the heat transfer from the region under separated flow. The laminar boundary-layer analysis upon which the numerical value of the coefficient of the first term is based is an asymptotic analysis, valid when the boundary-layer thickness is very small compared with the radius of the cylinder. For moderate Reynolds numbers, it becomes necessary to correct the numerical value of the coefficient to account for the finite thickness of the laminar boundary layer with respect to the cylinder radius. In order to obtain a reasonable estimate for this correction, it appears suitable to adapt an idea once proposed by Langmuir[6] in connection with the analysis of natural convection from a heated horizontal cylinder. In the asymptotic analysis, it is assumed that the boundary layer is locally a flat film. In the vicinity of the cylinder surface, the heat transfer occurs predominantly by pure conduction in the gas, the net convection velocities being very small. With this in mind, it appears reasonable to suppose that, for finite Reynolds numbers, the conduction occurs in a thick-walled "tube" of the gas, the "tube" thickness being proportional to the boundary-layer thickness. A first-order estimate for the conduction thickness can be obtained from the asymptotic solution. If the heat transfer were indeed by conduction through the gas, the corresponding wall thickness of a plane slab is given by the reciprocal of the slope of the temperature profile at the wall surface. For the forward stagnation region, the corresponding conduction thickness is $1.01\,D/(Re_D)^{1/2}$. In the steady conduction problem, which corresponds to the situation at moderate Reynolds number, a logarithmic expression arises. The logarithm can be expanded as a series (the radius of convergence of which embraces all Reynolds numbers exceeding 4.04), and the leading term of the series can be used in a correction factor. The laminar boundary-layer thickness around the forward portion of a cylinder is roughly constant, so that, to the order of approximation which is involved, the correction factor calculated for the forward stagnation point can be applied to the term in the equation which represents the whole of the forward region on the cylinder. This equation therefore becomes

$$
\begin{aligned}
Nu &= 0.37\,Re^{1/2}\,\{1 + 1.01/Re^{1/2}\} + 0.057\,Re^{2/3} \\
&= 0.3737 + 0.37\,Re^{1/2} + 0.057\,Re^{2/3}
\end{aligned}
\tag{2}
$$

Since the contribution to the total heat transfer of the forward portion of the cylinder is greater than that of the rear portion, at moderate Reynolds numbers, it is appropriate that the term for the forward region is the first to undergo correction. As the Reynolds numbers considered become smaller, it is to be expected that it is necessary to take account of more terms in the series, to take account of the changing position of the separation of the laminar boundary layer, and of changes in the heat-transfer characteristics of the rearward surface. It seems that, to some extent, corrections for these various factors compensate each other, and it is not surprising that Eq. (2) correlates heat-transfer measurements down to Reynolds numbers below those for which the flow models used to obtain the equation are valid.

Comparison of Eq. (2) with the correlation of McAdams shows good agreement for Reynolds numbers as low as 1.0. Collis and Williams presented two equations to correlate their own measurements, the first being for $0.02 < Re < 44.0$ and the second for $44.0 < Re < 140$. Equation (2), when compared with these equations, shows differences ranging from 0 to 6%, with the largest differences occurring at $Re = 44.0$, for the range $1.0 < Re < 140$. The differences becomes more uniform and of the order of 3–4% if the coefficient of the first term in the equation is changed to 0.36 instead of 0.37.

It may be concluded that Eq. (2) represents convection from heated cylindrical surfaces within experimental uncertainty over a range of Reynolds number of about 1.0 to $10^5$, subject to the conditions that, at high Reynolds numbers, the relation is appropriate for streams with low turbulence intensity and, for all Reynolds numbers, the Grashof numbers are not significant. The correlation is based upon a physical understanding of the local heat-transfer distribution appropriate to high and moderate Reynolds numbers; it is a fortunate but accidental circumstance that the equation provides a good correlation for Reynolds numbers down to the order of unity. The correlation is for heat transfer that occurs with small temperature differences; when the temperature differences become large, it is necessary to include a factor to account for this, as is done by Collis and Williams. As a secondary matter, the correlation given here provides a hint of the reasons for which the empirical correlations having the form

$$Nu = A + B\,Re^n \tag{3}$$

work as well as they do. It may be noted from Eq. (2) that a numerical constant $A$ arises from the first-order correction of the laminar convection on the forward portion of the cylindrical body. When the range of Reynolds numbers used in a correlation is small, there is considerable latitude in the choice of the coefficients in fitting the data.

