]\right\} + 2x\left\{\mu_b^\circ + RT\ln\left[\frac{2xp}{(2+x)}\right]\right\} \tag{11}$$

$$F(T, V, x) = (2-x)\left\{\mu_a^\circ + RT\ln\left[(2-x)\frac{RT}{V}\right]\right\} + 2x\left\{\mu_b^\circ + RT\ln\left(\frac{2xRT}{V}\right)\right\} - (2+x)RT \tag{12}$$

In Eqs. (11) and (12), the subscripts a and b refer to N_2O_4 and NO_2, respectively. The equilibrium value of the degree of advancement is habitually obtained from the solution of

$$\left(\frac{\partial G}{\partial x}\right)_{T,p} = 2\mu_b^\circ - \mu_a^\circ + RT\ln\left[\frac{4x^2p}{(2+x)(2-x)}\right] = 0 \tag{13}$$

or

$$\left(\frac{\partial F}{\partial x}\right)_{T,V} = 2\mu_b^\circ - \mu_a^\circ + RT\ln\left[\frac{4x^2RT}{(2-x)V}\right] = 0 \tag{14}$$

Note that the argument of the logarithms in Eqs. (13) and (14) expresses the equilibrium constant K_p.

At the same time, the Gibbs and Helmholtz potentials [Eqs. (11) and (12)] can be inverted to yield, respectively,

$$\ln p = \frac{1}{2+x}\frac{G}{RT} - \frac{2-x}{2+x}\left(\frac{\mu_a^\circ}{RT} + \ln\frac{2-x}{2+x}\right) - \frac{2x}{2+x}\left(\frac{\mu_b^\circ}{RT} + \ln\frac{2x}{2+x}\right) \tag{15}$$

$$\ln V = -\frac{1}{2+x}\frac{F}{RT} + \ln(RT) - 1 + \frac{2-x}{2+x}\left[\frac{\mu_a^\circ}{RT} + \ln(2-x)\right] + \frac{2x}{2+x}\left[\frac{\mu_b^\circ}{RT} + \ln(2x)\right] \tag{16}$$

The application of the criteria indicated by Eqs. (8) and (9) leads to the equilibrium equations

$$\left(\frac{\partial p}{\partial x}\right)_{G,T} = -\frac{p}{2+x}\left\{2\mu_b^\circ - \mu_a^\circ + RT\ln\left[\frac{4x^2p}{(2+x)(2-x)}\right]\right\} = 0 \tag{17}$$

$$\left(\frac{\partial V}{\partial x}\right)_{F,T} = \frac{V}{2+x}\left\{2\mu_b^\circ - \mu_a^\circ + RT\ln\left[\frac{4x^2RT}{(2-x)V}\right]\right\} = 0 \tag{18}$$

which coincide with Eqs. (13) and (14) because the factors $p/(2+x)$ and $V/(2+x)$ never vanish.

Conclusions

The example considered in the preceding section illustrates in a simple manner the idea of the equivalence of the thermodynamic potentials (and not the rejection of the Gibbs potential) for the purpose of finding the chemical-equilibrium conditions. It favors a reconciliation of chemical and physical thermodynamics because it shows how the same equilibrium conditions can be reached using either chemical potentials G and F or physical potentials p and V when the appropriate mathematical constraints are selected. In this regard, note that other equilibrium criteria can be formulated by adopting any appropriate fundamental relation (Ref. 4, p. 88). For example, one could adopt the temperature as a function of Gibbs potential, pressure, and mole numbers

$$T = T(G, p, N_1, N_2, \ldots) \tag{17}$$

and proceed to its minimization

$$(\mathrm{d}T)_{G,p} = \frac{1}{S}\sum_i^n \mu_i\,\mathrm{d}N_i = 0 \tag{18}$$

for prescribed G and p.

