Table 1 Eigenvalues and coefficients

	$u/\bar{u} = 0$	$\frac{2}{5}$	$\frac{2}{3}$	1
$\lambda_1^{1/2}$	2 531		2 65	2 710
$\lambda_2^{1/2}$	4 578	4 71	4 75	4 955
$\lambda_3^{1/2}$	6 599	6 78	6 88	7 195
$\lambda_4^{1/2}$	8 610	8 81	9 00	9 425
D_1	−0 1985		−0 1670	−0 1360
D_2	−0 0693	−0 0594	−0 0515	−0 0406
D_3	−0 0365	−0 0306	−0 0247	−0 0194
D_4	−0 0230	−0 0217	−0 0145	−0 0113

It should be mentioned that the first few eigenvalues apparently become slightly inaccurate (i e , do not fit) as ($u_s/\bar{u} \rightarrow 0$) Also, interactions between the velocity and temperature fields, such as thermal creep, have been neglected, as noted earlier

From this comparison it appears that the method of Sellars et al has definite application for determining the eigenvalues and coefficients for heat transfer in laminar tube slip flow The author is currently extending the treatment outlined here to the problem of heat transfer to laminar slip flow in a parallel plate channel

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Numerical Study of Hydrogen-Fluorine Kinetics in Nozzles

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A NUMBER of groups now have general computer programs for the study of complex chemical reactions in adiabatic flow [1–5] A program written here in FORTRAN language has been used to compare calculated and experimental performances in the H_2-F_2 system

The equations and techniques necessary have been amply described in the references cited Briefly, the usual hydrodynamic equations for one-dimensional, adiabatic, frictionless, ideal-gas flow were solved along with general equations in matrix form for coupled chemical reaction kinetics To begin the expansion from initial equilibrium, the chemical kinetic equations were linearized about the equilibrium composition and an analytical solution obtained by standard eigenvalue techniques The linear chemical kinetic equations were based on a straightforward generalization of the equations of Brokaw[6] for a single reaction When the departure from equilibrium became appreciable, the computation was switched to a conventional Runge-Kutta integration of the complete nonlinear kinetic equations Other approaches to the problem of starting the integration from an equilibrium state include starting with the nonlinear equations and a very small integration interval, after a small initial perturbation of the starting composition,[4] and another type of perturbation scheme which assumes equilibrium composition derivatives and density [1] It has been found here, as well as by other workers, that the initial portion of the computation is not critical as long as it can be carried out in some manner A possible advantage of linearization- or perturbation-type schemes would be the reduction in computing time for flows with substantial near-equilibrium portions Computing times on the IBM 7090 for the present work were in the range 5–20 min, depending on the chamber pressure and expansion ratio

A relatively simple approximate approach was used to find the mass flow rate and initial area The ratio of mass discharge rate to throat area has an eigenvalue nature[4 7] but does not vary markedly with initial area, velocity, or nature of the flow up to the throat Since the flow is usually near equilibrium from the chamber to the throat, it was decided to use throat area as the scale parameter and calculate the mass discharge rate w from a chosen throat area A_t and the equilibrium ratio of w/A_t, found from a conventional specific impulse program An arbitrary, small chamber velocity was assumed and the chamber area found from w Large variations in the initial velocity did not affect the subsequent quantities materially The actual throat area was always within 1% of the nominal area used initially If great accuracy were desired, an iterative procedure could have been used to find the true eigenvalue w/A_t

The following kinetic scheme involving HF, H_2, F, and H was used:

$$H + F + M = HF + M \tag{1}$$

$$2H + H_2 = 2H_2 \tag{2}$$

$$2H + H = H_2 + H \tag{3}$$

$$2H + HF = H_2 + HF \tag{4}$$

$$F + H_2 = HF + H \tag{5}$$

Since all mixtures studied were stoichiometric or hydrogen-rich, the concentration of F_2 was quite small and was neglected The recombination of H atoms was written with three different third bodies, since there are experimental data[8–10] on reactions (2) and (3) The forward rate constants were of the form

$$k_l = B_l T^{\nu_l} e^{-E_l/RT} \tag{6}$$

and the values used initially are given in Table 1

The values of B_2 and B_3 are the upper limits of the range of values obtained by different workers For example, values of B_2 of 3×10^{18} have been obtained by Rink[9] and $5\ 6 \times 10^{18}$ by Avramenko and Kolesnikova [10] Preliminary work indicated that the calculated performance would be lower than the available measurements,[12] and so the highest values of the most recent data were used Over-all performance values were not very sensitive to the range of experimental values

