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# THE IMPORTANCE OF THERMODYNAMICS TO THE MODELING OF NITROGEN COMBUSTION CHEMISTRY

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**ABSTRACT**

Modeling calculations have been performed to illustrate the effect of using five commonly accepted data bases of thermochemical properties on predictions of temporal species profiles. The thermochemical properties are those used for the determination of equilibrium constants employed in the calculation of reverse rate coefficients for a chemical mechanism where forward rate coefficients are specified. The modeling study was performed for hydrogen/oxygen/argon/nitrogen-compound mixtures where the nitrogen compound was either NO or $NH_3$. The mixtures reacted isothermally at 1600 K and isobarically at 1 atmosphere, and a single kinetic mechanism for which forward rate coefficients were specified was used throughout. Mixtures of equivalence ratios of 0.625, 1.0 and 1.6 were considered.

Modifications in sources of thermodynamic data have been substantial since 1971 for some species. Among the data bases, thermochemical properties varied greatly for the species NH, $NH_2$, NNH, and $HO_2$, and those for other species important in the mechanism had variations of less than 10 percent. The thermochemical property variations among the data bases in NH, $NH_2$ and NNH have substantial effects upon the temporal species profiles for nitrogenous species. While this result is not surprising, unfortunately, it is often overlooked when modeling results are compared. This effect is most pronounced for rich combustion, and varies directly with equivalence ratio. Use of different data bases had little effect on the H/O species profiles. Radical species profiles (with the exception of $HO_2$) tend to be influenced strongly by their own thermochemical properties. Computed profiles also were shown to be independent of algorithm (HCT or CHEMKIN) and thermodynamic property fitting procedure between 1000 and 2000 K.

## INTRODUCTION

Success in modeling combustion chemistry depends on the reliability of the kinetic mechanism used. A mechanism must not only provide accurate information about the forward rates of elementary reactions, it must also allow for reversibility of the individual steps. In accord with the principle of detailed balance, elementary reaction rates in the forward and reverse directions are related through the equilibrium constant. The importance of good thermochemical data to combustion computations is firmly underscored by reviewers on the subject [1-4].

Fortunately, the thermochemical properties of many combustion species are known with a great deal of confidence. For modeling applications that rely on detailed kinetics, small refinements in property values for these well-characterized species produce only infinitesimal changes in results. Because of this behavior, researchers frequently emphasize mechanism sensitivity to one or more kinetic rate coefficients, while taking for granted the input thermochemical data.

Thermodynamic properties (most notably enthalpies of formation) of some radical species, however, are undergoing substantial revisions due to improved measurement and theory. These property revisions may produce significant deviations in modeling results for some classes of combustion problems. In fact, the incorporation of a new thermodynamic data base into a kinetic model, may introduce variations in species profiles even larger than effects attributable to mass diffusion.

For some combustion modeling applications, there are only a few radical species which influence the outcome of the chemistry.

For example, the hydrogen oxidation problem described by Dixon-Lewis and Williams [5] requires a mechanism containing only 8 species and 20 reactions, to quantitatively reproduce such diverse physical phenomena as explosion behavior, flammability limits and induction times.

With nitrogen added to the H/O system, the kinetics are considerably more complex. Hanson and Salimian [6] enumerate 13 additional species and 110 additional reactions to account for the influence of nitrogen in a combustion environment which is still carbon-free. The mechanism of Glarborg, et al. [7] excludes some of the higher molecular weight $N_iH_j$ species, yet still contains 39 reactions in addition to the H/O set. The mechanism of Roby and Bowman [8], which was used to model fuel-rich nitrogen chemistry, contains only 29 nitrogen reactions in addition to the H/O set.

This paper describes how changes in thermodynamic parameters can affect calculated species profiles. It is specifically concerned with nitrogen combustion chemistry. The first part discusses species' thermodynamic properties, and their variation between five widely used thermochemical data bases. The second part compares results from two different FORTRAN chemical kinetic codes when they are supplied with identical rate coefficients, initial conditions and species' properties. The third part presents some striking comparisons of species profiles computed with identical kinetics and initial conditions, but with different thermochemical data bases.

Formal sensitivity analysis can be used to determine how

variations in a set of thermodynamic parameters can affect the concentrations of various species [9]. In a sense, this study represents a crude form of sensitivity analysis for determining the effects of variations in the thermodynamic properties on the concentrations of species. It is important to note that obtaining a global mapping by systematically employing the approach documented here is a notoriously difficult approach to sensitivity analysis. Our intent in the current study was to illustrate the importance of variations in species profiles that result from using the same set of elementary reactions, the same forward rate coefficients, and one of five data bases that are currently distributed to the combustion research community. Our conclusions are not profound, and, in some senses, they are obvious. They illustrate the importance of describing a model very carefully in terms of the complete set of parameters used. The results can also be used to provide a compelling argument for performing sensitivity analysis with respect to the entire set of parameters employed in a modeling study.

## METHODOLOGY

Thermochemical data for combustion species are available in a variety of formats from a number of sources. As a result, it was convenient to utilize two different computational models in this study. The codes HCT [10] and CHEMKIN [11], which are well-known to combustion modelers, were executed on a microcomputer to solve an initial value problem involving isobaric, isothermal, homogeneous H-N-O combustion. The microcomputer versions of these codes were developed at Princeton [12] and Stanford [13]

for use on hardware compatible with an IBM-AT or IBM-XT with math co-processor, fixed-disk and 640K RAM.

Table 1 presents the reaction mechanism which was common to all computations described here. This mechanism is an assembly of individual rate coefficients from Glarborg, et al. [7], Miller, et al. [14], Hanson and Salimian [6] and Chang and Kaufman [15]. Forward rate coefficients and thermodynamic properties were input to the codes. Reverse rate coefficients were determined from the forward value and the equilibrium constant.

The algebraic format used to represent thermodynamic data is different for the two codes. CHEMKIN utilizes a pair of six parameter polynomials, fitted over a low (300-1000 K) and high (1000-5000 K) temperature range to compute species' heat capacity at constant pressure ($\hat{c}_p$), enthalpy ($\hat{h}$) and entropy ($\hat{s}$). Continuity in each expression and its first derivative are enforced at 1000 K, the temperature common to both regimes. Equilibrium constants are determined from the difference in Gibbs free energy ($\hat{g} = \hat{h}-T\hat{s}$) between products and reactants. In contrast, HCT accepts an Arrhenius-type expression for each species equilibrium constant of formation ($K^f_{eq}$) as a function of temperature. $K^f_{eq}$ is the equilibrium constant of a "fictitious" reaction, where one mole of the compound of interest is formed from reactants comprised only of reference elements (e.g. $H_2$, $N_2$, etc.).

Five different thermochemistry data bases were compared in this study. They are identified by Roman numerals, and listed in

Table 2. The original CHEMKIN set [11] (data base I) and two revisions [16,17] (data bases II and III) were utilized with the CHEMKIN solver. Kee and his co-authors chose JANAF (2nd and 3rd editions) [18,19] as their primary source for thermodynamic properties, and incorporated results from ab initio calculations and more recent interpretation of experiments into some of the species' data as well. Westbrook and Chase [20] (data base IV) developed their set of HCT thermochemical data from the 2nd edition of the JANAF tables [18], and when not available there, from the data of Bahn [21]. These species equilibrium constants were fitted to an Arrhenius expression of the form (1), and did not include any pre-exponential temperature dependence. We generated a fifth set of expressions for species equilibrium

$$K_{eq}^{f} = A \exp(-E/RT) \qquad (1)$$

constants (data base V) from the 3rd edition of the JANAF tables [19]. This was accomplished by fitting a straight line through two points (at 900 and 1600 K) on a plot of $\ln(K_{eq}^{f})$ versus 1/T, to yield an equation of the form (1). JANAF data for $H_2O_2$ are not available explicitly at 1600K, thus the two parameter fit to Eq. (1) was performed at 900 and 1500 K for this species. No data are available for NNH from data bases I and V. For completeness, these two data bases were supplemented with NNH properties from data base III when the computations were performed.

