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APOLLO: A Computer Program for the Calculation of Chemical Equilibrium and Reaction Kinetics of Chemical Systems

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APOLLO: A COMPUTER PROGRAM FOR THE CALCULATION OF CHEMICAL EQUILIBRIUM AND REACTION KINETICS OF CHEMICAL SYSTEMS

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APOLLO: A COMPUTER PROGRAM FOR THE CALCULATION OF CHEMICAL EQUILIBRIUM AND REACTION KINETICS OF CHEMICAL SYSTEMS

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ABSTRACT

This document presents the mathematical methodology of the APOLLO computer code. APOLLO is a computer code that calculates the products of both equilibrium and kinetic chemical reactions. The current version, written in FORTRAN, is readily adaptable to existing transport programs designed for the analysis of chemically reacting flow systems. Separate subroutines EQREACT and KIREACT for equilibrium and kinetic chemistry respectively have been developed. A full detailed description of the numerical techniques used, which include both Lagrange multipliers and a third-order integrating scheme is presented. Sample test problems are presented and the results are in excellent agreement with those reported in the literature.

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NOMENCLATURE

A_i	Symbol representing chemical species
$A_{p,ij}$	See Equation (3)
b_j	Total number of atomic weights of element j
c_p	Heat capacity
C_i	Concentration of species i
E, E′	Truncation errors
f_j, $f_{p,i}$	Functionals defined by Equations (10) and (9)
F_i	Rate expression of species i
g	Total Gibbs free energy of the system
G	Functional defined by Equation (4)
h	Enthalpy
h_{n+1}	Elapsed interval between two time levels t_{n+1} and t_n
k_j, k_j'	Rate constants of forward and reverse reactions respectively
K_i^{n+1}	Concentration difference between two time levels, see Equation (41) for definition
L	Number of chemical elements present in the system
M_p	Number of species in phase p

$n_{p,i}$	Mole number of species i in phase p
N_p	Total mole numbers in phase p
NQ	Number of condensed phases
NS	Number of invariant condensed phases
P	Total pressure of the system
R	Universal gas constant
s	Entropy
t	Time
T	Temperature of the system
$Z_{1,\ldots,5}$	Coefficients of heat capacity, see Equation (29)
Z_6	Integrating constant of enthalpy
Z_7	Integrating constant of entropy

Greek

α	Pre-exponential factor of rate constant
β	Empirical parameter of rate constant
γ	Activity coefficient
η	Accelerating parameter, see Equation (27)

λ	Lagrangian multiplier
ν_{ij}	Stoichiometric coefficient of species i associated with reaction j
ω_{ij}	Time rate of net change of species i in reaction j

Subscripts

298	Temperature at which the property is evaluated
f	Pertains formation

Superscripts

0	Standard state
n	Time level

APOLLO: A COMPUTER PROGRAM FOR THE CALCULATION OF CHEMICAL EQUILIBRIUM AND REACTION KINETICS OF CHEMICAL SYSTEMS

1. INTRODUCTION

Several of the technologies being evaluated for the treatment of waste material involve chemical reactions. One example is the in situ vitrification (ISV) process where electrical energy is used to melt soil and waste into a "glass like" material that immobilizes and encapsulates any residual waste. During the ISV process, various chemical reactions may occur that produce significant amounts of gaseous products which must be contained and treated. The APOLLO program was developed to assist in predicting the composition of the gases that are formed. Although the development of this program was directed toward ISV applications, it should be applicable to other technologies where chemical reactions are of interest.

