

Fig. 3 Correlation of reciprocal time parameter β with pressure.

rates at the same pressures. The burning zone advanced by the appearance of discrete groups of tiny flames, rather than by the movement of a continuous flame front. Tiny "secondary ignition spots" appeared somewhat in advance of the main flame front and spread at a slower rate than the advance of the main front, so that they were usually overtaken by and consolidated with the main burning area before spreading to an appreciable extent. Although the flame spread in small, discrete jumps, the position-time points formed reasonably smooth curves when plotted.

Values of α and β , obtained from the flame-spread data by a curve-matching technique, are presented in Figs. 2 and 3, which show that α is a strong function of gas velocity ($\alpha u^{0.55} = 41.3$) but apparently not of pressure, and β increases with approximately the 1.25 power of pressure but is not affected significantly by velocity.

The composition of β is known from its definition. The increase in f_0/T_i with increasing pressure is explained qualitatively by the increase in density of the hot gas from the burning zone. Apparently, for transport of hot gas from the burning zone to a contiguous unignited surface, all of the velocities studied here (>10 m/sec) are equally effective, i.e., transport effectiveness is complete over a wide range of velocities, including the range studied and extending to a velocity sufficient to extinguish the flame.

The inverse relationship between α and u is to be expected from boundary-layer considerations. The empirical origin of α , however, makes it difficult to comment on the degree of velocity dependence and the absence of pressure dependence. Two effects of increasing velocity are easily conceived: heat transfer is enhanced; and, at a given x , the hot gas has less time to radiate or otherwise lose its energy to the surroundings.

Several runs were made with oxygen as the tube gas in place of nitrogen (Figs. 2 and 3). Since no appreciable consistent effect was found, it is concluded that, except to provide the aerodynamic environment, the tube gas did not participate significantly.

Conclusions

In rocket-design practice, we are confronted with the problem of anticipating, perhaps of regulating, the progress of ignition over large areas of propellant surface under conditions of changing pressure, energy distribution, and internal flow patterns. Flame spread is the concluding phase of the complex sequence of events that comprises the over-all igni-

tion transient. It is, therefore, the one most susceptible to influence by igniter behavior, propellant response, geometry, and scale, insofar as these affect the time-dependent heat-flux distribution. From laboratory experiments conducted with constant process conditions, therefore, the principal products expected are clues to the influence of the process conditions. The analysis of this study produces two flame-spread parameters in which, fortuitously, the pressure and velocity effects are isolated. The influence of pressure appears to be greater than the influence of velocity.

References

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Further Comments on Correlations for Shifting Rocket Thrust

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PREVIOUSLY mentioned¹ were the empirical correlations between 1) theoretical enthalpy drops in rocket-combustion products on equilibrium expansion from 1000 psia to 1 atm and 2) heats of reaction of the propellants at 298°K. With the exception of a few anomalies,² they apply when all products are gaseous and the systems are arranged with respect to the average number of atoms per mole of major (i.e., "effective") species, regardless of dissociations or inter-reactions. This note presents correlations that hold when the effective species are not all gases so the original correlations are not applicable. It also comments on choosing effective species for the correlations and on the subordinate nature of rocket temperatures.

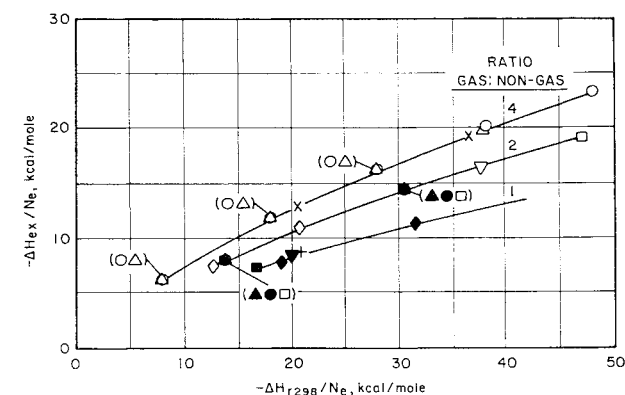
Table 1 Adjusted ΔH_{f298} for correlations with some nongaseous products

