Nonequilibrium Combustion and Nozzle Flow in Propellant Performance

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Attempts to improve theoretical propellant performance calculations have included "kinetic-expansion" solutions[1] and further refinements of the nozzle expansion process.[2] The common approximation of one-dimensional fluid flow has been replaced by a two-dimensional or axisymmetric solution based on the method of characteristics. The velocity and/or thermal lag of condensed phases detract from propellant performance and have been treated in the "phase lag solutions." Composition variations in the radial direction, as arising from nonuniform injector distributions or transpiration wall cooling, have been considered through approximate "two-zone solutions." The possibility of combining some or all of these sophistications to the theoretical treatment of the expansion process has been considered.

A common feature of the foregoing solutions, which are summarized in Table 1, is the assumption that combustion results in equilibrium composition products. There exist at least some experimentally observed cases for which the nozzle expansion initial condition is not that of equilibrium. The possibility and consequences of a nonequilibrium initial condition on the theoretically predicted propellant performance is considered in the present work.

Nonequilibrium Initial Conditions

Perhaps the most striking case of a propellant yielding nonequilibrium combustion products is that of hydrazine. Both as a monopropellant and in fuel rich mixtures, hydrazine produces reaction products containing greater than equilibrium concentrations of ammonia.[4] Under a variety of experimental conditions hydrazine has been observed to decompose to give NH_3, H_2, and N_2 in the approximate mole ratio of 2:1:1 as the dominant product species, whereas equilibrium-combustion products are predicted to be dominantly H_2 and N_2 in the volume ratio 2:1.

Other experimentally observed cases of nonequilibrium combustion include the greater than equilibrium concentrations of nitric oxide in oxidizer rich mixtures of hydrazine and nitrogen tetroxide. The effect in this case detracts from performance. Greater than equilibrium concentrations of chlorine monofluoride have been observed in the rocket combustion products of N_2H_4/ClF_5.[5] A simple and preliminary approach to predicting the effect of nonequilibrium initial conditions, based on a "part equilibrium expansion" in the nozzle has been presented previously for N_2H_4/N_2O_4.[6]

In the present investigations, part of the fuel or oxidizer was assumed unreacted or only partially decomposed, or the combustion was assumed to proceed to arbitrary nonequilibrium products. Two propellant combinations were considered, H_2/F_2 and N_2H_4/ClF_5. Initial conditions for H_2/F_2 were based upon unreacted fuel or oxidizer or excess radical species. The effect of greater than equilibrium ClF concentrations was investigated for the N_2H_4/ClF_5 combination.

Table 1 Summary of rocket propellant performance calculations[a]

Thrust chamber initial condition	Equilibrium NPL	Equilibrium PL	Frozen NPL	Frozen PL	Part equilibrium NPL	Part equilibrium PL	Kinetic NPL	Kinetic PL
				One-dimensional				
Equilibrium	A[b]	D	A[b]	D	F		B[b]	D
Equilibrium, 2 zone								
Nonequilibrium			G[b]		F,G[b]		G[b]	
			Two-dimensional (axisymmetric)					
Equilibrium	C	D	C	D			C	D
Equilibrium, 2 zone							E	

[a] NPL: no phase lag; PL: phase lag; A: equilibrium, frozen expansion solutions, e.g., Ref. 3; B: kinetic expansion solutions, e.g., Ref. 1; C: two-dimensional solutions, e.g., Ref. 2; D: phase lag solutions, e.g., Ref. 2; E: two-zone solutions, e.g., Ref. 2; F: part-equilibrium solutions, e.g., Ref. 6; G: nonequilibrium initial condition, this work.
[b] Cases compared with this work.

