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Investigation of Chemical Affinity for Reacting Flows of Non-Local Thermal Equilibrium Gases

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Use of chemical affinity for analyzing reacting flows of gases not in local thermal equilibrium (LThE) is investigated. The affinity is used as a parameter to define the degree of reaction extent in reacting flows. The relation between the reaction rate and the affinity for a multitemperature ideal gas mixture is also investigated and discussed. Each gas species in the mixture is assumed to have a Maxwellian velocity distribution, and the particle distribution for each internal energy mode is characterized by a Boltzmann or an equivalent population temperature. It is found that the relation between the reaction rate and the affinity for non-LThE gases can be reduced to that for LThE gases if modified stoichiometric coefficients and modified mole fractions are employed in the exponential function relationship. Results of the present investigation are applied to the ionization reaction of argon with nonequilibrium translational and electronic excitation temperatures. Equations and charts for computing the composition and thermodynamic properties of singly ionized argon plasma are presented for various non-LThE temperatures and different affinity values. An example of argon ionization reaction is given to illustrate the use of these charts.

Nomenclature

C = mole fraction
e^- = free electron
F = chemical affinity
g_m = degeneracy of energy level m
H^0 = negative value of the heat of reaction
h = enthalpy
$\underline{h}$ = Planck's constant
K_p = equilibrium constant
k = Boltzmann's constant
m = mass
N = particle number
N_0 = Avogadro's number
n = number density
p = pressure
$\underline{p}$ = equilibrium pressure
$\bar{q}$ = heat transfer rate per unit mass flow
s = entropy
T = temperature
t = time
V = volume
w = reaction rate
Z = partition function
Δh = enthalpy of formation
ε_m = energy of level m referred to the ground state
κ = reaction constant
λ = reaction rate ratio
μ = chemical potential
ν = stoichiometric coefficient
ξ = extent of reaction
ω = forward reaction rate

Subscripts

b = backward reaction
chem = chemical energy
e = electron
f = forward reaction
g = heavy particles
j = species j
k = internal energy modes
m = energy level
r = rotational energy mode
t = translational energy mode
v = vibrational energy mode
x = electronic excitation energy mode

Introduction

IN advanced combustion techniques and manufacturing processes such as laser or microwave heating, electric arcs, plasma jets and plumes, the gas (ionized or not) may not be in local thermal equilibrium (LThE), and different species and energy modes of the gas are found to be at different temperatures.[1] For example, in the ionization reaction of microwave or radio-frequency (rf) plasmas, the input electromagnetic energy is primarily picked up by the lightweight electrons. Consequently local electron kinetic energy may be much higher than the translational energy of the heavy particles. The translational temperatures of the high- and low-speed particles will eventually become identical after a large number of collisions. The time required for the gas to reach local thermal equilibrium depends on the collision rate. The two-temperature model has been widely employed for the calculation of plasmas with translational nonequilibrium. Nonequilibrium measurements in nitrogen-containing arcs and inductively coupled plasmas have measured rotational, vibrational, and excitation temperatures of different values.[1] Excitation nonequilibrium was also observed near the center of a plasma torch in recent experimental measurements of argon/helium plasma,[2,3] indicating non-LThE condition is very common in thermal plasmas.

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A generalized mutithermodynamic equilibrium (GMTE) model was proposed by the authors and co-workers[4–6] for handling gases or gas mixtures not in local thermodynamic equilibrium (LTE). In this model each gas species is assumed to behave as an ideal gas and has a Maxwellian velocity distribution, but different species may have different translational temperatures if their kinetic energy levels are not equal. A non-Maxwellian velocity distribution that was observed at high field strengths or low pressures can also be handled by the multitemperature model if the relation between the velocity distribution and the translational temperature is determined theoretically or experimentally. In thermal plasmas the assumption of a Maxwellian velocity distribution is generally valid.[4]