Predicting the composition and volume of the off-gas, necessitates a chemistry model which is capable of addressing the behavior of an extremely complex mixture consisting of soil and buried wastes whose components are likely to react or pyrolyze to elemental forms. Such capability provides a way to obtain required information for the design of an effective gas containment and treatment system. Since processes associated with ISV are operated at high temperatures, the assumption of equilibrium chemistry may be adequate. To date, the use of an equilibrium constant and the free energy minimization method are the two most common approaches[1] for calculating the equilibrium composition of a mixture of chemicals, with the latter method being more readily extendable to general problems. In the free energy minimization approach, the Gibbs function is minimized; via Lagrange undetermined coefficients, subject to the conservation of mass constraints imposed by the elements from which chemical compounds are made. Utilizing this technique, a computer program SOLGAS[2] and its later extensions[3,4] have been developed and in use since the early 1970's. Although SOLGAS is adequate for many applications, its computation time is too long for inclusion as a subroutine in the ISV suite of codes. To correct this shortcoming, it would require a major revision. In a reacting flow study, though somewhat different in context, Pratt and Wormeck[5] demonstrated that it is possible to reduce the

size of the system of equations as formulated in SOLGAS by orders of magnitude, hence, suggesting a significant saving in computational time. This report describes the equilibrium chemistry computer program called APOLLO, that utilizes this size reduction. Additionally, a subroutine for the integration of chemical kinetic equations based on a third-order scheme is also provided for calculations involving nonequilibrium applications.

2. THERMODYNAMIC APPROACH TO REACTION EQUILIBRIUM

2.1 Minimization of Gibbs Free Energy

From the thermodynamic point of view, equilibrium is a unique state at which Gibbs free energy of a system attains its minimum. Using the fundamentals of thermochemistry as a guide, we shall formulate the problem on the underlying foundation. To make the derivation general, consider a system composed of a gas phase, NQ liquid and solid mixtures, and NS pure condensed phases without any limit on the number of components allowed in any particular phase, and that each constituent is made up from a set of L chemical elements. For this multiphase system, the total free energy, g, at a given temperature and pressure is the sum of the products of partial molar free energies and mole numbers over all species and phases. That is,

$$g = \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} n_{p,i}\,\mu_{p,i} \tag{1}$$

where $n_{p,i}$ and $\mu_{p,i}$ are mole number and chemical potential of component i associated with phase p respectively, and M_p is the number of species in phase p. In writing Equation (1) we have replaced the molar Gibbs free energy of specie i by the corresponding chemical potential whose functional dependence on temperature, pressure, and mole numbers is given as

$$\mu_{p,i} = \begin{cases} \mu^0_{p,i} + RT\left[\ln P + \ln\left(n_{p,i}/N_p\right)\right] & p=1 \\ \mu^0_{p,i} + RT\left[\ln\gamma_{p,i} + \ln\left(n_{p,i}/N_p\right)\right] & p=2,\ldots,NQ+1 \\ \mu^0_{p,i}, & p=NQ+2,\ldots,1+NQ+NS \end{cases} \tag{2}$$

where

P = total pressure of the system, (atm, due to the standard state taken to be 1 atm)

R = universal gas constant

T = absolute temperature

N_p = total mole number in phase p

$\gamma_{p,i}$ = activity coefficient (takes a value of one for perfect mixture, and a value either greater or lower than one as the system departs from ideality)

^{0} = standard state.

A simplifying assumption has been made in the expression of the chemical potential in that the gas phase is assumed to obey the ideal gas equation of state, and that the effects due to pressure are negligible in condensed solutions.

Equation (1) will serve as the starting point of our development. The minimization of g is performed, subject to the following constraint arising from mass conservation

$$\sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i} = b_j \qquad j = 1, \ldots, L \tag{3}$$

Equation (3) simply says that the total mass of any individual chemical element comprising the substances present in the system, b_j for example, is constant regardless of the nature of the reactions. In order to minimize Equation (1), and to satisfy Equation (3) at the same time we shall apply Lagrange's method of undetermined multipliers, which hypothesizes that the optimum solution of Equation (1) is the same as the optimization of the following:

$$G = g + \sum_{j=1}^{L} \lambda_j \left\{ \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i} - b_j \right\} \tag{4}$$

where $\{\lambda_j,\ j \in [1,L]\}$ is a set of unknown multipliers to be determined. From elementary calculus, it is known that the derivatives of a well-behaved function of several variables vanish at every critical point that lie within the domain of interest. However, the determination of absolute minimum/maximum values requires additional tests on the sign of the second derivatives. Due to the unique property of the Gibbs free energy whereby G is a monotonically increasing function, it could be concluded that there exists only one set of mole numbers which yields a minimum value of G.