A series of computed values for vacuum specific impulse $I_{v\ c}$ is shown in Fig 1, along with the frozen, equilibrium, and

Table 1 Hydrogen-fluorine rate parameters

Reaction	B_l, cm³-mole-sec	v_l	E_l, kcal/mole	Source
1	$7\ 5 \times 10^{18}$	−1	0	Assumed same as reaction (2)
2	$7\ 5 \times 10^{18}$	−1	0	Ref 8
3	5×10^{19}	−1	0	Ref 8
4	$7\ 5 \times 10^{18}$	−1	0	Assumed same as reaction (2)
5	5×10^{12}	0	5 7	By analogy with O + H_2 (Ref 11)

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experimental impulses Pertinent parameters, chosen to allow comparison with experiment, were as follows: chamber pressure, 300 psia; nominal throat diameter, 10 cm; expansion cone half-angle 15°; and area ratio (A/A_t), 25 An initial velocity of 2×10^4 cm/sec was arbitrarily assumed The equilibrium values are from a conventional specific impulse program, whereas the frozen ones were obtained from the kinetic flow program with a very small throat diameter (10^{-6} cm) The experimental data as reported[12] were already corrected to 100% combustion efficiency and zero flow divergence by dividing the observed impulse by the measured c^* efficiency (94–97%) and the flow divergence correction The calculated values are seen to be close to the experimental ones near stoichiometric but fall off for hydrogen-rich mixtures This trend would indicate that the rate constant assumed for the $2H + HF$ reaction was low, resulting in insufficient recombination as H_2 increases in importance relative to HF It is not likely that H or H_2 is responsible, since the upper limits of these rates are being used The good agreement near stoichiometric indicates that the rate constant assumed for $H + F + M$ is about right, since this reaction is most important in that region An alternative explanation of the calculated (and experimental) results for hydrogen-rich mixtures is the participation of H_2F in the reaction scheme as a catalyst for H-atom recombination:

$$H + HF = H_2F^* \tag{7}$$

$$H_2F^* + M = H_2F + M \tag{8}$$

$$H + H_2F = H_2 + HF \tag{9}$$

where H_2F^* represents an excited form that must be stabilized by a further collision Benson[13] has shown that, if the "complex" formed in such a scheme is sufficiently stable, the recombination rate can be enhanced by several orders of magnitude However, it was decided that estimation of the properties of H_2F and H_2F^* and the rates of reactions (7–9) would be too uncertain to justify the added complications Instead, the effect of a stable complex of H and HF was simulated by increasing the third-order rate of the reaction $2H + HF$, reaction (4) For $k_4 \times 10$ and 100, I_{vac} was essentially the same as with the initial value, whereas $k_4 \times 10^3$ gave an impulse in the range of the experimental data, as shown in Fig 1 Increasing $k_4 \times 10^4$ and 10^5 gave essentially equilibrium flow Variation of the rate parameters of the two-body reaction (5) had little effect, as was found by Westenberg and Favin[4] for this type of reaction

A few runs were made at a lower chamber pressure, 60 psia, and a higher expansion ratio, $A/A_t = 100$, with k_4 10^3 times larger than the maximum experiment value The results are given in Table 2 The throat diameter was still 10 cm and the expansion half-angle 15°

The calculated kinetic performance, especially near stoichiometric, is seen to be less than the experimental at this lower pressure This may indicate that the rate enhancement of H_2 recombination by HF is more akin to a two-body process and does not fall off as rapidly with decreasing pressure as the three-body process by which it was simulated

