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A STUDY OF THE SENSITIVITY OF COUPLED
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RATE COEFFICIENTS. II. APPLICATIONS

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A STUDY OF THE SENSITIVITY OF COUPLED

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IN RATE COEFFICIENTS

II. APPLICATIONS‡

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I. INTRODUCTION

In the preceding paper, hereafter referred to as I,[1] we developed a diagnostic technique to investigate the sensitivity of the solution of large sets of coupled, non-linear equations to uncertainties or changes in the coupling parameters. For brevity, we will refer to this method as FAST, the Fourier Amplitude Sensitivity Test. In this paper we wish to demonstrate the utility of FAST by applying it to a study of the sensitivity of two sets of coupled non-linear rate equations describing, respectively, the high temperature dissociation of air and the high temperature $H_2 - O_2$ reaction. The specific objective of the calculations described here was to determine the sensitivity of the various species concentrations at a particular time to assumed uncertainties in the rate coefficients which enter into these calculations.

In Section II we summarize the steps which must be carried out in the application of FAST to any system of coupled non-linear equations and discuss the choice of frequencies and the number of sampling points to be used. In Section III, we present the sensitivity analysis for the two chemical reaction systems. Section IV contains some concluding remarks.

II. GENERAL REMARKS ON APPLICATION OF FAST

We wish to determine the sensitivity of an "output function", in our case the calculated concentration of a particular species at a particular time, to assumed uncertainties in the rate coefficients entering the rate equations. We write this output function as

$$c(k_1, k_2, \ldots, k_n) \equiv c(\vec{k}) \tag{2.1}$$

where $\vec{k}$ is the n-component vector of the rate coefficients $k_1, k_2, \ldots, k_n$.

The application of FAST is carried out via the following steps:

Step 1) One must choose a set of n integer frequencies, $\{\omega_1, \omega_2, \ldots, \omega_n\}$, where n is the number of independent rate coefficients which determine the value of the output function.

Step 2) One frequency of this set is now assigned arbitrarily to each rate coefficient by (see I.2.2):

$$k_i = k_i^{(o)} e^{u_i} \tag{2.2}$$

$$u_i = u_i^{(o)} \sin \omega_i s \tag{2.3}$$

where $k_i^{(o)}$ is the best estimate of the rate coefficient, s is a parameter and the $u_i^{(o)}$ are the endpoints of the estimated ranges of uncertainties of the rate coefficients k_i. If a rate coefficient is known precisely, i.e. with zero uncertainty, then $k_i = k_i^{(o)}$ which implies $u_i^{(o)} = 0$. The endpoints $u_i^{(o)}$ are specified as part of the input data and their values should be based on the best judgement of the investigator.

Step 3) The output function $c(\vec{k}) = c[\vec{k}(s)]$ is now Fourier analyzed in s to obtain the sine amplitudes A_{ω_i} corresponding to the input frequencies ω_i. This analysis requires the evaluation of $c[\vec{k}(s)]$ for N values of s, where N is an integer which depends on the frequency spectrum of $c[\vec{k}(s)]$.

These steps will now be discussed in more detail.

a) Choice of Frequencies ω_i

In section III of part I we have presented a discussion of the choice of the set of frequencies $\{\vec{\omega}\}$ and have also given there a set of references (ref. 4) which contain both discussions of optimal choices of sets of frequencies

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as well as tables of frequencies which could be used for FAST. For the calculations presented here we have developed our own set of frequencies. We have done so to obtain a better insight in how to handle the calculations involved in the Fourier analysis method. In a follow-on study we plan to investigate whether our method of choosing frequencies yields better, equivalent or worse sets for use in FAST than those presented in reference 4 of part I.

Since we will carry out computer calculations, we are limited to rational (or, equivalently, integer) frequencies. For the coupled non-linear equations under study here, this means that in addition to the input frequencies ω_i and their multiples, various linear combinations of integer multiples of ω_i ("interference frequencies") will appear in the spectrum of $c[\vec{k}(s)]$. This presents a problem in our analysis since the Fourier sine amplitude of frequency ω_ℓ is to reflect only the effect of the uncertainty in the value of the rate coefficient k_ℓ. Clearly, if an interference frequency coincides with one of the input frequencies ω_i, say ω_ℓ, the corresponding Fourier amplitude A_{ω_ℓ} will not only reflect changes in k_ℓ but also in other rate coefficients. Thus, for example, if $\omega_1 + \omega_3 - \omega_4 = \omega_2$, the amplitude A_{ω_2} is identical with $A_{(\omega_1 + \omega_3 - \omega_4)}$ and will therefore reflect not only changes in k_2, but also in k_1, k_3 and k_4.

One therefore needs to choose a linearly independent set of input frequencies ω_i such that

$$\sum_{i=1}^{n} a_i \omega_i \neq 0 \; ; \qquad a_i \text{ integer} \tag{2.4}$$

for

$$\sum_{i=1}^{n} |a_i| \leq M + 1 \tag{2.5}$$

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where M is a parameter at the disposition of the investigator. We refer to such a set as being free of interferences to order M. The larger the chosen value of M, the greater the likelihood that the Fourier amplitude of each input frequency reflects solely the uncertainty of the corresponding rate coefficient. On the other hand, as discussed in section III of part I and below, the larger the chosen value of M, the larger the maximum value, ω_{max}, of the input frequencies ω_i which will still satisfy (2.4) and (2.5) and, correspondingly, the larger the set N of points s which will be required for the evaluation of the Fourier amplitudes. For the calculations presented in this paper we have chosen M = 4. In Table I we present sets of frequencies which are free of interferences to 4th order for systems with dimensionality n from 5 to 19, i.e. for systems with from 5 to 19 independent rate coefficients. These frequencies were determined via computer by a trial and error procedure. The sets of frequencies listed here have the smallest value of ω_{max} satisfying conditions (2.4) and (2.5) and are referred to as "minimal sets".

b) Assignment of Frequencies to Rate Coefficients

The frequencies $\{\omega_1, \omega_2, \ldots, \omega_n\}$ are assigned to the rate coefficients $\{k_1, k_2, \ldots, k_n\}$ arbitrarily since the results of these calculations, in order to be useful, must be independent of both the frequency set and the assignment of the frequencies. To check that the spectrum of the output function does not contain interfering frequencies which coincide with the input frequencies, and thus affect the results, one should reassign the frequencies to the various rate coefficients and repeat the Fourier analysis. If the calculated Fourier amplitudes are invariant in magnitude and sign to these permutations, then the set of frequencies is free of interferences to the order of the dimensionality of the set of rate equations and the results of these calculations are reliable. If,

