

EFFECT OF VIBRATIONAL EXCITATION ON  
THE THEORETICAL PERFORMANCE OF THE  
STOICHIOMETRIC CARBON-OXYGEN PROPELLANT SYSTEM

Thesis by

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## SUMMARY

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.

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## I. INTRODUCTION

It is well-known that the overall performance of rocket propellant systems is dependent on the extent to which physico-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 sizeable 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)

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\*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 non-viscous 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, for example, "Quantitative Evaluation of Rocket Propellants" by S. S. Penner, American Journal of Physics, Vol. 20, 1952, pp. 26-31.

Approximate estimates of the effect of vibrational excitation on performance of rockets have been carried out previously. (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 occurs 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 shown\* that equations (7), (8), (11) and (12) of reference (4) become, respectively:

(a) For equilibrium flow

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

(b) For frozen flow

$$\frac{1}{2} \bar{M}_c u_e^2 = \Delta H_{oe}^c = \sum_{k=1}^n N_{kc}^o [ H_{okc} - H_{oke} ] \quad (1b)$$

(c) For chemically-equilibrium and vibrationally-frozen flow

$$\frac{1}{2} \bar{M}_c u_e^2 = \Delta H_e^{oc} = \Delta H_{oe}^{oc} + (\bar{M}_c / \bar{M}_e) \sum_{k=1}^n N_{ke}^o [ H_{ke}^{vib} - H_{kc}^{vib} ] \quad (1c)$$

(d) For chemically- and vibrationally-frozen flow

$$\frac{1}{2} \bar{M}_c u_e^2 = \Delta H_e^c = \Delta H_{oe}^c + \sum_{k=1}^n N_{kc}^o (H_{ke}^{vib} - H_{kc}^{vib}) \quad (1d)$$

In equations (1a) to (1d),  $u_e$  represents the linear flow velocity at the nozzle exit position,  $N_{kc}^o$  and  $N_{ke}^o$  are the equilibrium mole fractions of species  $k$  evaluated at the chamber exit and nozzle exit positions, respectively;  $H_{okc}$  and  $H_{oke}$  equal the total enthalpy (sensible

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 \*For the relatively simple case of flow with frozen vibrational energy states, it is not necessary to use the analysis given in reference (4) since equations (1a) to (1d) can be written down immediately.

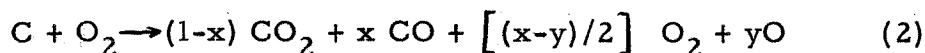
plus chemical enthalpy) per mole of species  $k$  if complete internal equilibrium exists at the nozzle entrance and exit positions, respectively; the superscript  $vib$  signifies that only the vibrational enthalpy is involved; the subscript  $o$  denotes complete energy equilibrium exists for all constituents; the superscript  $o$  denotes complete chemical equilibrium exists for all constituents.

From equations (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  $N_{kc}^o$  as well as of total and vibrational enthalpies. Since the exit temperature is determined by the assumption that the flow process is isentropic, it is obvious that the exit temperature  $T_e$ , and hence the numerical values of  $N_{ke}^o$ ,  $H_{ke}^{vib}$ , and  $H_{oke}$ , 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 O<sub>2</sub>(g)] the equilibrium mole fractions at any temperature may be determined conveniently by writing the overall chemical reaction in the form



We arrive at equation (2) by assuming that the first chemical reaction taking place in the combustion chamber is  $C+O_2 \rightarrow CO_2$  which is followed by a dissociation of part of the carbon dioxide to carbon monoxide and oxygen according to the relation  $xCO_2 \rightarrow xCO + (x/2) O_2$ . This decomposition is then followed by a dissociation of part of the molecular oxygen to atomic oxygen according to the relation  $(y/2) O_2 \rightarrow yO$ . In equation (2) x is the number of moles of carbon dioxide dissociated and y/2 is the number of moles of molecular oxygen dissociated.

From equation (2) we have

$$n_t = (2 + x + y)/2 \quad (3)$$

where  $n_t$  = total number of moles of reaction products.

For the chemical reactions under discussion two equilibrium constants are obtained

$$K_1 = p_O (p_{O_2})^{-\frac{1}{2}} \quad (4)$$

$$K_2 = p_{CO} (p_{O_2})^{\frac{1}{2}} / (p_{CO_2}) = K_9 / K_{10} \quad (5)$$

where  $K_1$ ,  $K_9$  and  $K_{10}$  are in the notation of data compiled from reference (5)\* and  $p_k$  is the partial pressure of species k.