The calculated equilibrium and arbitrarily selected nonequilibrium initial conditions, labeled equilibrium combustion (EC) and nonequilibrium combustion (NEC), for the H_2/F_2 combination are compared in Table 2. Equivalence ratios $[\phi = (f/o)/(f/o)_{\text{stoich}}]$ of 1.0 and 2.0 were selected. The $\phi = 2.0$ case is near the optimum for equilibrium expansion. The nonequilibrium case for $\phi = 1.0$ is based on 93.5% formation of the equilibrium HF with the remainder appearing primarily as unreacted, undissociated H_2 and F_2. For $\phi = 2.0$, the NEC case is based on 91.6% formation of the equilibrium HF with the remainder appearing primarily as unreacted, undissociated H_2 and F_2. This corresponds to an arbitrary shift to the right in the reaction $2HF \rightleftarrows H_2 + F_2$.

Similar initial condition data are presented for N_2H_4/ClF_5 in Table 3. In this case the observed excess of ClF was treated as occurring through displacement of the equilibrium $HF + HCl \rightleftarrows ClF$ to the right by an amount resulting in a ClF mole fraction increase of 0.03. Two different nonequilibrium-combustion initial conditions, NEC(1) and NEC(2) arise from two different treatments of the expansion process. Case 1 is that for a kinetic nozzle expansion and is simply as previously described. Case 2 is for a part equilibrium expansion which results in further equilibration of some product species to alter the initial condition even further than the original 0.03 mole fraction ClF increase. The departure from equilibrium expressed in the shift of the fraction of the fluorine appearing in HF molecules is included in the table. Again two equivalence ratios are considered, $\phi = 1.0$ and $\phi = 2.0$. In this case, however, the mixture ratio giving maximum specific impulse at equilibrium expansion conditions is near the stoichiometric value, $\phi = 1.0$.

Table 2 Initial conditions, H_2/F_2 at a chamber pressure of 100 psia

	$\phi = 1.0$ EC	$\phi = 1.0$ NEC(1)	$\phi = 2.0$ EC	$\phi = 2.0$ NEC(1)
Composition, mole fraction × 10^5:				
F	18356	18313	1080	1560
H	14647	14657	18929	18961
HF	65142	58542	58918	50938
H_2	1855	5145	21074	25044
F_2	0	3383	0	4000
Temperature, °K	4357	3470	3789	3400
Departure from equilibrium, %[a]	0	6.5[a]	0	8.4

[a] The fraction of fluorine appearing as HF in the nonequilibrium composition is 93.5% (or 91.6 at $\phi = 2.0$) of the fraction appearing as HF in the equilibrium composition.

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Table 3 Initial conditions, N_2H_4/ClF_5 at a chamber pressure of 500 psia

	ϕ = 1.0			ϕ = 2.0		
	EC	NEC(1)	NEC(2)	EC	NEC(1)	NEC(2)
Composition, mole fraction × 10^5:						
Cl	6819	6830	2519	2102	719	190
ClF	7	3007	6357	1	3000	4121
Cl_2	11	12	2	2	1	...
F	3020	2992	1313	361	67	21
H	4800	4795	5516	5439	3368	1978
HCl	5507	2527	3830	7743	4460	3931
HF	58755	55777	55878	48894	37728	37069
H_2	2537	5503	5514	13288	26159	27961
N	16	16	10	4	1	...
NH	3	...	3	3	...	1
NH_2	...	...	1	1	...	1
NH_3	...	...	...	...	...	2
N_2	18525	18541	19057	22161	24498	24725
Temperature, °K	4060	3301	3918	3346	3176	3111
ΔHF, %	0	5.0	7.5	0	6.2	9.6

Although the magnitudes of departure from equilibrium were selected as reasonable estimates based on available experimental information, they are arbitrary and difficult to substantiate. Should the values be grossly unrealistic, the effect upon performance, of course, would be altered. Should departures from equilibrium of the magnitude considered exist, the effect upon the propellant performance which would result is presented in the following section.

Nozzle Expansion and Propellant Performance

From among the many possible expansion models summarized in Table 1, three were selected to be used in determining the relation between the initial condition and the propellant performance. The simple one-dimensional cases of equilibrium, kinetic, and frozen expansion were chosen. Six possible types of performance calculations then resulted, based upon the two initial conditions and three nozzle expansions.

