Correlation of Chemical Freezing in a Freejet Expansion

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The chemical freezing process in a freejet is studied using an activation energy concept. The numbers of activated collisions for bimolecular reactions with various activation energies are computed along the freejet centerline for gases of specific heat ratios $\gamma = 5/3$, 7/5, and 9/7. It is found that the number of activated collisions in a freejet can be characterized by a dimensionless kinetic parameter defined by the ratio of the chemical activation energy divided by the random thermal energy, and by a dimensionless scaling parameter defined by the ratio of the flow time divided by the collision time. The chemical freezing point in a freejet determined using a last-activated-collision criterion is plotted as a function of the scaling and the kinetic parameters. It is found that complete chemical freezing in a freejet is obtained if the ratio of the logarithmic scaling parameter divided by the kinetic parameter is less than 0.5. An application of the present study to molecular-beam sampling from a reacting-species source is demonstrated.

Nomenclature

A = reactant species of interest
B = reactant-partner species
Ch_f = chemical-freezing-point parameter defined by Eq. (18)
E^* = activation energy
$\tilde{E}^*$ = kinetic parameter
Kn = Knudsen number
M = Mach number
$\dot{N}_{AB}$ = rate of activated collisions of a given A molecule with any B molecule
$N_{AB}^{\bar{x}-d}$ = total number of activated collisions of a given A molecule with any B molecule between point $\bar{x}$ and detector d
R,S = reaction-product species
T = temperature
$(T_{\mathrm{ch}})_f$ = temperature evaluated at the chemical freezing point
a = speed of sound
d^* = sonic diameter of the sampling orifice
d_{AB} = zero-energy collision diameter of the collision pair $A+B$
f = mole fraction
k = Boltzmann constant
m^* = $m_A m_B/(m_A+m_B)$, reduced molecular mass
n = number density
p = pressure
t = time
u = hydrodynamic speed
x = distance measured from the sonic orifice
$\Omega^{(1,1)*}$ = reduced collision integral
γ = average specific heat ratio of the gas mixture
τ_{AB} = average time between collisions of a given A molecule with any B molecule
$\tilde{\tau}$ = scaling parameter
$\tilde{\ }$ = normalized quantity, variously defined
$(\ )_l$ = evaluated using the last-activated-collision criterion
$(\ )_f$ = evaluated at the freezing point

Subscripts

B = species B
0 = quantity evaluated at the sampling source
$1,2$ = quantity evaluated at points 1 and 2

Introduction

APPLICATIONS of the supersonic molecular beam to sampling of high-temperature reactive gas mixtures have increased steadily in the past few years. A major difficulty encountered in this sampling technique is the possible composition distortions caused by a) chemical relaxation, b) vibrational relaxation, c) species condensation, d) pressure diffusion, and e) Mach number focusing. Many of these have been discussed previously; in some cases, criteria for either avoiding or minimizing the distortions have been suggested.[1-5] As a result of the rapid quenching rate encountered in the freejet, the effect of chemical relaxation has been ignored often in low-temperature sampling. However, since the chemical relaxation time decreases drastically at high temperature, the effect of chemical relaxation is no longer negligible. In a freejet expansion, since the chemical freezing takes place before vibrational relaxation and/or species condensation (if any) become significant, attention in this paper is focused on chemical relaxation alone; possible distortions by other mechanisms are referred to in the literature cited above.

The chemical reactions in nonequilibrium flows have been studied by numerous authors. Using a sudden-freezing model, Bray[6] found that the reservoir entropy can be used to correlate the nonequilibrium flow. Later, Harris and Warren,[7] and Ring and Johnson[8] extended Bray's correlation parameter to include a term corresponding to a linear scale shift of the entropy due to the flow-time scaling factor. Since both the reservoir entropy and the flow-time scaling parameter are not normalized, and since only the dissociations of air species are considered in those studies, applications of their results to other systems are limited. In a recent review, Knuth[9] studied the chemical relaxation processes in flow systems and combined Bray's sudden-freezing model with Phinney's relaxation-time-freezing-point criterion to obtain a chemical relaxation equation characterized by two dimensionless parameters; namely, the kinetic parameter defined by the ratio of the chemical activation energy divided by the random thermal energy, and the scaling parameter defined by the ratio of the flow time divided by the collision time. Since Knuth used dimensionless correlation parameters, his results are valid not only for general chemical relaxation processes, but also for other types of relaxation

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processes (e.g., vibrational relaxation) so long as the dimensionless correlation parameters are properly chosen.

