

Communications

Afterburning of solid rocket exhaust

DONALD H. STEDMAN[†], JOHNSON AY[‡],
JEFFREY R. WILLIAMS[§], AND THOMAS C. ADAMSON[¶]

University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

(Received 19 August 1974; Communicated by A. K. Oppenheim)

AN EQUILIBRIUM CALCULATION of the solid fueled rocket exhaust of the proposed NASA Space Shuttle has been carried out and parameterized in terms of oxidant/fuel ratio. Results comparing the equilibration times with experimentally determined dilution times show that H₂ and CO are completely burned to H₂O and CO₂, whereas HCl, although thermodynamically usable, is not oxidized to Cl₂. NO formation is less certain, but an upper limit of HCl/NO > 5 can be determined.

Studies to date on exhaust product reactions by Susko and Kaufman[1] and Nybakken and Harris[2] either include an assumption of intense afterburning of H₂ and CO, or use as an arbitrary parameter zero or complete afterburning[3]. In this paper a simplified model is used to estimate the extent of afterburning. Data are parameterized in terms of oxidant/fuel ratio (derived from the work of Rhein[4]). Effluent from the proposed Space Shuttle is fuel (F) and oxidant (O) is air. The lifetime (τ) of several key reactions in the afterburning equilibria are compared to the time rate of change of species concentration. When reaction lifetimes (τ) become long compared to cloud dilution times then the equilibria will clearly be frozen.

An inventory of exhaust products HCl, H₂O, CO, CO₂, N₂ and N₂O₄ at $\tau = 13$ sec after ignition (solid particles are excluded) results in 1932 moles of products assumed evenly distributed throughout a cloud volume of 1.25×10^6 m³ (Hart[5]). This gives an oxidant-to-fuel ratio of 26.9 at $\tau = 13$ sec, which increases logarithmically through O/F = 1100 at 40 sec. Applying cloud rise and growth factors from Nybakken and Harris[2] one finds an O/F ratio of 7000 at $\tau = 150$ sec. This curve enables one to set an approximate dilution time.

Equilibrium analysis was carried out by the minimization of Gibbs free energy with mass balance constraints. The thermodynamic state of the gas mixture was specified by a given pressure and enthalpy. Our model makes use of two main assumptions: (a) that stagnation enthalpy is constant throughout the mixing region

[†]Assistant Professor of Chemistry.

[‡]Research Assistant, Aerospace Engineering.

[§]Research Assistant, Department of Chemistry.

[¶]Professor of Aerospace Engineering.

(this is equivalent to assuming a turbulent Prandtl number of unity) and (b) that thermodynamic equilibrium is maintained using the computer program of Gordon and McBride[6]. Because the exhaust gases pass through several shock waves before impinging on the ground and mixing with air, the assumption of constant stagnation enthalpy appears to be most plausible. One set of calculations was based on chemical equilibrium throughout the complete region of the nozzle throat and frozen flow from throat to exit. Chemical equilibrium computations were then made at constant static and total enthalpy exhaust for dry or wet (100% relative humidity) air at 293°K and atmospheric pressure. Equilibrium compositions of species calculated from the above two approaches differed by less than 8% in species concentration at O/F > 1000. Humidity was not a significant factor under any conditions. The assumption of thermodynamic equilibrium at early time is reasonable in view of the high temperature, but at a later time all the equilibria will be frozen, and the species concentrations will just be diluted proportional to O/F.

A time constant characteristic of processes of formation or decomposition of a species to approach its equilibrium was used to study the validity of the chemical equilibrium assumption, and to estimate where in the afterburning freezing would take place. The characteristic time was based on a rate equation of the key reaction: for example, for H₂: O + H₂ = OH + H. Thus for this reaction, the time constant τ was derived from the formula $\tau = (k_2[\text{O}][\text{H}_2])^{-1}$. The concentrations used were the instantaneous equilibrium concentrations (the appropriate value of the rate constants at the equilibrium temperatures were taken from Hampson *et al.*[7]).