| Atoms/mole | Species | Accepted ΔH_{f298} , kcal/mole | Adjustment, kcal/mole | Adjusted ΔH_{f298} , kcal/mole |
|------------|------------------------------------|--|-----------------------|--|
| 2 | BeO(l) | -129.1 | 0.0 ^a | -129.1 |
| | BeO(s) | -143.1 | +1.0 | -142.1 |
| | BN(s) | -60.3 | -3.0 | -63.3 |
| | LiF(l) | -140.7 | +7.0 | -133.7 |
| | LiF(s) | -145.1 | +3.0 | -142.1 |
| | MgO(s) | -143.7 | +3.0 | -140.7 |
| 3 | ZrO ₂ (l) | -245.5 | 0.0 ^a | -245.5 |
| | ZrO ₂ (s) | -261.5 | -4.0 | -265.5 |
| | Li ₂ O(l) | -132.3 | +5.0 | -127.3 |
| | Li ₂ O(s) | -142.6 | -0.5 | -143.1 |
| | SiO ₂ (l) | -209.4 | -3.5 | -212.9 |
| 5 | Al ₂ O ₃ (l) | -356.5 | 0.0 ^a | -356.5 |
| | Al ₂ O ₃ (s) | -400.4 | +9.0 | -391.4 |

^a No adjustment, reference species.

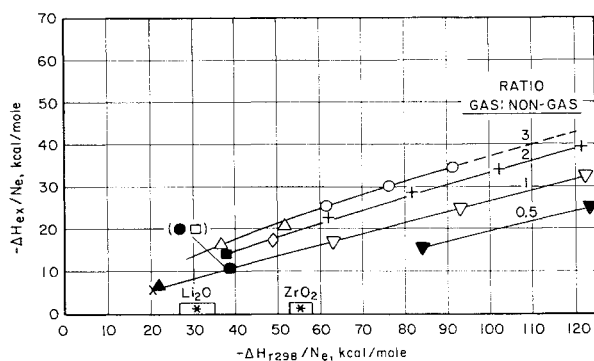
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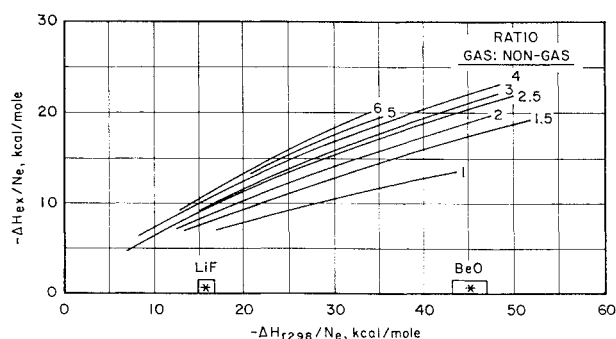
| MOLAR RATIO GAS: NON-GAS | SYSTEM | SYMBOL |
|-----------------------------|--|--------|
| 1/1 | LiF (l) (H ₂) | ■ |
| | BN (c) (H ₂) | ◆ |
| | MgO (c) (H ₂) | ▼ |
| | BeO (c) (H ₂) | + |
| 2/1 | BN (c) (H ₂) ₂ | ▲ |
| | MgO (c) (H ₂) ₂ | ◇ |
| | BeO (c) (H ₂) ₂ | □ |
| | BeO (c) (N ₂) (H ₂) | ● |
| | BeO (l) (H ₂) ₂ | ▽ |
| 4/1 | BN (c) (H ₂) ₄ | x |
| | MgO (c) (N ₂) (H ₂) ₃ | ○ |
| | BeO (c) (H ₂) ₄ | △ |

a) Diatomic nongaseous species



| MOLAR RATIO GAS: NON-GAS | SYSTEM | SYMBOL |
|-----------------------------|---|--------|
| 0.5/1 | ZrO ₂ (l) (H ₂) _{0.5} | ▼ |
| | ZrO ₂ (l) (H ₂) | ▽ |
| | Li ₂ O (l) (H ₂) | ● |
| | Li ₂ O (l) (N ₂) | ▲ |
| 1/1 | Li ₂ O (c) (H ₂) | ■ |
| | Li ₂ O (c) (N ₂) | x |
| 2/1 | ZrO ₂ (l) (H ₂) ₂ | + |
| | ZrO ₂ (c) (H ₂) ₂ | ◇ |
| | SiO ₂ (l) (H ₂) ₂ | ■ |
| 3/1 | ZrO ₂ (l) (H ₂) ₃ | ○ |
| | ZrO ₂ (c) (H ₂) ₃ | △ |

