Effect of Vibrational Excitation on the Theoretical Performance of the Stoichiometric Carbon-Oxygen Propellant System

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Accurate calculations to evaluate the performance of the stoichiometric carbon-oxygen propellant system have been carried out for nozzle flow with and without chemical reactions and with and without vibrational adjustment. The calculations show that, for frozen chemical flow, a lag of vibrational energy states at chamber conditions nearly doubles the reduction in $l_m$, as compared with flow in which complete vibrational equilibrium is maintained. On the other hand, lags in vibrational adjustment have practically no effect on the theoretical performance of hot propellant systems if chemical equilibrium is maintained during nozzle flow. The preceding conclusions are in agreement with the results on other propellant systems obtained previously by use of an approximate evaluation procedure.

I Introduction

It is well known that the over-all performance of rocket propellant systems is dependent on the extent to which physical-chemical changes occur during nozzle flow. Thus it is customary to report specific impulse data for "equilibrium flow" (the chemical reactions are fast enough to maintain thermodynamic equilibrium at all times) and for "frozen flow" (the chemical composition remains unchanged at the concentrations corresponding to thermodynamic equilibrium in the combustion chamber). Practical experience has shown that this method of estimating reasonable upper and lower bounds for performance evaluation is generally in accord with experimental results.

Implicit in the customary propellant evaluation procedures is the assumption that complete thermodynamic equilibrium is maintained during flow with respect to excitation of internal degrees of freedom. It is apparent, however, that sizable departures from equilibrium internal excitation may occur, for example, for the vibrational degrees of freedom, particularly for non-hydrogen-containing propellant systems in small motors for which the vibrational relaxation times may not be short compared to the residence time (1, 2). Approximate estimates of the effect of vibrational excitation on performance of rockets have been carried out previously by Penner (3).

It is the purpose of the present analysis to present the first accurate evaluation of the probable combined effects of chemical and vibrational lags during nozzle flow. Performance calculations have been carried out for the following special cases: (a) Complete thermodynamic equilibrium is maintained (equilibrium flow). (b) Complete thermodynamic equilibrium is maintained with respect to internal energy states but no chemical reactions occur during nozzle flow (frozen flow). (c) Complete thermodynamic equilibrium is maintained except that no adjustments of vibrational degrees of freedom occur during flow (chemically equilibrium and vibrationally frozen flow). (d) Complete thermodynamic equilibrium is maintained except that no chemical reactions and no adjustment of the vibrational degrees of freedom occur during flow (chemically and vibrationally frozen flow).

II Basic Equations

The requisite basic equations for cases (a) to (d) have been given elsewhere (4). For the present purposes it will be convenient to express the chemical composition by the mole fractions of the various chemical species. In terms of mole fractions it is readily shown (4) that [7], [8], [11], and [12] of Reference (4) become, respectively:

(a) For equilibrium flow

$$v \bar{M}_{ke} a^2 = \Delta H_{ke} e = \sum_{k=1}^{n} N_{ke} [H_{ke} - H_{ke}^{e}]$$

(b) For frozen flow

$$\bar{M}_{ke} a^2 = \Delta H_{ke} e = \sum_{k=1}^{n} N_{ke} [H_{ke} - H_{ke}^{e}]$$

(c) For chemically equilibrium and vibrationally frozen flow

$$\bar{M}_{ke} a^2 = \Delta H_{ke} e + (\bar{M}_{ke} / \bar{M}) \sum_{k=1}^{n} N_{ke} [H_{ke}^{vib} - H_{ke}^{vib}]$$

(d) For chemically and vibrationally frozen flow

$$\bar{M}_{ke} a^2 = \Delta H_{ke} e + \sum_{k=1}^{n} N_{ke} (H_{ke}^{vib} - H_{ke}^{vib})$$

1 Numbers in parentheses refer to the References on page 27.

2 The usual simplifying assumptions in propellant evaluation, which do not involve consideration of rate processes, are the following: Thermodynamic equilibrium is reached in the combustion chamber after adiabatic reaction; expansion of the combustion products through the Laval nozzle is adiabatic; the products of combustion behave as ideal gases; the adiabatic expansion may be considered to involve one-dimensional flow (parallel to the nozzle axis) of nonviscous ideal gases; the velocity of the gases at the nozzle entrance position is negligibly small compared to that at the exit position. For further details concerning customary evaluation techniques see, e.g., "Quantitative Evaluation of Rocket Propellants," by S. S. Penner, American Journal of Physics, Vol. 20, 1952, pp. 26–31.
In [1a] to [1d], \( u_e \) represents the linear flow velocity at the nozzle exit position, \( N_{r_a}^* \) and \( N_{s_b}^* \) are the equilibrium mole fractions of species \( k \) evaluated at the chamber exit and nozzle exit positions, respectively; \( H_{r_a}, H_{s_b}, H_{r_a}^*, \) and \( H_{s_b}^* \) equal the total enthalpy (sensible plus chemical enthalpy) per mole of species \( k \) if complete internal equilibrium exists at the nozzle entrance and exit positions, respectively; the subscript \( vib \) signifies that only the vibrational enthalpy is involved; the subscript \( o \) denotes chemical equilibrium during flow; without the subscript \( o \) the flow process occurs without composition change \((H_{r_a}^{*o} = H_{s_b}^{*o})\).

