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**Development of Constrained Equilibrium Codes and Their Applications in
Non-equilibrium Thermodynamics**

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Abstract

Two constrained equilibrium codes, GNASA and GSTANJAN, have been developed which determine the composition of constrained equilibrium gas mixture. These codes use NASA and STANJAN equilibrium programs as the basis for generalized equilibrium routines. Gas mixture composition is determined by minimizing Gibbs free energy of the mixture subject to any specified constraints in addition to elemental constraints. Performances of these two codes have been compared to each other and it has been found that GSTANJAN converges over a wider range of constraints while the convergence of GNASA is limited. These codes have been applied in non-equilibrium evolution process of hydrogen-oxygen mixture. The non-equilibrium process has been modeled by using only two constraints in addition to elemental constraints. The results are in good agreement with detailed kinetic solution.

Introduction

The development of models to describe the time evolution of complex reacting systems is one of the main objectives of non-equilibrium thermodynamics. The equations describing the behavior of such systems can be obtained from the laws of thermodynamics and laws of quantum mechanics, but solution of these equations is difficult due to large numbers of degrees of freedom. The alternative way to model these systems is by reducing the number of variables to be integrated or the number of chemical reactions describing them. In the past work, mostly two general approaches have been used in attempts to solve these problems. The first method involves truncation of species list used by Frenklach (1984,1987,1991), Hautman et. al (1981) and Peters (1988). The second method involves mathematical approximations which convert differential equations into algebraic equations and it is discussed by Benson (1952), Bowen et. al (1963), Lam and Goussis (1992), Rein (1992), and Mass and Pope (1992). An alternative approach, proposed originally by Keck and Gillespie (1971) and later developed by Metghalchi and Keck (1988,1993), is the Rate Controlled Constrained Equilibrium (RCCE) method which is based on the maximum entropy principle of thermodynamics. This method is based on the assumption that slow reactions in a complex reacting system impose constraints on its composition which retard its relaxation to complete equilibrium while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. As a consequence, the system relaxes to complete equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. The constrained equilibrium state at any time is determined either by maximizing the entropy or minimizing the appropriate free energy of the system subject to the instantaneous values of the constraints. These constraints are chosen by the user and imposed upon the system in addition to the fixed atomic elemental constraints. Instead of a full set of rate equations for the species, only the rate equations for the constraints are needed to determine the state of the system and since the number of constraints required is expected to be very much smaller than the number of species, the task of integrating these equations should be very much simplified. In addition, only those reactions which change the constraints are considered and this further simplifies the calculations.

Rate equations for the additional variable constraints are integrated in the RCCE method over the time domain. A generalized equilibrium program, capable of accepting additional variable constraints in addition to the elemental fixed constraints, is needed to calculate the constrained compositions. The purpose of the paper is to present two such generalized constrained equilibrium routines. These two generalized equilibrium programs, GNASA and GSTANJAN, have been developed from NASA (Gordan and McBride, 1994) and STANJAN (Reynolds, 1986) programs respectively.

Equilibrium Calculations

Method of Equilibrium Constants :

The chemical reactions can be written as follows :



where B_j is the species symbol, Nr is the total number of reactions and Nsp is the total number of species and v_{jk}^+ and v_{jk}^- are the corresponding stoichiometric coefficients for forward and reverse directions of the k -th reaction. At equilibrium we can write :

$$K_{ck}(T) = \prod_{j=1}^{Nsp} [N_j]^{v_{jk}} \quad k=1, \dots, Nr \quad (2)$$

where $K_{ck}(T)$ is the equilibrium constant for the reaction k , $[N_j] = N_j/V$ is the species concentration, V is the volume, and $v_{jk} = v_{jk}^- - v_{jk}^+$. Given a subset of Nsp ($Nsp \leq Nr$) independent reactions, equations (2) can be solved in conjunction with the equation for conservation of atoms to obtain the Nsp number of species equilibrium concentrations.

