

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 I_{sp} , 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 physicochemical 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.²

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 nonhydrogen-containing propellant systems in small

motors for which the vibrational relaxation times may not be short compared to the residence time (1, 2).³ 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 for the various chemical species. In terms of mole fractions it is readily shown⁴ that [7], [8], [11], and [12] of Reference (4) become, respectively:

(a) For equilibrium flow

$$\frac{1}{2} \bar{M}_c u_c^2 = \Delta H_{oc}^{oc} = \sum_{k=1}^n N_{kc}^o H_{okc} - (\bar{M}_c / \bar{M}_e) \sum_{k=1}^n N_{ke}^o H_{oke} \dots [1a]$$

(b) For frozen flow

$$\frac{1}{2} \bar{M}_c u_c^2 = \Delta H_{oc}^c = \sum_{k=1}^n N_{kc}^o [H_{okc} - H_{kc}] \dots [1b]$$

(c) For chemically equilibrium and vibrationally frozen flow

$$\frac{1}{2} \bar{M}_c u_c^2 = \Delta H_{oc}^{oc} + (\bar{M}_c / \bar{M}_e) \sum_{k=1}^n N_{ke}^o [H_{oke}^{vib} - H_{oke}^{vib}] \dots [1c]$$

(d) For chemically and vibrationally frozen flow

$$\frac{1}{2} \bar{M}_c u_c^2 = \Delta H_{oc}^c + \sum_{k=1}^n N_{kc}^o (H_{kc}^{vib} - H_{kc}^{vib}) \dots [1d]$$

³ Numbers in parentheses refer to the References on page 27.

⁴ For the relatively simple case of flow with frozen vibrational energy states, it is not necessary to use the analysis given in (4) since [1a]-[1d] are obvious expressions for conservation of energy.

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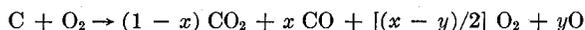
² The usual simplifying assumptions in propellant evaluation, which do not involve consideration of rate processes, are the following: Thermodynamic equilibrium is reached in the combustion chamber after adiabatic reaction; expansion of the combustion products through the Laval nozzle is adiabatic; the 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_{ke}^o and N_{ke}^e are the equilibrium mole fractions of species k evaluated at the chamber exit and nozzle exit positions, respectively; H_{ke} , H_{oke} , H_{ke} , and H_{oke} 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 superscript *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 ($H_{ke}^{vib} \equiv H_{oke}^{vib}$).

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_{ke}^o and N_{ke}^e as well as of total and vibrational enthalpies. Since the exit temperature is determined by the assumption that the flow process is isentropic,² it is obvious that the exit temperature T_e , and hence the numerical values of N_{ke}^o , H_{ke} , H_{ke}^{vib} , H_{oke} , and H_{oke}^{vib} 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(c) reacting with 1 mole of O₂(g)] the equilibrium mole fractions at any temperature may be determined conveniently by writing the over-all chemical reaction in the form



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

$$x^3(P_T + K_1K_2 - K_2^2) + x(3K_2^2 - K_1K_2) - 2K_2^2 = 0 \dots [2]$$

and

$$y = K_1x^2[x(K_1 - 2K_2) + 2K_2]^{-1} \dots [3]$$

where P_T represents the total pressure and the equilibrium constants,⁵ K_1 and K_2 are defined, respectively, by the relations $K_1 = P_o/(P_{O_2})^{1/2}$ and $K_2 = P_{CO}(P_{O_2})^{1/2}/P_{CO_2}$.

Using appropriate values (5) for K_1 and K_2 , the equilibrium chamber temperature T_c was found to be 3750°K for $P_T = 20$ 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 $P_T = 20$ atm, and at various temperatures for $P_T = 1$ atm, in Table 1.

TABLE 1 EQUILIBRIUM MOLE FRACTIONS N_k^o AND AVERAGE MOLECULAR WEIGHTS \bar{M} AS A FUNCTION OF PRESSURE AND TEMPERATURE FOR THE STOICHIOMETRIC CARBON-OXYGEN PROPELLANT SYSTEM

T_c , °K	P_T , atm	N_{CO_2}	N_{CO}	N_{O_2}	N_O	\bar{M}
3750	20	0.2900	0.4443	0.1787	0.0870	32.3
3250	1	0.2502	0.4631	0.1762	0.1106	31.39
3000	1	0.4283	0.3652	0.1587	0.0479	34.91
2750	1	0.6190	0.2480	0.1150	0.0160	38.09

A Equilibrium Flow

Equilibrium flow calculations have been carried out in the usual way.² For equilibrium flow it is found that $T_e = 2970$ °K, $u_e = 2.220 \times 10^5$ cm/sec, $I_{sp} = 227$ sec.