From [1a] to [1d] it is apparent that the evaluation of \( u_e \) and hence of \( I_{sp} = u_e/g \) requires the calculation of equilibrium mole fractions \( N_{r_a}^* \) and \( N_{s_b}^* \) as well as of total and vibrational enthalpies. Since the exit temperature is determined by the assumption that the flow process is isentropic,\(^6\) it is obvious that the exit temperature \( T_e \) and hence the numerical values of \( N_{r_a}^*, H_{r_a}, H_{r_a}^{*o}, H_{s_b}, \) and \( H_{s_b}^{*o} \) will depend upon the assumed type of flow process.

### III Outline of Calculations

For the stoichiometric solid-carbon gaseous- oxygen propellant system [1 mole of C(e) reacting with 1 mole of \( O_2 \) (g)] the equilibrium mole fractions at any temperature may be determined conveniently by writing the overall chemical reaction in the form

\[
C + O_2 \rightarrow (1 - x) CO_2 + x CO + [(x - y)/2] O_2 + y O
\]

The values of \( x \) and \( y \) are given by the solution of the following pair of simultaneous equations

\[
x(P_r + K_rK_v - K_v) + x(3K_v^2 - K_rK_v) - 2K_v^2 = 0 \quad [2]
\]

and

\[
y = K_vx^2[K_v(2 - 2K_v) + 2K_v^{-1}] \quad [3]
\]

where \( P_r \) represents the total pressure and the equilibrium constants,\(^9\) \( K_r \) and \( K_v \) are defined, respectively, by the relations \( K_r = P_0/(P_{CO}P_{O})^{1/2} \) and \( K_v = P_{CO}/P_{O}^{1/2}P_{CO} \).

Using appropriate values (5) for \( K_r \) and \( K_v \), the equilibrium chamber temperature \( T_e \) was found to be 3750°K for \( P_r = 20 \) atm using standard procedures for the calculation of the adiabatic flame temperature (6). The mole fractions and average molecular weights \( \bar{M} \) are given at 3750°K and \( P_r = 20 \) atm, and at various temperatures for \( P_r = 1 \) atm, as shown in Table 1.

### Table 1 Equilibrium Mole Fractions \( N_{r_a}^* \) and Average Molecular Weights \( \bar{M} \) for the Stoichiometric Carbon-Oxygen Propellant System

<table>
<thead>
<tr>
<th>( T_e ), °K</th>
<th>( P_r ), atm</th>
<th>( N_{CO} )</th>
<th>( N_{CO}^* )</th>
<th>( N_{O_2} )</th>
<th>( N_{O} )</th>
<th>( \bar{M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3750</td>
<td>20</td>
<td>0.2990</td>
<td>0.4443</td>
<td>0.1787</td>
<td>0.0870</td>
<td>32.3</td>
</tr>
<tr>
<td>2850</td>
<td>1</td>
<td>0.2502</td>
<td>0.4631</td>
<td>0.1762</td>
<td>0.1106</td>
<td>31.39</td>
</tr>
<tr>
<td>2500</td>
<td>1</td>
<td>0.4283</td>
<td>0.3652</td>
<td>0.1587</td>
<td>0.0479</td>
<td>34.91</td>
</tr>
<tr>
<td>2575</td>
<td>1</td>
<td>0.6190</td>
<td>0.2480</td>
<td>0.1150</td>
<td>0.0160</td>
<td>38.09</td>
</tr>
</tbody>
</table>

### A Equilibrium Flow

Equilibrium flow calculations have been carried out in the usual way.\(^5\) For equilibrium flow it is found that \( T_e = 2970 \) °K, \( u_e = 2.229 \times 10^6 \) cm/sec, \( I_{sp} = 227 \) sec.

### B Frozen Flow

For frozen flow it is found\(^2\) that \( T_e = 2110 \) °K, \( u_e = 2.105 \times 10^6 \) cm/sec, \( I_{sp} = 215 \) sec.

\(^5\)The effect of lag in vibrational energy states on the equilibrium constants has been neglected. It can be shown that the changes in equilibrium constant will not affect the numerical values obtained in the present calculations (cf. AE thesis of J. H. Schroeder, California Institute of Technology, Pasadena, 1952).