Method of Element Potentials :

The element potential method is based on minimization of Gibbs free energy (or maximization of entropy) subject to conservation of elements (elemental constraints). It has the important advantage over the method of equilibrium constants that it does not depend on a reaction model. For a system of Nsp species, the dimensionless Gibbs free energy of mixture is given by :

$$\tilde{\mu} = \sum_{j=1}^{Nsp} \tilde{\mu}_j N_j \quad \text{where } \tilde{\mu} = \mu / RT \quad (3)$$

where

$$\tilde{\mu}_j(T, p_j) = \tilde{\mu}_j^{\circ}(T) + \ln p_j \quad j=1, \dots, Nsp \quad (4)$$

is the dimensionless Gibbs free energy for species j and p_j is the partial pressure of j -th species. The element constraints are linear combinations of the species :

$$C_i = \sum_{j=1}^{N_{sp}} a_{ij} N_j \quad i=1, \dots, Ne \quad (5)$$

where coefficient a_{ij} is the number of atoms of i -th element in the j -th species and Ne is the number of elements in the system. Minimization of the Gibbs free energy (3), subject to elemental fixed constraints (5), is done by the method of Lagrange Multipliers and this leads to the following result :

$$\ln p_j = -\tilde{\mu}_j^o - \sum_{i=1}^{Ne} a_{ij} \gamma_i \quad j=1, \dots, N_{sp} \quad (6)$$

where γ_i is the dimensionless "element potential" (Lagrange Multiplier) conjugate to the elemental constraint C_i . Substituting p_j from equation (6) into the ideal gas equation of state $p_j = N_j RT/p_o V$, number of moles of the j -th species can be calculated as :

$$N_j = \frac{p_o V}{RT} \exp(-\tilde{\mu}_j^o) \exp\left(-\sum_{i=1}^{Ne} a_{ij} \gamma_i\right) \quad j=1, \dots, N_{sp} \quad (7)$$

where p_o is the standard atmospheric pressure. For systems which include a large number of species, the number of constraints is much smaller than the number of species and solving for the element potentials is easier than solving equilibrium equations for the species concentrations. NASA and STANJAN equilibrium programs, that can only accept elemental constraints, use this method to calculate equilibrium compositions.

Constrained Equilibrium

The above method may also be used to find the constrained equilibrium state of systems subject to any number of constraints, linear in the species concentrations in addition to those imposed by conservation of the atomic elements. A system is always constrained by elemental constraints but the term 'constrained equilibrium' refers to those systems which are constrained by additional constraints in addition to elemental constraints (Keck, 1990). To determine the constrained equilibrium state, one simply replaces equation (5) by

$$C_i = \sum_{j=1}^{N_{sp}} a_{ij} N_j \quad i=1, \dots, Ne, Ne+1, \dots, Nc \quad (8)$$

where Nc is the total number of constraints, the elemental and additional constraints. The constrained equilibrium composition is then found by maximizing the entropy or minimizing the Gibbs free energy subject to constraints given by equations (8), as in the preceding section and hence equation (7) becomes

$$N_j = \frac{p_o V}{RT} \exp(-\tilde{\mu}_j^o) \exp\left(-\sum_{i=1}^{Nc} a_{ij} \gamma_i\right) \quad j=1, \dots, N_{sp} \quad (9)$$

NASA and STANJAN equilibrium codes have been modified to accept any constraint in addition to elemental or atomic fixed constraints. The modified programs, called Generalized NASA (GNASA) and Generalized STANJAN (GSTANJAN), are capable of calculating the constrained equilibrium compositions of gas mixture subject to any

additional variable constraint imposed on the system in addition to elemental constraints which are always needed for the conservation of atoms in the system in absence of any nuclear reaction. These codes in the form of callable subroutines can be used in RCCE method to calculate non-equilibrium composition of gas mixture.