In addition to translational energy, each species in a gas mixture has electronic energy. Diatomic and polyatomic species also have rotational and vibrational energies. In LThE condition, the particle density distribution for each of these internal energy modes is characterized by a temperature called the Boltzmann temperature. The translational and Boltzmann temperatures for all species and every energy mode are identical for the LThE case. However, for non-LThE gases, not only the temperatures of different energy modes and species may be different, but the particles of the gas mixture may not be distributed over their allowed energy levels according to the Boltzmann distribution. Graphically, this means the plot of the number density distribution, divided by the degeneracy of the energy level, vs the allowed energy levels (or quantum states) is not a straight line on a semilog chart. If the distribution of an energy mode is not Boltzmann distribution, it may be approximated by several population temperatures for different energy levels. Alternative methods for handling non-Boltzmann distributions are discussed in detail in Eddy and Cho's recent paper.[4] In the GMTE model, an equivalent population temperature is used for thermodynamic calculation if the distribution does not follow the Boltzmann distribution. Chemical affinity is employed in the GMTE model[5,6] to handle the non-local chemical equilibrium (LChE) effects. It was used to measure the departure from chemical equilibrium for composition and property computations in a reacting flow. The relations between the affinity and the reaction rate and other properties for non-LThE gases have not been studied in detail in previous papers of the GMTE model.

In this article a detailed investigation of chemical affinity for reacting flows of non-LThE gases is presented. A generalized relation between the reaction rate and the affinity is derived for multitemperature gas mixtures. For simplicity, either the particles for each internal energy mode in the gas mixture are assumed to be distributed over their quantum states according to the Boltzmann distribution, or a single population temperature is used for non-Boltzmann distributions. Different species may have different translational temperatures, but are assumed to have a Maxwellian velocity distribution.

The law of mass action used in the present study is based on open subsystems in dynamic nonequilibrium such that the control of the local thermodynamic state is nonlocal, as discussed by Thomas and Athay.[7,8] For these conditions the equilibrium criteria is the minimization of the Gibbs energy, yielding $\Sigma\ \nu_j \mu_j$ equal to zero in chemical equilibrium, and not equal to zero in chemical nonequilibrium.[6] A different form of the law of mass action is obtained if one assumes that the subsystems are isolated so that the equilibrium criteria is maximizing the entropy[9,10] (with the energy constant), apparently yielding $\Sigma_{jk}\ (\nu_j \mu_{jk}/T_{jk})$ equal to zero in chemical equilibrium and Saha ionization equations similar to those used in partial local thermal equilibrium (PLTE) models. A detailed discussion of the differences between these models is beyond the scope of this article. Callen indicates that there is little reason to believe that the subsystems are isolated.[11] Methods to determine this are discussed by Thomas.[8] In chemical equilibrium with multitemperatures, the isolated subsystem case is a subset of the more general open subsystem assumption considered here, as has been shown in a comparison by Cho and Eddy.[12]

In the present investigation equations for chemical potential and equilibrium constant calculations are first introduced. Then the relation between the reaction rate and the affinity is determined for gas mixtures with non-LThE temperatures. It is shown that the equilibrium constant of a non-LThE gas mixture is a function of all the temperatures involved. When modified stoichiometric coefficients and modified mole fractions are used, the relation between the reaction rate and the affinity can be reduced to the exponential function relation for LThE gases. The composition and thermodynamic properties for singly ionized argon at different degree of reactions (different affinity values) are computed for various translational and excitation nonequilibria, and an example is given to illustrate the application of the present non-LThE analysis for reacting flow calculation.

Equilibrium Constant, Affinity, and Reaction Rate Equations for a GMTE Gas Mixture

Affinity is used in nonequilibrium thermodynamic processes as a measure of the degree of reaction extent. The affinity of a thermodynamic system is zero if the system is in chemical equilibrium. Affinity has been studied in great detail for LThE gases and the results were summarized in many nonequilibrium thermodynamics texts (e.g., Refs. 13 and 14). Since affinity is a thermodynamic property, it is very convenient to use affinity for the analysis of reacting flows. Because the change of a thermodynamic property depends on the state of the system and is independent of the path by which the system arrived at the given state, thermodynamic tables and charts can be constructed at different affinity values for gases not in chemical equilibrium.

The relationship between the reaction rate and the affinity for LThE gases is given in Haase's book.[13] Consider the following elementary reaction as an example

$$\sum \nu_r(M_r) \leftrightarrow \sum \nu_p(M_p) \tag{1}$$

where (M_r) and (M_p) denote the various reacting species. The affinity of the above reaction is calculated from the appropriate law of mass action for open systems[4]

$$F = -\sum \nu_j \mu_j \tag{2}$$

where the sign of F has been selected to give positive values in recombination.