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on the other hand, some of the Fourier amplitudes vary greatly with the permutions of the frequency assignments, a better set of input frequencies must be generated. By "better" we refer to a set $\{\omega\}$ with a larger parameter M and a higher ω_{max}. We have carried out such a permutation analysis for the $N_2 - O_2$ system discussed below and verified that our sets of input frequencies yielded Fourier amplitudes $A_{\omega_\ell}^{(i)}$ which were invariant to the frequency permutations.

c) Calculation of Fourier Amplitudes

As discussed in section II of part I, we are only interested in the Fourier sine amplitudes. For an input frequency ω_ℓ, the amplitude is

$$A_{\omega_\ell} = \frac{1}{2\pi} \int_0^{2\pi} c[\vec{k}(s)] \sin \omega_\ell s \, ds \qquad (2.6)$$

To compute this integral, one must evaluate the function $c[\vec{k}(s)]$ at a set of points in the interval $0 \leq s \leq 2\pi$. In the absence of any information on the form of the output function c we take the points to be equally spaced in that interval,

$$s = \frac{2\pi q}{N} \quad , \quad q = 1, 2, \ldots, N \qquad (2.7)$$

where N is some integer. With these equally spaced points we can now conveniently relate the Fourier coefficient A_{ω_ℓ} as defined by the integral (2.6) to the sum

$$A_{\omega_\ell}^* = \frac{2}{N} \sum_{q=1}^{N} \sin \omega_\ell s_q \, c[\vec{k}(s_q)] \qquad (2.8)$$

where

$$A_{\omega_\ell}^* = A_{\omega_\ell} + \varepsilon_{\omega_\ell} \qquad (2.9)$$

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The error term $\varepsilon_{\omega_\ell}$ is given by

$$\varepsilon_{\omega_\ell} = \sum_{m=1}^{\infty} \sum_{j} A(mN-\omega_j)$$

(2.10)

where ω_j is any frequency in the spectrum of $f[k(s)]$ which satisfies

$$mN - \omega_j = \omega_\ell$$

(2.11)

This error term is due to "aliasing" which inevitably occurs whenever a finite number of points are chosen on an interval to evaluate Fourier amplitudes. For example, if N equally spaced points are used, the amplitudes $A_{\omega_\ell}^{(i)}$ for ω_ℓ will unavoidably include the amplitudes of a component of frequency ω_j present in $c(s)$ which satisfies the relation $\omega_\ell = mN-\omega_j$ where m is an arbitrary integer. The value of N is chosen to be the smallest integer such that

$$\sum_{i=1}^{n} b_i \omega_i \neq mN \qquad , \qquad b_i, m \text{ integers}$$

(2.12)

for

$$\sum_{i=1}^{n} |b_i| \leq M + 1$$

(2.13)

The Fourier amplitudes A_{ω_ℓ} have been evaluated using Eqs. (2.8) through (2.10).

If the output function $c(k)$ could be expressed as a polynomial of degree less than or equal to M in the variables u_i, $i = 1, \ldots, n$, where (see Eq. 2.2)

$$u_i = \ln (k_i / i_i^{(0)})$$

(2.14)

then the conditions (2.12) and (2.13) imply that $\varepsilon_{\omega_\ell} = 0$ so that

$$A_{\omega_\ell}^* = A_{\omega_\ell}$$

(2.15)

The conditions (2.11) through (2.13) also determine N the minimum number of s points required for the evaluation of $c[\bar{k}(s)]$. These are listed in Table I.

The Fourier amplitudes are related to a multiple integral of an output function over the uncertainty space (see I. 2.12). One way of obtaining the Fourier amplitudes without the troublesome interferences and aliasing involved in the method discussed above would be to evaluate the n-dimensional integral of Eq. (I. 2.12) directly. We have done this _via_ simple Monte Carlo integrations. Our results show that the number of integration points required by the Monte Carlo method to give a comparable accuracy is much greater than the number required in the Fourier analysis. Stated another way, for a given number of integration points (we used 200), the degree of accuracy of the Fourier method detailed above far surpasses that of the Monte Carlo integration.

d) Choice of the Weight Function

As emphasized in I, our final result, i.e. the relation

$$A^{(i)}_{\omega_\ell} \propto \langle \partial c_i / \partial u_\ell \rangle \tag{2.16}$$

involves a weight function $p(u_i)$ which can be interpreted as a distribution function in u space which weights the uncertainty in the rate coefficients. In our treatment in part I, we used the weight function (see Eq. 2.20)

$$p(u_i) = \frac{a_i}{\cosh a_i u_i} \tag{2.17}$$

which had several desirable properties. It is, for instance, bell shaped about $u_i = 0$ corresponding to $k_i = k_i^{(o)}$, the "best" value of the rate coefficient k_i. For computational convenience, we have used two different weight functions for the calculations presented in section III below corresponding to two different

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transformations $u_i = u(\omega_i s)$. As we had hoped and expected, our results did not depend significantly on the choice of the weight function. This indicates that our output functions $c(k)$ were "well behaved", i.e. did not have any large local excursions in $\vec{u}$ space. It is also in agreement with the discussion in the last paragraph of section III of part I.