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# Near-Equilibrium Criterion for Complex Reacting Flows

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## Introduction

A near-equilibrium criterion is required when determining the point in a nozzle where integration of an initially equilibrium flow should be started. A similar criterion is required if a "sudden-freezing" analysis is to be performed. Although it is easy to examine the proximity to equilibrium of a simple reacting system (a dissociating gas, for example), the problem is more complicated in the general case when several reactions may be simultaneously taking place among several species.[1]

An examination of the closeness to equilibrium can be made from a comparison of the characteristic reaction time with the characteristic flow time. This method was first developed by Penner[2] for flow with a single reaction and extended by Bray and Appleton[3] to an arbitrary number of reactions. When applied to complex systems, it suffers from the disadvantage that each reaction is considered independently. No account is taken of the coupling between reactions whereby a slow reaction can be held close to equilibrium by the action of a set of fast reactions.

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The proximity to equilibrium can also be examined by a perturbation method. Such a method has been suggested by Penner, Porter, and Kushida.[4] They derive a set of first-order, nonlinear differential equations. They reduce these to a set of nonlinear algebraic equations by neglecting the differential terms, but substitution of some typical values shows that these terms are not always negligible. Elsewhere, it appears to have been quite widely held[5] that, when more than $n$-$L$ reactions were considered, where $n$ is the number of species, and $L$ the number of independent species, a perturbation technique was inapplicable as the system at equilibrium was overspecified. This belief is behind the group-testing method of Bray and Appleton.[6] It is the purpose of this note to show that this restriction is an imaginary one and that a perturbation method, leading to a set of algebraic equations, can be applied.

### Analysis

The differential continuity equation for the $i$th species in steady, one-dimensional, reacting flow, is

$$\rho V \frac{d\sigma_i}{dx} = \sum_{j=1}^{N} (\alpha_i{}^{j''} - \alpha_i{}^{j'})(R_f{}^j - R_b{}^j) \tag{1}$$

where $\rho$ is the density; $V$ the velocity; $x$ the distance along the nozzle; $\sigma_i$ the molal concentration of the $i$th species; $\alpha_i{}^{j'},\alpha_i{}^{j''}$ the stoichiometric coefficients of the $i$th species in the $j$th reaction, reactants and products, respectively; $R_f{}^j R_b{}^j$ the rates of the $j$th reaction, forward and backward, respectively; and $N$ the number of reactions.

The reaction rates are given by the expressions

$$R_f{}^j = k_f{}^j \prod_{i=1}^{n} (\rho\sigma_i)^{\alpha_i{}^{j''}} \tag{2}$$

$$R_b{}^j = k_b{}^j \prod_{i=1}^{n} (\rho\sigma_i)^{\alpha_i{}^{j''}} \tag{3}$$

where $k_f{}^j k_b{}^j$ are the reaction rate constants of the $j$th reaction, forward and backward, respectively.

When computing the equilibrium solution, an independent set of reactions that can be used conveniently is

$$\sum_{e=1}^{L} \beta_{ei} M_e \rightleftharpoons M_i \tag{4}$$

where the $L$ elementary species are arranged to be the first species in the series; $M_i$ is a molecule of the $i$th species; $\beta_{ei}$ is the number of times the $e$th elementary species occurs in the $i$th species; and $i = L + 1, L + 2 \ldots n$.

The reactions given by Eq. (4) may not be very important from a reaction kinetic point of view, but this does not matter; what is important is their independence. The equilibrium constants $K_c{}^i$ for the independent set of reactions are given by

$$K_c{}^i = (\rho\sigma_i) \prod_{e=1}^{L} (\rho\sigma_e)^{-\beta_{ei}} \tag{5}$$

However, when the system is not in equilibrium, and it cannot be exactly so in nozzle flows, as the reactions are not infinitely fast, the relation between the equilibrium constants and the concentrations is

$$K_c{}^i(1 + \zeta_i) = (\rho\sigma_i) \prod_{e=1}^{L} (\rho\sigma_e)^{-\beta_{ei}} \tag{6}$$

where $\zeta_i$ is a measure of the deviation of the independent reaction from equilibrium.

Note that for $i = 1, 2, \ldots L$, Eqs. (4) are degenerate, and reduce to reactions in which the reactant and product are the same. These "reactions" are, of course, always in equilibrium, with an "equilibrium constant" equal to unity. $\zeta_i$, for $i = 1, 2, \ldots L$, is therefore zero.