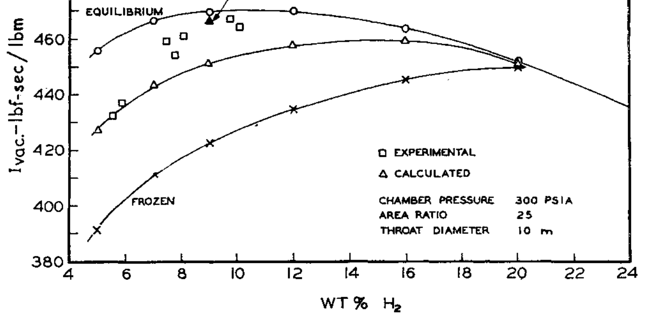

Fig 1 Comparison of calculated and experimental vacuum specific impulse

Table 2 $H_2 + F_2$ performance ($P = 60$ psia, area ratio $= 100$)

	Vacuum specific impulse, sec			
Wt % H_2	Frozen	Kinetic	Experimental	Equilibrium
7	397	463	470	488
12	430	482	485	485

Table 3 Catalysis of hydrogen recombination by HF

Mole ratio F_2/H_2	Chamber temp K	Specific impulse, sec		
		Frozen	Kinetic[a]	Equilibrium
0	3500	989 6	1050 3	1159 4
0 0025	3504	969 8	1039 0	1137 6
0 005	3507	950 5	1021 9	1115 2
0 01	3515	915 9		1074 9

[a] Throat diameter 10 cm ; expansion half angle 15

The experimental data at 60 psia indicated that an expansion half-angle of 25° resulted in substantially lower performance than a 15° cone However, a kinetic calculation with a 25° cone was virtually identical with the 15° case, possibly indicating that the observed difference was due to factors other than chemical kinetic lag It was felt that any further "curve fitting" would not be warranted in view of the many uncertainties in the rate parameters and the limited extent of the experimental data It is possible to reproduce the experimental trends with reasonable rate and species parameters, including a marked effect of HF on H atom recombination which results in an effective increase of 10^2–10^3 in the rate of the reaction $2H + HF = H_2 + HF$

The apparent catalysis of hydrogen recombination by HF suggests the possibility of adding small amounts of fluorine to high-temperature hydrogen systems contemplated for nuclear propulsion Other agents that have been suggested are carbon[2] and methane[13] The indications have not been encouraging, principally because the increased H recombination may not compensate for the increased molecular weight It was thought that small amounts of F_2, added to a hydrogen stream, would be more effective since a much more exothermic product would be formed

Calculations were made for a hydrogen stream at 3500°K plus $F_2(l)$ at various chamber pressures and expansion to a pressure ratio of 100 The results for the most favorable case, chamber pressure 1 atm, are shown in Table 3 but are no more encouraging than previous work The rate data cited previously which gave the best fit with experimental vacuum impulse were used

It is seen that the decrease in kinetic impulse with added fluorine parallels the decrease with frozen and equilibrium flow However, it was shown in Ref 2 that increased rate constants will result in an optimum catalyst concentration, balancing molecular weight and catalytic activity The need is evident for more and better data on elementary reaction rates

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Optimal Functional Approximation Using Dynamic Programming

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Introduction

The problem of approximating some general curve $y = y(x)$, $x_a \leq x \leq x_b$ by some simpler curve $y^*(x)$ is a well-known one For example, Stone[1] considers the case where y^* is a finite number of line segments, i e , $y^* = a_i + b_i x$, $\bar{x}_i \leq x \leq \bar{x}_{i+1}$, $i = 0, \quad , NP$, where $\bar{x}_0 = x_a$, $\bar{x}_{NP+1} = x_b$, and NP is the number of partitions He determines the optimal $y^*(x)$, in the least-squares sense, using the conventional techniques of calculus His solution requires the iterative solution of $(3NP + 2)$ simultaneous linear equations

Bellman and Kotkin[2] obtain a solution to the same problem by the technique of dynamic programming Their solution is much simpler than Stone's, both conceptually and computationally, since the use of the dynamic programming technique enables them to solve for the $(3NP + 2)$ quantities a_i, b_i, and $\bar{x}_i$ in groups of three rather than simultaneously