As is shown in part I, the form of the weight function $p(u_i)$ depends upon the choice of the transformation function f of Eq. (I.2.3). For the Fourier amplitude method to be at all useful, our results on the relative magnitudes of the Fourier amplitudes must clearly be independent of the explicit form of the transformation function. The insensitivity of our results to our choice of transformation function (and thus of the weight functions) verifies the validity of FAST in this respect.
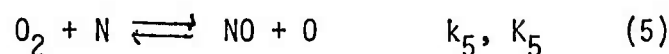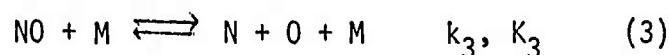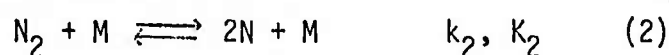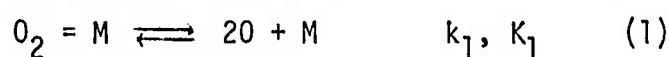
III. APPLICATION OF FAST TO CHEMICAL SYSTEMS

We have applied FAST to two relatively simple reaction systems as a test of its utility as a diagnostic tool. Both systems were assumed, for simplicity, to react at constant temperatures and volume. These restrictions are in no way necessary for the application of FAST. The concentrations were

integrated in time with a code using Gear's[2] algorithm. These integrations
were carried out once for each of the N values of s with the corresponding
values of the n rate coefficients, $\vec{k}(s)$, up to some time t. This yielded the
output function $c_i[\vec{k}(s),t]$, i.e. the concentration of species i, i=1, 2, ..., m,
as a function of time. The Fourier analysis of $c_i[\vec{k}(s),t]$ was then carried out
at several selected times. The uncertainties in the rate coefficients were
arbitrarily assumed to be much larger than warranted by the available experi-
mental data in order to check out FAST. It should therefore be pointed out
again that the primary purpose of the calculations presented here is to demonstrate
the validity and utility of FAST as a diagnostic tool and not to provide new
information about the selected reaction systems.

a) High Temperature Air Reaction

We consider the following simplified reaction system[3]

$$O_2 = M \rightleftharpoons 2O + M \qquad k_1, K_1 \qquad (1)$$

$$N_2 + M \rightleftharpoons 2N + M \qquad k_2, K_2 \qquad (2)$$

$$NO + M \rightleftharpoons N + O + M \qquad k_3, K_3 \qquad (3)$$

$$N_2 + O \rightleftharpoons NO + N \qquad k_4, K_4 \qquad (4)$$

$$O_2 + N \rightleftharpoons NO + O \qquad k_5, K_5 \qquad (5)$$

The rate coefficients k_i, i=1, ..., 5, refer to the forward reactions, the rate
coefficients k_{-i} for the reverse reactions are obtained from the equilibrium
constant K_i through the relation $K_i = k_i/k_{-i}$. In the system and the one dis-
cussed below in IIIb, the equilibrium constants are assumed to be known exactly,
i.e. with zero uncertainty. The forward and reverse rate coefficients k_i, k_{-i}
for each reaction therefore have identical uncertainties and the number of

independent uncertainties is equal to the number of equilibrium constants. It is, of course, not necessary to proceed this way and one can instead assign different uncertainties to the forward and reverse rate coefficients which reflect uncertainties in the equilibrium constants.

The system was assumed to react at a constant temperature of 6000°K and constant volume. The rate coefficients, equilibrium constants and initial conditions used in this calculation are shown in Table II.

The equilibrium constants represent the latest and "best" literature values we could find and the rate coefficients listed in this table are the $k_i^{(o)}$ of Eq. (2.2). In Fig. 1 we show a plot of the time evolution of this reaction system obtained from the integration of the rate equations using the rate coefficients $k_{\pm i}^{(o)}$ of Table II.

While the real uncertainty of these rate coefficients is not too large, we assumed arbitrarily for the purpose of testing FAST that the experimental uncertainties were ± two orders of magnitude for each of the five independent sets of rate coefficients. To take account of this uncertainty we then write (see Eq. (2.2))

$$k_i^{(o)} e^{-4.606} \leq k_i \leq k_i^{(o)} e^{4.606} \quad ; \quad i = 1, \ldots, 5 \quad . \tag{3.1}$$

For our sensitivity analysis we used the frequency set (see Table I)

$$\{\omega\} = (2, 42, 62, 74, 90) \tag{3.2}$$

for which the smallest number N of evenly spaced points satisfying the conditions of Eqs. (2.4, 2.5, 2.12, 2.13) in the s interval, $0 \leq s \leq 2\pi$, is 191.

We carried out the Fourier analysis of the output function $c_i[\vec{k}(s)]$ at $t = 10^{-6}$ sec and 10^{-4} sec. From Eqs. (2.2), (2.3) and (3.1) we have

$$u_i = 4.606 \sin \omega_i s \tag{3.3}$$

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The concentrations of the various species, N_2, O_2, NO, O, N, were calculated at 10^{-6} sec and 10^{-4} sec for each of the 191 s values by integrating the rate equations. The 191 values of the concentration of the above species at a given time define the output function $c_i[\bar{k}(s)]$ which is now Fourier analysed by computing the Fourier coefficients from Eqs. (2.8) through (2.13) using the set of input frequencies of Eq. (3.2). An example of the function $c_i[\bar{k}(s)]$ for NO at $t = 10^{-4}$ sec is shown in Fig. 2. This curve has been drawn by connecting the 191 calculated concentrations of NO (one for each of the 191 evenly spaced values of s) by straight lines.

The results of the Fourier analysis at $t = 10^{-6}$ sec are shown in Table III. The high values of the Fourier amplitudes associated with the rate coefficients k_1, k_{-1} for the concentration of O and O_2 (see blocks 1 and 2 of Table III) indicate that a variation in k_1 and k_{-1} has a greater effect on the concentration of O and O_2 than the variation of any of the other rate coefficients. This follows immediately from Eq. (2.16), where now i refers to the O atoms and O_2 molecules and $\omega_\ell = 2$ refers to the rate coefficients k_1 and k_{-1}. We can rephrase this by saying that, at this early time in the reaction, only reaction (1) is important in the production of O atoms and the disappearance of O_2 molecules. The sign of the amplitudes in the last column can be understood from Eq. (2.16) according to which the amplitude $A_{\omega_\ell}^{(i)}$ is proportional to $\langle \partial c_i/\partial u_\ell \rangle$. Thus the negative sign of the Fourier amplitude for k_1 for the concentration of O_2 (block 1, Table III) simply indicates that $[O_2]$ decreases with increasing k_1. The positive sign for the Fourier amplitude for k_1 for the concentration of O atoms (block 2, Table III) indicates that $[O]$ increases with increasing k_1. From the relative magnitudes of the Fourier amplitudes in blocks 4 and 5 of Table III, it will be noted that the formation of N and NO at these early times

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in the reaction is most sensitive to reactions (1) and (4). This is quite reasonable since at $t = 10^{-6}$ sec the formation of N and NO via reactions (2) and (5) cannot play any important role owing to the small value of $k_2^{(o)}$ as compared to $k_1^{(o)}$ (see Table II). A number of other conclusions as to the sensitivity of the concentrations of the various species with respect to variation of the rate coefficients can be drawn from a study of the results in Table III. All these conclusions are in accord with one's knowledge and intuition of this rather simple reaction system.