Proceeding as outlined above, we differentiate the functional G, and upon incorporation of the Gibbs-Duhem equation, the resulting expression can be rearranged in the following form

$$dG = \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} \left\{ \mu_{p,i} + \sum_{j=1}^{L} \lambda_j A_{p,ij} \right\} dn_{p,i} + \sum_{j=1}^{L} \left\{ \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i} - b_j \right\} d\lambda_j \quad . \tag{5}$$

Equating the differential of G to zero and utilizing the fact that both $dn_{p,i}$ and $d\lambda_j$ are independent, Equation (5) may be broken down to

$$\mu_{p,i} + \sum_{j=1}^{L} \lambda_j A_{p,ij} = 0 \qquad \begin{matrix} p = 1, \ldots, 1+NQ+NS \\ i = 1, \ldots, M_p \end{matrix} \tag{6}$$

and

$$\sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i} = b_j \qquad j=1,\ldots,L \tag{7}$$

Equations (6) and (7) constitute a system of $M_1 + M_2 + \ldots + M_{1+NQ+NS} + L$ equations with an identical number of unknowns, hence equilibrium mole numbers can, at least in theory, be obtained. There are two difficulties that prevent direct solution to the mole numbers, (1) even for a simple system, the number of possible species are sufficiently large that it is inconvenient for hand calculation, and (2) chemical potential is a nonlinear function of mole numbers. In the subsequent section we shall describe an iterative technique for obtaining the solution of a large system of nonlinear equations.

2.2 Modified Newton-Raphson Method

Due to the difficulties imposed by nonlinearity, we shall employ an iterative scheme to refine the solution, which begins with a rough estimate, until it converges to desired accuracy. For the standard Newton-Raphson method, the general recursive formula for successive corrections is

$$\sum_{j=1}^{N} \left.\frac{\partial F_i}{\partial x_j}\right|^n \Delta x_j^{n+1} = -F_i^n \tag{8}$$

where $F_i^n = F_i(x_1^n, x_2^n, \ldots, x_N^n)$, $\Delta x_i^{n+1} = x_i^{n+1} - x_i^n$, and the superscript n represents the iteration index. Instead of using Equation (8) as normally done in practice, the algorithm was modified. This modification is discussed in the remainder of this subsection. As a first step, we define the following functionals

$$f_{p,i} \equiv \frac{\mu_{p,i}}{RT} + \sum_{j=1}^{L} \frac{\lambda_j}{RT} A_{p,ij} \qquad \begin{matrix} p=1,\ldots,1+NQ+NS \\ i=1,\ldots,M_p \end{matrix} \tag{9}$$

$$f_j \equiv \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i} - b_j \qquad j=1,\ldots,L \tag{10}$$

where for the sake of convenience, we have normalized the chemical potentials and the Lagrangian multipliers by RT. Unless otherwise stated, the normalizing factor is herein omitted instead of being written.

Next, the partial derivatives of Equations (9) and (10) are calculated. The results are:

$$\frac{\partial f_{p,i}}{\partial(\ln n_{q,j})} = \delta_{ij}\,\delta_{pq} \tag{11}$$

$$\frac{\partial f_{p,i}}{\partial(\ln N_q)} = -\delta_{pq} \tag{12}$$

$$\frac{\partial f_j}{\partial(\ln n_{p,i})} = A_{p,ij}\, n_{p,i} \tag{13}$$

where δ_{ij} is the usual Kronecker Delta that has a value of one if the indices i and j are equal, and of zero when such a condition is false. It should be noted that $\ln(n_{p,i})$ has been treated as an independent variable instead of $n_{p,i}$ with the reason to be clear shortly. Substitution of these quantities into Equation (8) leads to the following correction equations

$$(\Delta \ln n_{p,i})^{n+1} - (\Delta \ln N_p)^{n+1} = -f_{p,i}^{n} \qquad \begin{matrix} p=1,\ldots,1+NQ+NS \\ i=1,\ldots,M_p \end{matrix} \tag{14}$$

$$\sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij}\, n_{p,i}^{n} (\Delta \ln n_{p,i})^{n+1} = -f_j^n \qquad j=1,\ldots,L \tag{15}$$