### C Chemically Equilibrium, Vibrationally Frozen Flow

For chemically equilibrium but vibrationally frozen flow, the isentropic relation which is used to determine \( T_e \) becomes

\[
\sum_{k=1}^{n} \frac{N_{r_a}^*[S_h(S_h - S_{r_a} - (S_{r_a}^{*o} - S_{r_a}^{*o})] = R \ln \frac{P_r}{P_e} \quad [9]
\]

### D Constant-Composition and Vibrationally Frozen Flow

For constant-composition and vibrationally frozen flow the isentropic relation, which is used to determine \( T_e \), becomes

\[
\sum_{k=1}^{n} \frac{N_{r_a}^*[S_h(S_h - S_{r_a} - (S_{r_a}^{*o} - S_{r_a}^{*o})] = R \ln \frac{P_r}{P_e} \quad [9]
\]
By trial and error calculation we find that $T_e = 1600\text{K}$. By use of [16] and [17] it is readily shown that $\frac{1}{2} F_{\nu_{1}, \nu_{2}, \nu_{3}}^2 = \Delta H_e = 15.144 \text{ kcal/mole}, u_e = 1981 \text{ meters/sec},$ and $I_{sp} = 202 \text{ sec.}$

In using [5] to [8] we assumed harmonic oscillations. It can be shown (7) that satisfactory approximations to the anharmonicity correction terms are

$$S^\text{out}_{\nu_{k}}(\nu_{e}) = R \frac{4v^2 \nu_{e}^{\nu_{k}}}{(e^{\nu_{e}} - 1)^2} \quad \quad \quad \quad \quad [5a]$$

and

$$H^\text{vib}_{\nu_{k}}(\nu_{e}) = RT \left[ \frac{4v^2 \nu_{e}^{\nu_{k}}}{(e^{\nu_{e}} - 1)^2} - \frac{2\nu_{k}}{(e^{\nu_{e}} - 1)^2} \right] \quad \quad \quad \quad \quad [7a]$$

Detailed calculations show that inclusion of corrections obtained from [5a] and [7a] does not change the numerical values summarized in Table 4.

### TABLE 4 SUMMARY OF RESULTS

<table>
<thead>
<tr>
<th>Type of Flow</th>
<th>$T_e$ (K)</th>
<th>$u_e$ (m/s)</th>
<th>$I_{sp}$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically equilibrium and energy-equilibrium flow</td>
<td>2970</td>
<td>2220</td>
<td>227</td>
</tr>
<tr>
<td>Chemically frozen and energy-equilibrium flow</td>
<td>2110</td>
<td>2105</td>
<td>215</td>
</tr>
<tr>
<td>Chemically equilibrium and vibrationally frozen flow</td>
<td>2910</td>
<td>2203</td>
<td>225</td>
</tr>
<tr>
<td>Chemically frozen and vibrationally frozen flow</td>
<td>1600</td>
<td>1981</td>
<td>202</td>
</tr>
</tbody>
</table>

### IV Discussion of Results

Reference to Table 4 shows that the effect of vibrationally frozen flow is of no consequence when chemical equilibrium is maintained. In this case, lag in vibrational adjustment lowers the performance by roughly one per cent.

On the other hand, the effect of vibrationally frozen flow for frozen chemical flow is such as to decrease $I_{sp}$ approximately six per cent. In this connection it is of interest to note that lags in vibrational adjustment, for a given propellant system, become more likely as the nozzle size is reduced because a reduction in nozzle size means increased cooling rates. In particular, it has been postulated that frozen-vibrational flow occurs in the small nozzles used in the pneumatic method for measuring temperatures in combustion chambers (8).

The calculations on the carbon-oxygen propellant system have been repeated by using Penner's approximate procedure (3) which permits ready estimates of the effect of vibrational lag on performance for propellant systems for which the usual theoretical performance data are available. The results of these calculations are summarized in Table 5, together with data for other propellant systems which were obtained by utilizing the concept of a constant average vibrational heat capacity during flow (3). Reference to Table 5 shows that lag in vibrational energy states produces a similar effect on performance for widely different propellant systems. A simple physical explanation for this observation is obtained by noting that frozen vibrational flow reduces the effective heat capacity during expansion by nearly the same extent for chemically frozen and for chemically equilibrium flow. On the other hand, the effective heat capacity is much larger for frozen flow in which chemical changes occur, provided the propellant system is sufficiently hot. Hence the effect of vibrational lags will always be more pronounced for flow without chemical change than for chemically equilibrium flow. Furthermore, the disparity will be largest for the hottest propellant systems.

The preceding remarks are obviously in accord with the data given in Table 5, which show a large effect of vibrational lag on performance for chemically equilibrium flow only for the relatively cool RFNA-aniline propellant system.

<table>
<thead>
<tr>
<th>Propellant system</th>
<th>$I_{sp}$ (energy equilibrium flow)</th>
<th>$I_{sp}$ (vibrationally frozen flow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-oxygen</td>
<td>1.009</td>
<td>1.004</td>
</tr>
<tr>
<td>Carbon-oxygen</td>
<td>1.01</td>
<td>1.06</td>
</tr>
<tr>
<td>Hydrogen-fluorine</td>
<td>1.008</td>
<td>1.034</td>
</tr>
<tr>
<td>Hydrogen-oxygen</td>
<td>1.006</td>
<td>. . .</td>
</tr>
<tr>
<td>RFNA-aniline</td>
<td>1.039</td>
<td>1.056</td>
</tr>
</tbody>
</table>

* Accurate calculations.
* Approximate calculations.
* Results given in (3).

### References