B Frozen Flow

For frozen flow it is found² that $T_e = 2110$ °K, $u_e = 2.105 \times 10^5$ 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

$$\sum_{k=1}^n N_{ke}^o (S_{ke}^o - R \ln P_e - R \ln N_{ke}^o) = (\bar{M}_c/\bar{M}_e) \sum_{k=1}^n N_{ke}^o [S_{ke}^o - R \ln P_e - R \ln N_{ke}^o - (S_{ke}^{vib} - S_{ke}^{vib})] \dots [4]$$

where S_{ke}^o and S_{ke}^e denote the total molar entropies at the chamber and exit conditions, respectively; the superscript *vib* indicates that only the vibrational entropy is involved; R is the molar gas constant.

For diatomic molecules the vibrational contribution to the entropy is, in good approximation (7)

$$S^{vib} = R \{ u [\exp(u) - 1]^{-1} - \ln [1 - \exp(-u)] \} \dots [5]$$

Here $u = hc\omega^*/kT$, h represents Planck's constant, c is the velocity of light, k the Boltzmann constant, and ω^* the wave number corresponding to an energy transition from the ground vibrational energy level to the first excited vibrational state for the nonrotating diatomic molecule. For the linear triatomic molecule CO₂, the total vibrational entropy is given by the approximate relation (7)

$$S^{vib} = R \sum_{i=1}^4 \{ u_i [\exp(u_i) - 1]^{-1} - \ln [1 - \exp(-u_i)] \} \dots [6]$$

where u_i corresponds to the four normal vibration frequencies of CO₂. For the present calculations, the numerical values of the characteristic temperatures $\theta = hc\omega^*/k$ which are listed in Table 2 were used.

TABLE 2 CHARACTERISTIC TEMPERATURES FOR O₂, CO, AND CO₂

Molecule	O ₂	CO	CO ₂
θ , °K	2228	3067	955.6, 955.6, 1925, 3493

The left-hand side of [4] is found to be 67.65 cal/°K mole at $T_c = 3750$ °K; the right-hand side of [4] is found to be 67.557 at $T_e = 2900$ °K, 69.012 at $T_e = 3000$ °K, and by linear interpolation it is found that $T_e = 2910$ °K.

For diatomic molecules the vibrational contribution to the enthalpy is in good approximation (7)

$$H^{vib} = RTu[\exp(u) - 1]^{-1} \dots [7]$$

For the linear triatomic molecule CO₂ the total vibrational enthalpy is given by the approximate relation

$$H^{vib} = RT \sum_{i=1}^4 u_i [\exp(u_i) - 1]^{-1} \dots [8]$$

Using these relations, the values for H^{vib} (in cal/mole) listed in Table 3 were obtained.

TABLE 3 H^{vib} AS A FUNCTION OF TEMPERATURE FOR O₂, CO, AND CO₂

Molecule	H^{vib} (cal/mole) at		
	3750°K	3000°K	2900°K
O ₂	5455.8	4018.0	3829.3
CO	4815.0	3423.6	3242.6
CO ₂	23,247	17,424	16,869

For case (a) we find that $\Delta H_{oc}^{oc} = +22.26$ kcal/mole at $T_e = 2910$ °K, whence it follows that $1/2 M_c u_e^2 = \Delta H_{oc}^e = 18.72$ kcal/mole, $u_e = 2203$ meters/sec, and $I_{sp} = 225$ sec.

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

$$\sum_{k=1}^n N_{ke}^o [S_{oke}^o - S_{oke} - (S_{ke}^{vib} - S_{ke}^{vib})] = R \ln \frac{P_c}{P_e} \dots [9]$$

By trial and error calculation we find that $T_e = 1600^\circ\text{K}$. By use of [1d] and [7] it is readily shown that $\frac{1}{2}\bar{M}_e u_e^2 = \Delta H_e^c = 15.144$ kcal/mole, $u_e = 1981$ meters/sec, and $I_{sp} = 202$ sec.