## RESULTS AND DISCUSSION

Thermochemical properties from the five data bases utilized in this study are compared in Table 3. The data shown are

equilibrium constants of formation ($K^f_{eq}$) computed at 1600 K, for the fifteen non-reference species used in the model. Four reference elements, Ar, $H_2$, $N_2$ and $O_2$ were also used in this mechanism, and $K^f_{eq}$ is, by definition, 1.0 for each of them. Five of the species shown in the table, (O, NO, $NO_2$, HNO and $NH_3$) agree to within 2 percent among all of the data bases, and six others (H, N, OH, $H_2O$, $N_2O$ and $H_2O_2$) agree to within 10 percent. In contrast, the remaining four species (NH, $NH_2$, NNH and $HO_2$) exhibit wide variability among the five data bases.

Figure 1 presents a graphic comparison of $\log(K^f_{eq})$ versus T for each of the four species whose properties vary considerably among the data bases. Aside from the wide variation in properties among some of the data bases, it is also important to observe that in each case, two or three of the data bases are in close agreement with each other. When two data bases agree, it is because their data sources are identical, and no artifacts have been introduced by the fitting procedure. The small differences in $K^f_{eq}$ (of the order 10 percent) seen in Table 3 for some of the species (e.g. H, N, OH, etc.) are most likely due to fitting artifacts. Deviations of this magnitude are not noticeable in the logarithmic scale of Fig. 1, hence the variations seen in this figure can only be attributable to differences in data sources.

Data bases I, IV and V compare well for NH, because each used the data from the 2nd edition-JANAF tables [18]. No recent measurements of the enthalpy of formation of NH are available, hence data base V concurs with the earlier JANAF (1971) version.

Data bases II and III differ from the others because Miller has estimated [17] the enthalpy of formation of NH to be 85.2 kcal/mol, which is 4.7 kcal/mol less than the JANAF value, and 2.3 kcal/mol less than the Bond Additivity Correction to Moller-Plesset fourth-order perturbation theory (BAC-MP4) calculations of Melius and Binkley [22]. The JANAF [19] evaluation specifies an uncertainty of 4 kcal/mol for the enthalpy of formation of NH, which encompasses nearly all of the values itemized here. Such an uncertainty in enthalpy of formation, leads to a factor of 3.6 variability in $K^f_{eq}$, at 1600 K.

Properties for $NH_2$ were recalculated in the 3rd edition-JANAF tables [19], and data bases III and V utilize these updated properties. $NH_2$ properties computed from data base II yield values for $K^f_{eq}$ which are lower than the others. The JANAF [19] authors indicate an uncertainty of 1.5 kcal/mol for their recommended heat of formation of $NH_2$. At 1600 K, this uncertainty gives rise to a factor of 1.6 variability in $K^f_{eq}$.

The compound NNH was included in neither the 2nd [18] nor the 3rd [19] edition of the JANAF tables, because it had not yet been observed experimentally. Many researchers consider NNH to be an important intermediate in the oxidation of ammonia and in the chemistry of Thermal De-NOx. Recently, Bian, et al. [23] have provided convincing evidence for the mass spectrometric detection of NNH in low pressure ammonia flame studies. Data bases II and III agree to within a factor of two for this species, and values for III are based on BAC-MP4 calculations [17].

For $HO_2$, data bases I and IV are in agreement again because each uses the 2nd edition JANAF tables [18] as its source. New

measurements and a critical review by JANAF editors in 1978 have led to a change in the recommended JANAF properties for $HO_2$ between the second and third editions. Data base II, although compiled before the 3rd edition JANAF tables [19] were published, most likely used the same source material to compute $HO_2$ properties. Data base III differs from the others because its enthalpy of formation is based on an estimate by Miller [17] which is higher than JANAF-3rd Ed. [19] by 2 kcal/mol. Miller's [17] value for the enthalpy of formation of $HO_2$ is in good agreement with the experiments and analysis of Howard [24].

The rather consistent agreement between data bases I and IV, which use the same data source (2nd Ed. JANAF [18]) gives credibility to the idea that fitting two very different parametric forms has not produced important artifacts. The differences evident in Fig. 1 are due to changes in species properties from one data base generation to the next. Generally speaking, revisions in species properties represent improvements in the measurement and theory of these difficult-to-study radical compounds. However, for the purposes of this paper, no judgement has been made as to which set is best.

Because of differences in the forms of fitting functions, it is conceivable, indeed unavoidable, that two data bases which share good agreement over one range of temperatures will be in poor agreement at other temperatures. Figure 1 shows that no such fitting problems exist for the species depicted, when temperatures are between 1000 and 2000 K. The polynomial and exponential fits are nearly coincident over this range whenever

the source data are identical.

In addition to thermochemical data and kinetic rate coefficients, a model may also be sensitive to the mathematical algorithm used to generate the solution to the governing equations. Since HCT and CHEMKIN utilize different methods of O.D.E. solution, it was necessary to verify that the two codes produced comparable output when executed with identical initial conditions and governing equations. To allow this comparison, a third set of Arrhenius-type (HCT) thermochemistry parameters was derived from the data of Kee, et al. [17] (data base III), using the same two parameter fitting procedure described earlier. Because the two parameter exponential fit was forced through 900 and 1600 K, and the kinetic computations were carried out at 1600 K, there was no difference whatsoever in the thermodynamic data between HCT and CHEMKIN for this comparison.

Figure 2 presents four species profiles, calculated separately by HCT and CHEMKIN using identical kinetics (Table 1), thermodynamics (Kee, et al. [17]), and fuel-rich initial conditions which shall be referred to as Case A. Case A corresponds to homogeneous combustion, taking place isothermally at 1600 K, isobarically at 1 atm, and with $H_2/O_2/Ar/NO$ reactants in the ratio 3.2/1.0/8.0/0.024 by mole. The four individual species concentration profiles shown in Fig. 2 agree to within a few percent at all reaction times, and the agreement is equally good among the other species computed for this case. When non-isothermal calculations are performed, however, consideration should be given to possible deviations in thermochemistry, especially if temperatures are far-removed from the fitting

points in the two parameter expression (1).

The sensitivity of modeling results to the various thermodynamic data bases will now be demonstrated. In addition to Case A computations, comparable model executions were performed for Cases B, C and D. These conditions correspond to (Case B) lean (Phi=0.625) and (Case C) stoichiometric (Phi=1.0) reactant mixtures with NO as the nitrogen additive, and (Case D) a lean (Phi=0.625) mixture with $NH_3$ added. The largest contrasts were observed for rich combustion (Case A), so that it will be discussed in greatest detail. All calculations were performed using the five thermochemical data bases identified in Table 2 and the forward kinetic rate coefficients of Table 1. The variation in equivalence ratio (Cases A through C) was accomplished by holding mole fractions of Ar and NO constant, while altering the $H_2$ and $O_2$ mole fractions accordingly.

Figure 3 presents species profiles for OH and $HO_2$ for Case A calculations. The agreement among profiles computed with the various data bases is quite good over the range of reaction times computed. Deviations among profiles are insignificant between times of 10 and 100 us. Some disagreement is apparent very early (prior to 10 us) in the $HO_2$ profile, however these deviations do not significantly alter the maximum $HO_2$ concentration, nor the timing of its occurrence. One might expect larger deviations for $HO_2$ profiles at lower temperatures, especially considering the behavior noted in Fig. 1. In contrast, small deviations in the OH profile are noted at times greater than 0.13 ms, during the approach to equilibrium. With lean combustion (Case B), there

are no significant discrepancies among the five data bases for either OH or $HO_2$. Modelers who focus on macroscopic flame properties such as extinction limits and flame speeds will be reassured to see good agreement, among profiles for these two important radicals.