Application of GNASA and GSTANJAN

The main objective of this work is the development and application of GNASA and GSTANJAN in RCCE calculation. Mixture of hydrogen and oxygen gases has been chosen to test the new generalized equilibrium routines because the kinetics in the above gas mixture are well known and the full set of rate equations can be integrated easily to obtain exact or detailed solutions for comparison with RCCE calculations using GNASA and GSTANJAN. For RCCE calculation, stoichiometric mixture of hydrogen and oxygen with initial conditions of 1500 K temperature and 1 atm. pressure in constant energy and constant volume system has been used in this study. The species included are H_2 , O_2 , H_2O , OH , H_2O_2 , HO_2 , H and O . Overall four constraints have been used. Two elemental fixed constraints (elemental hydrogen EH and the elemental oxygen EO) and two additional variable constraints (total moles M and active valences AV) have been used. Total moles as a constraint (M) is due to slow dissociation and recombination reactions and active valence constraint (AV) includes the most active radicals such as H , O and OH . For the present system these constraints can be defined as follows for the present system :

$$EH = 2H_2 + 2H_2O + 2H_2O_2 + HO_2 + H + OH = 4 \text{ (in the present case)}$$

$$EO = 2O_2 + 2H_2O_2 + 2HO_2 + O + OH + H_2O = 2 \text{ (in the present case)}$$

$$M = H_2 + O_2 + H_2O + H_2O_2 + HO_2 + H + O + OH$$

$$AV = 2O + H + OH$$

Allowed Ranges of Constraints :

For the present system the constraint coefficient matrix (a_{ij} matrix), which is used in the equation (8), is given in table 1. As discussed before, NASA and STANJAN take into account only the first two rows of the a_{ij} matrix which form elemental constraints where as GNASA and GSTANJAN consider all the rows of the a_{ij} matrix. Elemental constraints are fixed in nature to ensure the conservation of atoms where as additional constraints are not fixed and their values can range between a minimum and maximum which can be determined uniquely for any system. For additional constraints, which are also functions of time during non-equilibrium calculation, the following non-equalities are true for any system : $EH + EO > 0$; $0 < M \leq A$; $AV \geq 0$ where A = total number of atoms for the system. For the present system, the following ranges for additional variable constraints can be deduced from the a_{ij} matrix using the above inequalities :

$$AV \geq 2M - (EH + EO) \quad \text{(Lower Bound)}$$

$$AV \geq 4M - 3EH - 2EO \quad \text{(Lower Bound)}$$

$$AV \leq 2M - EH \quad \text{(Upper Bound)}$$

For the present H₂-O₂ system with given initial condition (EH=4 and EO=2), M can vary from 2 to 6 and AV can vary from 0 to 8. The additional constraints M and AV are variable and time dependent in case of non-equilibrium evolution of the system. Using the above inequalities, the allowed domain for the present system (in terms of M and AV) is shown in figure 1 which gives the 2-dimensional representation of the M-AV domain.

Both GNASA and GSTANJAN have been used to find the constrained equilibrium compositions of H₂-O₂ system for two cases. In one case, as the static demonstration for the programs, they have been used to calculate constrained compositions for stoichiometric mixture of H₂-O₂ system at temperature of 1500 K and pressure of 1 atm. under different combinations of the additional variable constraints. In another case, the non-equilibrium evolution of a constant volume and constant energy H₂-O₂ system, starting from stoichiometric compositions at 1500 K and 1 atm. was studied by RCCE method using GNASA and GSTANJAN. The variable constraints, considered in both cases, were M and AV which were used in addition to fixed atomic constraints (EH and EO) to determine constrained compositions with the help of GNASA and GSTANJAN. The trapezoid ABCD represents the possible domain on M-AV plane. The points outside the trapezoid are on the forbidden zone which means it is impossible to have the mixture on those zones.

Static Calculation

The purpose of the static calculation was to find the effectiveness of the two programs GNASA and GSTANJAN in extreme cases of combinations of additional constraints which might arise in the non-equilibrium problems studied by RCCE at various instants of time. Static calculations were carried out for stoichiometric mixtures of H₂-O₂ at constant temperature of 1500 K and pressure of 1 atmosphere by GNASA and GSTANJAN. Table 2 gives the results from GNASA and GSTANJAN for different combinations of M and AV within the ranges of permissible values derived earlier and shown in figure 1. It can be seen from table 2 that GSTANJAN is more stable and accurate than GNASA in extreme cases of combinations for M and AV. For example, in the case of M=5 and AV=4 (point C), GNASA failed to converge where as GSTANJAN converged precisely. In another instance, when M=3 and AV=0, GNASA failed to converge on point B and it gave solution only when the point is well within domain by the range of 1.e-6.