In Table IV we present our results for $t = 10^{-4}$ sec. At this time, as can be seen from Fig. 1, the concentrations of reactants and products are, except for N_2, significantly different from their initial values. The coupling between the various reactions has come into play much more strongly at this later time and one would expect that the influence of the uncertainties in the rate coefficients on the concentrations of the various species is more complex. This can readily be verified from the data in Table IV, where there is now no longer such a pronounced order of magnitude effect in the Fourier amplitudes. Let us arbitrarily use a factor of about 10 to distinguish between the "relatively important" amplitudes (i.e. the concentration of the species is very sensitive to the change of a specific rate coefficient) and the "relatively unimportant" amplitudes (i.e. the concentration of the species is not very sensitive to the change of a specific rate coefficient). Then the data of Table IV indicates that $[O_2]$ and $[O]$ are affected primarily by uncertainties in k_1, $[N_2]$ is affected about equally by uncertainties in all of the rate coefficients, $[N]$ is least affected by uncertainty in k_1, and $[NO]$ is least affected by uncertainty in k_2. The least "sensitive" rate coefficient is k_2, which determines the rate

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of dissociation of N_2. This is not surprising since $k_2^{(o)}$ is smaller than the other rate coefficients by 2 to 4 orders of magnitude. The important point to note is that owing to the strong coupling of all the reactions at this stage of the kinetic development, a number of the elementary rate processes contribute significantly to the production and removal of most of the species, so that the concentration of these species are quite sensitive to uncertainties in several rather than just one rate coefficient. This result is certainly not unexpected.

b) The H_2 - O_2 Reaction

The H_2 - O_2 combustion system was modeled by the following set of chemical reactions[4]:

$$H_2 + M \rightleftharpoons 2H + M \qquad k_1, K_1 \qquad (1)$$

$$O_2 + M \rightleftharpoons 2O + M \qquad k_2, K_2 \qquad (2)$$

$$OH + M \rightleftharpoons O + H + M \qquad k_3, K_3 \qquad (3)$$

$$H_2O + M \rightleftharpoons H + OH + M \qquad k_4, K_4 \qquad (4)$$

$$H + O_2 \rightleftharpoons OH + O \qquad k_5, K_5 \qquad (5)$$

$$O + H_2 \rightleftharpoons OH + H \qquad k_6, K_6 \qquad (6)$$

$$H_2 + OH \rightleftharpoons H_2O + H \qquad k_7, K_7 \qquad (7)$$

$$O_2 + H_2 \rightleftharpoons 2OH \qquad k_8, K_8 \qquad (8)$$

$$OH + OH \rightleftharpoons H_2O + O \qquad k_9, K_9 \qquad (9)$$

The system was assumed to react at a constant temperature of 2000°K and constant volume, with only H_2 and O_2 present at t = 0.

The initial conditions, rate coefficients and equilibrium constants are shown in Table V. The rate coefficients listed in this table are the $k_i^{(o)}$ of Eq. (2.2); the equilibrium constants are assumed to be known with zero uncertainty.

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We assumed arbitrarily that the experimental uncertainties for each of the nine independent rate coefficients were ± one order of magnitude so that

$$k_i^{(o)} e^{-2.303} \leq k_i \leq k_i^{(o)} e^{2.303} \quad ; \quad i = 1, 2, ..., 9 \quad . \tag{3.4}$$

For our analysis we used the frequency set

$$\{\omega\} = (19, 59, 91, 113, 133, 143, 149, 157, 161) \tag{3.5}$$

for which the smallest number N of evenly spaced points in the s interval, $0 \leq s \leq 2\pi$, is 630.

A plot of the concentrations of the various species for the time interval $10^{-4} \leq t \leq 10$ seconds, calculated with the $k_i^{(o)}$ of Table V is shown in Fig. 3. We have employed FAST to study the sensitivity of the species concentrations to uncertainties in the rate coefficients at 10^{-8} seconds and 10^{-3} seconds. These results are shown in Tables VI and VII.

At the very early time of 10^{-8} seconds (Table VI), the H_2 and O_2 concentrations have not changed significantly from their original value (to within 8 significant places) and the Fourier amplitudes are merely round-off error. For H atoms, reaction (1) seems to be the major contributor to its formation at this early time and its rate coefficient is the most sensitive in determining the accuracy of [H]. Reactions (7) and (8), which together also produce H atoms, are also important but the concentration of H atoms is not as sensitive to k_7 and k_8 as it is to k_1. The sensitivity of [H] to these two rate coefficients has identical values which is not surprising since [H] is proportional to $k_7 \cdot k_8$ at this early time. The same argument also holds for the production of H_2O since its concentration at 10^{-8} seconds is proportional to $k_7 \cdot k_8$. The H_2O concentration

is also sensitive to k_5, since reaction (5) appears to be partly responsible for the production of the OH which enters into reaction (7). The concentration of O atoms is most sensitive to k_2 which is again as expected. Finally, the OH concentration is most sensitive to k_8 which is also most reasonable, since at this early time, only the direct reaction between O_2 and H_2 would be expected to effect the OH concentration. Again, the results of FAST are in good agreement with what could be predicted on the basis of chemical knowledge.

At $t = 10^{-3}$ seconds (Table VII) the story is quite different. As can be seen from Fig. 3, significant changes from the initial concentrations have occured by this time, and the reactions are now strongly coupled. This is reflected in the array of Fourier amplitude in Table VII as compared to those of Table VI. Now, for instance, rate coefficient k_5 corresponding to the chain branching step (5) which produces H and O atoms is the most influential one in controlling the concentration of all species. The H atoms concentration, in addition, is equally sensitive to k_7. All other rate coefficients, except for k_3, which is very small for all species, have about equal sensitivities to within a factor of 10 as measured by their Fourier amplitudes. According to our theory and calculations then, the rate coefficient which needs to be determined with the highest accuracy for the accurate calculation of all species concentration at 10^{-3} seconds is k_5 with k_7 next in line. Uncertainties in the other rate coefficients will have a smaller effect on the species concentrations.