The stoichiometric coefficients ν_j in the affinity equation are positive if they appear on the right side, and negative if on the left side of the reaction equation, Eq. (1). The reaction rate of the above reaction for a LThE gas at T is related to the affinity F by the following equation:

$$w = \omega\{1 - \exp[-F/(kT)]\} \tag{3}$$

The second term on the right side represents the ratio of the backward reaction rate to the forward reaction rate. The two reaction rates are equal, and chemical equilibrium is reached when F equals zero. A negative affinity indicates a faster backward reaction, and a positive affinity indicates a slower backward reaction than the forward reaction.

The affinity equation for non-LThE gases is much more complicated because there are many different temperatures involved. If we assume the velocity distribution of species j in the mixture of a non-LThE gas is Maxwellian and is characterized by a translational temperature $T_{t,j}$, and a Boltzmann or an equivalent population temperature can be used for the particle distribution for each internal energy mode k of species j, then the chemical potential for species j is given by

$$\begin{aligned}\mu_j &= \mu_{t,j} + \sum \mu_{k,j} + \mu_{\text{chem}} \\ &= -kT_{t,j} \ln(Z_{t,j}/N_j) - \sum kT_{k,j} \ln Z_{k,j} + \mu_{\text{chem}} \qquad (4)\end{aligned}$$

where subscript k = internal energy modes (rotational, vibrational, and electronic)

The translational partition function for species j is

$$Z_{t,j} = V(2\pi m_j k T_{t,j}/\underline{h}^2)^{3/2} \qquad (5)$$

Only the translational energy has a contribution to the pressure. As a result, the ideal gas law for species j is written as

$$p_j V = N_j k T_{t,j} \qquad (6)$$

Combining Eqs. (5) and (6), we obtain

$$\begin{aligned}Z_{t,j}/N_j &= (2\pi m_j/\underline{h}^2)^{3/2}(kT_{t,j})^{5/2}/p_j \\ &= (2\pi m_j/\underline{h}^2)^{3/2}[(kT_{t,j})^{5/2}/p^0](p^0/p_j) \\ &= (Z_{t,j}/N_j)^0(p^0/p_j) \qquad (7)\end{aligned}$$

where p^0 is a reference pressure (e.g., 1 atm). Substituting Eq. (7) into Eq. (4), we obtain

$$\mu_j = \mu_j^0 - kT_{t,j} \ln(p^0/p_j) = \mu_j^0 + kT_{t,j} \ln(p_j/p^0) \qquad (8)$$

where

$$\begin{aligned}\mu_j^0 &= \mu_{t,j}^0 + \sum \mu_{k,j} + \mu_{\text{chem}} \\ &= -kT_{t,j} \ln(Z_{t,j}/N_j)^0 + \sum \mu_{k,j} + \mu_{\text{chem}} \\ &= \text{a function of } T_{t,j} \text{ and } T_{k,j}\end{aligned}$$

The affinity F for a chemical reaction of multitemperature gases is calculated from

$$\begin{aligned}F &= -\sum \nu_j \mu_j \\ &= \Delta\mu = \Delta\mu^0 + k \sum -\nu_j T_{t,j} \ln(p_j/p^0) \qquad (9)\end{aligned}$$

If $T_{t,1}$ is chosen as the reference temperature, the affinity equation can be rewritten as

$$\begin{aligned}F &= \Delta\mu^0 + kT_{t,1} \sum -\nu_j(T_{t,j}/T_{t,1}) \ln(p_j/p^0) \\ &= \Delta\mu^0 + kT_{t,1} \ln\left[\prod (p_j/p^0)^{-\nu_j(T_{t,j}/T_{t,1})}\right] \\ &= \Delta\mu^0 + kT_{t,1} \ln\left[\prod (p_j/p^0)^{-\nu_j^*}\right] \qquad (10)\end{aligned}$$

where the modified stoichiometric coefficient ν_j^* is defined as

$$\nu_j^* = \nu_j(T_{t,j}/T_{t,1}) \qquad (11)$$

A modified mole fraction C_j^* that is equal to the pressure ratio of species j is defined as

$$C_j^* = p_j/p = C_j(T_{t,j}/T_{t,1})\Big/\left[\sum C_j(T_{t,j}/T_{t,1})\right] \qquad (12)$$

where C_j = mole fraction of species $j = N_j/\Sigma N_j$. Note that, if all translational temperatures are identical, $C_j^* = C_j$ and $\nu_j^* = \nu_j$.