Non-Equilibrium Calculation (Dynamic Calculation)

Detailed Kinetic :

The rate equation for an individual species j in equation (1) is given by :

$$\dot{N}_j = V \sum_{k=1}^{Nr} v_{jk} r_k \quad j=1, \dots, Nsp \quad (10)$$

where Nr is the number of reactions, $r_k = r_k^+ - r_k^-$ is the net rate of reaction k per unit volume, and r_k^+ and r_k^- are the forward and reverse reaction rates given by

$$r_k^\pm = k_k^\pm(T) \prod_j^{Nsp} [N_j]^{v_{jk}^\pm} \quad k=1, \dots, Nr \quad (11)$$

where $k_k^+(T)$ and $k_k^-(T)$ are the rate constants for the forward and reverse reaction k and $[N_j] = N_j / V$ is the species concentration. At equilibrium the species composition must be independent of time and r_k must vanish. This gives the detailed balancing condition $K_{ck} = k_k^+ / k_k^-$ where $K_{ck}(T)$ is the equilibrium constant for the reaction k given by the equation (2). Given a subset of Nsp ($Nsp \leq Nr$) independent reactions, equations (10) can be solved in conjunction with the equation for conservation of atoms to obtain the Nsp species concentrations. In the case where the complete reaction mechanism of a chemically reacting system is known, the most accurate method of describing the evolution of the system is the integration of full set of rate equations. In the case where the energy and volume are specified, an additional equation for the temperature is needed. This can be obtained by differentiating the expression for the energy

$$E = \sum_{j=1}^{Nsp} N_j E_j(T) \text{ with respect to time which gives}$$

$$\dot{T} = (\dot{E} - \sum_{j=1}^{Nsp} \dot{N}_j E_j) / \sum_{j=1}^{Nsp} N_j C_{vj} \quad (12)$$

where $C_{vj} = dE_j / dT$ is the specific heat at constant volume for j -th species.

Rate Controlled Constrained Equilibrium (RCCE)

The rate controlled constrained equilibrium (RCCE) method (Keck, 1990) as discussed before is a very good alternative in modeling of reaction kinetic. In this method, chemical systems evolve through a sequence of constrained-equilibrium states determined by the slow rate-limiting reactions. In chemical systems, additional constraints can occur as a result of slow reactions having time scales long compared to those of interest, and in this context it may be helpful to remember that conservation of atomic elements is a result of extremely slow nuclear reactions having time scale compared to the age of the earth. The constrained equilibrium compositions can be determined by integrating the rate equations for the constraints in stepwise fashion and then the species constrained compositions can be calculated by using a constrained equilibrium program such as GNASA and GSTANJAN.

The constraints imposed on the reacting system are given by equation (8). Differentiating these equations with respect to time yields :

$$\dot{C}_i = \sum_{j=1}^{Nsp} a_{ij} \dot{N}_j \quad i=1, \dots, Ne, Ne+1, \dots, Nc \quad (13)$$

Substituting species rate equation (10) for \dot{N}_j in the equation (13), we get

$$\dot{C}_i = V \sum_{j=1}^{Nrc} b_{ik} r_k \quad i=1, \dots, Ne, Ne+1, \dots, Nc \quad (14)$$

where $b_{ik} = \sum_{j=1}^{N_{sp}} a_{ij} v_{jk}$ and N_{rc} = Number of reactions for which $b_{ik} \neq 0$.

Note that b_{ik} gives the change in C_i due to reaction k . Given energy, volume, and the initial conditions, the N_c+1 rate equations can be integrated to calculate temperature and values of constraints at each time step. Then concentrations of species are determined by using GNASA or GSTANJAN.