IV. CONCLUDING REMARKS

It should be realized that the applications presented here are only a first cut at the subject. It appears that FAST is a useful diagnostic tool in determining the sensitivity of the results of complex calculations to the parameters which enter the calculations. The Fourier amplitude method clearly needs further testing on more complicated systems than the ones dealt with in this paper. Such tests should also involve comparison with various types of "brute force" calculations.

In addition to applications to larger systems, there are also a number of theoretical-computational questions which need further investigation. Some examples are: the influence of the range of uncertainties, with different uncertainties for different coupling parameters, on the relative magnitudes of the Fourier amplitudes; the influence of the choice of the input frequencies $\{\omega\}$ and the spacing of the N values of the parameter s on the Fourier amplitudes; and the question whether the absolute magnitude of the Fourier amplitudes can be used as a predictor for the actual change of the output function for a given change of the coupling parameter. Additional work is being carried out to answer these questions.

V. ACKNOWLEDGEMENT

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We are aware that more recent "nominal" values of the various rate coefficients
exist in the literature but feel that the values used in our calculations are
adequate for the purpose of this paper.

4) The equilibrium constants were calculated from the data in Mc Bride
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FIGURE CAPTIONS

Fig. 1.   Time evolution of the N_2 - O_2 system based on the kinetic data in Table II.

Fig. 2.   The function $c_i[\vec{k}(s)]$ for NO at 10^{-4} sec between 0 and 2π as a function of s. This curve has been drawn by connecting the 191 calculated values of the concentrations of NO (corresponding to the 191 values of s) by straight lines.

Fig. 3.   Time evolution of the H_2 - O_2 systems between t = 10^{-4} sec to t = 10 sec based on the kinetic data in Table V.
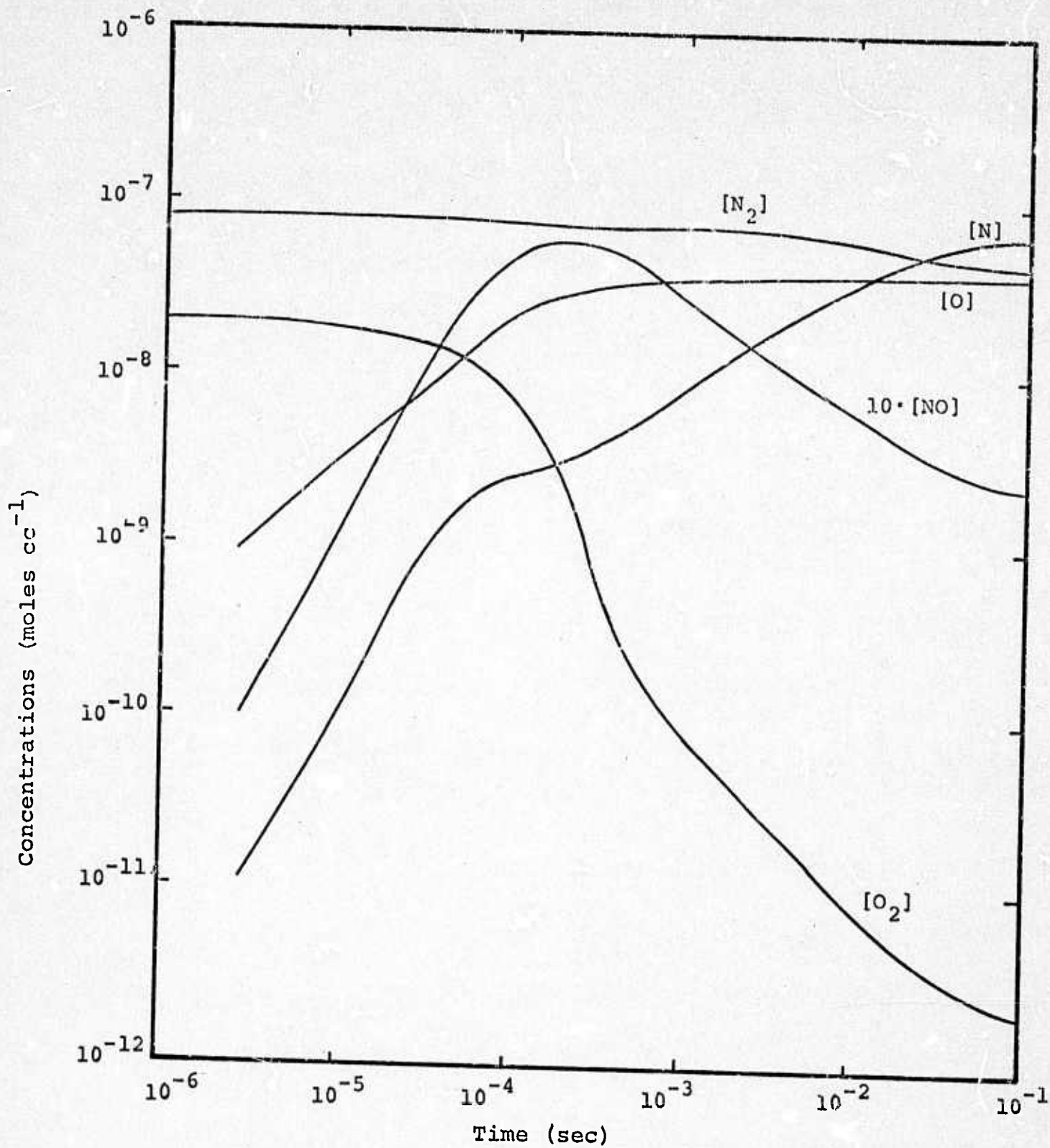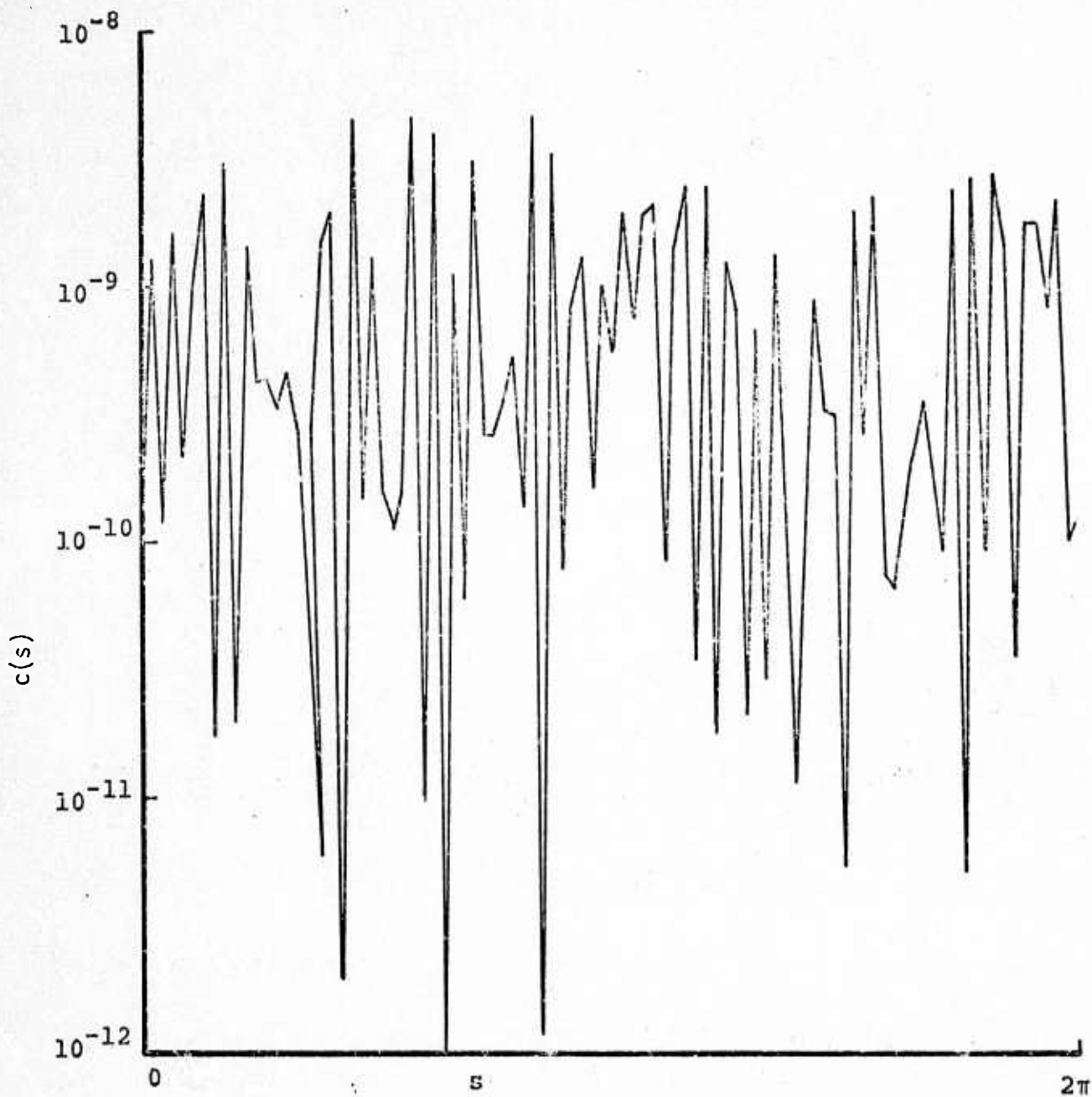
Fig. 2,   Scharfly + Shuler