Profiles illustrated in Figs. 4 through 6 were computed under Case A conditions. Figure 4 contains temporal profiles for NO, and examination of this figure indicates that NO is ultimately reduced from its initial concentration of 2000 ppm to varying levels which are strongly data base dependent. Except at short times, (less than 1 ms), NO profiles computed with data bases I, IV and V agree quite well. The use of data bases II and III to determine reverse rate coefficients predicts significantly less NO survival during combustion, approximately 50 percent, as compared to 90 percent predicted from the other data bases.

The destruction of NO results in the formation of $N_2$, and the temporal profiles for $N_2$ are also shown in Fig. 4. The production of $N_2$ is significantly greater when using reverse rate coefficients computed with data bases II and III and quite similar when I, IV and V are used. Data base V allows the smallest fixation of $N_2$ at only 170 ppm, while use of data base II results in a value of 680 ppm, a factor of 4 higher.

The differences noted in the NO and $N_2$ profiles among the five thermodynamic data sets can be attributed to the species NH. Examination of Fig. 1 indicates that NH is the substance for which data bases I, IV and V agree, and for which data bases II and III are similar. The disagreement in $K_{eq}^{f}$ for NH between these two groups of data bases is approximately a factor of 5.

Data bases II and III differ from each other by 35 percent in NH properties, and this is responsible for the variation in $N_2$ and NO profiles determined using these two data sets.

Figure 5 illustrates temporal profiles for three species produced from NO decomposition which are are of intermediate concentration. HNO plays an important role in the combustion chemistry of nitrogen, because the reverse of reaction 51 (see Table 1) is the principal route for NO disappearance in a rich system. The HNO profile shapes in Fig. 5 are similar, with the exception of data base IV. The one species in this mechanism, whose properties differ distinctly (by several orders of magnitude) in data base IV alone, is NNH. The anomalously high $K_{eq}^{f}$ for this species affects the chemistry and results in a rapid and large increase in HNO.

Calculated $NH_3$ concentrations are strongly influenced by thermodynamic properties. A factor of four difference exists between the extreme profiles in Fig. 5, at time equal to 5 ms. Profiles of $NH_3$ generated by using data sets II, III and V exhibit some interesting similarities and differences which are worthy of comment. At shorter times (less than 2.5 ms), profiles associated with III and V are quite similar, while at 5 ms, the $NH_3$ concentrations associated with data bases II and V are nearly equal. Profile shapes for II and III remain similar throughout, and must be strongly influenced by the NH properties associated with these two data bases. The short time agreement between III and V and the lack of agreement between each of these and II are influenced by the properties of $NH_2$. Property differences in NNH

must be responsible for the short time differences between IV and I, since these two data bases agree for every species except NNH. The longer time behavior of $NH_3$ cannot be explained by differences in $HO_2$ properties. Recalling Fig. 3, $HO_2$ had almost completely disappeared by 200 us, therefore it could not be playing any important role in the $NH_3$ chemistry beyond 1 ms.

Relative to NO and $N_2$, $N_2O$ is a minor species, but its chemistry is quite active during the intermediate stages of the combustion, as seen in Fig. 5. The longer time behavior (greater than 2 ms) of $N_2O$ is strongly influenced by NH, because the profiles computed with data bases II and III are in closer agreement with each other and are in wider disagreement with the others. The anomalously high value of NNH associated with data base IV influences the distinct shape of this profile.

Figure 6 presents profiles of the radical species $NH_2$, NH and NNH for the Case A initial conditions. Concentrations are very low, however, these highly reactive radical species strongly influence nitrogen chemistry. The character of the early and intermediate behavior of $NH_2$ profiles indicates that the $NH_2$ thermochemical properties strongly influence its own abundance in combustion calculations. Use of data bases IV and I results in $NH_2$ concentrations which are more than a factor of four larger than those predicted by data bases III and V. Referring again to Fig. 1, the properties of $NH_2$ are in closest agreement between data bases I and IV and between sets III and V. A similar trend is evident in the NH profile graph of Fig. 6. More NH is predicted with data bases II and III, which, by comparison in Fig. 1, differ the most from the other three data bases in NH

properties. The anomalous values for $K_{eq}^{f}$ of NNH in data base IV are sufficient to explain the unusual short-time behavior of this species. However, $NH_2$ properties also appear to influence NNH concentrations, as evidenced by the higher NNH levels computed with data base I, than with sets II, III and V.

Calculated species profiles of NH, $NH_2$ and $NH_3$ are especially sensitive to variations in the thermodynamic properties of NH and $NH_2$ for conditions of rich combustion. Under these conditions, many of the bimolecular shuffling reactions involving these species are nearly equilibrated.

Predictions of nitrogenous species temporal profiles under lean conditions are also influenced by the particular data base used for reverse rate coefficient calculations. There is, however, very little effect on the major stable species, NO. The computations presented in Fig. 7 were executed using the fuel-lean Case B initial conditions. As illustrated by this figure, NO remains principally as NO, and there is relatively less nitrogen chemistry occurring than for the rich Case A. The major product of NO destruction is $N_2$, and its concentration is less than 25 ppm. Differences seen in the $N_2$ profiles of Fig. 7 can be attributed to NH property variations, just as they were in the rich comparison discussed earlier.

For fuel-lean Case B calculations, HNO profiles maintain good agreement among all five data bases, and so do $NH_3$ profiles. The $N_2O$ chemistry is strongly influenced by NH property differences among the data bases for Case B as well as Case A computations.

For Case B calculations, radical species are sensitive to values of their own thermochemical properties, just as they were for Case A. Concentrations of $NH_2$ and NH are several orders of magnitude lower for Case B calculations than for Case A. Variations in $NH_2$ and NH profiles due to differences in data bases follow the same trends for both Cases A and B. Concentrations of NNH for Case B are too low to be significant for each of the data base computations.

Differences in composition profiles also have been observed in calculations performed with stoichiometric $H_2/O_2/Ar/NO$ reactant mixtures (Case C). The magnitude of these variations is intermediate to those observed under lean and rich conditions. Differences in thermodynamic properties play a less significant role in determining the NO and $N_2$ profiles in Case D (Phi=0.625, $H_2/O_2/Ar/NH_3$) combustion than in Case B.

## CONCLUSIONS

Modeling calculations have been performed to illustrate the effect of using five commonly accepted data bases of thermochemical properties on predictions of temporal species profiles. The thermochemical properties are those used for the determination of equilibrium constants employed in the calculation of reverse rate coefficients for a chemical mechanism where forward rate coefficients are specified. The modeling study was performed for hydrogen/oxygen/argon/nitrogen-compound mixtures where the nitrogen compound was either NO or $NH_3$. The mixtures reacted isothermally at 1600 K and isobarically at 1 atmosphere, and a single kinetic mechanism for which forward rate

coefficients were specified was used throughout. Mixtures of equivalence ratios of 0.625, 1.0 and 1.6 were considered.

Modifications in sources of thermodynamic data have been substantial since 1971 for some species. Among the data bases, thermochemical properties varied greatly for the species NH, $NH_2$, NNH, and $HO_2$, and those for other species important in the mechanism had variations of less than 10 percent. The thermochemical property variations among the data bases in NH, $NH_2$ and NNH have substantial effects upon the temporal species profiles for nitrogenous species. While this result is not surprising, unfortunately, it is often overlooked when modeling results are compared. This effect is most pronounced for rich combustion, and varies directly with equivalence ratio. Use of different data bases had little effect on the H/O species profiles. Radical species profiles (with the exception of $HO_2$) tend to be influenced strongly by their own thermochemical properties. Computed profiles also were shown to be independent of algorithm (HCT or CHEMKIN) and thermodynamic property fitting procedure between 1000 and 2000 K.

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**TABLES**

1. Reaction Mechanism. Units of Pre-Exponential (A) are moles, $cm^3$ and sec. Units of Activation Energy (E) are cal/mole. Numbers bracketed with slanted lines are third-body efficiencies.