In order to check performance of GNASA and GSTANJAN in nonequilibrium calculation, premixed hydrogen-oxygen mixture in an adiabatic constant volume chamber has been used. A full set of rate equations with 19 reactions and 8 species were integrated to obtain exact solution for comparisons with RCCE calculation. The 19 reactions used in the calculation are listed in table 3 along with their standard reaction enthalpies ΔH_{300}^0 and the parameters A , n , and E_a for calculating the exothermic rate constants using the form $k^+ = AT^n \exp(-E_a / RT)$. The coefficients b_{ik} appearing in equation (14) are given in the last two columns of table 3. When $b_{ik} = 0$, the k -th reaction does not change the i -th constraint. In table 3, there are 5 reactions that do not change any constraint and these reactions are in equilibrium. In the RCCE calculations, the number of rate equations to be integrated is reduced from 9 to 3 and the number of reaction rates required is reduced from 19 to 14. For more complex systems, such as C/H/O system, the reduction in both number of rate equations and the number of reactions can be of orders of magnitude larger. It is anticipated that this will reduce the computational time substantially.

Figure 2 shows a plot of temperature as a function of time for a stoichiometric mixture of hydrogen-oxygen with initial conditions of 1500 K and 1 atm. The solid curve represents the detailed or exact calculation, the dashed curve represents RCCE calculation using GNASA, and the dotted curve represents RCCE calculation using GSTANJAN. It can be seen that RCCE calculation using two generalized equilibrium codes are almost same and they are very close to detailed calculation while using only two constraints. It should be noted that there were some difficulties using GNASA to start the computation. The first step in the dynamic calculation involves the determination of the time dependent constraints at initial time in order to start the integration loop and it is at this stage that all variable constraints other than M are identically zero. However GNASA fails to start from the given initial conditions which involve zero values for additional constraints except M . What happens in such case of failure of GNASA is that the iteration equations sometimes give very large corrections which result in very large increases in mole fractions of those species that are actually present in very small quantities and eventually these large calculations lead to divergence. Hence a small number, instead of zero, had to be used for active valence constraint at initial time when GNASA was used in the calculations. On the other hand, there was no problem using GSTANJAN with zero initial condition for active valence.

Figure 3 shows species concentration as a function of time. Note that the major species are well predicted by the constrained method but the minor species are not predicted as well during early stages but nonetheless they reach the correct equilibrium concentration. Difference of results obtained by GNASA and GSTANJAN during early times are due to the starting problem with GNASA as mentioned earlier. Overall, results of RCCE calculations using GNASA and GSTANJAN with only two additional constraints are very close to detailed calculations.

Conclusion

The generalized constrained equilibrium routines in callable form, required for constrained equilibrium and also Rate Controlled Constrained Equilibrium calculations, have been developed. They have been used in this paper successfully for calculation of temperature and composition time history for a stoichiometric mixture of hydrogen and oxygen. GSTANJAN performed better than GNASA for both static and dynamic calculations in terms of stability of the code and computation speed, though the results from both routines were in good agreement with the detailed calculation.

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Table 1 : a_{ij} matrix for Hydrogen - Oxygen System