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Fig. 2, Solarsky + Slater

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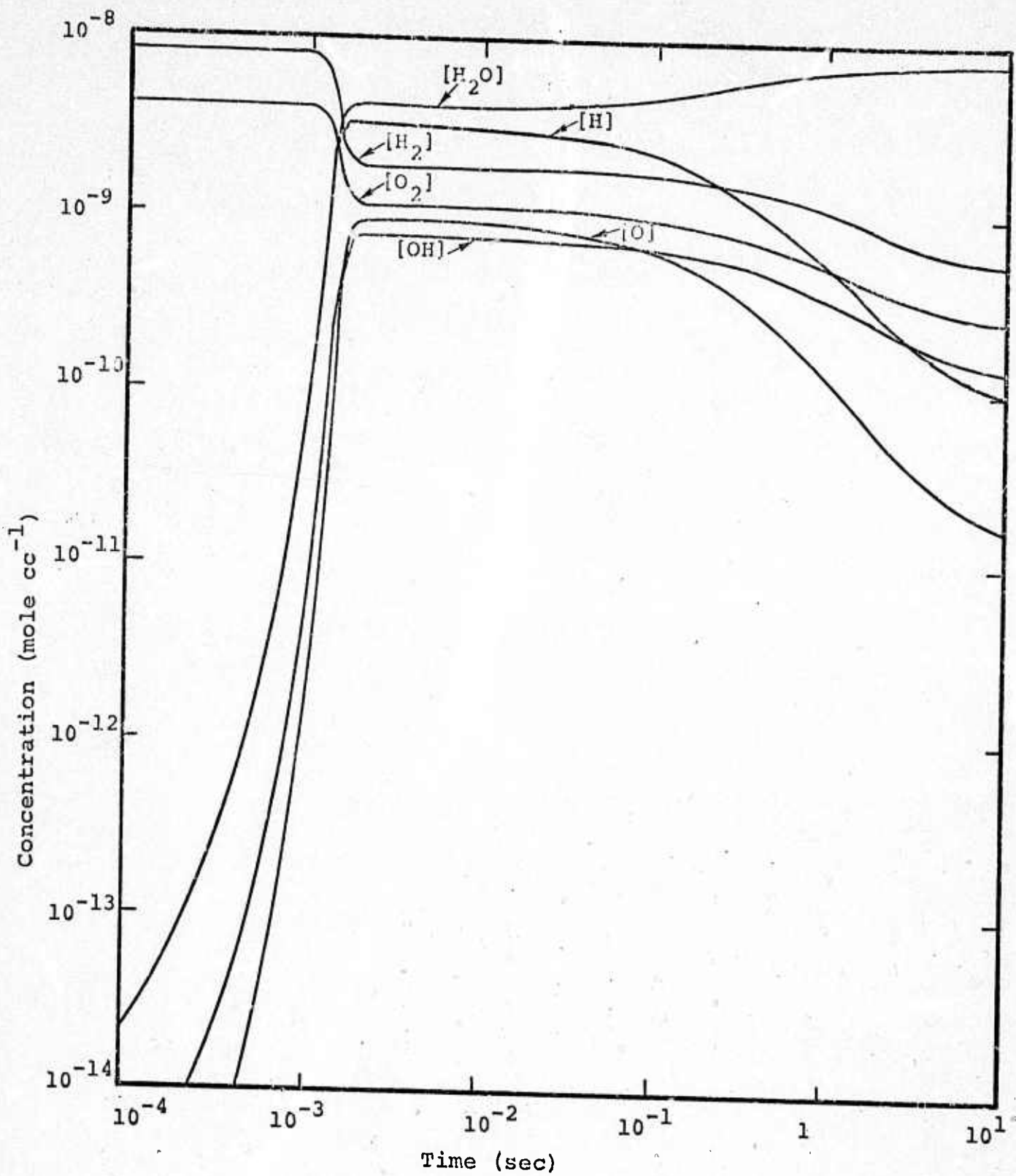
Fig. 3, Schärtly + Shuler