In terms of the modified mole fraction, the pressure ratio term in Eq. (10) can be expressed as

$$\prod (p_j/p^0)^{-\nu_j^*} = \left(\prod C^{*-\nu_j^*}\right)(p/p^0)^{\Sigma-\nu_j^*} \qquad (13)$$

Now consider the equilibrium condition. Inserting the equilibrium condition $F = 0$ into Eq. (10) gives

$$\ln\left[\prod (\underline{p}_j/p^0)^{-\nu_j^*}\right] = \ln(1/K_p) = -\Delta\mu^0/(kT_{t,1}) \qquad (14)$$

where $\underline{p}_j$ is the equilibrium partial pressure for species j. Thus, Eq. (10) can be rewritten in terms of the equilibrium constant K_p:

$$\begin{aligned}F &= kT_{t,1} \ln K_p + kT_{t,1} \ln\left[\prod (p_j/p^0)^{-\nu_j^*}\right] \\ &= kT_{t,1} \ln\left\{\left[\prod (p_j/p^0)^{-\nu_j^*}\right] K_p\right\} \qquad (15)\end{aligned}$$

Rearranging, we obtain

$$\left[\prod (p_j/p^0)^{-\nu_j^*}\right] = \exp[F/(kT_{t,1})]/K_p \qquad (16)$$

Note that

$$\ln K_p = \Delta\mu^0/(kT_{t,1}) = \text{a function of } T_{t,j} \text{ and } T_{k,j} \text{ only} \qquad (17)$$

Therefore, K_p can be computed for various values of $T_{t,j}$ and $T_{k,j}$. Then, the product of the partial pressure ratios can be calculated from Eq. (16) for a given F. The number density for each species can be computed from Eq. (6) for a given total pressure p if Dalton's rule of additive pressure is employed, and other information such as the initial composition of the gas mixture is known or the assumption of electric neutrality is made. With the composition determined, thermodynamic properties can be calculated as the sum of the contributions of all species and every energy mode in the mixture. Detailed description and derivation for property calculation of a non-LTE gas can be found in the authors' and co-workers' previous papers.[4,6,15,16]

We shall now investigate the relation between the affinity and the reaction rate constants. If the forward and backward reaction constants for Eq. (1) are designated as κ_f and κ_b, the reaction rate of Eq. (1) can be calculated from

$$w = \frac{d\xi}{dt} = \kappa_f \prod C_r^{\nu_r} - \kappa_b \prod C_p^{\nu_p} \qquad (18)$$

For multitemperature gases, it is convenient to use a modified forward rate constant defined as

$$\kappa_f^* = \kappa_f\left(\prod C_r^{\nu_r}\right)\Big/\left(\prod C_r^{*\nu_r^*}\right) \qquad (19)$$

Similarly, the backward reaction constant for non-LThE gases is modified as

$$\kappa_b^* = \kappa_b\left(\prod C_p^{\nu_p}\right)\Big/\left(\prod C_p^{*\nu_p^*}\right) \qquad (20)$$

The reaction rate equation for a multitemperature gas mixture can be written as

$$w = \frac{\mathrm{d}\xi}{\mathrm{d}t} = \kappa_f^* \prod C_r^{*\nu_r^*} - \kappa_b^* \prod C_p^{*\nu_p^*}$$

$$= \omega^* \left(1 - \lambda^* \prod C_j^{*\nu_j^*}\right) \tag{21}$$

where

$$\omega^* = \kappa_f^* \prod C_r^{*\nu_r^*}$$

$$\lambda^* = \kappa_b^* / \kappa_f^*$$

$$\prod C_j^{*\nu_j^*} = \left(\prod C_p^{*\nu_p^*}\right) \Big/ \left(\prod C_r^{*\nu_r^*}\right)$$

From Eqs. (12) and (16)

$$\prod C_j^{*\nu_j^*} = (p/p^0)^{\Sigma - \nu_j^*} \Big/ \prod (p_j/p^0)^{-\nu_j^*}$$

$$= [K_p(p/p^0)^{\Sigma - \nu_j^*}]\exp[-F/(kT_{t,1})] \tag{22}$$

Thus, Eq. (21) becomes

$$w = \omega^*\{1 - \lambda^* K_p(p/p^0)^{\Sigma - \nu_j^*} \exp[-F/(kT_{t,1})]\} \tag{23}$$

When in equilibrium, $w = F = 0$. Thus

$$0 = 1 - \lambda^* K_p(p/p^0)^{\Sigma - \nu_j^*} \tag{24}$$

$$K_p(p/p^0)^{\Sigma - \nu_j^*} = 1/\lambda^* \tag{25}$$

In terms of ω^*, a simple relationship between w and F can be obtained for non-LThE gases:

$$w = \omega^*\{1 - \exp[-F/(kT_{t,1})]\} \tag{26}$$

If all temperatures are identical, the above equation is reduced to that for LThE gases.