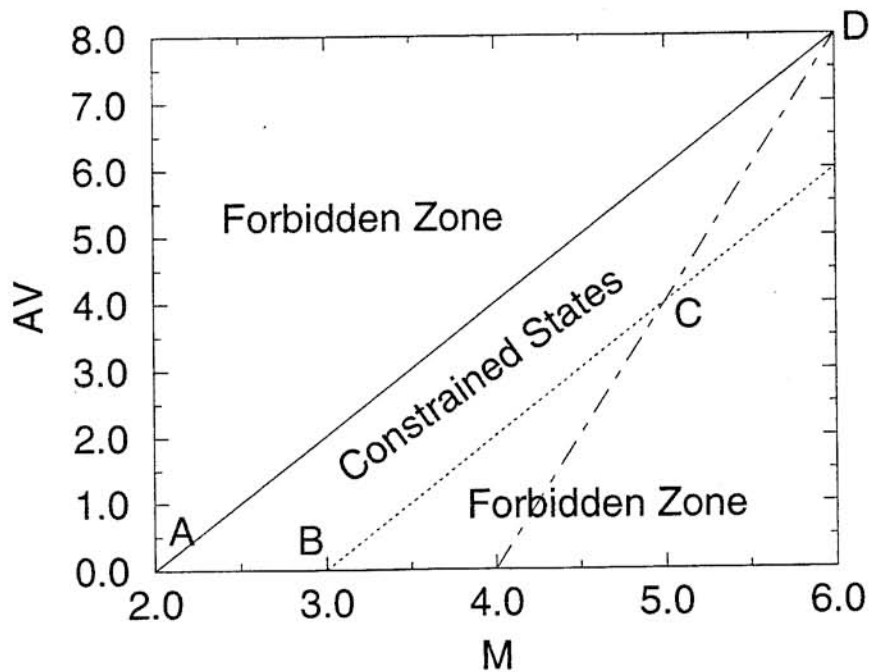
		Species (N_j)							
		H ₂	O ₂	H ₂ O	H ₂ O ₂	HO ₂	H	O	OH
Constraints (C_i)									
	EH	2	0	2	2	1	1	0	1
	EO	0	2	1	2	2	0	1	1
	M	1	1	1	1	1	1	1	1
	AV	0	0	0	0	0	1	2	1

Table 2 : Species Mole Fractions for Hydrogen-Oxygen System
(EH=4 and EO=2)T = 1500 K and P = 1 ATM.

Figure 1	M	AV	O ₂	H ₂	H ₂ O	H ₂ O ₂	O	H	OH	HO ₂	Method
A	2	0	4.80E-14	6.24E-07	1.00E+00	6.24E-07	0	0	0	1.73E-12	GSTANJAN
		0	3.70E-08	6.64E-07	1.00E+00	6.00E-07	9.30E-27	4.07E-19	1.80E-14	1.50E-09	GNASA
B	3	0	1/3	2/3	3.33E-07	6.50E-26	2.06E-21	3.33E-07	4.71E-15	1.47E-15	GSTANJAN
		1.00E-06	1/3	2/3	2.66E-07	4.24E-26	1.65E-21	3.33E-07	3.91E-15	1.19E-15	GNASA
C	5	4	1/5	0	0	0	1.33E-13	4/5	0	0	GSTANJAN
		4	x	x	x	x	x	x	x	x	GNASA
D	6	8	0	0	0	0	3.33E-01	6.67E-01	0	0	GSTANJAN
		6 - 1.E-12	8 - 1.E-12	0	0	0	0	3.33E-01	6.67E-01	0	0
Equilibrium Method			8.98E-05	1.98E-04	1.00E+00	1.92E-09	3.80E-08	2.46E-07	3.65E-05	2.18E-09	GSTANJAN
			8.99E-05	1.98E-04	1.00E+00	2.01E-09	3.82E-08	2.46E-07	3.65E-05	4.27E-09	GNASA

Table 3 : Hydrogen - Oxygen Reaction Mechanism and Rate Data
in cm³, sec and kcal units