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

$$S_{k \text{ (corr)}}^{vib} = R \frac{4u^2 e^u x}{(e^u - 1)^3} \dots \dots \dots [5a]$$

and

$$H_{k \text{ (corr)}}^{vib} = RT \left[\frac{4u^2 x e^u}{(e^u - 1)^3} - \frac{2ux}{(e^u - 1)^2} \right] \dots \dots [7a]$$

Detailed calculations show that inclusion of corrections obtained from [5a] and [7a] does not change the numerical values summarized in Table 4.⁶

TABLE 4 SUMMARY OF RESULTS

Type of Flow	T_e , °K	u_e , m/s	I_{sp} , sec
Chemically equilibrium and energy-equilibrium flow	2970	2220	227
Chemically frozen and energy-equilibrium flow	2110	2105	215
Chemically equilibrium and vibrationally frozen flow	2910	2203	225
Chemically frozen and vibrationally frozen flow	1600	1981	202

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

⁶ This statement should not be interpreted to mean that the vibrational entropies and enthalpies for CO_2 are given accurately by using harmonic oscillator approximations with anharmonicity corrections. Calculation utilizing the known energy levels of CO_2 to determine the partition function raises an interesting question concerning the assignment to vibration or rotation of the quantized angular rotation associated with the doubly degenerate ν_2 -vibration. It is perhaps most reasonable to express the total energy of the CO_2 -molecule as $W = W_V(n_1, n_2, n_3, l) + W_R(j)$, where W_V and W_R denote the vibrational and rotational energy

levels, respectively; n_1, n_2 , and n_3 are vibrational quantum numbers l is the quantum number for angular rotation associated with the ν_2 -vibration, and j is the rotational quantum number. Detailed numerical calculations have been carried out utilizing the energy levels of Adel and Dennison (see, e.g., D. M. Dennison, *Reviews of Modern Physics*, vol. 12, 1940, pp. 175-214). These laborious calculations show that the required corrections to S_{vib} and H_{vib} for CO_2 are not small at the temperatures of interest for the present analysis. Nevertheless, the effect on over-all performance is negligibly small. For this reason an outline for the more exact work, which would necessarily be lengthy, is not included in the present discussion.

TABLE 5 EFFECT OF LAG IN VIBRATIONAL ENERGY STATES ON PERFORMANCE FOR VARIOUS PROPELLANT SYSTEMS

Propellant system	I_{sp} (energy equilibrium flow) \div I_{sp} (vibrationally frozen flow) for	
	Equilibrium flow	Frozen flow
Carbon-oxygen ^a	1.009	1.064
Carbon-oxygen ^b	1.01	1.06
Hydrogen-fluorine ^c	1.008	1.034
Hydrogen-oxygen ^c	1.006	...
RFNA-aniline ^c	1.039	1.056

^a Accurate calculations.

^b Approximate calculations.

^c Results given in (3).

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 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.

References

- 1 "Zur Theorie der Schalldispersion," by L. Landau and E. Teller, *Physik. Zeits. Sowjetunion*, vol. 10, 1936, pp. 34-43.
- 2 "Heat-Capacity Lag in Gas Dynamics," by A. Kantrowitz, *Journal of Chemical Physics*, vol. 14, 1946, pp. 150-164.
- 3 "Flow Through a Rocket Nozzle With and Without Vibrational Equilibrium," by S. S. Penner, *Journal of Applied Physics*, vol. 20, 1949, pp. 445-447.
- 4 "Thermodynamics and Chemical Kinetics of One-Dimensional Nonviscous Flow Through a Laval Nozzle," by S. S. Penner, *Journal of Chemical Physics*, vol. 19, 1951, pp. 877-881.
- 5 National Bureau of Standards, Tables of Selected Values of Chemical Thermodynamic Properties, series III, vol. I, March 31, 1947 to June 30, 1949.
- 6 "Calculation of the Equilibrium Composition of Systems of Many Constituents," by S. R. Brinkley, Jr., *Journal of Chemical Physics*, vol. 15, 1947, pp. 107-110.
- 7 "Statistical Mechanics," by J. E. Mayer and M. G. Mayer, John Wiley & Sons, New York, N. Y., 1st edition, 1940, pp. 440-449.
- 8 "Sonic-Flow-Orifice Temperature Probe for High-Gas-Temperature Measurements," by Perry L. Blackshear, Jr., *NACA Technical Note 2167*, September 1950, pp. 1-20.