It should be noted that the case of nonequilibrium initial conditions followed by equilibrium expansion is excluded as being inconsistent. Any initial nonequilibrium would be immediately adjusted to the equilibrium composition upon entrance into the nozzle section. An alternate nozzle flow based upon part equilibrium expansion was used. In this model, departures from equilibrium at the initial condition are maintained through freezing the composition of departure species. For example, the excess ClF over the equilibrium concentration is given a separate name and not allowed to react in the nozzle. Other species, including that part of nonequilibrium component which would be present under equilibrium conditions, are maintained at local equilibrium in the nozzle.

Consideration of kinetic expansion is especially important to determine if nozzle reactions are capable of returning any initial departure from equilibrium to a local near equilibrium composition. If this were the case, initial nonequilibrium conditions would have little bearing on performance of the propellant.

Equilibrium and frozen expansion solutions were obtained with the NASA Equilibrium Program.[3] Kinetic-expansion solutions were based on the ICRPG (Interagency Chemical Rocket Performance Group) standard program.[1] Thermodynamic data were those of the JANAF (Joint Army-Navy Air Force) Thermochemical Tables.[7] The two propellant combinations considered and the nozzle contours were based upon similar cases reported by Cherry and Van Nice.[8] The reaction mechanisms and kinetic rate constants used were those of Ref. 8.

Hydrogen/fluorine

The stoichiometric reaction of H_2 and F_2 forms HF which is extremely stable. During the expansion process for equilibrium flow, conditions favor substantial recombination of atomic species to form HF. Hence, there is a wide difference, about 10%, between the frozen and equilibrium expansion specific impulse. Equilibrium-combustion initial condition calculations were made and indicate that the maximum specified impulse for equilibrium expansion occurred at an equivalence ratio of 2.0. The equilibrium-combustion—kinetic-expansion (EC/KE) solution provided by the one-dimen-

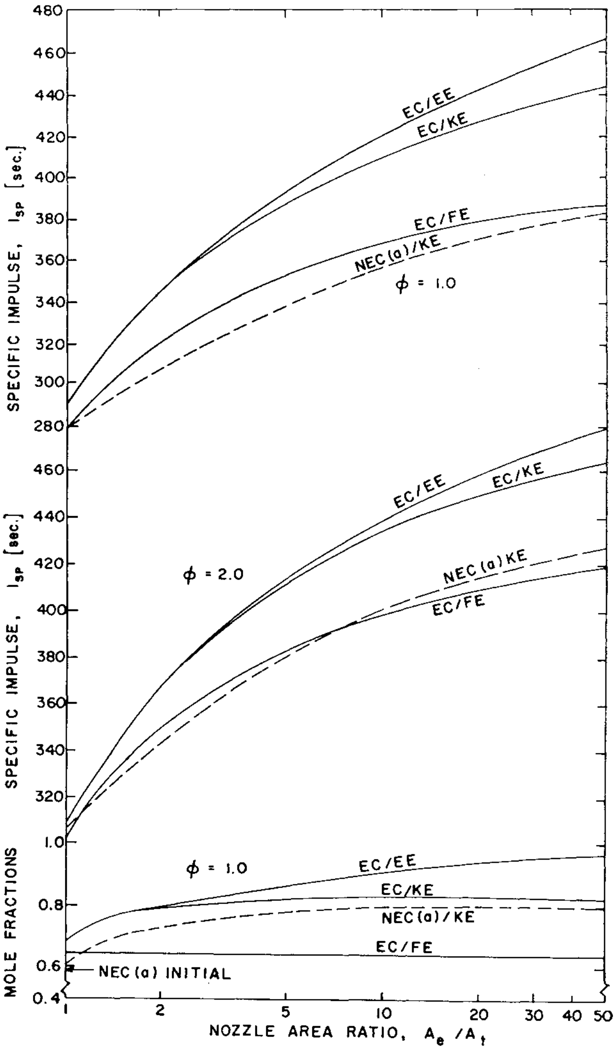

Fig. 1 Theoretical I_{sp} for ϕ = 1.0 and ϕ = 2.0, and HF concentration in nozzle for ϕ = 1.0 for H_2/F_2 (P_c = 100 psia, P_a = 0.0 psia, F = 5000 lbf nom).