The deviation of each of the chemical reactions which is in fact taking place, even though there may be more than $n - L$ to be considered, can be expressed in terms of the deviations of the independent set of reactions.

From Eqs. (2) and (3),

$$\frac{R_f{}^j}{R_b{}^j} = \frac{k_f{}^j}{k_b{}^j} \prod_{i=1}^{n} (\rho\sigma_i)^{(\alpha_i{}^{j'} - \alpha_i{}^{j''})} \tag{7}$$

Substituting in (7) from (6),

$$\frac{R_f{}^j}{R_b{}^j} = \frac{k_f{}^j}{k_b{}^j} \prod_{i=1}^{n} \left\{ K_c{}^i(1 + \zeta_i) \prod_{e=1}^{L} (\rho\sigma_e)^{\beta_{ei}} \right\}^{[\alpha_i{}^{j'} - \alpha_i{}^{j''}]}$$

By continuity,

$$\prod_{i=1}^{n} \prod_{e=1}^{L} (\rho\sigma_e)^{\beta_{ei}(\alpha_i{}^{j'} - \alpha_i{}^{j''})} = 1$$

Therefore,

$$\frac{R_f{}^j}{R_b{}^j} = \frac{k_f{}^j}{k_b{}^j} \prod_{i=1}^{n} \{K_c{}^i(1 + \zeta_i)\}^{(\alpha_i{}^{j'} - \alpha_i{}^{j''})} \tag{8}$$

However, the relationship between equilibrium constants gives

$$\frac{k_f{}^j}{k_b{}^j} \prod_{i=1}^{n} (K_c{}^i)^{(\alpha_i{}^{j'} - \alpha_i{}^{j''})} = 1$$

Equation (8) therefore becomes

$$\frac{R_f{}^j}{R_b{}^j} = \prod_{i=1}^{n} (1 + \zeta_i)^{(\alpha_i{}^{j'} - \alpha_i{}^{j''})} \tag{9}$$

If $\zeta_i \ll 1$, as will be the case near equilibrium,

$$\frac{R_f{}^j}{R_b{}^j} \simeq 1 + \sum_{i=1}^{n} (\alpha_i{}^{j'} - \alpha_i{}^{j''})\zeta_i \tag{10}$$

$$R_f{}^j - R_b{}^j \simeq R_f{}^j \sum_{i=1}^{n} (\alpha_i{}^{j'} - \alpha_i{}^{j''})\zeta_i \tag{11}$$

Substituting Eqs. (11) into (1),

$$\rho V \frac{d\sigma_i}{dx} = \sum_{j=1}^{N} \left\{ (\alpha_i{}^{j'} - \alpha_i{}^{j''}) R_f{}^j \sum_{h=L+1}^{n} (\alpha_h{}^{j'} - \alpha_h{}^{j''})\zeta_h \right\} \tag{12}$$

where the index $h$ is used to avoid confusion with the index $i$. The summation limits have been changed since the first $L$ values of $\zeta_h$, corresponding to the independent species, are zero.

In a near-equilibrium flow, the left-hand side of Eqs. (12) can be found from an equilibrium analysis, as can the values of $R_f{}^j$. Thus, Eqs. (12) provide a set of $n - L$ linear equations in $n - L$ unknowns and can be solved for $\zeta_h$ without difficulty. A comparison of the forward and backward rates of any reaction can then be made using Eqs. (10).

### Conclusions

The choice of the correct set of variables enables a linear perturbation method, unrestricted by the number of reactions to be considered, to be used in developing a near-equilibrium criterion for reacting flows. The method can also be applied to finding the freezing points if a "sudden-freezing" analysis is to be performed on a complex system. In this case, however, the linearization possible when the system is close to equilibrium is not justified, and a set of nonlinear algebraic equations must be solved iteratively.

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# Hexanitroethane Propellant Slurries

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## Introduction

RECENT developments in the synthesis of hexanitroethane (HNE) have renewed interest in its use as a possible high energy oxidizer. The chemical reactivity and the physical properties of HNE have recently been reported.[1] As might be expected for such an energetic compound, HNE is chemically reactive with many compounds, particularly curable organic binders. HNE does not lend itself well to a castable, curable propellant system because 1) it requires low-temperature mixing and casting, 2) it is incompatible with standard binders and curing agents, and 3) it may undergo phase transition. The problems associated with using HNE in a conventional composite type of propellant could possibly be circumvented by utilizing noncurable slurries of HNE. This paper describes the preparation and evaluation of noncurable HNE propellant slurries.