In this paper, the chemical reaction of a given species in freejet is studied using an activation energy theory. The number of activated collisions of a molecule of a given species is computed along the flow path, and the chemical freezing point is determined using a last-activated-collision model; in this model, a given chemical reaction freezes approximately at the location where the sample molecule encountered its last activated collision. In an agreement with Knuth's study, the present analysis also shows that the extent of chemical reaction in a freejet is characterized by the dimensionless kinetic and scaling parameters. More importantly, the present analysis reveals that complete chemical freezing in a freejet is obtained if the ratio of the logarithmic scaling factor divided by the kinetic parameter is less than 0.5. This result can be used as a design criterion to develop a sampling system which avoids composition distortions by chemical reactions in the sampling jet.

Analysis

Essentially all chemical reactions can be divided into three groups: unimolecular, biomolecular, and trimolecular. Reactions of a higher order are improbable due to the negligible probability of the simultaneous collision of four molecules. Of the three reaction mechanisms cited, the bimolecular reaction is encountered most frequently in practice. Therefore, in the following analysis, we consider only the bimolecular reaction.

Consider two species A and B reacting according to

$$A+B=R+S+\ldots \tag{1}$$

where R, S, etc. denote the reaction products. Furthermore, since in a freejet both the density and the temperature decrease drastically, the reverse reaction is negligible and thus is not considered here. Activation energy theory states that only those binary collisions with energies higher than the activation energy E^* are responsible for the reaction. Since the fraction of species A removed by reaction (1) equals the probability of a given A molecule reacting with any B molecule, the latter approach is adopted here for simplicity. The number of activated collisions of a given A molecule with any B molecule per unit time is given by

$$\begin{aligned}\dot{N}_{AB} &= (1/\tau_{AB})\exp(-E^*/kT)\\ &= (8kT/\pi m^*)^{1/2}\cdot \pi d_{AB}^2\Omega^{(1,1)*} n_B \exp(-E^*/kT)\end{aligned} \tag{2}$$

where τ_{AB} is the mean time between collisions of a given A molecule with any B molecule, n_B is the local number density of species B, T is the static temperature in the freejet, d_{AB} is the average diameter of the collision pair, m^* is the reduced molecular mass, E^* is the activation energy, k is the Boltzmann constant, and $\Omega^{(1,1)*}$ is the reduced collision integral.

Equation (2) can be simplified using the following normalized quantities

$$\tilde{\dot{N}}_{AB} \equiv \dot{N}_{AB}/\dot{N}_{AB_0} \tag{3a}$$

$$\tilde{n}_B \equiv n_B/n_{B_0} \tag{3b}$$

$$\tilde{T} \equiv T/T_0 \tag{3c}$$

and the kinetic parameter

$$\tilde{E}^* = E^*/kT_0 \tag{3d}$$

where the subscript 0 denotes the stagnation condition. With the assumption that the reduced collision integral is inversely proportional to the one-third power of the temperature, Eq. (2) is reduced to

$$\tilde{\dot{N}}_{AB} = \tilde{n}_B \tilde{T}^{1/6} \exp\{-\tilde{E}^*(1/\tilde{T}-1)\} \tag{4}$$

Introduce the following dimensionless distance and time

$$\tilde{x} \equiv x/d^* \tag{5a}$$

$$\tilde{t} \equiv \tilde{x}/\tilde{u} = (a_0/d^*)\ (x/u) = (1/\tilde{a}M)\tilde{x} \tag{5b}$$

where x is the distance measured from the sonic orifice, d^* is the sonic diameter of the sampling orifice, u is the hydrodynamic speed, a is the speed of sound, and M is the Mach number. Then, the normalized number of activated collisions of a given A molecule between two states $(\tilde{x}_1, \tilde{t}_1)$ and $(\tilde{x}_2, \tilde{t}_2)$ is calculated from

$$\tilde{N}_{AB}^{1-2} = \int_{\tilde{t}_1}^{\tilde{t}_2} \tilde{\dot{N}}_{AB}\,d\tilde{t} = \int_{\tilde{x}_1}^{\tilde{x}_2} \tilde{n}_B \tilde{T}^{-1/3} \exp\{-\tilde{E}^*(\frac{1}{\tilde{T}}-1)\}\,d\tilde{x}/m \tag{6}$$