b) Triatomic nongaseous species



c) Loci curves for diatomic nongaseous species

Fig. 1 Theoretical energy conversions of diatomic and triatomic nongaseous effective species with added diatomic gaseous species (1000 psia/1 atm, shifting expansion, $-\Delta H_{r298}$ computed with adjusted $-\Delta H_{f298}$ of nongases).

Table 2 Examples of effective species

| | | | |
|------------------------------------|------------------------------------|----------------------|-----------------------------------|
| AlF ₃ (g) | B ₂ O ₃ (l) | H ₂ O(g) | TiO ₂ (l) |
| Al ₂ O ₃ (c) | B ₂ O ₃ (g) | HCl(g) | ZrO ₂ (l) |
| Al ₂ O ₃ (l) | BeO(c) | LiF(c) | P ₄ O ₆ (g) |
| BOF(g) | BeF ₂ (g) | LiF(g) | SiF ₄ (g) |
| BF ₃ (g) | Be ₂ N ₂ (c) | MgF ₂ (g) | SiO ₂ (l) |
| HOB(O)(g) | H ₂ (g) | MgO(c) | F(g) |
| BN(c) | HF(g) | N ₂ (g) | Pb(g) |

Intercorrelations between systems with identical proportions of diverse types of nongaseous and gaseous products are obtained when an adjusted heat of formation is used for the nongaseous effective species.³ The adjustment is added to the accepted heat of formation and is the average displacement in kilocalories of the plot of enthalpy increase above 298°K vs temperature for the particular nongaseous species, as compared with an arbitrarily selected nongaseous species of the same atoms per molecule. It is applied to the heat of reaction term (as indicated below) and is not used in performing the exact computation.

Accepted heats of formation of some nongaseous effective species, derived adjustments, and consequential heats for use in the correlations are given in Table 1, as generated from Ref. 4. The customary excellence of plots of $-\Delta H_{ex}/N_e$ vs $-\Delta H_{r298}/N_e$, prepared in the manner of Ref. 1 but with adjusted heats used to determine $-\Delta H_{r298}$, are shown in Figs. 1a and 1b: the former for mixtures of a diatomic nongaseous with diatomic gases and the latter for a triatomic nongaseous with diatomic gases. Such results lead to loci curves as exemplified in Fig. 1c for the former case. The asterisks on the abscissas of Figs. 1b and 1c show approximate melting ranges. These curves (and others in Ref. 3) can be used to compute theoretical thrust or specific impulse to a better accuracy than 2% by the simple and rapid procedure described in Ref. 1, although they do not intercorrelate with the all-gaseous loci of Ref. 1.

Examples of gaseous and nongaseous effective species are given in Table 2, ignoring certain anomalies.² Customarily their elements are proportioned in accordance with normal valence rules, so they generally are the compounds that exist at room temperatures. However, in case the propellant elements can give rise to other normal-valence compounds, those with greater stabilities at rocket conditions will be the effective species. Thus, the elemental formulation, B, 2-O, H, will act effectively as HOB(O)(g), instead of $\frac{1}{2}$ B₂O₃(g) and $\frac{1}{2}$ H₂O(g), because of the instability at high temperatures of boric oxide in the presence of water vapor. Molecular fragments, such as OH, BO, BF₂, H, etc., are rarely effective species, although they often exist in notable amounts within the rocket. Exceptions occur when normally unstable diatomic gases dissociate virtually completely to monatomic elements at rocket conditions, such as 2 F(g) from F₂(g) or 2 Pb(g) from Pb₂(g).

The empirical correlations do not directly involve combustor or exhaust temperatures, or their ratios, because thermodynamic efficiencies based on temperatures do not apply to the noncyclic rocket process, and its temperatures per se are dependent properties and not fundamental ones.

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