For an ideal gas

$$p_k = n_k p_t / n_t \quad (6)$$

where  $n_k$  is the number of moles of species k and  $p_t$  is the total pressure.

By use of equation (6) in equation (4) we obtain

$$K_1 = y \left[ \frac{(x-y)}{2} \right]^{-\frac{1}{2}} \left[ \frac{2p_t}{(2+x+y)} \right]^{\frac{1}{2}} \quad (7)$$

and, similarly, equation (5) becomes

$$K_2 = x \left\{ \left[ \frac{(x-y)}{2} \right]^{\frac{1}{2}} / (1-x) \right\} \left[ \frac{2p_t}{(2+x+y)} \right]^{\frac{1}{2}} \quad (8)$$

Equations (7) and (8) form a system of two equations in two unknowns, x and y. By solving the equations for the expression  $\left[ \frac{p_t(x-y)}{(2+x+y)} \right]^{\frac{1}{2}}$  and equating the results it is readily shown that

$$x^3(p_t - K_2^2 + K_1 K_2) + x(3K_2^2 - K_1 K_2) - 2K_2^2 = 0, \quad (9)$$

and

$$y = K_1 x^2 / \left[ x(K_1 - 2K_2) + 2K_2 \right] \quad (10)$$

From equations (9) and (10), the quantities x and y, and the number of moles of each of the combustion products, can be determined\*\* provided  $p_t$  and  $T_c$ , the adiabatic flame temperature, are known.

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 \*Class notes for JP 200, California Institute of Technology, 1951.  
 \*\* The effect of lag in vibrational energy states on the equilibrium constants has been neglected. It will be shown in Section IIIC that the changes in equilibrium constant will not materially affect the numerical values obtained in the present calculations.

In the calculations for finding  $T_c$  the following relations are used

$$Q_{av} = -(n_{CO} \Delta H_{f,CO}^{\circ} + n_{CO_2} \Delta H_{f,CO_2}^{\circ} + n_O \Delta H_{f,O}^{\circ}) \quad (11)$$

$$Q_c = \sum_k n_{kc} [H_{okc} - H_{ok}(298.16^{\circ}K)] \quad (12)$$

and

$$Q_{av} = Q_c \quad (13)$$

where  $Q_{av}$  is the heat released by the chemical reaction,  $Q_c$  is the heat absorbed by the combustion products, and  $\Delta H_{fk}^{\circ}$  is the standard heat of formation of species  $k$ .

With equations (9) to (13) it is found by trial and error that the adiabatic flame temperature is  $3750^{\circ}K$  for  $p_t = 20$  atmos. (6)

The mole fractions as found by use of equations (9) and (10) and the average molecular weight  $\bar{M}$ , as calculated from the relation

$$\bar{M} = \sum_k N_k M_k \quad (14)$$

are given at  $3750^{\circ}K$  and  $p_t = 20$  atmos. and at various temperatures for  $p_t = 1$  atmos. in Table I. Here  $N_k$  and  $M_k$  are the mole fraction and molecular weight, respectively of species  $k$ .

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

T, °K	$p_t$ , atmos.	$N_{CO_2}$	$N_{CO}$	$N_{O_2}$	$N_O$	$\bar{M}$
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

The evaluation of the performance for equilibrium flow requires the introduction of an additional assumption, namely, isentropic flow during the expansion process through the nozzle. This condition can be expressed in terms of the component entropies by the relation

$$\sum_k N_{kc}^0 (S_{oke} - R \ln p_c - R \ln N_{kc}^0) = (\bar{M}_c / \bar{M}_e) \sum_k N_{ke}^0 (S_{oke} - R \ln p_e - R \ln N_{ke}^0) \quad (15)$$

where  $S_{okc}$  and  $S_{oke}$  denote the total molar enthalpies at the chamber and exit conditions, respectively and  $R$  is the molar gas constant.

The exit temperature,  $T_e$ , can now be found by computing the right-hand side of equation (15) for several temperatures and comparing the results with the value of the left-hand side. By using the values of  $\bar{M}$  and  $N_k^0$  as given in Table I and the entropies tabulated in reference (5), the left-hand side of equation (15) is found to be 67.65 cal./ $^{\circ}$ K-mole for  $T_c = 3750^{\circ}$ K and  $p_c = 20$  atmos. and the right-hand side is found to be 66.43 cal./ $^{\circ}$ K-mole and 68.16 cal./ $^{\circ}$ K-mole at  $2900^{\circ}$ K and  $3000^{\circ}$ K respectively for  $p_e = 1$  atmos. By linear interpolation it is found that  $T_e = 2970^{\circ}$ K.