Since we are interested in a near chemically frozen freejet, the number density n_B does not deviate much from the isentropic-expansion value, and thus $\tilde{n}_B$ is related to the Mach number by

$$\tilde{n}_B \equiv n_B/n_{B0} = [1+(\gamma-1)M^2/2]^{-1/(\gamma-1)} \tag{7}$$

where γ is the averaged specific heat ratio of the gas mixture. Furthermore, the temperature $\tilde{T}$ is related to M by

$$\tilde{T} = T/T_0 = [1+(\gamma-1)M^2/2]^{-1} \tag{8}$$

Combining Eqs. (6-8), we obtain

$$\begin{aligned}\tilde{N}_{AB}^{1-2} &= \int_{\tilde{x}_1}^{\tilde{x}_2} (1+\frac{\gamma-1}{2}M^2)^{(\gamma-4)/3(\gamma-1)}\\ &\times \exp\{-\frac{\gamma-1}{2}\tilde{E}^* M^2\}\,d\tilde{x}/M\end{aligned} \tag{9}$$

The Mach number along the jet centerline has been reported by Ashkenas and Sherman[10]

$$\begin{aligned}M &= 3.26(\tilde{x}-0.075)^{0.67}\\ &\quad -0.536/(\tilde{x}-0.075)^{0.67} \qquad \gamma=5/3\end{aligned} \tag{10a}$$

$$\begin{aligned}M &= 3.65(\tilde{x}-0.40)^{0.4}\\ &\quad -0.822/(\tilde{x}-0.40)^{0.4} \qquad \gamma=7/5\end{aligned} \tag{10b}$$

$$\begin{aligned}M &= 3.96(\tilde{x}-0.85)^{0.286}\\ &\quad -1.01/(\tilde{x}-0.85)^{0.286} \qquad \gamma=9/7\end{aligned} \tag{10c}$$

Equation (10) is valid for $\tilde{x} \geq 2$.

In the flow region near the sonic orifice, the centerline Mach number is calculated using Eq. (8) with T evaluated from[2]

$$M = \{(\gamma+1)/(\gamma-1)\exp[4(\gamma-1)\tilde{x}/(\gamma+1)] - 2/(\gamma-1)\} \tag{11}$$

The Mach number in the range $0<x<2$ is obtained by joining the two solutions; Eqs. (10) and (11).

It is seen that Eq. (9) can be readily integrated along the jet centerline once the quantity $\tilde{E}^*$ is given. If, in Eq. (9), we let $\tilde{x}_2 \to \infty$, then the integral gives the total normalized number of activated collisions which a given A molecule would encounter after it passes point $\tilde{x}_1$. In a typical molecular-beam-sampling application, the detector is located far downstream from the sampling source. Therefore, the normalized number of activated collisions between a point $\tilde{x}$ and the detector is given approximately by

$$\tilde N_{AB}^{\tilde x - d} \simeq \int_{\tilde x}^{\infty} \left(1+\frac{\gamma-1}{2}M^2\right)^{(\gamma-4)/3(\gamma-1)} \times \exp\left\{-\frac{\gamma-1}{2}M^2\tilde E^*\right\} \mathrm{d}\tilde x/M \qquad (12)$$

The corresponding actual number of activated collisions, $N^{\tilde x}{}_{AB}^{-d}$ is related to the normalized number by

$$\dot N_{AB} = \dot N_{AB_0}\tilde N_{AB}$$

which yields

$$N_{AB}^{\tilde x - d} = \int_t^{\infty} \dot N_{AB}\mathrm{d}t$$

$$= \int_t^{\infty} \dot N_{AB_0}\tilde N_{AB}\mathrm{d}t$$

$$= \dot N_{AB_0}\frac{d^*}{a_0}\int_{\tilde t}^{\infty} \tilde N_{AB}\mathrm{d}\tilde t$$

or

$$N_{AB}^{\tilde x - d} = (d^*/a_0)\dot N_{AB_0}\tilde N_{AB}^{\tilde x - d} \qquad (13)$$

It is seen that the actual number of activated collisions $N_{AB}^{\tilde x - d}$ is the product of the sampling source parameter $\dot N_{AB_0}d^*/a_0$, and the normalized quantity $\tilde N_{AB}^{\tilde x - d}$, which depends on the quenching process. In molecular-beam sampling, the detected composition of species A will correspond to its equilibrium value at the location where the last activated collision takes place. In other words, the chemical freezing of species A will take place approximately at the location where $N_{AB}^{\tilde x - d} = 1$. The corresponding value of $\tilde N_{AB}^{\tilde x - d}$ follows from Eq. (13)

$$(\tilde N_{AB}^{\tilde x - d})_f \approx (a_0/d^*)\ (1/\dot N_{AB_0}) \qquad (14)$$

where $(\ )_f$ represents the freezing value based on the last-activated-collision criterion.