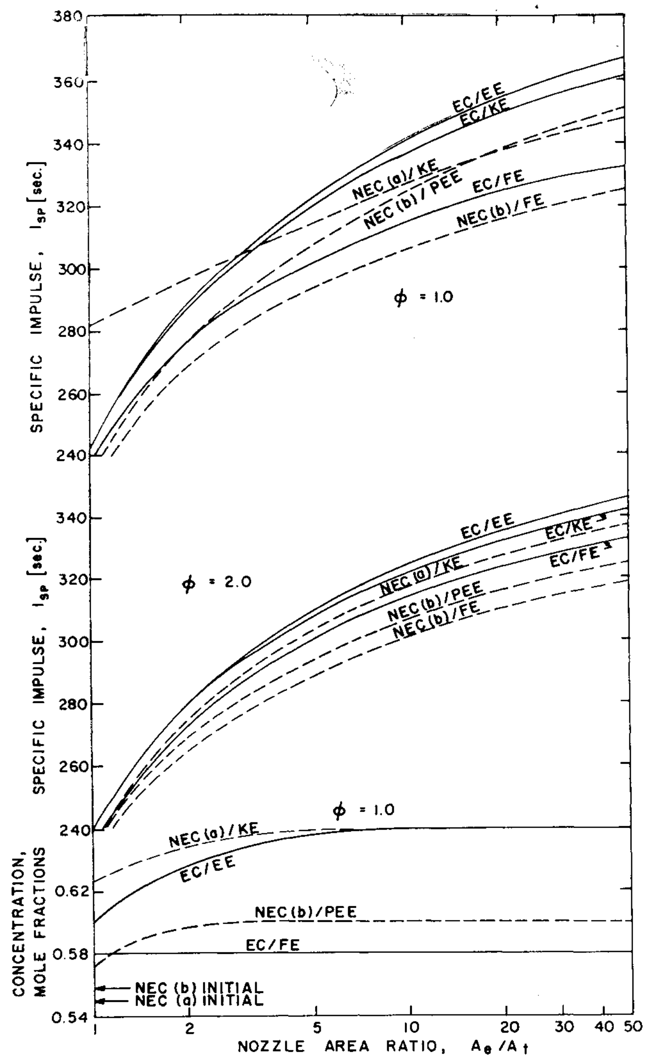

Fig. 2 **Theoretical I_{sp} for $\phi = 1.0$ and $\phi = 2.0$, and HF concentration in nozzle for $\phi = 1.0$ for ClF_5/N_2H_4 ($P_c = 500$ psia, $P_a = 0.0$ psia, $F = 3000$ lbf nom).**

sional kinetics program follows the equilibrium nozzle flow solution to a certain nozzle location and then diverges. A sudden freezing assumption is sometimes made to approximate this behavior. Equilibrium combustion cases for equivalence ratios of 1 and 2 are given for H_2/F_2 in Fig. 1. Figure 1 also shows the variation of HF concentration with area ratio for the $\phi = 1$ cases.

The nonequilibrium-combustion case proposed for the H_2/F_2 combination is the lack of completion of the combustion reaction. HF concentrations would exist at the expansion initiation plane at lower than equilibrium-combustion concentrations. Additionally, H_2 and F_2 concentrations are higher. For both equivalence ratios, the effect of the assumed nonequilibrium initial conditions on the specific impulse is significant. A smaller degree of nonequilibrium would be expected to have a proportionately smaller effect on the specific impulse.