2. References corresponding to the five thermochemical data bases compared in this study.

3. Values of equilibrium constant of formation (Keq,f) at 1600 K for 15 species, computed from five data bases.

**FIGURES**

1. Equilibrium constant of formation (Keq,f) as a function of temperature for four species, evaluated from five thermochemical data bases.

2. Composition profiles for four species computed from two codes, HCT and CHEMKIN, when they were supplied with identical kinetic, thermodynamic and initial parameters. Initial conditions correspond to Case A.

3. OH and $HO_2$ concentration profiles computed using identical reaction mechanisms (Table 1) and rich initial conditions (Case A) but with five different thermochemical data bases.

4. Concentration profiles of major stable species NO and $N_2$, computed using identical reaction mechanisms (Table 1) and rich initial conditions (Case A) but with five different thermochemical data bases.

5. Concentration profiles of species HNO, $NH_3$ and $N_2O$, computed using identical reaction mechanisms (Table 1) and rich initial conditions (Case A) but with five different thermochemical data bases.

6. Concentration profiles of radical species $NH_2$, NH and NNH, computed using identical reaction mechanisms (Table 1) and rich initial conditions (Case A) but with five different thermochemical data bases.

7. Concentration profiles of major stable species NO and $N_2$, computed using identical reaction mechanisms (Table 1) and lean initial conditions (Case B) but with five different thermochemical data bases.

**TABLE 1**

| | Reaction | (Ref) | A | n | E |
|---|---|---|---|---|---|
| 1. | H+O2=OH+O | [7] | 5.10E+16 | -0.820 | 16510. |
| 2. | O+H2=OH+H | [7] | 1.80E+10 | 1.000 | 8830. |
| 3. | OH+H2=H2O+H | [7] | 1.20E+9 | 1.300 | 3630. |
| 4. | 2OH=O+H2O | [7] | 6.00E+8 | 1.300 | 0. |
| 5. | H2+O2=2OH | [7] | 1.70E+13 | 0.000 | 47780. |
| 6. | H2+M=H+H+M | [14] | 2.23E+12 | 0.500 | 92600. |
| | H2O/6./ H/20./ H2/5./ | | | | |
| 7. | H+OH+M=H2O+M | [7] | 7.50E+23 | -2.600 | 0. |
| | H2O/20./ | | | | |
| 8. | O2+M=O+O+M | [7] | 1.90E+11 | 0.500 | 95560. |
| 9. | H+O2+M=HO2+M | [7] | 2.10E+18 | -1.000 | 0. |
| | H2O/21./ H2/3.3/ O2/0./ | | | | |
| 10. | H+O2+O2=HO2+O2 | [7] | 6.70E+19 | -1.420 | 0. |
| 11. | H+HO2=2OH | [7] | 2.50E+14 | 0.000 | 1900. |
| 12. | H+HO2=H2+O2 | [7] | 2.50E+13 | 0.000 | 700. |
| 13. | O+HO2=O2+OH | [7] | 4.80E+13 | 0.000 | 1000. |
| 14. | OH+HO2=H2O+O2 | [7] | 5.00E+13 | 0.000 | 1000. |
| 15. | HO2+HO2=H2O2+O2 | [7] | 2.00E+12 | 0.000 | 0. |
| 16. | H2O2+M=OH+OH+M | [7] | 1.20E+17 | 0.000 | 45500. |
| 17. | H2O2+H=HO2+H2 | [7] | 1.70E+12 | 0.000 | 3750. |
| 18. | H2O2+OH=H2O+HO2 | [7] | 1.00E+13 | 0.000 | 1800. |
| 19. | N2O+M=N2+O+M | [6] | 6.90E+23 | -2.500 | 64960. |
| 20. | N+NO=N2+O | [7] | 3.30E+12 | 0.300 | 0. |
| 21. | N+O2=NO+O | [7] | 6.40E+9 | 1.0000 | 6280. |
| 22. | O+N2O=NO+NO | [6] | 6.90E+13 | 0.000 | 26610. |
| 23. | O+N2O=N2+O2 | [6] | 1.00E+14 | 0.000 | 28000. |
| 24. | NO2+O=NO+O2 | [7] | 1.00E+13 | 0.000 | 600. |
| 25. | NNH+M=N2+H+M | [7] | 2.00E+14 | 0.000 | 20000. |
| 26. | NH3+M=NH2+H+M | [7] | 1.40E+16 | 0.000 | 90600. |
| 27. | NNH+H=N2+H2 | [7] | 3.70E+13 | 0.000 | 3000. |
| 28. | NH3+H=NH2+H2 | [6] | 1.26E+14 | 0.000 | 21490. |
| 29. | NH2+H=NH+H2 | [7] | 6.90E+13 | 0.000 | 3650. |
| 30. | NH+H=N+H2 | [7] | 3.00E+13 | 0.000 | 0. |
| 31. | NH+N=N2+H | [7] | 3.00E+13 | 0.000 | 0. |
| 32. | NH3+O=NH2+OH | [7] | 2.10E+13 | 0.000 | 9000. |
| 33. | NH2+O=NH+OH | [7] | 6.80E+12 | 0.000 | 0. |
| 34. | NH2+O=HNO+H | [7] | 6.60E+14 | -0.500 | 0. |
| 35. | NH3+OH=NH2+H2O | [7] | 2.04E+6 | 2.040 | 566. |
| 36. | NH2+OH=NH+H2O | [7] | 4.50E+12 | 0.000 | 2200. |
| 37. | NH+OH=N+H2O | [7] | 5.00E+11 | 0.500 | 2000. |
| 38. | NH+OH=HNO+H | [7] | 2.00E+13 | 0.000 | 0. |
| 39. | N2O+OH=N2+HO2 | [15] | 6.00E+11 | 0.000 | 7500. |
| 40. | HNO+OH=NO+H2O | [7] | 3.60E+13 | 0.000 | 0. |
| 41. | HO2+NO=NO2+OH | [7] | 2.10E+12 | 0.000 | -480. |
| 42. | N+OH=NO+H | [7] | 3.80E+13 | 0.000 | 0. |
| 43. | NO2+H=NO+OH | [7] | 3.50E+14 | 0.000 | 1500. |
| 44. | N2O+H=N2+OH | [7] | 7.60E+13 | 0.000 | 15200. |
| 45. | HNO+H=H2+NO | [7] | 5.00E+12 | 0.000 | 0. |
| 46. | HNO+N=NH+NO | [6] | 1.00E+13 | 0.000 | 1990. |
| 47. | NH+NO=N2O+H | [7] | 4.30E+14 | -0.500 | 0. |
| 48. | NH2+NO=N2+H2O | [7] | 3.80E+15 | -1.25 | 0. |
| 49. | NH2+NO=N2O+H2 | [6] | 5.01E+13 | 0.000 | 24620. |
| 50. | NH+O2=HNO+O | [7] | 1.00E+13 | 0.000 | 12000. |
| 51. | HNO+M=H+NO+M | [7] | 1.50E+16 | 0.000 | 48680. |
| | H2O/6./ H2/2./ O2/2./ | | | | |
| 52. | NH+O2=NO+OH | [7] | 1.40E+11 | 0.000 | 2000. |
| 53. | NH2+NO=NNH+OH | [7] | 8.80E+15 | -1.25 | 0. |
| 54. | NNH+NO=N2+HNO | [7] | 5.00E+13 | 0.000 | 0. |

**TABLE 2**

I. Kee, R.J., Miller, J.A. and Jefferson, T.H.: "CHEMKIN: A general-purpose transportable, Fortran chemical kinetics code package", SAND80-8003, 1980.

II. SANDIA-Interim: Unpublished, interim thermodynamic data base, provided by R.J. Kee, F.M. Rupley and J.A. Miller, between their published data bases in 1980 and 1987, (c.1983).

III. Kee, R.J., Rupley, F.M. and Miller, J.A.: "The CHEMKIN thermodynamic data base", SAND 87-8215, 1987.

IV. Westbrook, C.K. and Chase, L.L.: "Chemical kinetics and thermochemical data for combustion applications", UCID-17833 Rev. 3, 1983.