The calculated times of NO, H₂, CO and HCl for the case of constant total enthalpy in dry air were plotted versus O/F ratios together with the related equilibrium compositions. In all cases characteristic times increase rapidly as the O/F ratio increases beyond about two, which occurs in a few seconds. All equilibria are well frozen by then. Even if one puts a conservative limitation of freezing (characteristic time greater than one second) then all concentrations are frozen by O/F = 10. All the H₂ will then be oxidized to H₂O before the equilibrium freezes, similarly for CO burning to CO₂. By contrast, the reverse is true for HCl. Here, the equilibrium HCl concentration will be frozen at HCl/Cl₂ > 100; thus the thermodynamically stable product (Cl₂) will not be formed to any great extent.

The case of NO is not so clear. In order to make NO, excess O₂ must be mixed with the exhaust, so at early times τ is never much less than 1 msec. Thus equilibrium NO may never form. Furthermore, although relative humidity is unimportant for NO formation the assumption of constant static or total enthalpy is important and unspecifiable. Thus, the best that can be done with this study is an upper limit calculation for NO in the stabilized ground cloud. This upper limit is obtained by assuming constant static enthalpy with freezing occurring at log₁₀ O/F = 0.4, and then following the frozen slope out to log₁₀ O/F = 3.8 (the stable ground cloud O/F). This gives about 5 ppm NO. This value is an upper limit for many reasons, but if the actual concentration were within two orders of magnitude it would still be a significantly measurable perturbation over the ambient atmosphere. (Non-equilibrium chemical kinetic calculations could give a

better estimate of NO concentrations within the limitations of the instantaneous mixing assumptions).

At the same time as our study, Rhein[8] modeled a similar exhaust cloud. His study was aimed at prediction of aerosol concentrations and his results on equilibrium agree well with ours. He does not include experimental data on dilution versus time, nor does he use the equilibration time constant approach which enables us to be sure that the HCl/Cl₂ ratio will be frozen at greater than 100.

References

1. Susko, M. and Kaufman, J. W., Exhaust cloud rise and growth for Apollo Saturn engines, *J. Spacecraft & Rockets*, **10**, 341 (1973).
2. Nybakken, T. W. and Harris, N. A., Solid rocketry effluent analysis, Final Report Contract No. F04701-72-C-0274, proposed by EG&G, Santa Barbara Division, Report No. S-573-R (1972).
3. Rhein, R. A., The formation of hydrochlorine acid aerosol from the interaction of the Space Shuttle rocket exhaust with the atmosphere, Technical Memorandum 33-619, Jet Propulsion Laboratory, C.I.T. (1973).
4. Rhein, R. A., Shuttle solid booster exhaust environmental effects, Task Number 909-02-47-01, Task Title: Exhaust Plume Chemistry, Interim Letter (1973).
5. Hart, W. S., Dynamics of large buoyant clouds generated by rocket launches, *J. Basic Eng.*, **1**, 53-60 (1972).
6. Gordon, S. and McBride, B. J., Computer program for calculations of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouquet detonations, NASA SP-273, Lewis Research Center, Cleveland, Ohio (1971).
7. Hampson, R. F., Braun, W., Brown, R. L., Garvin, D., Herron, J. T., Huie, R. E., Kurylo, M. J., Laufer, A. H., McKinley, J. D., Okabe, H. A., Scheer, M. D., Tsang, W. and Stedman, D. H., Survey of photochemical and Rate Data for Twenty-eight Reactions of Interest in Atmospheric Chemistry. *J. Phys. Chem. Reference Data*, **2**, 267-311 (1973).
8. Rhein, R. A., Some Environmental Considerations Relating to the Interaction of the Solid Rocket Motor Exhaust with the Atmosphere: Predicted Chemical Composition of Exhaust Species and Predicted Conditions for the Formation of HCl Aerosol, Technical Memorandum 33-659, Jet Propulsion Laboratory, C.I.T. (1973).