In counting the number of unknowns and equations, it is found that Equations (14) and (15) constitute an ill-posed linear system unless 1 + NQ + NS equations are provided. However, this difficulty is easily eliminated by utilizing the definition of the total mole number of a phase.

$$N_p = \sum_{i=1}^{M_p} n_{p,i} \qquad p=1,\ldots,1+NQ+NS \quad . \tag{16}$$

For a typical and relatively simple chemical process, L may be on the order of 5. But the number of different compounds formed may be much higher and is on the order of the number of all combinations of the elements that are in the system. Such a number is usually large, because as long as a combination satisfies the octet rule, it is (at least in principle) a possible compound. Furthermore, since the final composition of the system is rarely known prior to the course of reaction, it is prudent not to omit any potential compounds without careful justification. This implies that for many systems, a sizable system of equations must be solved. However, the inspection of Equation (14) indicates that the number of equations may be reduced significantly by using simple algebraic manipulations. This reduction in size will improve the computational time. To demonstrate this point, we need to rewrite Equation (16) in a functional form as

$$f_p^* \equiv \sum_{i=1}^{M_p} n_{p,i} - N_p \qquad p=1,\ldots,1+NQ+NS \tag{17}$$

whose associated partial derivatives may be evaluated to give

$$\frac{\partial f_p^*}{\partial(\ln n_{q,i})} = n_{q,i}^n \delta_{pq} \tag{18}$$

$$\frac{\partial f_p^*}{\partial(\ln N_q)} = - N_q \delta_{pq} \tag{19}$$

and the corresponding correction equation is

$$\sum_{i=1}^{M_p} n_{p,i}^n (\Delta \ln n_{p,i})^{n+1} - N_p^n (\Delta \ln N_p)^{n+1} = -f_p^{*n} \quad p=1,\ldots,1+NQ+NS \ . \tag{20}$$

Solving for $\Delta(\ln n_{p,i})^{n+1}$ from Equation (14), and substituting it into Equations (15) and (20) yields

$$\begin{aligned} \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} A_{p,ij} n_{p,i}^n \left\{ (\Delta \ln N_p)^{n+1} - \sum_{k=1}^{L} A_{p,ki} \lambda_k^{n+1} \right\} \\ = - f_j^n + \sum_{p=1}^{1+NQ+NS} \sum_{i=1}^{M_p} n_{p,i}^n A_{p,ij} \mu_{p,i}^n \qquad j=1,\ldots,L \end{aligned} \tag{21}$$

and

$$\begin{aligned} \sum_{i=1}^{M_p} n_{p,i}^n \left\{ (\Delta \ln N_p)^{n+1} - \sum_{j=1}^{L} A_{p,ij} \lambda_j \right\} - N_p^n (\Delta \ln N_p)^{n+1} \\ = - f_p^{*n} + \sum_{i=1}^{M_p} n_{p,i}^n \mu_{p,i}^n, \qquad p=1\ldots,1+NQ+NS \ . \end{aligned} \tag{22}$$