V. Chase, Jr., M.W., Davies, C.A., Downey, Jr., J.R., Frurip, D.J., McDonald, R.A. and Syverud, A.N.: **J. Phys. Chem. Ref. Data, 14**, Suppl. 1, "JANAF Thermochemical Tables, 3rd Edition", 1985.

TABLE 3

| Species | Data Base I Keq,f | Data Base II Keq,f | Data Base III Keq,f | Data Base IV Keq,f | Data Base V Keq,f |
|---|---|---|---|---|---|
| H | 5.408E-05 | 5.408E-05 | 5.408E-05 | 5.649E-05 | 5.445E-05 |
| N | 6.668E-13 | 6.668E-13 | 6.653E-13 | 6.871E-13 | 6.684E-13 |
| O | 1.439E-05 | 1.439E-05 | 1.436E-05 | 1.466E-05 | 1.449E-05 |
| NH | 5.358E-12 | 3.733E-11 | 2.547E-11 | 5.260E-12 | 5.637E-12 |
| OH | 3.119E-01 | 3.119E-01 | 3.296E-01 | 3.055E-01 | 3.296E-01 |
| NO | 5.129E-03 | 5.129E-03 | 5.129E-03 | 5.105E-03 | 5.129E-03 |
| NH2 | 3.358E-08 | 2.780E-09 | 6.166E-09 | 3.281E-08 | 6.124E-09 |
| NNH | — | 7.329E-11 | 1.312E-10 | 2.673E-03 | — |
| H2O | 1.510E+05 | 1.510E+05 | 1.521E+05 | 1.476E+05 | 1.510E+05 |
| HO2 | 6.761E-04 | 3.350E-03 | 1.782E-03 | 6.699E-04 | 3.319E-03 |
| N2O | 3.055E-07 | 3.055E-07 | 3.062E-07 | 3.251E-07 | 3.041E-07 |
| NO2 | 4.286E-05 | 4.286E-05 | 4.286E-05 | 4.335E-05 | 4.266E-05 |
| HNO | 1.892E-06 | 1.892E-06 | 1.897E-06 | 1.897E-06 | 1.884E-06 |
| NH3 | 4.710E-05 | 4.710E-05 | 4.797E-05 | 4.797E-05 | 4.732E-05 |
| H2O2 | 5.370E-02 | 5.370E-02 | 5.358E-02 | 5.521E-02 | 5.433E-02 * |

* JANAF value for H2O2 extrapolated from 1500K.

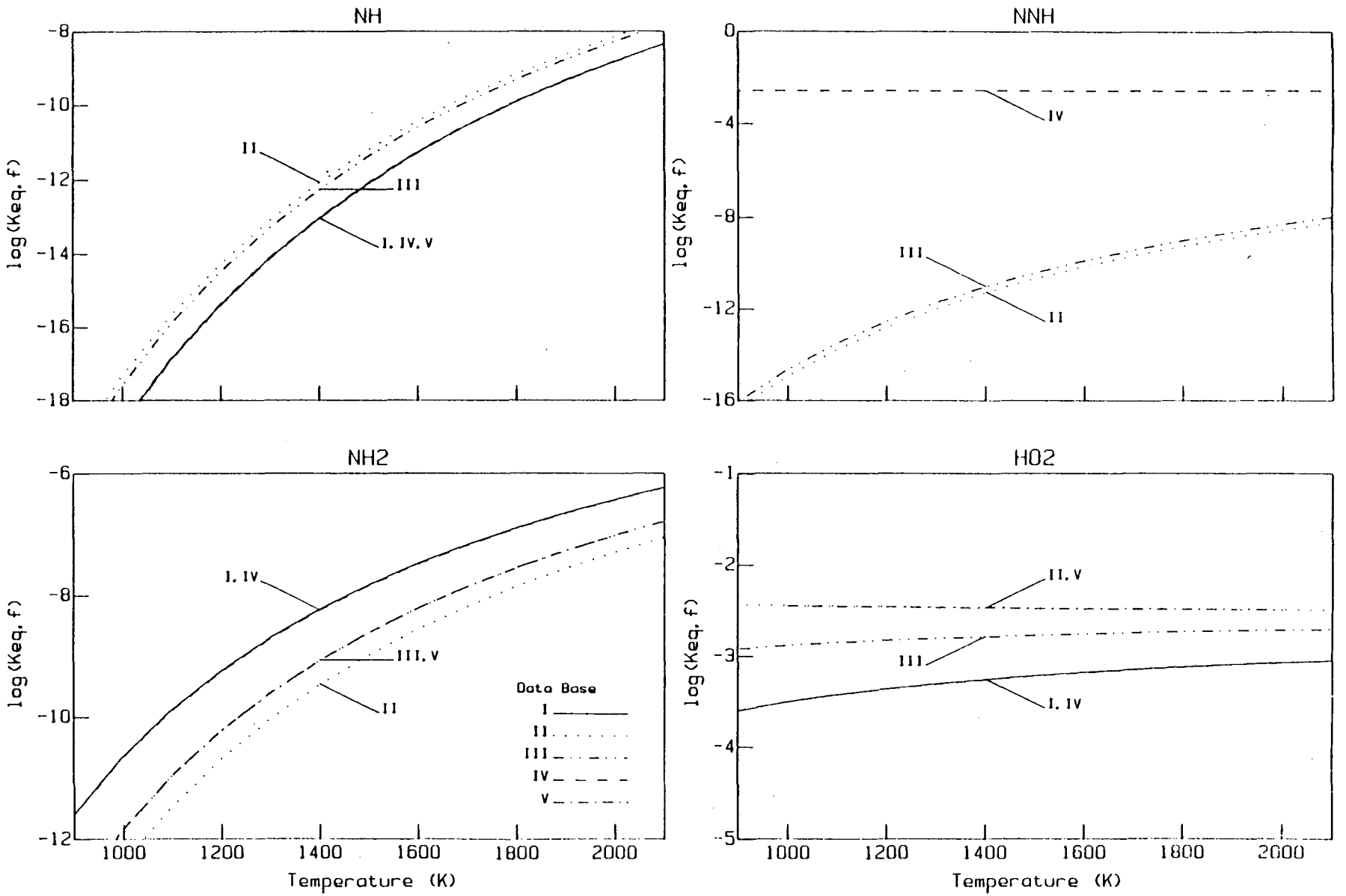
NH
NNH
NH2
HO2
log(Keq, f)
Temperature (K)
II
III
I, IV, V
IV
III, V
I, IV
II, V
Data Base
I
II
III
IV
V