The equivalence of the thermodynamic potentials also emphasizes that the search of the equilibrium conditions is based on a mathematically virtual process and that the knowledge of the real physicochemical transformation that brings the system into the equilibrium state is irrelevant. This conclusion may seem startling to those in the chemical community used to conceiving of the equilibrium conditions as an end result determined by a real transformation. Their hesitation rests on the conceptual prejudice that 1) the constraints (T, p) and (T, V) appear more natural than the constraints (G, T), (F, T), or (G, p) because the former constraints lend themselves to easy control in the laboratory and 2) the feasibility of a real transformation consistent with the latter constraints is difficult to imagine. Yet, these arguments become untenable when subjected to deeper scrutiny because all constraints have a mathematically virtual nature and are associated exclusively with the final state of equilibrium, rather than with the transformation that the system actually follows to reach that state. Such an interpretation is the only one consistent with Eqs. (13) and (14) and Eqs. (17) and (18) being equivalent and leading to the same equilibrium conditions.

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Thermal Effects of Particles on Hypersonic Ablation

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Nomenclature

a = particle radius
a_1 = particle temperature profile parameter
D = particle drag in the melt layer
H_1, H_2 = functions of $\tilde{h}$, Eqs. (19a) and (19b)
h = average heat convection coefficient
$\tilde{h}$ = dimensionless convection coefficient, Eq. (13a), Biot number
Q = total heat loss from the particle to the melt
$\dot{q}$ = rate of heat loss from the particle to the melt
r = radial distance from the particle center
$\tilde{r}$ = dimensionless radial distance, r/a
T = temperature
t = time
$\tilde{t}$ = dimensionless time, t/t_f
$\tilde{u}$ = dimensionless temperature inside the particle, Eq. (13b)
V = particle velocity in the melt layer
$\tilde{V}$ = dimensionless particle velocity, $V/(z^*/t_f)$
z = distance from the melt–solid interface
$\bar{z}$ = distance from the air–melt interface, $z^* - z$
z^* = melt-layer thickness
α_p = particle thermal diffusivity
$\tilde{\alpha}_p$ = dimensionless particle thermal diffusivity, Eq. (13a)
η_2 = z/z^*
λ_a = $(\rho_2/\rho_p)(z^*/a)$
$\bar{\nu}_2$ = average kinematic viscosity of the melt
ρ = density

Subscripts

f = final
m = conditions on the ablation surface
p = particle
2 = conditions in the melt layer
∞ = freestream conditions

Superscript

$*$ = conditions at the air–melt interface

I. Introduction

IT is well known (for example, see Ungar[1]) that thermal protection systems used in severe aerodynamic heating environments associated with hypersonic flights are often subject to the effects of particles, either in solid form or in the form of liquid droplets, or both, in the gas stream. These particles carry large thermal and kinetic energies as they enter the thermal protection system, and their effects on the performance of the system are, thus, expected to be significant.

In this Note, we present a simplified model to assess the thermal effects of these particles on aerodynamic ablation near the stagnation point of a circular-nosed body in hypersonic flight. Only the case of sparse particles of small size is considered, and the particles will be considered as rigid spheres. These assumptions allow considerable simplifications to be made in the analysis. Some preliminary results are also presented, and their possible refinements are discussed. The dynamic effects that could contribute significantly to the mechanical erosion of the ablative materials will require a separate model for material responses, and they will not be considered here.

The study will be based on the earlier work by Zien and Wei[2,3] on the modeling of particle-free hypersonic ablation. The central part of the model is a thin melt layer formed by the molten ablative material (see also Lees[4] and Hidalgo,[5] among others), which is coupled to the airflow on the one side and to the ablating solid on the other (Fig. 1). The melt layer plays a critical role in providing a heat shield to the aerodynamic body through conduction and convection currents in the layer. Because we consider only the case of sparse particles of small size (compared to the dimension of the melt layer), the interaction between particles and the effects of particles on the basic ablation field can be neglected in the first approximation.

To fix the idea, we consider the case where the particle enters the melt layer at a given (high) velocity, and it is in thermal equilibrium with the hot carrier gas on entry. The particle travels through the nonuniform but known temperature field of the melt layer as given in Refs. 2 and 3, and its motion is inertia dominated. The temperature field inside the spherical particle is assumed to be one dimensional (in the radial direction) and time dependent, and the heat loss to the surrounding melt is expressed approximately by a constant average heat transfer coefficient.

The simplified model is, thus, amenable to analytical treatments. Relevant dimensionless parameters for the problem are also identified, and they are used in the presentation of results. Possible refinements of these preliminary results are discussed. It is hoped that the results of the present study will be useful as a starting point for the study of dynamic effects of particles on ablation, for which additional models for material response will need to be incorporated

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