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Influence of Heterogeneous Reaction Processes on Atomic Recombination Rates in Rocket Nozzles[1]

Influence of Heterogeneous Reaction Processes on Atomic Recombination Rates in Rocket Nozzles[1]

By

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Abstract — Zusammenfassung — Résumé

Influence of Heterogeneous Reaction Processes on Atomic Recombination Rates in Rocket Nozzles. Approximate relations are derived for determining under what conditions in two-phase flow heterogeneous two-body processes are expected to proceed as rapidly as the homogeneous three-body recombination reaction.

Über den Einfluß heterogener Reaktionsprozesse auf die atomare Rekombinationsrate in Raketendüsen. Näherungsbeziehungen für heterogene Rekombinationsprozesse werden angegeben, um zu untersuchen, welche Größenordnung diese Prozesse im Vergleich zu der Größenordnung des gleichzeitig vorhandenen homogenen Rekombinationsprozesses besitzen.

Influence de réactions hétérogènes sur le taux des recombinaisons atomiques dans les tuyéres de fusèes. On établit à l'aide de relations approchées dans quelles conditions les processus de réaction hétérogènes à deux constituants ont une rapidité d'évolution comparable aux processus homogène de recombinaison à trois constituants.

List of Symbols

k	Boltzmann constant
k_{2a}, k_{2b}	specific reaction rate constants, in $(\text{mole})^{-1}$-cm^3-sec^{-1}
k_3	specific reaction rate constant for the three-body recombination reaction, in $(\text{mole})^{-2}$-$(\text{cm}^3)^2$-sec^{-1}
m_A	mass of molecule A
N	Avogadro's number
n_A	number of molecules of type A per cm^3
$\sigma_{1,2}$	distance at collision between molecular centers for molecules of type 1 and type 2 $= \frac{1}{2}(\sigma_1 + \sigma_2)$ for rigid elastic spheres
(A)	concentration of A in mole/cm^3
$Z_{1,2}$	total number of collisions per sec per cm^3 for molecules of type 1 with molecules of type 2
σ_A	collision diameter of molecule A

I. Introduction

In two-phase nozzle flow processes, it is of interest to consider the relative importance of a three-body gas-phase recombination reaction and of a succession of heterogeneous two-body reactions. We confine the following considerations to a uniform mixture of gaseous hydrogen and small liquid or solid particles[3].

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[3] The argument may be modified, without difficulty, to the case where a large molecule plays the role of the solid particles.

These computations are of interest in connection with the development of experimental procedures for improving the performance of nuclear rockets using hydrogen as driving fluid. They are readily modified to infer conditions under which the flow processes in hypersonic air-breathing engines can be influenced by induced, heterogeneous chemical reactions.

II. Outline of Theoretical Considerations

The two assumed reaction paths for the recombination of hydrogen atoms are:

$$2H + X \xrightarrow{k_3} H_2 + X, \tag{1}$$

$$H + Y \xrightarrow{k_{2a}} H --- Y, \tag{2 a}$$

$$H + H --- Y \xrightarrow{k_{2b}} H_2 + Y. \tag{2 b}$$

The quantities k_3, k_{2a}, k_{2b} denote appropriate specific reaction rate coefficients, X represents the dominant species (i.e., either H or H_2), Y is a small solid or liquid particle, and $H --- Y$ denotes a hydrogen atom adsorbed on the surface of Y.

According to Eqs. (1) and (2), the rate of disappearance of hydrogen atoms by three body processes is

$$-\left[\frac{d(H)}{dt}\right]_3 = 2\,k_3 (H)^2 (X)$$

or

$$-\left[\frac{dn_H}{dt}\right]_3 = \frac{2\,k_3}{N^2}\, n_H{}^2\, n_X; \tag{3}$$

the rate of disappearance of hydrogen atoms by two-body processes is,

$$-\left[\frac{d(H)}{dt}\right]_2 = k_{2a}(H)\,(Y) + k_{2b}(H)\,(H --- Y)$$

or

$$-\left[\frac{dn_H}{dt}\right]_2 = \frac{1}{N}\,(k_{2a}\, n_H\, n_Y + k_{2b}\, n_H\, n_{H---Y}). \tag{4}$$

Hence the ratio

$$R \equiv \frac{-(dn_H/dt)_2}{-(dn_H/dt)_3} = \frac{N\,(k_{2a}\, n_H\, n_Y + k_{2b}\, n_H\, n_{H---Y})}{2\,k_3\, n_H{}^2\, n_X} \tag{5}$$

is a measure of the relative importance of heterogeneous two-body to three-body processes in the removal of hydrogen atoms.