	Reactions	ΔH_{300}^0	$\log_{10}A$	n	Ea	ΔM	ΔAV
1.	H + O ₂ + M → HO ₂ + M	-47.10	18.32	-1	0	-1	-1
2.	OH + OH + M → H ₂ O ₂ + M	-51.40	12.50	0	-1.1	-1	-2
3.	O + H + M → OH + M	-102.23	15.90	0	0	-1	-2
4.	H + H + M → H ₂ + M	-104.20	16.08	0	0	-1	-2
5.	O + O + M → O ₂ + M	-119.12	17.11	-1	0	-1	-4
6.	H + OH + M → H ₂ O + M	-119.33	9.92	1	-6.95	-1	-2
7.	H ₂ O ₂ + H → HO ₂ + H ₂	-14.60	12.20	0	-3.80	0	-1
8.	O + H ₂ O ₂ → OH + HO ₂	-14.70	12.10	0	-8.00	0	-1
9.	O + OH → H + O ₂	-16.90	13.17	0	-0.68	0	-2
10.	H ₂ O ₂ + OH → HO ₂ + H ₂ O	-29.70	13.00	0	-1.80	0	-1
11.	H + HO ₂ → H ₂ + O ₂	-38.20	14.40	0	-1.90	0	-1
12.	HO ₂ + O → O ₂ + OH	-55.10	13.70	0	-1.00	0	-1
13.	H + HO ₂ → OH + OH	-57.10	13.40	0	0.70	0	-1
14.	OH + HO ₂ → H ₂ O + O ₂	-72.20	13.70	0	-1.00	0	-1
15.	H + H ₂ O ₂ → OH + H ₂ O	-68.10	13.00	0	-3.60	0	0
16.	H + OH → H ₂ + O	-1.970	23.88	-3	0	0	0
17.	OH + H ₂ → H + H ₂ O	-15.13	13.34	0	-5.15	0	0
18.	OH + OH → H ₂ O + O	-17.10	11.67	0	6.07	0	0
19.	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	-42.53	12.30	0	0	0	0



- AV $\leq 2M - EH$ (Upper Boundary)
- ⋯ AV $\geq 2M - EH - EO$ (Lower Boundary)
- - - AV $\geq 4M - 3EH - 2EO$ (Lower Boundary)

Figure 1 : Domain of possible states of H₂-O₂ system (EH=4 and EO=2)