Equation (14) can be written in the alternative form

$$(\tilde N_{AB}^{\tilde x - d})_f\tilde\tau = \exp\tilde E^* \qquad (15)$$

where

$$\tilde\tau \equiv \text{scaling parameter} = d^*/a_0\tau_{AB_0} \qquad (16)$$

Note that the scaling parameter is related to the Knudsen number Kn_{0B} by

$$\tilde\tau = (4/\gamma\pi)^{1/2}(m/m^*)^{1/2}1/Kn_{0B} \qquad (16')$$

where

$$1/Kn_{0B} = \sqrt{2}\pi d_{AB}^2 n_{B0}d^*\Omega_0^{(1,1)^*} \qquad (17)$$

and m is the average molecular weight of the gas mixture. Hence the scaling parameter is proportional to, and of the same order of magnitude as, the inverse Knudsen number.

Results

The normalized numbers of activated collisions described by Eq. (12) are computed for $\gamma = 5/3$, $7/5$, and $9/7$, and are shown in Figs. 1a-c. During the numerical integration of Eq. (12), an upper limit of $\tilde x = 1000$ was used. In all cases for $\tilde E^* = 0$, the calculated $\tilde N_{AB}^{\tilde x - d}$ is smaller than 10^{-15} for $\tilde x > 10$. Therefore, the use of $\tilde x = 1000$ for the upper limit in-

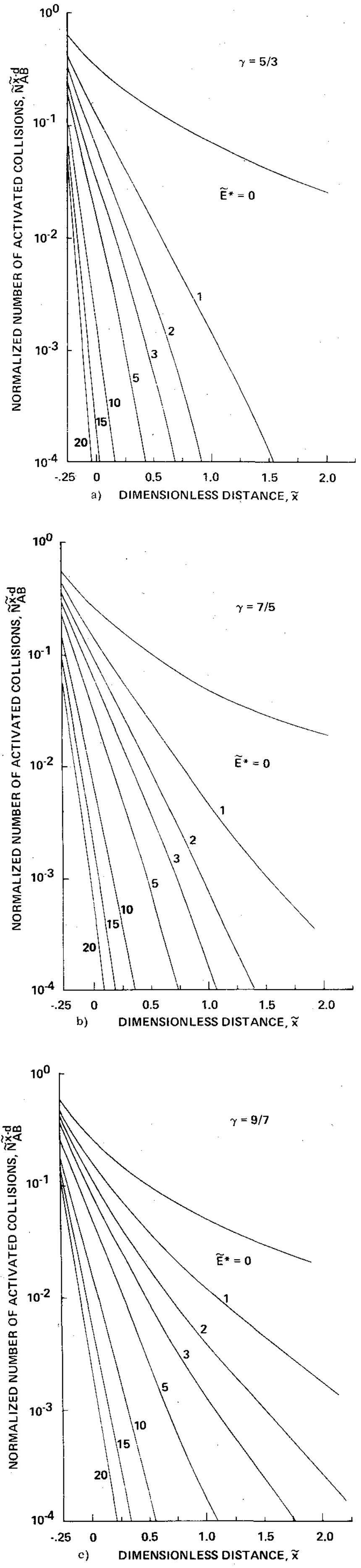

Fig. 1 Normalized number of activated collisions measured from $\tilde x \to \infty$ [see Eq. (12)]; a) $\gamma = 5/3$; b) $\gamma = 7/5$; c) $\gamma = 9/7$.