Fig. 1

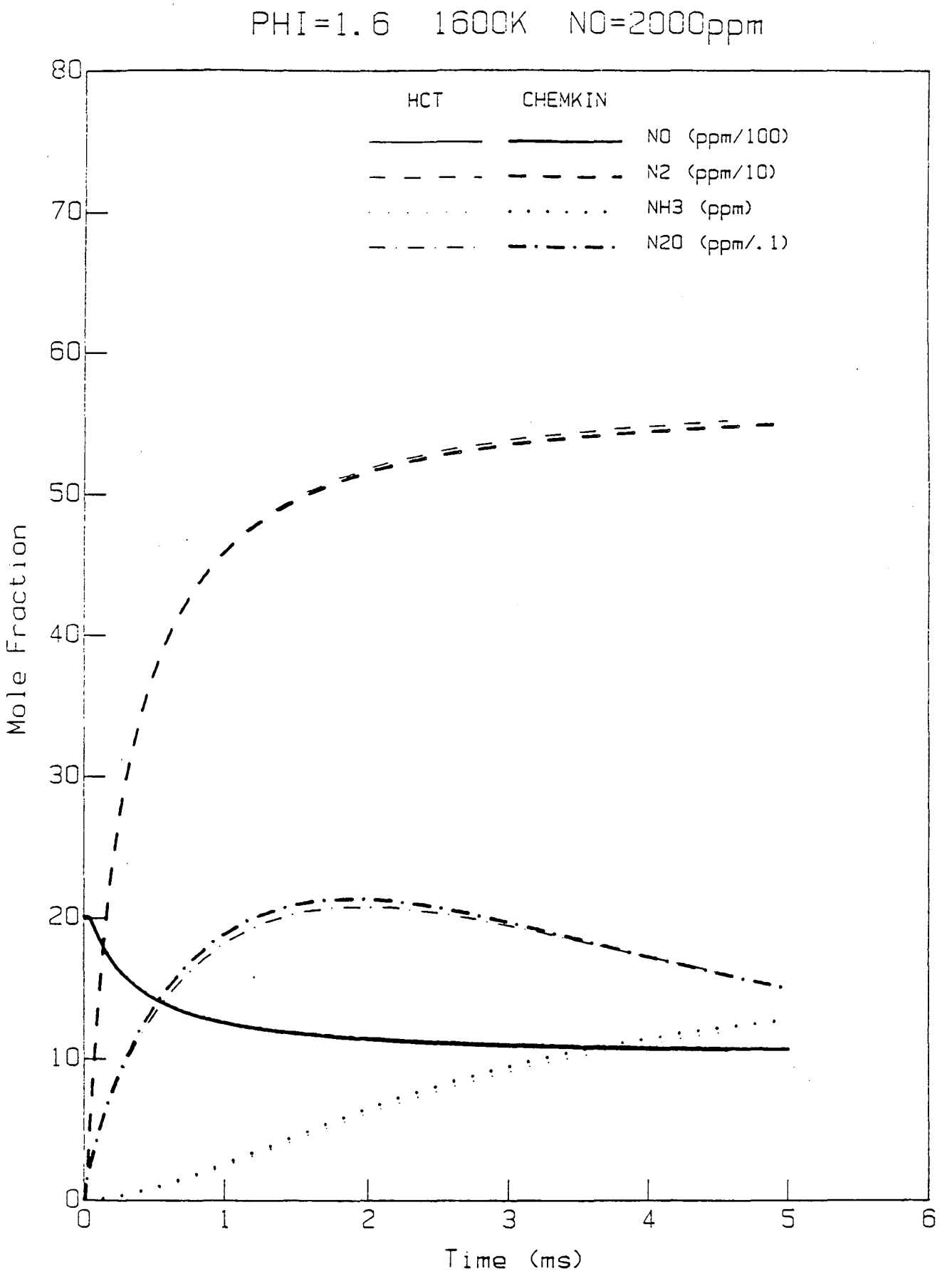
PHI=1.6 1600K NO=2000ppm
HCT
CHEMKIN
NO (ppm/100)
N2 (ppm/10)
NH3 (ppm)
N2O (ppm/.1)
Mole Fraction
Time (ms)
0
10
20
30
40
50
60
70
80
0
1
2
3
4
5
6

Fig. 2

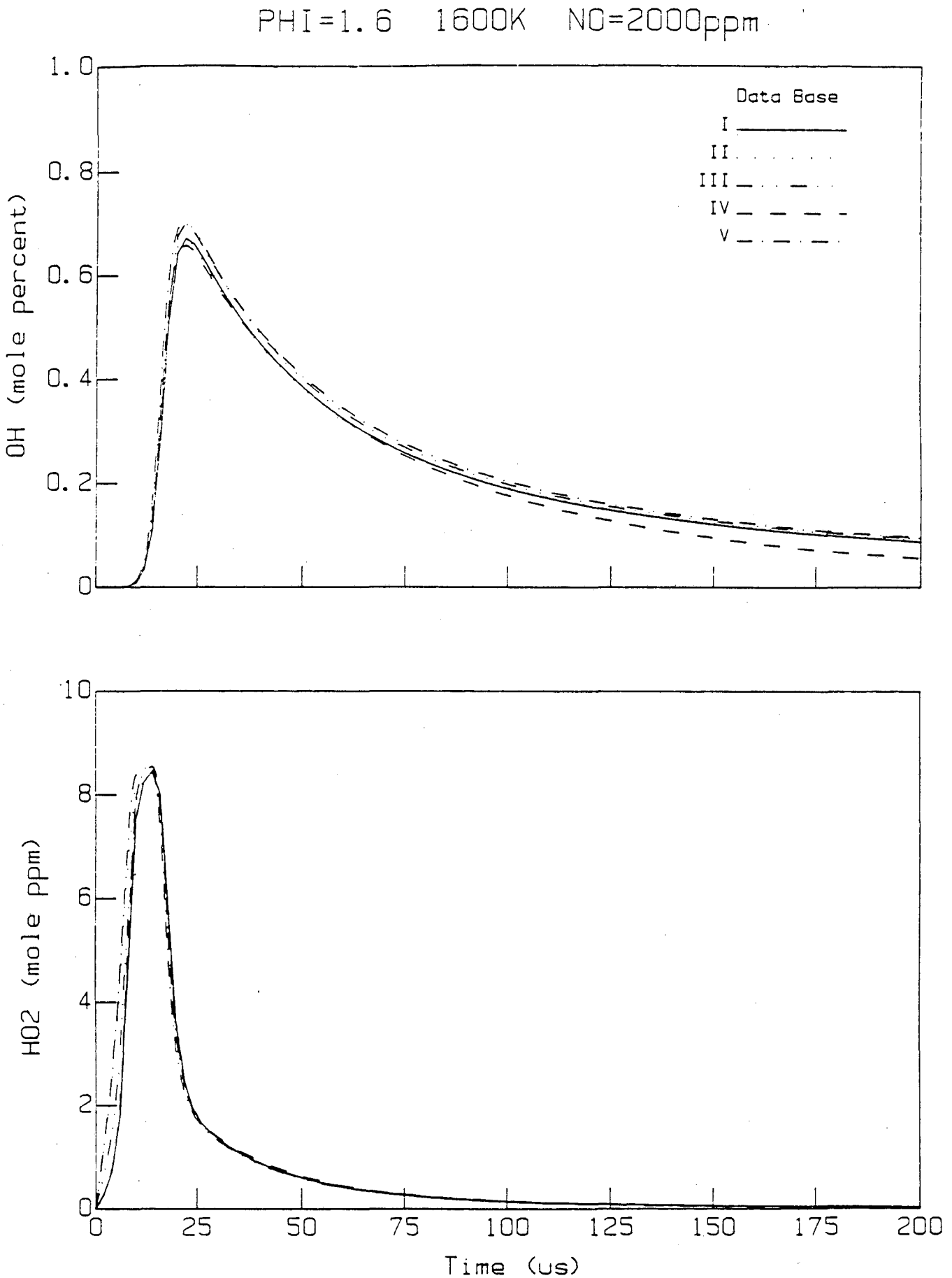
PHI=1.6 1600K NO=2000ppm
Data Base
I
II
III
IV
V
OH (mole percent)
1.0
0.8
0.6
0.4
0.2
0
HO2 (mole ppm)
10
8
6
4
2
0
0
25
50
75
100
125
150
175
200
Time (us)