## Performance Calculations

Performance calculations§ were made of propellant systems composed of HNE with the following fuels: polyethylene, decane, 1-nitropropane, 1-nitrobutane, 1,1-dinitroethane, 1,1-dinitropropane, 1,1,1-trinitropropane, ethyl nitramine, propylnitramine, diethyl nitramine, and trimethyolethanetrinitrate. The propellant systems containing the saturated hydrocarbons, mononitroalkanes, and the primary and secondary nitramines gave calculated specific impulses of 275–278; the main difference is that 84% HNE was required for the hydrocarbon systems, whereas 70–72% HNE was needed for the mononitroalkanes and only 55–65% was required for the nitramines. The hydrocarbon system has too high a solids loading for a castable slurry, but the mononitroalkanes and nitramines with the lower solids loading would qualify as castable systems. 1,1-dinitroethane has an optimum specific impulse of 270 at 24% HNE, whereas 1,1-dinitropropane peaks at 273 with 46% HNE. The higher homologs of the 1,1-dinitroalkanes, such as 1,1-dinitrobutane and 1,1-dinitropentane, will undoubtedly give a specific impulse of 275–277 at a practical oxidizer loading. Nitrate esters such as trimethyolethane trinitrate do not give specific impulses in excess of 270 and are not of interest. The results are summarized in Fig. 1. The heats of formation of the liquid fuels that were used in the performance calculations are compiled in Table 1.

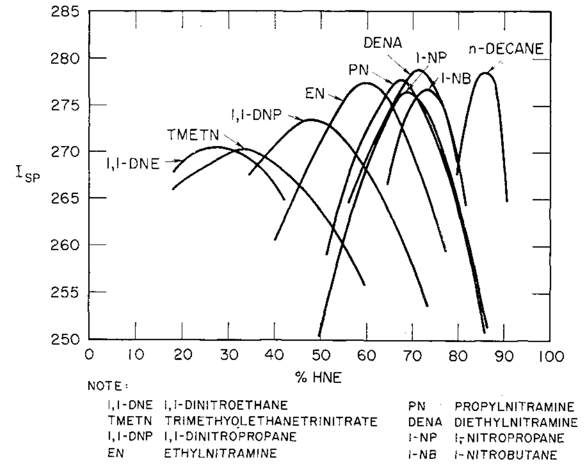

**Fig. 1 Performance calculations of HNE propellant slurries.**

## Compatibility Studies

Compatibility studies were run on HNE and the following compounds: decane, oronite polybutene #6, 1-nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, 1,1-dinitropropane, 1,1-dinitrobutane, butyl nitramine, methyl ethyl nitramine, and diethyl nitramine. The mononitroalkanes were samples from Commercial Solvents Company and were used as received with the exception of 1-nitrobutane that was purified by fractional distillation. The 1,1-dinitroalkanes were prepared by the Lockheed Missiles and Space Company, and the nitramines were synthesized at Stanford Research Institute. Both the 1,1-dinitroalkanes and the nitramines had purities greater than 99% as indicated by vapor phase chromatography.

Stoichiometric mixtures of HNE and the liquids were placed in manometric tubes and the gas evolution was measured as a function of time at ambient temperature. HNE showed excellent compatibility with decane and the 1,1-di-

**Table 1 Heat of formation data on HNE propellant components**

| Compound | Heat of formation, kcal/100 g |
|---|---|
| Hexanitroethane | 9.53 |
| Polyethylene | −42.99 |
| Decane | −50.56 |
| 1-nitropropane | −45.32 |
| 1-nitrobutane | −44.69 |
| 1,1-dinitroethane | −28.87 |
| 1,1-dinitropropane | −29.85 |
| 1,1,1-trinitropropane | −15.66 |
| Ethyl nitramine | −22.85 |
| Propyl nitramine | −25.79 |
| Diethyl nitramine | −21.57 |
| Trimethyolethane trinitrate | −39.70 |

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§ Performance calculations are based on mobile equilibrium, isentropic expansion between 1000 psia chamber pressure and an exhaust pressure of 14.7 psia.