Examination of the HF concentration curve given in Fig. 1 shows HF below equilibrium at the nozzle throat. Recombination takes place sufficiently rapidly, however, so that the HF concentration approaches that of the equilibrium-combustion case as the expansion occurs. The behavior of the HF concentration for $\phi = 2.0$ is not given but was found to be similar to the stoichiometric case. The higher equivalence ratio case indicates less of a departure from the equilibrium-combustion performance for the same mole fraction of HF assumed unreacted as compared to the stoichiometric equivalence ratio case. In both cases, however, the nonequilibrium initial condition results in a significant reduction of propellant performance, as is shown in Table 4 which summarizes the results of the performance calculations for the H_2/F_2 combination.

Table 4 Summary of specific impulse (sec) at an area ratio of 50 for H_2/F_2 (p_c = 100 psia) and ClF_2/N_2H_4 (p_c = 500 psia)

Initial condition	Equivalence ratio	Nozzle expansion FE[a]	KE[b]	PEE[c]	EE[d]
1) H_2/F_2					
EC	1.0	386.2	444.1	...	465.5
	2.0	419.8	464.0	...	477.8
NEC	1.0	...	383.0	...	...
	2.0	...	427.2	...	...
2) N_2H_4/ClF_5					
EC	1.0	332.2	361.9	...	366.8
	2.0	332.4	342.0	...	346.0
NEC	1.0	324.8	347.2	351.1	...
	2.0	318.2	336.8	323.9	...

[a] FE: frozen expansion.
[b] KE: kinetic expansion.
[c] PEE: part equilibrium expansion.
[d] EE: equilibrium expansion.

Hydrazine/chlorine pentafluoride

Equilibrium-combustion cases were computed for ClF_5/N_2H_4 and are given in Fig. 2. Many general features remain similar to the H_2/F_2 system. The solution for kinetic expansion closely parallels the equilibrium flow solution until the nozzle velocities become so great that the finite rate reactions cannot completely adjust to equilibrium. The predicted performances for the different expansion conditions are much closer at higher equivalence ratios than at the stoichiometric mixture.

It can be seen again that there is a significant effect on the propellant performance predictions when the expansion initial condition is nonequilibrium. A further effect, much more clearly demonstrated in the $\phi = 1.0$ case, is the influencing of the kinetics of the nozzle expansion process as well. The behavior at low expansion ratios is caused by a very rapid reaction forming HF induced by the nonequilibrium ClF. This can be seen from Fig. 2. In the nonequilibrium-combustion case at $\phi = 1.0$ the HF concentration increases from 0.55 to 0.62 between the expansion initiation plane and the nozzle throat, whereas the corresponding increase for equilibrium combustion is from 0.57 to 0.60. This continued combustion reaction in the converging portion of the nozzle raises the specific impulse above that for equilibrium combustion at low expansion ratios, A_e/A_t. Eventually the HF concentrations approach nearly the same value. The higher equivalence ratio case does not have this behavior since the change in HF concentration between the chamber and the throat is substantially less. In both cases the ClF reacts immediately and is found only in trace amounts at the throat.

Another nonequilibrium-combustion case which was calculated for ClF_5/N_2H_4 was for part equilibrium expansion. The initial ClF concentration was above the equilibrium level by 0.04 mole fractions at $\phi = 1.0$. This excess ClF was not allowed to react during the part equilibrium expansion. Neither rapid HF formation nor the continued combustion into the nozzle is found. For the $\phi = 2.0$ case the ClF concentration is above equilibrium by 0.06 mole fractions and the departures from equilibrium combustion are correspondingly greater. Calculated specific impulse values are summarized in Table 4 and show significant effects from nonequilibrium combustion.

Conclusions

Features of the nonequilibrium-combustion initial condition with general significance have been noted. The analysis verified that chamber conditions different from equilibrium prior to expansion could change significantly the equilibrium, kinetic, and frozen nozzle performance calculations from equilibrium-combustion performance for the propellant systems under study. Incomplete combustion of H_2 and F_2 to HF was particularly important in influencing H_2/F_2 performance. Greater than equilibrium concentrations of ClF in the ClF_5/N_2H_4 system also were found to alter performance from the equilibrium-combustion values. Increasing equivalence ratio above 1.0 was found to decrease slightly the effects of the departure from equilibrium. Attempts to refine propellant performance predictions as by kinetic nozzle calculations also should consider nonequilibrium combustion since this effect was shown to be of comparable importance to uncertainties in rate data.[8] It also was found that far down the nozzle, concentration differences from equilibrium which were introduced in the chamber began to approach the equilibrium values. Exhaust samples would appear to have limited value in gauging the effects considered here. What is needed to increase the value of this approach to propellant performance studies is more extensive measurement of actual chamber conditions.