By use of equation (1a) it is found that  $\Delta H_{oe}^{oc} = 22.800$  kcal/mole and  $17.437$  kcal/mole at  $2900^{\circ}$ K and  $3000^{\circ}$ K, respectively. Linear interpolation yields the result  $\Delta H_{oe}^{oc} = 19.04$  kcal/mole at  $T_e = 2970^{\circ}$ K whence it follows that  $u_e = 2,200$  meters/sec. From the relation

$$I_{sp} = u_e / g \quad (16)$$

the specific impulse is seen to have a value of 227 seconds.

### B. Frozen Flow

For frozen flow equation (15) simplifies to

$$\sum_k N_{kc}^0 (S_{okc} - S_{oke}) = R \ln(p_c/p_e) \quad (17)$$

since  $N_{ke} = N_{kc}^0$  and  $\bar{M}_e = \bar{M}_c$ . By proceeding as in Section IIIA we find

$$T_e = 2110^\circ K;$$

from equation (1b)

$$\Delta H_{oe}^C = 17.12 \text{ kcal/mole}$$

is obtained; finally  $u_e = 2105$  meters/sec. and  $I_{sp} = 215$  sec.

### C. Chemically-Equilibrium, Vibrationally-Frozen Flow

For chemically-equilibrium but vibrationally-frozen flow, the isentropic relation which is used to determine  $T_e$  becomes

$$\begin{aligned} & \sum_{k=1}^n N_{kc}^0 (S_{okc} - R \ln p_c - R \ln N_{kc}^0) = (\bar{M}_c / \bar{M}_e) \\ \times & \sum_{k=1}^n N_{ke}^0 [ S_{oke} - R \ln p_e - R \ln N_{ke}^0 - (S_{ke}^{vib} - S_{kc}^{vib}) ] \end{aligned} \quad (18)$$

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

$$S^{vib} = R \left\{ u \left[ \exp(u) - 1 \right]^{-1} - \ln \left[ 1 - \exp(-u) \right] \right\}. \quad (19)$$

Here  $u = hc\omega^*/kT$ ,  $h$  represents Planck's constant,  $c$  is the velocity of light,  $k$  the Boltzmann constant, and  $\omega^*$  the wave number corresponding to an energy transition from the ground vibrational energy level to the first excited vibrational state for the non-rotating diatomic molecule. For the linear triatomic molecule  $CO_2$ , the total vibra-

tional entropy is given by the approximate relation<sup>(7)</sup>

$$S^{\text{vib}} = R \sum_{i=1}^4 \left\{ u_i \left[ \exp(u_i) - 1 \right]^{-1} - \ln \left[ 1 - \exp(-u_i) \right] \right\} \quad (20)$$

where  $u_i$  corresponds to the four normal vibration frequencies of  $\text{CO}_2$ . For the present calculations the numerical values of the characteristic temperatures  $\theta = hc\omega^*/k$  which are listed in Table II were used.

TABLE II. CHARACTERISTIC TEMPERATURES FOR  $\text{O}_2$ , CO, AND  $\text{CO}_2$

Molecule	$\text{O}_2$	CO	$\text{CO}_2$
$\theta, ^\circ\text{K}$	2228	3067	955.6, 955.6, 1988, 3493

The thermodynamic function  $S^{\text{vib}}$ , as found by use of equations (19) and (20), is listed in Table III for various temperatures.

TABLE III.  $S^{\text{vib}}$  (cal. / $^\circ\text{K}$ -mole) AS A FUNCTION OF TEMPERATURE FOR  $\text{O}_2$ , CO AND  $\text{CO}_2$

Component	$\theta, ^\circ\text{K}$	3750 $^\circ\text{K}$		3000 $^\circ\text{K}$		2900 $^\circ\text{K}$		1600 $^\circ\text{K}$	
		u	$S^{\text{vib}}$	u	$S^{\text{vib}}$	u	$S^{\text{vib}}$	u	$S^{\text{vib}}$
$\text{O}_2$	2228	.5941	3.050	0.7427	2.628	0.7683	2.5597	1.393	1.482
CO	3067	.8178	2.442	1.0223	2.027	1.0575	1.9689	1.917	0.972
1 $\text{CO}_2$	1988	.5301	3.271	0.6627	2.839	0.6855	2.7769	1.243	1.677
2 $\text{CO}_2$	955.6	.2548	4.709	0.3185	4.270	0.3295	4.2025	0.597	3.039
3 $\text{CO}_2$	3493	.9314	2.198	1.1645	1.774	1.2045	1.7384	2.184	0.789
$\text{CO}_2$ Total		---	14.887	---	13.153	---	12.920	---	8.544