Fig. 3

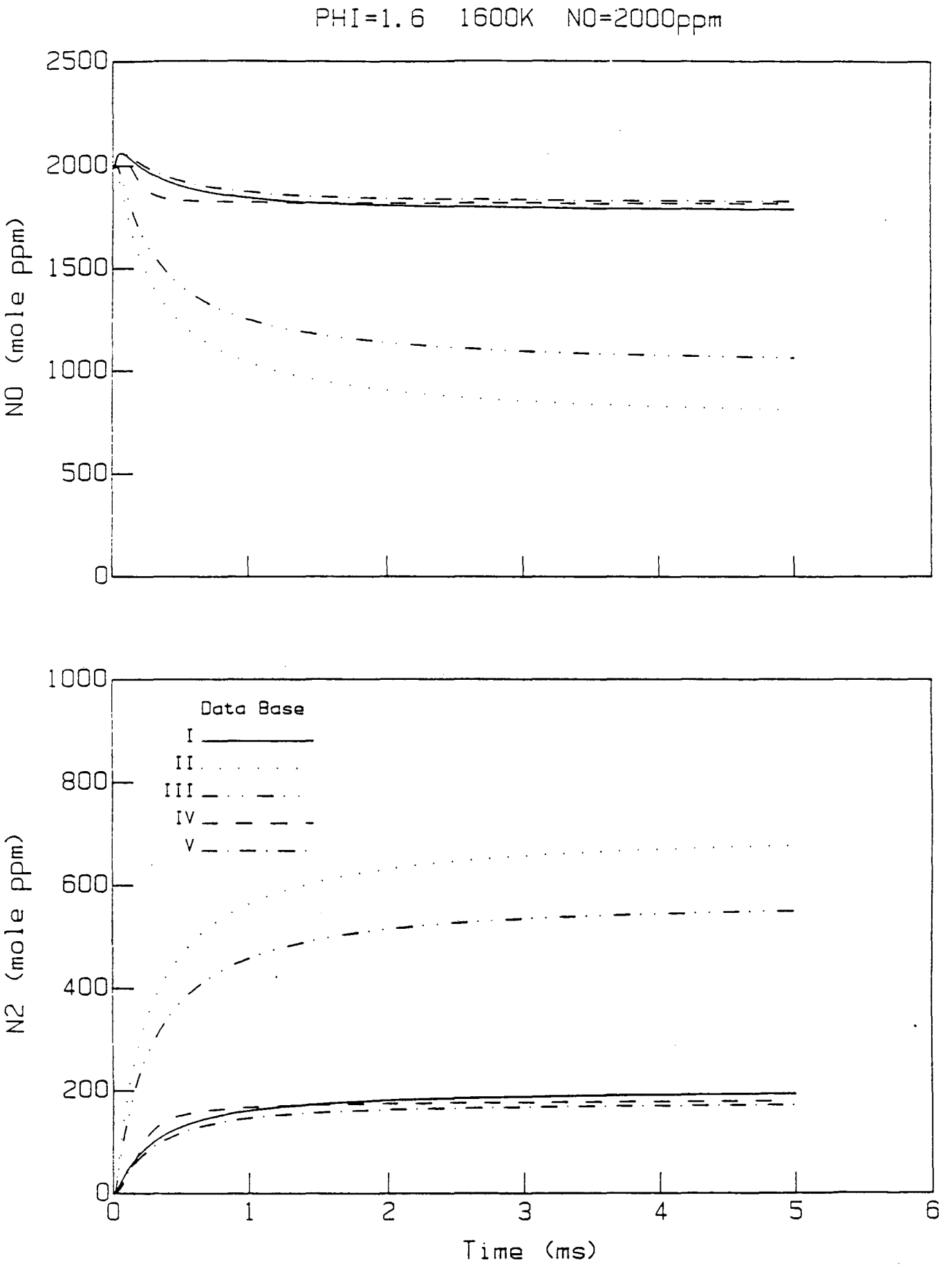
PHI=1.6 1600K NO=2000ppm
NO (mole ppm)
2500
2000
1500
1000
500
0
N2 (mole ppm)
1000
800
600
400
200
0
Data Base
I
II
III
IV
V
0
1
2
3
4
5
6
Time (ms)

Fig. 4

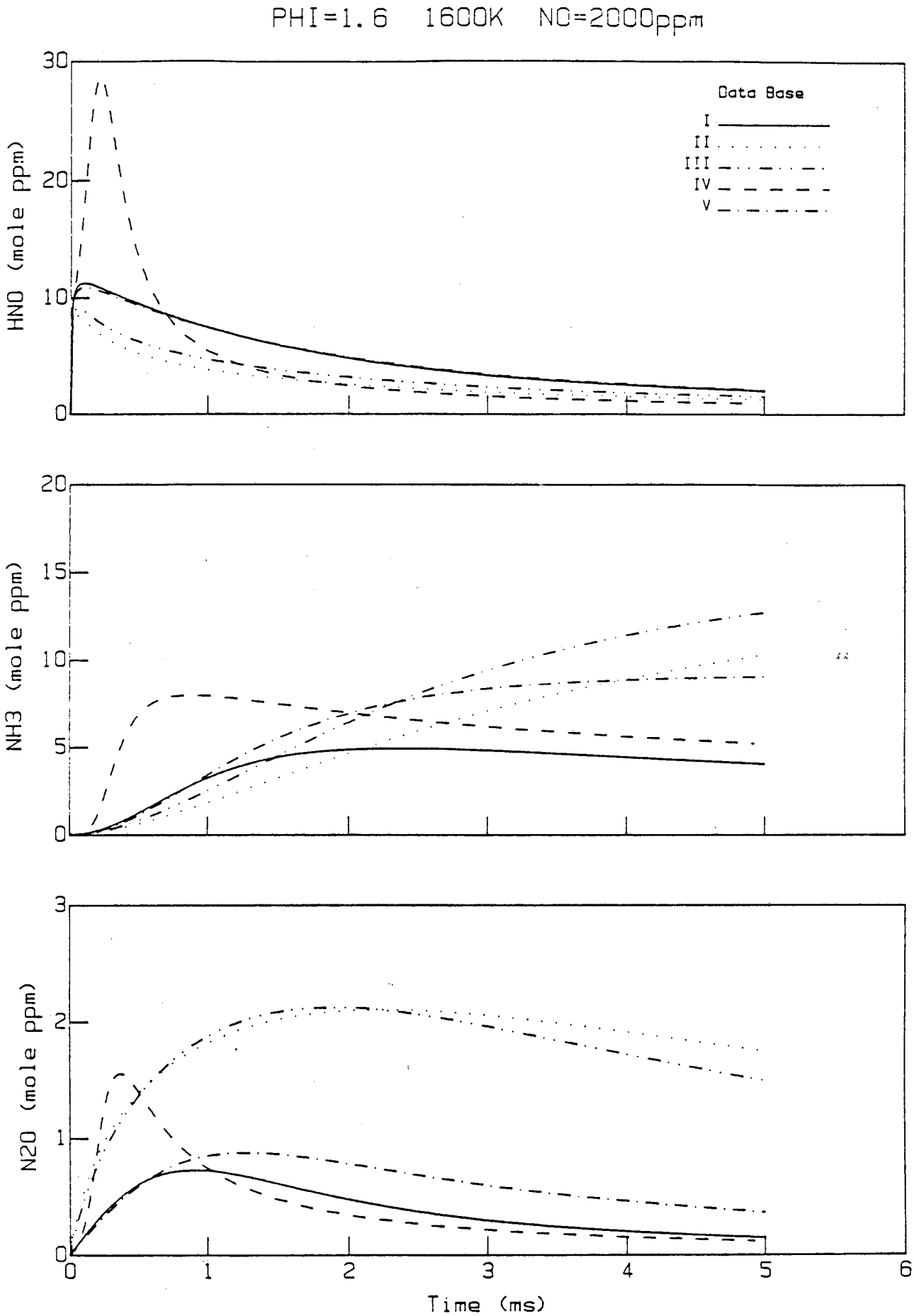
PHI=1.6 1600K NO=2000ppm
Data Base
I
II
III
IV
V
HNO (mole ppm)
NH3 (mole ppm)
N2O (mole ppm)
Time (ms)
0
10
20
30
5
15
1
2
3
4
5
6