We shall now estimate this ratio in terms of $(n_Y + n_{H---Y})/n_H$. Observations by various investigators have shown conclusively that the three-body recombination process occurs without appreciable activation energy [1]. We denote by α the fractional number of collisions that lead to adsorption in reaction (2 a), and by β the fractional number of collisions leading to H_2 formation in reaction (2 b).

For a mixture of gases containing molecules of different sizes and concentrations, the total number of collisions of molecules of type 1 with molecules of type 2 in unit volume in unit time is [2]

$$Z_{1,2} = 2\, n_1\, n_2\, \sigma_{1,2}{}^2 \sqrt{2\pi k T\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}. \tag{6}$$

Hence

$$-\left[\frac{dn_H}{dt}\right]_2 = \alpha Z_{H,Y} + \beta Z_{H,H---Y} \tag{7}$$

and

$$-\left[\frac{dn_H}{dt}\right]_2 = 2\,\alpha\, n_H\, n_Y\, \sigma_{H,Y}{}^2 \sqrt{2\pi k T\left(\frac{1}{m_H}+\frac{1}{m_Y}\right)} + $$
$$+ 2\,\beta\, n_H\, n_{H---Y}\, \sigma_{H,H---Y}{}^2 \sqrt{2\pi k T\left(\frac{1}{m_H}+\frac{1}{m_{H---Y}}\right)}. \tag{8}$$

For the case where $m_Y \gg m_H$, $m_{H---Y} \gg m_H$, and $\sigma_Y \simeq \sigma_{H---Y} \gg \sigma_H$, we obtain

$$-\left[\frac{dn_H}{dt}\right]_2 \simeq \sqrt{\frac{2\pi k T}{m_H}}\,\frac{n_H}{2}\,\sigma_Y{}^2\,(\alpha\, n_Y + \beta\, n_{H----Y}). \tag{9}$$

If the concentrations (H), (Y), and $(H---Y)$ are small compared with that of (H_2), then $n_X \approx n_{H_2}$ and we obtain for R from Eqs. (3), (5) and (9) the result

$$R \simeq \sqrt{\frac{2\pi k T}{m_H}}\,\frac{N^2 \sigma_Y{}^2}{4 k_3 n_{H_2}}\left(\frac{\alpha\, n_Y + \beta\, n_{H---Y}}{n_H}\right). \tag{10}$$

III. Numerical Estimates and Conclusions

The ratio R has been calculated from Eq. (10) for the following numerical values: $T = 1365°$ K, pressure = 5 atmos, $\sigma_Y = 3 \times 10^{-6}$ cm, and $k_3 = 5.4 \times 10^{15}$ (mole)$^{-2}$-(cm^3)^2-sec^{-1}. We find that

$$R \simeq (4.7 \times 10^6)\left(\frac{\alpha\, n_Y + \beta\, n_{H---Y}}{n_H}\right).$$

We therefore conclude that heterogeneous two-body processes will become of comparable importance with the three-body gas-phase collisions if

$$\left(\frac{\alpha\, n_Y + \beta\, n_{H---Y}}{n_H}\right) \gtrsim 2 \times 10^{-7}$$

or

$$\left(\frac{n_Y + n_{H---Y}}{n_H}\right) \gtrsim 2 \times 10^{-6}$$

for $\alpha = \beta = 0.1$. But, for a representative propellant system in two-phase nozzle flow, $(n_{H_2}) \simeq 10^{20}$ cm^{-3}, $(n_H) \simeq 10^{18}$ cm^{-3}, and $[(n_Y) + (n_{H---Y})] \simeq 10^{12}$ to 10^{15} cm^{-3}. Hence $(n_Y + n_{H---Y})/n_H \simeq 10^{-6}$ to 10^{-3}, i.e., the heterogeneous recombination processes may actually become dominant.

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