By use of the appropriate values of  $N_k^0$  and  $\bar{M}$  listed in Table I and the appropriate values of  $S^{\text{vib}}$  listed in Table III we can now proceed to find  $T_e$  from equation (18) by a trial and error method similar to the method described previously. With the values already obtained we find the left-hand side of equation (18) to be 67.65 cal/°K-mole at  $T_c = 3750^\circ\text{K}$ , and  $p_c = 20$  atmos. The right-hand side of equation (18) is found to be 67.557 cal/°K-mole and 69.012 cal/°K-mole at  $2900^\circ\text{K}$  and  $3000^\circ\text{K}$ , respectively. By linear interpolation the result  $T_e = 2910^\circ\text{K}$  is obtained.

For diatomic molecules the vibrational contribution to the enthalpy is, in good approximation, <sup>(7)</sup>

$$H^{\text{vib}} = RTu \left[ \exp(u) - 1 \right]^{-1} \quad (21)$$

For the linear triatomic molecule  $\text{CO}_2$  the total vibrational enthalpy is given by the approximate relation:

$$H^{\text{vib}} = RT \sum_{i=1}^4 u_i \left[ \exp(u_i) - 1 \right]^{-1} \quad (22)$$

Using these relations the values for  $H^{\text{vib}}$  (in cal. /mole) listed in Table IV are obtained.

TABLE IV.  $H^{\text{vib}}$  AS A FUNCTION OF TEMPERATURE FOR  $\text{O}_2$ , CO AND  $\text{CO}_2$ .

Molecule	$H^{\text{vib}}$ (cal/mole) at			
	$3750^\circ\text{K}$	$3000^\circ\text{K}$	$2900^\circ\text{K}$	$1600^\circ\text{K}$
$\text{O}_2$	5455.8	4018.0	3829.3	1462.3
CO	4815.0	3423.6	3242.6	1049.1
$\text{CO}_2$	23,247	17,424	16,869	7116.8

As has already been noted, the effect of lag in the vibrational energy states on the equilibrium constants has been neglected. In order to see just how much of an error this assumption introduces we will now proceed with the computation of  $K_2$  for  $T = 3000^\circ\text{K}$  by taking the effect of lag in the vibrational energy states into account. The starting relations for the reaction  $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$  at the temperature  $T_e = 3000^\circ\text{K}$  are

$$\Delta F^e = -RT \ln K_p^e \quad (23)$$

and

$$\Delta F^e = \frac{1}{2} \Delta F_{298.16}^e(\text{O}_2) + \Delta F_{298.16}^e(\text{CO}) + \Delta F_{298.16}^e(\text{CO}_2) + \Delta F \text{ (resulting from the given chemical reaction at } 298.16^\circ\text{K)} \quad (24)$$

where  $F$  is the Gibbs free energy as defined by the relation

$$F = H - TS, \quad (25)$$

and the superscript  $e$  again denotes conditions at the exit temperature. The enthalpy,  $H_{ke}$ , and the entropy,  $S_{ke}$ , are found from the relations

$$H_{ke} = H_{oke} - (H_{ke}^{\text{vib}} - H_{kc}^{\text{vib}}) \quad (26)$$

$$S_{ke} = S_{oke} - (S_{ke}^{\text{vib}} - S_{kc}^{\text{vib}}), \quad (27)$$

respectively. By use of the enthalpies and entropies tabulated in reference (5) and of equations (25) to (27), together with the appropriate values for  $S^{\text{vib}}$  and  $H^{\text{vib}}$  listed in Tables III and IV, the data listed in Table V are obtained.



TABLE V. THERMODYNAMIC FUNCTIONS AT 3000°K AND 1 ATMOS. FOR CO<sub>2</sub>, CO AND O<sub>2</sub> WITH VIBRATIONAL DEGREES OF FREEDOM FROZEN AT T<sub>c</sub> = 3750°K.

	1	2	3	4	5	6
	H <sub>ke</sub>	S <sub>ke</sub>	-F <sub>ke</sub>	-F <sub>k(298.16)</sub>	ΔF <sub>f</sub> <sup>o</sup>	ΔF <sub>298.16</sub> <sup>e</sup>
Component	kcal/mole	cal/°K-mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole
CO <sub>2</sub>	44.763	81.66	200.22	12.99	-94.260	+187.23
CO	25.825	65.87	171.78	12.03	-32.808	-159.75
O <sub>2</sub>	26.953	68.40	178.25	12.54	0.0	-165.71

In Table V, ΔF<sub>f</sub><sup>o</sup> represents the standard free energy of formation.