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System Requirements for Application of a Pulsed MPD to Electrical Propulsion

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THE concept of a pulsed MPD accelerator is simply quasi-steady operation at repetitively pulsed power levels two to three orders of magnitude higher than, but at average power levels comparable to those of steady-state MPD accelerators. Potential advantages arise because the efficiency of an MPD accelerator increases as the power input increases; indeed efficiencies as high as 80% might not be an unreasonable expectation for MPD operation at multimegawatt power levels. In comparison, efficiencies generally are not higher than 30% for steady-state MPD accelerators operated at powers of the order of 10 kw. A pulsed MPD accelerator is simpler because no externally applied magnetic field is necessary because the high currents involved (10,000–100,000 amp) provide a sufficiently strong self-magnetic field. Versatility results, in that a variable duty cycle is possible. The accelerator power input, and thus the efficiency, becomes virtually independent of the power delivered by the power supply, an important advantage for solar-powered spacecraft.

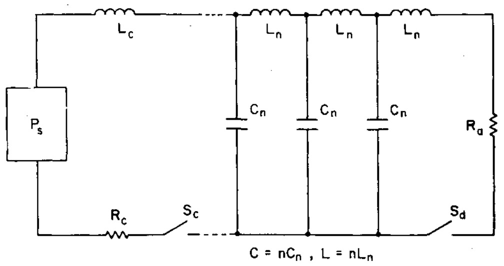

Fig. 1 Simplified network of pulsed MPD accelerator. R_a, thruster; C_nL_n, section of pulse forming network for discharge; S_d, S_c, switches; L_c, R_c, inductance and resistance in the charging loop; P_s, power supply.

However, the potential advantages of pulsed operation may not be realized when the complete propulsion system is considered. Whereas a steady MPD accelerator can be coupled to a solar power supply with very little or virtually no power conditioning, a pulsed one requires at least two additional components: a bank (most likely a capacitor bank) for energy storage between pulses, and a power conditioning unit for charging efficiently the bank from a solar power supply. As depicted in Fig. 1, the capacitor bank is structured, as a pulse-forming network, by nC_nL_n sections, and the power conditioner for charging C is represented symbolically by R_c and L_c. In practice, this conditioner must be substantially more sophisticated, especially if top utilization of the power supply and a high efficiency are desired for the energy transfer. These components required between the accelerator and the solar power supply are not 100% efficient; moreover, they have quite substantial masses, and they offset the supposed simplicity of a pulsed MPD thrustor.

This Note compares quasi-steady pulsed MPD systems with steady MPD systems. The physical phenomena imposing constraints are examined, and the acceptable ranges of the important parameters are determined. Finally, numerical results are produced for the comparison.

Parameters of a Pulsed MPD System

For quasi-steady MPD operation at very high currents (J), no external magnetic field appears to be necessary; under such conditions, the thrust is

$$F = bJ^2, b = 10^{-7}(\tfrac{3}{4} + \ln[r_a/r_c]) \quad (1)$$

where F and J are in N and amp, and r_a and r_c are the terminal radii of the current distribution at the anode and cathode, respectively. For simplicity it is assumed that the total power loss P_e in the accelerator may be represented by

$$P_e = JV_e \quad (2)$$

This assumption is realistic for the electrode losses, which represent a substantial fraction of the total losses. The use of Eq. (2) to express the electrical power not converted into thrust power, is a rough approximation, justified only by

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† The accelerator impedance R_a is obtained when Eq. (4) is divided through by J^2.