Use of Chemical Affinity for Ionization Analysis of Non-LThE Argon

To illustrate the application of the present non-LThE analysis for reacting flows, consider argon gas at 300 K and 1 atm heated in a microwave cavity or by a rf-inductive coil until the gas is partially ionized (see Fig. 1). The exit temperature considered in this example ranges from 5000 to 20,000 K. For temperatures below 20,000 K, the dominant ionization reaction is expected to be the formation of the singly ionized argon ions:

$$\mathrm{Ar} \leftrightarrow \mathrm{Ar}^+ + \mathrm{e} \tag{27}$$

Also, at low temperatures, only the first few electronic levels are important to equilibrium constant and property calculations. The electronic levels employed in the present calculation of argon composition and properties are those used in Sonntag and Van Wylen's book[17] for argon plasma around 10,000 K. At high temperatures ionizations of other argon ions such as Ar^{++} and Ar^{+++} should be taken into consideration, and a large number of electronic energy levels should be included. Sedghinasab and Eddy's calculation of argon properties[15] included the first 4 argon ions and for electronic energy levels of up to 70. The good agreement between the present calculation and Sedghinasab and Eddy's results of LTE argon properties[15] justifies the assumptions of one dominant ionization reaction and negligible high electronic energy levels for the temperature range considered here.

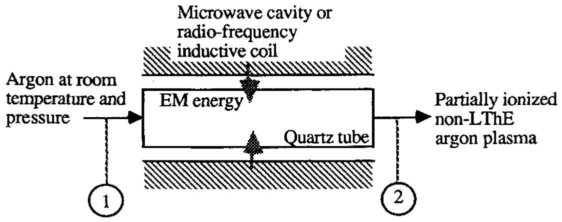

Fig. 1 Ionization of non-LThE argon gas by electromagnetic waves.

Argon atoms and ions are much heavier than electrons. It is therefore reasonable to assume that in high-frequency inductive heating T_{t,e^-} is higher than $T_{t,\mathrm{Ar}}$ and T_{t,Ar^+}, and the translational temperatures of Ar and Ar^+ are close to each other. Furthermore, we assume the excitation temperatures of all species are identical. Later we will see that the excitation temperature does not have a strong effect on the composition and thermodynamic properties. Therefore, the assumption of one excitation temperature for all species should not result in significant errors in our calculation.

Since there are no diatomic or polyatomic components in argon plasma, the temperatures involved in the present calculation for argon plasma are the translational temperature of the heavy particles T_g $(= T_{t,\mathrm{Ar}} = T_{t,\mathrm{Ar}^+})$, the translational temperature of free electrons T_e $(= T_{t,e^-})$, and the excitation temperature T_x. The equilibrium constant K_p can be calculated and charts for argon composition calculation can be constructed for various combinations of T_g, T_e, and T_x. Shown in Fig. 2 is the equilibrium constant for $p^0 = 1$ atm for various translational and excitation nonequilibria. Figure 2 shows that an increase in T_e results in a significant increase in K_p, whereas change in T_x has only a little effect on the equilibrium constant in the temperature range considered here. The difference between the equilibrium constants for $T_e/T_g = 1$ and 1.5 decreases as T_g decreases. This is because at very low temperatures the degree of ionization is low and a high electron translational temperature will not strongly affect the equilibrium constant.

If all the non-LThE temperatures at the exit can be measured, say via enthalpy probe and laser and/or emission spectroscopic techniques,[4] the equilibrium constant at the exit can be determined from Fig. 2. Then the number density of each species for neutral argon can be calculated from the ideal gas law for a given total pressure p. Alternatively, Eqs. (4), (6), and (9) can be combined to obtain a modified Saha equation for the ionization reaction of argon plasma, as done in Eddy and Cho's paper.[4] But use of the Saha equation is generally limited to ionization reactions, whereas Eq. (16) is applicable to all chemical reactions.