From column (5) of Table V we have

$$\begin{aligned} \Delta F \text{ (resulting from the given chemical reaction at } 298.16^\circ\text{K)} \\ = -32.808 - (-94.260) = + 61.452 \end{aligned}$$

and, using equation (24),

$$\Delta F^e = + 6.08 \text{ kcal. /mole.}$$

Using this value for ΔF<sup>e</sup> in equation (23) it is readily shown that

$$\ln K_2 = - \frac{\Delta F^e}{RT} = - 1.018$$

or

$$\log K_2 = - 0.442 \quad \text{at } T = 3000^\circ\text{K.}$$

On the other hand, for complete energy equilibrium,

$$\log K_2 = -0.4692 \text{ at } T = 3000^\circ\text{K,}$$

$$\log K_2 = -0.1091 \text{ at } T = 3250^\circ\text{K,}$$

and, using an appropriate linear interpolation,

$$\log K_2 \simeq -0.442 \text{ at } 1/T = .3314 \times 10^{-3} \text{ or } T = 3017^\circ\text{K.}$$

From the preceding results it is evident that neglecting the effect of lag in the vibrational energy states on the equilibrium constant  $K_2$  at  $T = 3000^\circ\text{K}$  has introduced an error equivalent to  $17^\circ\text{K}$ . Repetition of the preceding calculations shows that the error in  $K_1$  will be even smaller. Therefore, we arrive at the conclusion that the error in the mole fractions at  $T_e = 2910^\circ\text{K}$  is small enough so that the resultant  $T_e$  for this case is within  $15^\circ$  of the value which would be obtained if the effect of lag in the vibrational energy states on the equilibrium constants had been taken into account.

Using the calculations given for case (a) it is found that  $\Delta H_{oe}^{oc} = +22.26$  kcal/mole at  $T_e = 2910^\circ\text{K}$  from which it follows, by using appropriate values of  $N_k^o$  and  $\bar{M}$  from Table I and of  $H^{vib}$  from Table IV in equation (1c) that  $\frac{1}{2} \bar{M}_c u_e^2 = \Delta H_e^{oc} = +18.72$  kcal/mole,  $u_e = 2,203$  meters/sec, and  $I_{sp} = 225$  seconds.

#### 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

$$\sum_{k=1}^n N_{kc}^o \left[ S_{okc} - S_{oke} - (S_{kc}^{vib} - S_{ke}^{vib}) \right] = R \ln(pc/pe). \quad (28)$$

With the values of  $N_{kc}^o$  listed in Table I, the appropriate values of  $S^{vib}$  given in Table III, and the entropies tabulated in reference (5), it is found from equation (28), by use of a trial and error method,

that  $T_e = 1600^\circ\text{K}$ . Using the values of  $N_{kc}^0$  tabulated in Table I, the appropriate values of  $H^{\text{vib}}$  given in Table IV, and the enthalpies tabulated in reference (5), in equation (1d) it is found that  $\frac{1}{2} \bar{M}_c u_e^2 = \Delta H_e^C = 15.144 \text{ kcal/mole}$ ,  $u_e = 1,981 \text{ meters/sec}$ , and  $I_{sp} = 202 \text{ seconds}$ .

IV. DISCUSSION OF RESULTS

For convenience the results of the present analysis are summarized in Table VI. Reference to Table VI 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 percent.

TABLE VI. SUMMARY OF RESULTS

Type of Flow	$T_e(^{\circ}\text{K})$	$u_e(\text{m/s})$	Isp(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

On the other hand, the effect of vibrationally-frozen flow for frozen chemical flow is such as to decrease Isp approximately 6%. 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.<sup>(8)</sup>

The calculations on the carbon-oxygen propellant system have been repeated by using an approximate procedure,<sup>(3)</sup> 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 VII, together with data for other propellant systems which were obtained by utilizing the concept of a constant average vibrational heat capacity during flow.<sup>(3)</sup> Reference to Table VII 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 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 VII which show a large effect of vibrational lag on performance for chemically-equilibrium flow only for the relatively cool RFNA-Aniline propellant system.

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

Propellant System	Isp (energy equilibrium flow)÷ Isp (vibrationally frozen flow) for	
	Equilibrium Flow	Frozen Flow
Carbon-Oxygen*	1.009	1.064
Carbon-Oxygen**	1.01	1.06
Hydrogen-Fluorine***	1.008	1.034
Hydrogen-Oxygen***	1.006	-
RFNA - Aniline***	1.039	1.056

\* Accurate calculations.

\*\* Approximate calculations.

\*\*\* Results given in reference (3).

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