We wish to consider a simpler problem than the foregoing, namely, the optimal least-squares approximation of an arbitrary function by a step function of a given number of steps In spite of its simplicity, this problem has apparently not been treated elsewhere We give a solution using the technique of dynamic programming This solution is of interest for two reasons First, it provides an introduction to more complicated treatments, such as Ref 2 Also, the solution apparently has several practical applications One of these, the optimal approximation of the theoretical pitch-rate program of a rocket stage, is illustrated below Another possible use is for the optimal evaluation of Riemann-Stieltjes integrals as finite sums The application of this to problems of network synthesis is indicated in Ref 3

Formulation of the Problem

We wish to approximate the arbitrary function $y = y(x)$ $x_a \leq x \leq x_b$, by a step function $y^*(x)$ of the form

$$\begin{aligned} y^* &= \alpha_0 && x_a \leq x \leq \bar{x}_1 \\ &= \alpha_k && \bar{x}_k \leq x \leq \bar{x}_{k+1}; \ k = 1, \quad , NP - 1 \\ &= \alpha_{NP} && \bar{x}_{NP} \leq x \leq x_b \end{aligned}$$

where the constants $\bar{x}_1, \quad , \bar{x}_{NP}, \alpha_0, \alpha_1, \quad , \alpha_{NP}$ are chosen so as to minimize the integral

$$J = \int_{x}^{x_b} (y - y^*)^2 dx$$

Obviously,

$$J = \sum_{k=0}^{NP} \int_{\bar{x}_k}^{\bar{x}_{k+1}} [y(x) - \alpha_k]^2 dx = J\,(\alpha_0, \alpha_1, \quad \alpha_{NP}, \bar{x}_1, \quad , \bar{x}_{NP})$$

where $\bar{x}_0 = x_a$ and $\bar{x}_{NP+1} = x_b$

Solution

Let us first consider the much simpler problem of choosing the optimal α_k if the optimal $\bar{x}_k$ are given We introduce the function

$$A(x_k, x_{k+1}) = \min_{\alpha_k} \int_{\bar{x}_k}^{\bar{x}_{k+1}} [y(x) - \alpha_k]^2 dx$$

Setting the derivative of the integral with respect to α_k equal to zero, we obtain the optimal value of α_k:

$$\alpha_k = \frac{1}{\bar{x}_{k+1} - \bar{x}_k} \int_{\bar{x}_k}^{\bar{x}_{k+1}} y(x) dx \qquad (k = 0, 1, \quad , NP) \tag{1}$$

Using this value of α_k, we obtain an explicit expression for A:

$$A(\bar{x}_k, \bar{x}_{k+1}) = \int_{\bar{x}_k}^{\bar{x}_{k+1}} [y(x)]^2 dx - \frac{1}{\bar{x}_{k+1} - \bar{x}_k} \left[\int_{\bar{x}_k}^{\bar{x}_{k+1}} y(x) dx \right]^2 \tag{2}$$

Of course, $A(\bar{x}_k, \bar{x}_k) = 0$

We now return to the original problem Let us consider the quantity J, which we will call the minimum "error," to be a function f of the end point of the interval and of the number of partitions, i e , $f_{NP}(x_b) = \min\,[J]$ For the special case of no partitions (one step), $NP = 0$ and

$$f_0(x_b) = A(x_a, x_b)$$

For some arbitrary end point x_i where $x_a \leq x_i \leq x_b$,

$$f_0(x_i) = A(x_a, x_i)$$

Similarly, for the special case of one partition or two steps, we have

$$f_1(x_i) = \min_{x_a \leq x_j \leq x_i} [f_0(x_j) + A(x_j, x_i)]$$

This equation merely states the truism that, in order to minimize J with a single partition, the partition must be placed at the optimal point within the interval However, it indicates a method of solving the problem for $NP > 1$

The principle of optimality[4] states that an optimal policy has the property that, whatever the initial state and initial

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