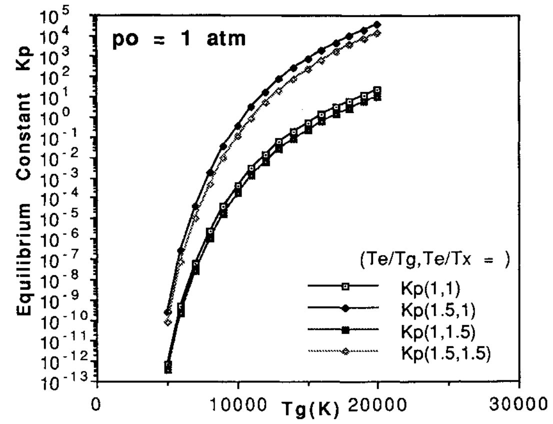

Fig. 2 Equilibrium constant for singly ionized argon at $p^0 = 1$ atm for various kinetic and excitation conditions.

For a gas mixture not in local chemical equilibrium, the properties and composition are functions of pressure, temperatures, as well as chemical affinity. If we assume the heating process in Fig. 1 is constant-pressure, the enthalpy, entropy, and other thermodynamic properties for neutral argon at 1 atm and at the measured exit temperatures can be computed for a variety of affinity values. The specific enthalpy of a GMTE argon plasma is calculated from

$$h = \sum m_j n_j h_j \tag{28}$$

where

$$\begin{aligned}
h_j &= h_{t,j} + h_{x,j} + h_{\mathrm{chem},j}\\
h_{t,j} &= 2.5kT_{t,j}\\
h_{x,j} &= kT_{x,j}Z'_{x,j}/Z_{x,j}\\
Z_{x,j} &= \sum g_{xm}\exp[-\varepsilon_{xm}/(kT_{x,j})]\\
Z'_{x,j} &= \sum g_{xm}[\varepsilon_{xm}/(kT_{x,j})]\exp[-\varepsilon_{xm}/(kT_{x,j})]\\
h_{\mathrm{chem},j} &= 0 \text{ for } j = \mathrm{Ar} \text{ and } \mathrm{e}^-\\
&= 2.5264 \times 10^{-9} \text{ erg for } j = \mathrm{Ar}^+
\end{aligned}$$

The entropy of the argon plasma is calculated from

$$s = \sum m_j n_j s_j \tag{29}$$

where

$$\begin{aligned}
s_j &= s_{t,j} + s_{x,j}\\
s_{t,j} &= k[\ln(Z_{t,j}/N_j) + 2.5]\\
s_{x,j} &= k(\ln Z_{x,j} + Z'_{x,j}/Z_{x,j})
\end{aligned}$$

For a one-dimensional steady flow of argon from state 1 to state 2, the first law of thermodynamics becomes

$$h_2 = h_1 + q_{12} + \Delta\mathrm{KE} + \Delta\mathrm{PE} \tag{30}$$

where q_{12} is the net heat input per unit mass flow between states 1 and 2. If the heat loss from the heating section can be measured and the changes in kinetic and potential energies, ΔKE and ΔPE, are negligible, the increase in argon enthalpy can be calculated from the mass flow rate and the power consumption rate of the electromagnetic heater. Suppose the inlet and exit conditions and the heat input are measured as shown in Table 1.

The enthalpy, entropy, and density of argon at the exit temperature ratios are computed for various affinity values and presented in Figs. 3–5. The dimensionless affinity F^* in these figures is the dimensional affinity F divided by the negative value of the heat of reaction at 0 K. That is

$$F^* = F/H^0 \tag{31}$$

where

$$H^0 = -\sum \nu_j \Delta h_j \tag{32}$$

With h_2 calculated from the first-law equation, the dimensionless affinity at the exit is determined to be approximately −0.2 from Fig. 3. The density and entropy at the exit then can be determined from Figs. 4 and 5. Since H^0 is negative for the ionization reaction, the dimensional F is positive, which implies a slower backward reaction than the forward reaction, as shown in Eq. (3). The slow backward reaction rate is due to the lower than LChE concentrations of argon ions and free electrons. Consequently, the enthalpy and entropy for $F^* = -0.2$ is lower than those for $F^* = 0$ (LChE), because of less ions and free electrons in the mixture.