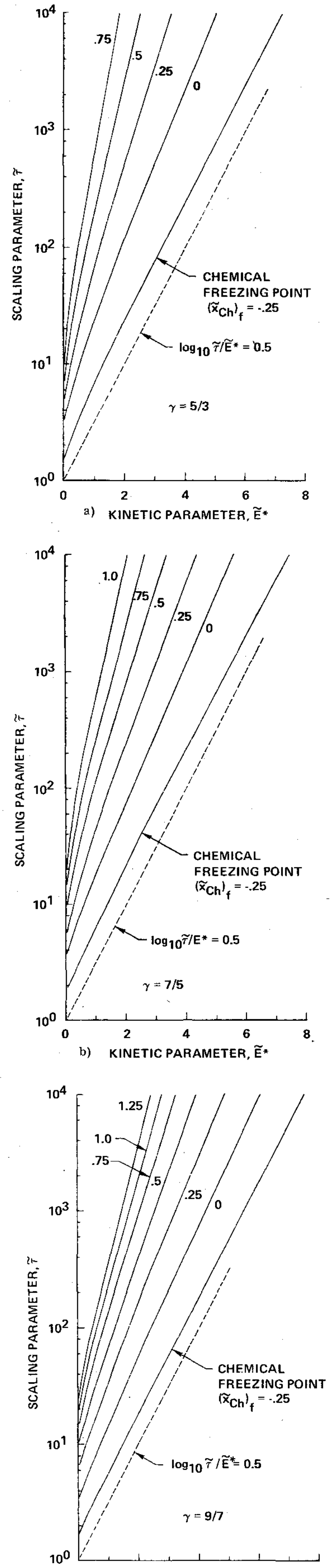

Fig. 2 **Chemical freezing point as function of dimensionless scaling parameter $\tilde{\tau}$ and kinetic parameter $\tilde{E}^*$. a) $\gamma=5/3$; b) $\gamma=7/5$; c) $\gamma=9/7$.**

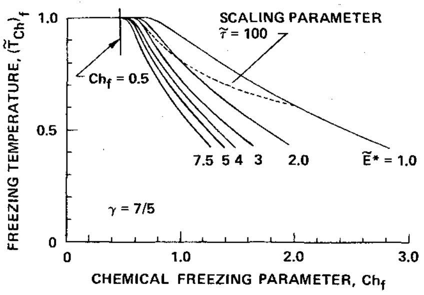

Fig. 3 **Normalized chemical freezing temperature $(\tilde{T}_{Ch})_f$ vs chemical freezing parameter Ch_f. The dashed line corresponds to scaling parameter $\tilde{\tau}=100$.**

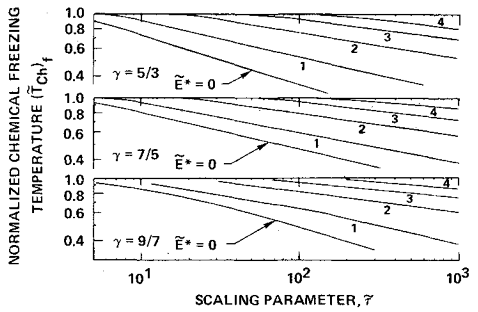

Fig. 4 **Normalized chemical freezing temperature $(\tilde{T}_{Ch})_f$ vs scaling parameter $\tilde{\tau}$.**

troduces negligible error in the final results. We see that, for a given $\tilde{x}$, the normalized number of activated collisions drops drastically, and chemical freezing occurs much earlier, as the kinetic parameter $\tilde{E}^*$ increases.

Using the chemical freezing criterion suggested by Eq. (14), we obtain the chemical freezing points directly from Figs. 1a-c. These freezing points are plotted as a function of the kinetic parameter and the scaling parameter in Figs. 2a-c. We see that, except of $\tilde{E}^* \approx 0$, the slope of each "freezing point" line is nearly constant. This observation motivates the chemical freezing point parameter Ch_f

$$Ch_f \equiv \log_{10}\tilde{\tau}/\tilde{E}^* \qquad (18)$$

For $Ch_f<0.5$, the chemical freezing takes place deep inside the orifice and the chemical reaction in the freejet is negligible. For $Ch_f>0.5$, chemical reaction occurs in the freejet and the extent of reaction increases as Ch_f increases. This is shown more clearly in Fig. 3, where the normalized chemical freezing temperature is plotted vs the chemical freezing parameter Ch_f for the case of $\gamma = 7/5$. We see that for $Ch_f<0.5$, $(\tilde{T}_{Ch})_f \approx 1.0$ for all cases. For $Ch_f>0.5$, the figure shows that, for a given value of Ch_f, the larger the kinetic parameter $\tilde{E}^*$, the lower the freezing temperature and hence the greater the effects of reactions in the freejet. However, since frequently the design of a molecular-beam system is determined by the scaling parameter, Ch_f varies with $\tilde{E}^*$. Figure 3 shows that if $\tilde{\tau}=100$ (indicated by the dashed line), then the chemical freezing temperature (determined from the intercept of $\tilde{E}^*$ curve and the dashed line) increases from 0.6 to approximately 1.0 when the kinetic parameter $\tilde{E}^*$ increases from 1.0 to 3.0. (See also Fig. 4.)