Fig. 5

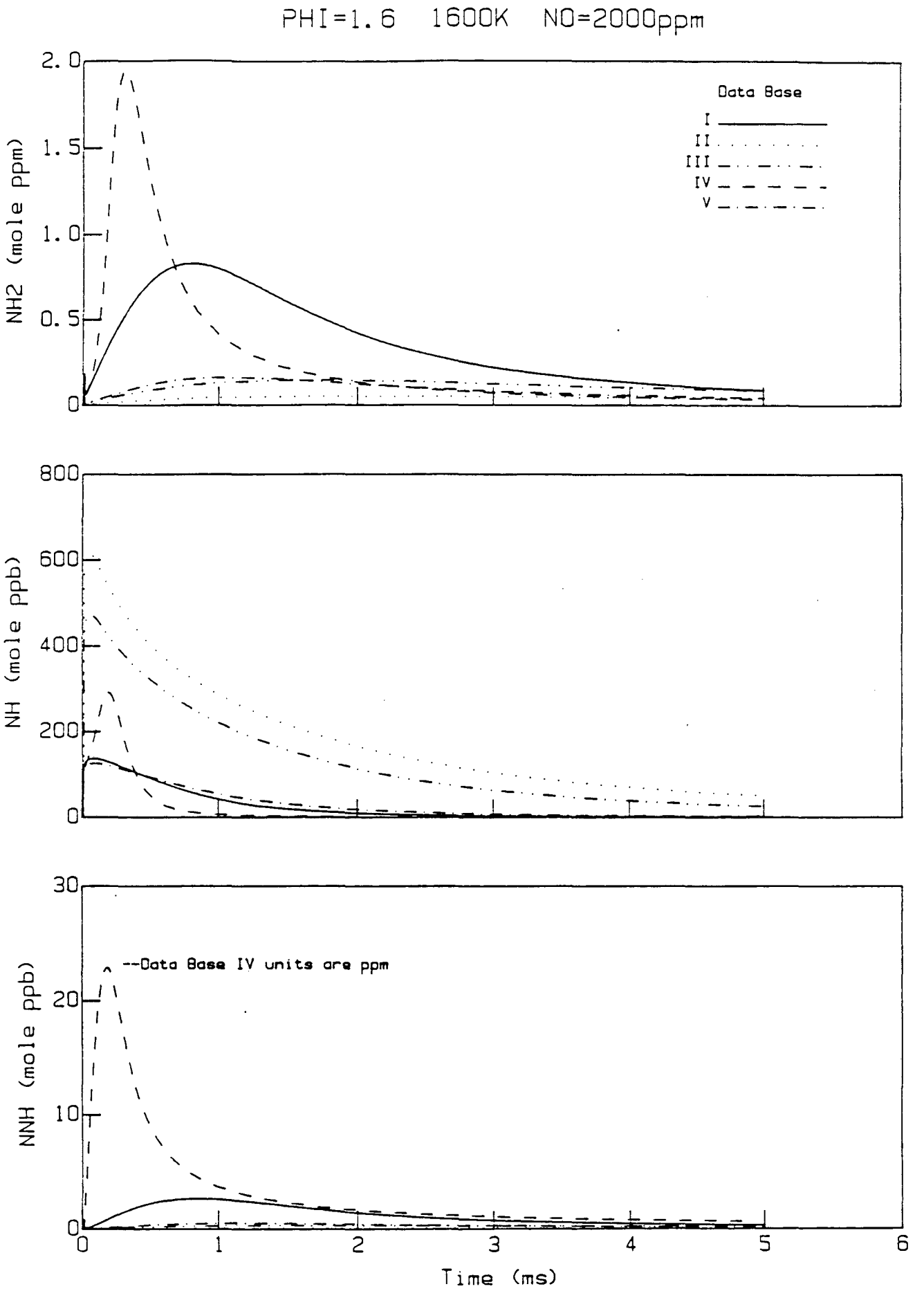
PHI=1.6 1600K NO=2000ppm
Data Base
I
II
III
IV
V
NH2 (mole ppm)
2.0
1.5
1.0
0.5
0
NH (mole ppb)
800
600
400
200
0
NNH (mole ppb)
30
20
10
0
--Data Base IV units are ppm
0
1
2
3
4
5
6
Time (ms)

Fig. 6

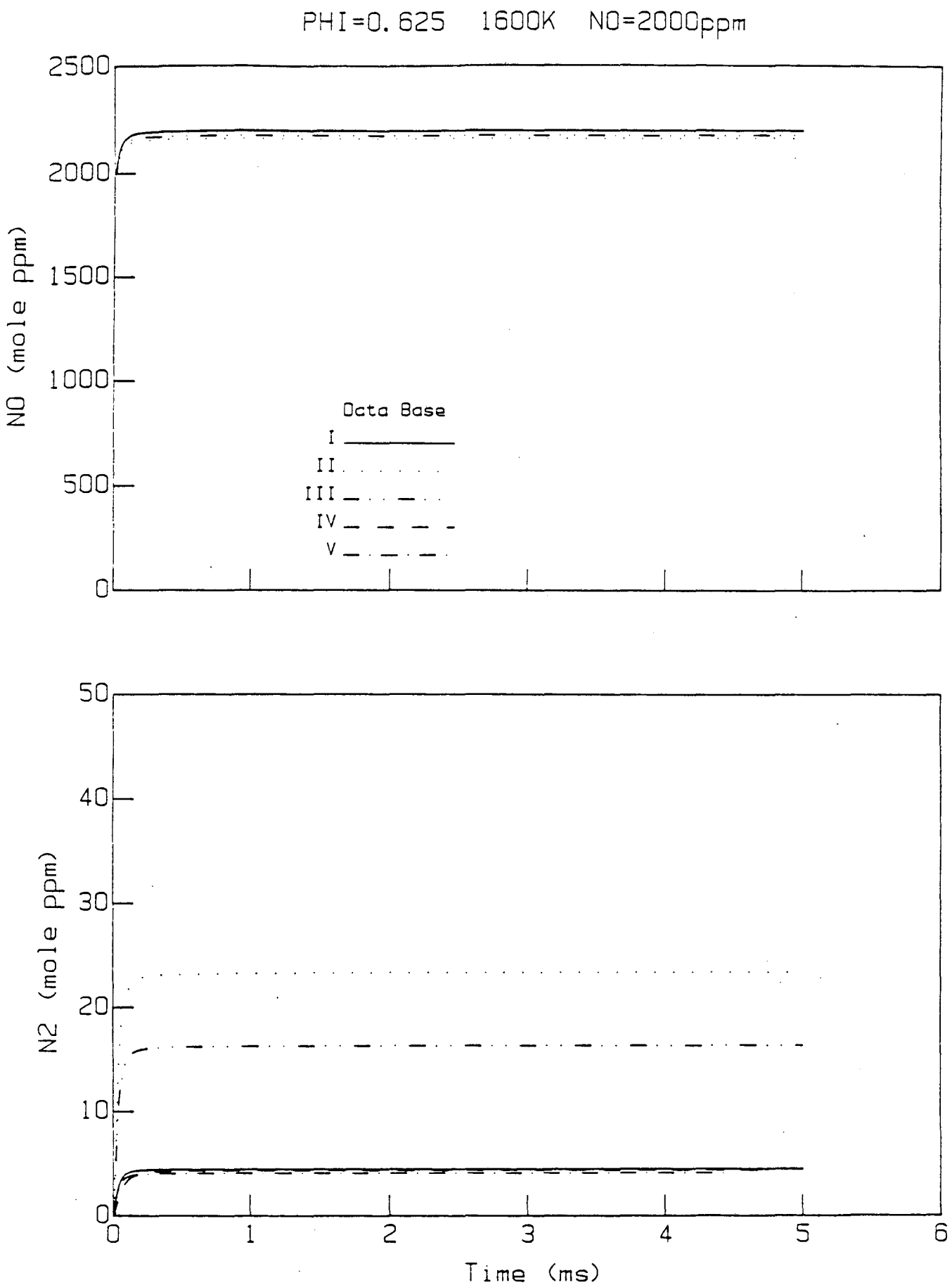
PHI=0.625 1600K NO=2000ppm
NO (mole ppm)
2500
2000
1500
1000
500
0
Data Base
I
II
III
IV
V
N2 (mole ppm)
50
40
30
20
10
0
0
1
2
3
4
5
6
Time (ms)

Fig. 7

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