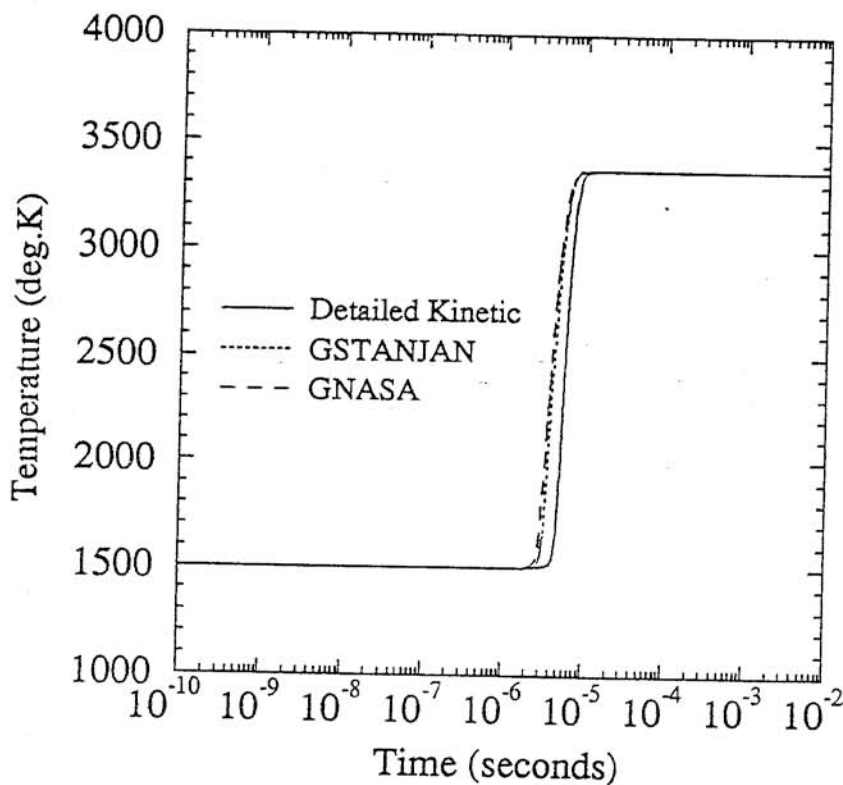


Figure 2 : Temperature as a function of time for H₂-O₂ system

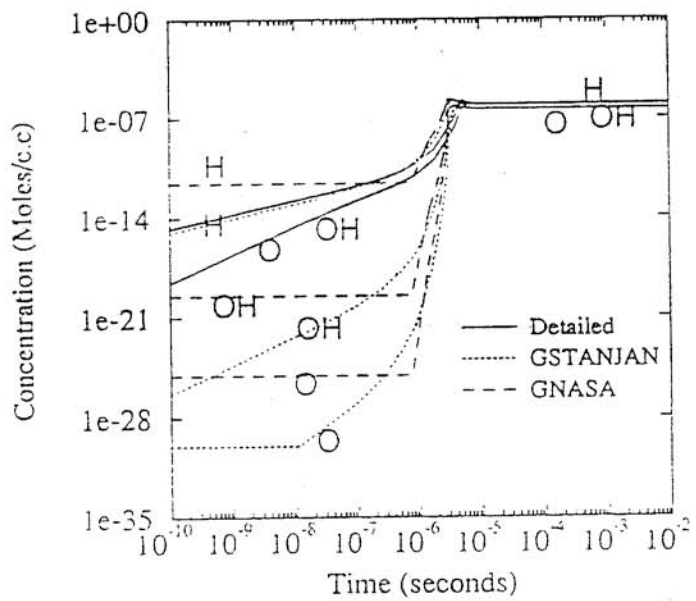
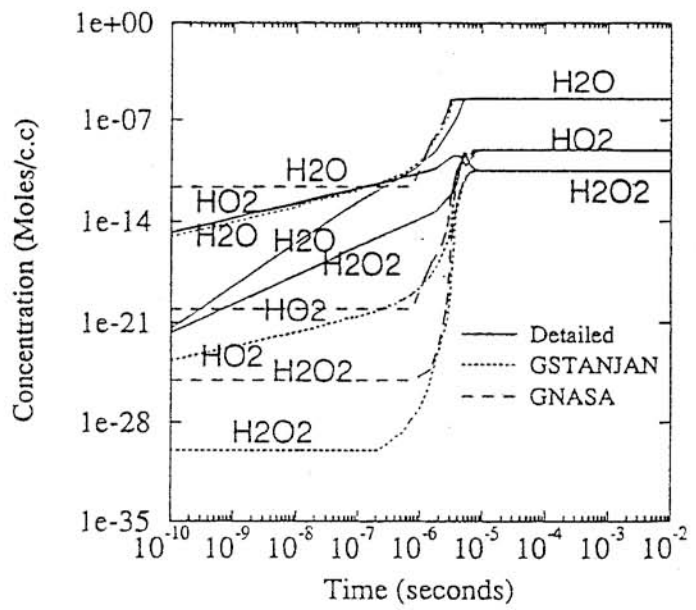
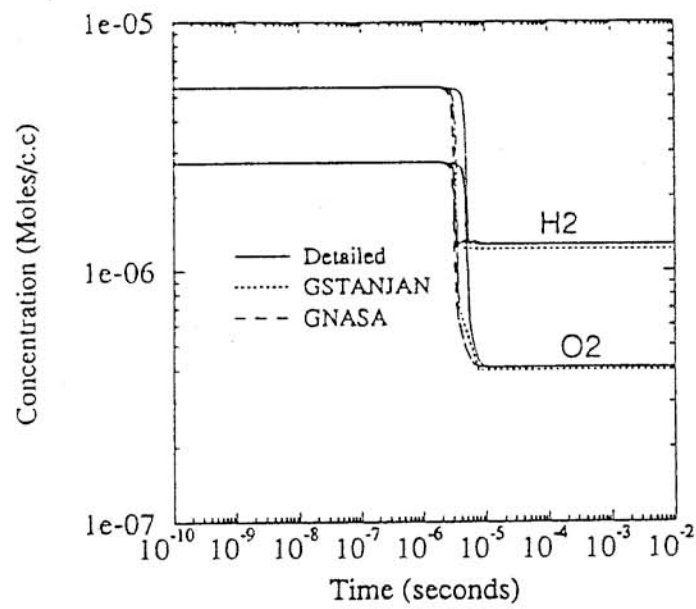


Figure 3 : Species concentration profiles for H₂-O₂ system