Table 1 Summary of the computed results for the example of NO sampling from an internal-combustion engine

Sampling nozzle diam d^*, cm	0.05
Knudsen number Kn_{00}	0.177
Kinetic parameter $\tilde{E}^*$	7.5
Scaling parameter $\tilde{\tau}$	8.98
Chemical freezing parameter Ch_f	0.127

If the chemical freezing parameter Ch_f is considerably larger than 0.5, then composition distortions due to chemical reaction in the freejet are not negligible and quantitative corrections to the sampling data are required. Since the freezing composition equals approximately the equilibrium composition calculated using the temperature evaluated at the chemical freezing point, the prediction of the chemical freezing temperature appears useful for practical applications. Hence the normalized chemical freezing temperature is plotted in Fig. 4 as a function of τ for several values of $\tilde{E}^*$ and for $\gamma = 5/3$, 7/5, and 9/7. We see that, for constant $\tilde{\tau}$, the freezing temperature increases as $\tilde{E}^*$ increases.

For most sampling systems, the scaling parameter is smaller than 1000. Figure 4 indicates that, for $\tilde{\tau}$ less than 1000, the composition distortion in the freejet is negligible if $\tilde{E}^* > 6$.

As an example, consider the sampling of NO from an internal-combustion engine when the piston is near the top dead center (where the chemical-reaction rate is highest). Consider the following reaction (which might lead to decomposition of NO during the expansion)

$$NO + 0 \rightarrow O_2 + N$$

The gas temperature, pressure, and the O-atom mole fraction inside the sampling source (i.e., the combustion chamber) are typically[11]

$$T_0 = 2665K$$

$$p_0 = 27.2 \text{ atm}$$

$$f_0 = 5.08 \times 10^{-4}$$

The O-atom number density calculated using the above cited data is $n_0 = 3.88 \times 10^{16}$ molecules/cm^3. Using the transport properties given by Brokaw,[12] we obtain $d_{NO\text{-}O} = 3.19 \times 10^{-8}$ cm, and $\Omega^{(1,1)*}_{NO-O} = 0.645$ at $T_0 = 2665K$. Table 1 shows the computed results for a sampling-orifice diameter of $d^* = 0.5$ cm, for which the chemical freezing parameter $Ch_f < 0.5$; thus no NO decomposition in the sampling freejet is expected.

Discussions and Conclusions

The chemical relaxation of a bimolecular reaction in a freejet is studied. The number of activated collisions along the jet centerline are computed for gases with specific heat ratios $\gamma = 5/3$, 7/5, and 9/7. A last-activated-collision criterion for determining the chemical freezing is characterized by two dimensionless parameters; namely, the scaling parameter $\tilde{\tau}$, and the kinetic parameter $\tilde{E}^*$.

A chemical freezing parameter Ch_f defined by Eq. (18) is introduced. This new parameter is found most convenient for estimating the condition under which complete chemical freezing is achieved. More specifically, if $Ch_f < 0.5$ then chemical freezing takes place deep inside the sampling orifice and composition distortion due to chemical reaction in the freejet expansion is minimized. This condition for complete chemical freezing appears to be more specific than the early freezing criterion given by Knuth [see Eq. (54), Ref. 2]. If $Ch_f > 0.5$, then chemical reaction takes place inside the freejet and composition corrections must be made in order to obtain quantitative sampling data. In principle, the extent of chemical reaction inside the freejet can be calculated using the measured chemical composition† together with the normalized chemical freezing temperature $(T_{Ch})_f$. However, these corrections are frequently tedious.

The analysis is made for the case of a single bimolecular reaction. For a system involving multiple bimolecular reactions, the freezing criterion must be evaluated for all reactions. Furthermore, since the hydrodynamic properties of the freejet depend on the gas mixture as a whole, the specific heat ratio of the mixture must be used. The results presented are for the cases of $\gamma = 5/3$, 7/5, and 9/7. However, in view of the fact that only small differences exist among results computed for those three different cases (see, for example, Figs. 2 and 4), it is believed that the results can be interpolated to obtain solutions for other values of γ.

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†Proper corrections for pressure diffusion, Mach number focusing, etc., must also be considered. See Refs. 2-5 for detailed descriptions.