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Table I

FREQUENCY SETS AND CORRESPONDING NUMBER OF POINTS AVOIDING INTERFERENCES THROUGH <u>4th</u> ORDER

Dimension (n)	Frequency Set {ω}	Minimum Number of Points (N)
5	11, 21, 27, 35, 39	142
5*	2, 42, 62, 74, 90	191
6	1, 21, 31, 37, 45, 49	182
6*	2, 42, 62, 74, 90, 98	231
7	17, 39, 59, 69, 75, 83, 87	334
8	23, 55, 77, 97, 107, 113, 121, 125	486
9	19, 59, 91, 113, 133, 143 149, 157, 161	630
10	25, 63, 103, 135, 157, 177, 187, 193, 201, 205	806
11	41, 67, 105, 145, 177, 199, 219, 229, 235, 243, 247	974
12	31, 87, 113, 151, 191, 223, 245, 265, 275, 281, 289, 293	1158
13	23, 85, 141, 167, 205, 245 277, 299, 319, 329, 335, 343, 347	1374
14	87, 133, 195, 251, 277, 315, 355, 387, 409, 429, 439, 445, 453, 457.	1814
15	67, 143, 189, 251, 307, 333, 371, 411, 443, 465, 485, 495, 501, 509, 513	2038
16	73, 169, 245, 291, 353, 409, 435, 473, 513, 545, 567, 587, 597, 603, 611, 615	2446
17	85, 145, 241, 317, 363, 425, 481, 507, 545, 585, 617, 639, 659, 669, 675, 683, 687	2734
18	143, 229, 289, 385, 461, 507, 569, 625, 651, 689, 729, 761, 783, 803, 813, 819, 827, 831	3310
19	149, 275, 361, 421, 517, 593, 639, 701, 757, 783, 821, 861, 893, 915, 935, 945, 951, 959, 963	3848

*These sets of 5 and 6 frequencies are not minimal, but have been used and are only included for completeness. They are also free of interferences to order less than 5.

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Table II

INITIAL CONDITIONS, RATE COEFFICIENTS AND EQUILIBRIUM CONSTANTS FOR THE HIGH TEMPERATURE AIR REACTION

Initial Conditions

$[N_2] = 8 \times 10^{-8}$ moles/cc

$[O_2] = 2 \times 10^{-8}$ "

Rate Coefficients

$k_1^{(o)} = 8.5 \times 10^{10}$ (moles/cc)$^{-1}$ sec^{-1}

$k_2^{(o)} = 3.0 \times 10^{7}$ "

$k_3^{(o)} = 8.0 \times 10^{9}$ "

$k_4^{(o)} = 9.0 \times 10^{10}$ "

$k_5^{(o)} = 8.0 \times 10^{11}$ "

Equilibrium Constants

$K_1 = 7.8 \times 10^{-4}$ (moles/cc)

$K_2 = 1.0 \times 10^{-7}$ "

$K_3 = 1.3 \times 10^{-5}$ "

$K_4 = 9.0 \times 10^{-3}$ -

$K_5 = 5.9 \times 10^{1}$ -

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A

Table III

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-6} SEC
FOR THE HIGH TEMPERATURE AIR SYSTEM

Input Frequency	Rate Coefficient	Fourier Amplitude
	$[O_2]$ x 10^9 moles/cc	
2	k_1	-4.47
90	k_5	-0.0244
74	k_4	-0.0227
42	k_2	-4.7×10^{-4}
62	k_3	-3.9×10^{-4}
	$[O]$ x 10^9 moles/cc	
2	k_1	8.53
74	k_4	-0.36
90	k_5	0.018
62	k_3	-0.029
42	k_2	0.0027
	$[N_2]$ x 10^9 moles/cc	
2	k_1	-0.389
74	k_4	-0.386

62	k_3	-3.9×10^{-4}

$[O] \times 10^9$ moles/cc		
2	k_1	8.53
74	k_4	-0.36
90	k_5	0.018
62	k_3	-0.029
42	k_2	0.0027

$[N_2] \times 10^9$ moles/cc		
2	k_1	-0.389
74	k_4	-0.386
42	k_2	-0.0087
62	k_3	-0.0039
90	k_5	-0.00103

$[N] \times 10^9$ moles/cc		
2	k_1	0.367
74	k_4	0.362
90	k_5	-0.028
62	k_3	-0.013
42	k_2	-0.011

$[NO] \times 10^{10}$ moles/cc		
2	k_1	0.412
74	k_4	0.410
90	k_5	0.031
42	k_2	-0.0066
62	k_3	-0.0048

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Table IV

A

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-4} SEC
FOR THE HIGH TEMPERATURE AIR SYSTEM

Input Frequency	Rate Coefficient	Fourier Amplitude
	$[O_2]$ x 10^8 moles/cc	
2	k_1	-1.1
90	k_5	-0.147
74	k_4	-0.087
62	k_3	-0.069
42	k_2	-0.044
	$[O]$ x 10^8 moles/cc	
2	k_1	2.17
62	k_3	0.228
90	k_5	0.164
42	k_2	0.078
74	k_4	-0.00146
	$[N_2]$ x 10^9 moles/cc	
74	k_4	-2.6
2	k_1	-2.3
62	k_3	-1.0
90	k_5	-0.70
42	k_2	-0.55
	$[N]$ x 10^9 moles/cc	
2	k_1	4.3
74	k_4	3.3
62	k_2	3.0