Table 1 Inlet and exit conditions of the flow in Fig. 1

Inlet	Exit
$T_e = T_g = T_x = 300$ K $p = 1$ atm	$T_g = 10{,}000$ K, $T_e = T_x = 15{,}000$ K $p = 1$ atm $q_{12} = 11{,}000$ kJ/kg

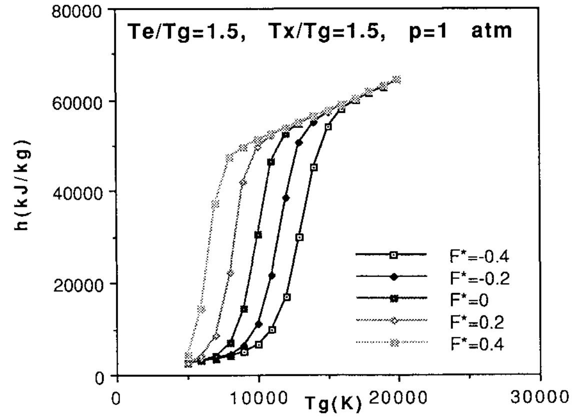

Fig. 3 Enthalpy of argon at $p = 1$ atm, $T_e/T_g = 1.5$, $T_e/T_x = 1$ for various affinity values.

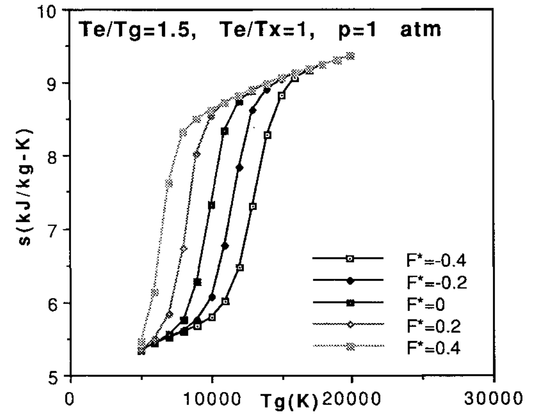

Fig. 4 Entropy of argon at $p = 1$ atm, $T_e/T_g = 1.5$, $T_e/T_x = 1$ for various affinity values.

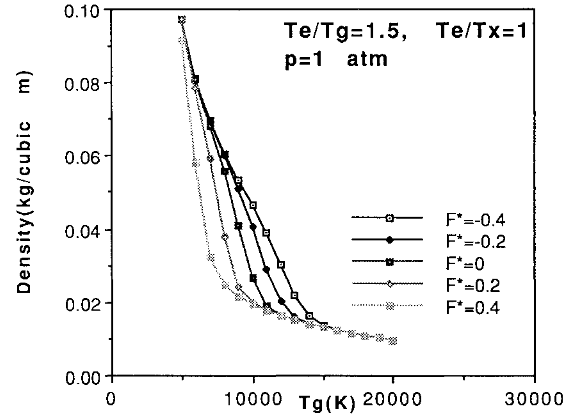

Fig. 5 Density of argon at $p = 1$ atm, $T_e/T_g = 1.5$, $T_e/T_x = 1$ for various affinity values.

If the change in kinetic energy is not negligible due to the high exit temperature, iteration on the exit affinity and density is needed until the first-law equation, Eq. (30), is satisfied. The composition of the argon plasma at the exit can be calculated from Eqs. (6) and (16). The ionization rate at the exit can be calculated from Eq. (21) if the reaction constants for the ionization of Ar to Ar$^+$ and e$^-$ at the exit temperatures can be determined experimentally or theoretically. It should be pointed out that the reaction constants are functions of all translational temperatures and the Arrhenius equation for reaction rate calculation must be modified accordingly for non-LThE gases.

Conclusions

Use of chemical affinity for the analysis of reacting flows that are not in LThE is investigated. Equations for composition and reaction rate computations are derived in terms of affinity for gases with thermal nonequilibrium. When modified stoichiometric coefficients and modified mole fractions are used, the relation between the affinity and the reaction rate for a multitemperature gas is reduced to the exponential function relation for LThE gases. Results of the present analysis are applied to the ionization reaction of non-LThE argon. Computed equilibrium constants for various kinetic and excitation nonequilibria show strong effects of the translational temperature, but only weak effects of the excitation temperature on argon composition and properties in the temperature range from 5000 to 20,000 K. An example is given to show that the analysis for non-LTE gas flows is similar to that for LTE gas flows, providing that thermodynamic tables or charts at different affinity values are available for various non-LThE temperatures.

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