[O] x 10⁶ moles/cc		
2	k_1	2.17
62	k_3	0.228
90	k_5	0.164
42	k_2	0.078
74	k_4	-0.00146

$[N_2]$ x 10^9 moles/cc		
74	k_4	-2.6
2	k_1	-2.3
62	k_3	-1.0
90	k_5	-0.70
42	k_2	-0.55

$[N]$ x 10^9 moles/cc		
2	k_1	4.3
74	k_4	3.3
62	k_3	3.0
42	k_2	0.98
90	k_5	0.125

$[NO]$ x 10^9 moles/cc		
74	k_4	1.77
90	k_5	1.29
62	k_3	-0.91
2	k_1	0.23
42	k_2	0.124

B

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Table V

Initial Conditions, the Rate Coefficients and Equilibrium Constants for the H_2 - O_2 Reaction

Initial Conditions

$$[H_2] = 8.0 \times 10^{-9} \text{ moles/cc}$$

$$[O_2] = 4.0 \times 10^{-9} \text{ moles/cc}$$

Rate Coefficients

$k_1^o = 5.78 \times 10^4 \text{ (moles/cc)}^{-1}\text{sec}^{-1}$ $k_6^o = 4.0 \times 10^{13} \text{ (moles/cc)}^{-1}\text{sec}^{-1}$

$k_2^o = 4.47 \times 10^3$ " $k_7^o = 1.51 \times 10^{13}$ "

$k_3^o = 1.03 \times 10^5$ " $k_8^o = 2.20 \times 10^6$ "

$k_4^o = 6.79 \times 10^5$ " $k_9^o = 1.6 \times 10^{14}$ "

$k_5^o = 1.23 \times 10^{12}$ "

Equilibrium Constants

$K_1 = 1.59 \times 10^{-11} \text{ moles/cc}$ $K_6 = 1.4$ -

$K_2 = 2.69 \times 10^{-12}$ " $K_7 = 9.76$ -

$K_3 = 1.14 \times 10^{-11}$ " $K_8 = 2.02$ -

$K_4 = 1.63 \times 10^{-12}$ " $K_9 = 6.76$ -

$K_5 = 2.37 \times 10^{-1}$ -

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Table VI

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-8} SEC FOR THE H_2 - O_2 REACTION

Rate Coefficient	Fourier Amplitude	Rate Coefficient	Fourier Amplitude
$[H_2]$		**$[O_2]$**	
Insensitive to uncertainties in any rate constant.		Insensitive to uncertainties in any rate constant.	
$[H] \times 10^{19}$		**$[O] \times 10^{20}$**	
k_1	4.67	k_2	1.79
k_8	0.202	k_6	-0.016
k_7	0.202	k_1	0.0065
k_5	0.010	k_5	0.0065
k_6	0.0023	k_3	2.25×10^{-5}
k_2	0.00165	k_4	-1.95×10^{-5}
k_4	8.0×10^{-5}	k_9	7.87×10^{-6}
k_9	4.1×10^{-5}	k_8	1.20×10^{-6}
k_3	-3.0×10^{-5}	k_7	-8.46×10^{-7}
$[OH] \times 10^{18}$		**$[H_2O] \times 10^{20}$**	
k_8	5.9	k_8	2.03
k_7	-0.0203	k_7	2.03
k_9	0.00176	k_5	0.121
k_5	0.0014	k_6	0.0066
k_2	1.61×10^{-4}	k_4	8.35×10^{-4}
k_6	9.73×10^{-5}	k_1	-6.35×10^{-4}
k_1	7.08×10^{-5}	k_9	4.22×10^{-4}
k_4	-7.43×10^{-6}	k_3	-2.81×10^{-4}
k_3	3.13×10^{-6}	k_2	1.33×10^{-4}

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Table VII

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-3} SEC
FOR THE $H_2 - O_2$ REACTION

Rate Coefficient	Fourier Amplitude	Rate Coefficient	Fourier Amplitude
$[H_2] \times 10^9$		$[H] \times 10^9$	
k_5	-3.71	k_5	1.92
k_7	-0.346	k_7	1.92
k_6	-0.313	k_6	0.122
k_8	-0.172	k_8	0.102
k_2	-0.108	k_2	0.061
k_4	-0.101	k_9	0.0466
k_9	-0.0905	k_4	0.0439
k_1	-0.0491	k_1	0.0176
k_3	0.0119	k_3	-0.00318
$[O_2] \times 10^9$		$[O] \times 10^{10}$	
k_5	-1.77	k_5	5.77
k_7	-0.153	k_7	0.420
k_6	-0.089	k_1	0.164
k_8	-0.070	k_6	0.162
k_2	-0.047	k_9	0.145
k_4	-0.047	k_2	0.116
k_9	-0.044	k_8	0.115
k_1	-0.031	k_4	0.10
k_3	0.0091	k_3	-0.061
$[OH] \times 10^{10}$		$[H_2O] \times 10^9$	
k_5	4.63	k_5	2.52
k_7	0.281	k_7	0.237
k_6	0.196	k_6	0.142

k_1	-0.0491	k_1	0.0176
k_3	0.0119	k_3	-0.00318

$[O_2] \times 10^9$		$[O] \times 10^{10}$	
k_5	-1.77	k_5	5.77
k_7	-0.153	k_7	0.420
k_6	-0.089	k_1	0.164
k_8	-0.070	k_6	0.162
k_2	-0.047	k_9	0.145
k_4	-0.047	k_2	0.116
k_9	-0.044	k_8	0.115
k_1	-0.031	k_4	0.10
k_3	0.0091	k_3	-0.061

$[OH] \times 10^{10}$		$[H_2O] \times 10^9$	
k_5	4.63	k_5	2.52
k_7	0.281	k_7	0.237
k_6	0.196	k_6	0.142
k_8	0.135	k_8	0.114
k_9	0.116	k_4	0.114
k_2	0.115	k_2	0.0718
k_4	0.0961	k_9	0.0614
k_1	0.0876	k_1	0.0358
k_3	-0.0359	k_3	-0.00851

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