It is now clear that we have reduced our original system to the one with $M_1 + M_2 + \ldots + M_{1+NQ+NS}$ less equations. For example, suppose we have a single

phase mixture containing 3 elements and 100 possible compounds. If the reduction had not been made, one would have to invert a matrix of 104 x 104 in contrast to 4 x 4 as would be the case when Equations (21) and (22) are used. Once $\Delta(\ln N_p)$ and λ_k are obtained, Equation (14) can be applied to compute the change of $\ln(n_{p,i})$ for all species. Updating the results may be accomplished by using the relations

$$n_{p,i}^{n+1} = n_{p,i}^{n} \exp\{\eta\,(\Delta \ln n_{p,i})^{n+1}\} \tag{23}$$

$$N_p^{n+1} = N_p^{n} \exp\{\eta\,(\Delta \ln N_p)^{n+1}\} \quad . \tag{24}$$

For the purpose of enhancing the rate of convergence, we have introduced an accelerating parameter η. As suggested by Gordon and McBride[6], the numerical value of η is determined from the following rules

$$\eta_1 = \frac{2}{\max\limits_{p,i}\,(|\Delta \ln N_p|,\ |\Delta \ln n_{p,i}|)} \tag{25}$$

for the species with relative concentration, $n_{p,i}/N_p$, greater than 10^{-8}, and

$$\eta_2 = \min_{p,i} \left| \frac{-\ln\left(\frac{n_{p,i}}{N_p}\right) - 9.2103404}{\Delta \ln n_{p,i} - \Delta \ln N_p} \right| \tag{26}$$

for those satisfying $n_{p,i}/N_p$ equal to or less than 10^{-8}. Finally, the factor η is chosen in such a way that controls the oscillations as the estimates approach the equilibrium solution.

$$\eta = \min\,(1, \eta_1, \eta_2) \quad . \tag{27}$$

Past numerical experiments show that η has a value of less than one (as estimates are far from the exact solution), and increases to one as the true solution is reached. For a more complete discussion, readers are referred to the document of Gordon and McBride[6]. The sequence of the steps described above may be repeated until the difference between the two consecutive estimates converges to a prescribed tolerance.

2.3 Evaluation of Thermodynamic Properties

In order to begin the iteration, the chemical potential of every single species must be determined. Several ways have been suggested in the published literature for assigning the chemical potential of a compound. For example, setting $\mu^0/RT = g^0/RT$, $\Delta g^0_f/RT$, $(g^0 - h^0_{298})/RT + \Delta h^0_{f,298.15}/RT$ would all lead to the same solution. The calculatory methods for these thermodynamic variables differ widely and can be cumbersome. However, the third alternative is adopted because of its relative straightforwardness.

Hence

$$\frac{\mu^0}{RT} = \frac{1}{RT}\left(g^0 - h^0_{298}\right) + \frac{1}{RT}\Delta h^0_{f,298} \tag{28}$$

where

$\Delta h^0_{f,298}$ = heat of formation at 298 K.

Perhaps, one of the most extensive sources of thermochemical data is the JANAF[7] Tables which contain information for more than 1000 compounds, at temperatures ranging from as low as zero to a few thousand degrees Kelvin. Since the Table is designed for hand calculations, the tabular data is of limited usefulness due to the enormous amount of computer memory necessary for data storage. To make the data more amenable for computers, the heat capacity has been fitted to a fourth-order polynomial of temperature,

$$\frac{C_p}{R} = Z_1 + Z_2 T + Z_3 T^2 + Z_4 T^3 + Z_5 T^4 \qquad (29)$$

and by integrating appropriate expressions, equations similar to Equation (29) can be derived for enthalpy and entropy.

$$\frac{h}{RT} = Z_1 + \frac{Z_2}{2} T + \frac{Z_3}{3} T^2 + \frac{Z_4}{4} T^3 + \frac{Z_5}{5} T^4 + \frac{Z_6}{T} \qquad (30)$$

$$\frac{s}{R} = Z_1 \ln(T) + Z_2 T + \frac{Z_3}{2} T^2 + \frac{Z_4}{3} T^3 + \frac{Z_5}{4} T^4 + Z_7 \qquad (31)$$

where Z_6 and Z_7 are essentially constants of integration. To obtain numerical values for those coefficients, reference temperature, enthalpy, and entropy must be specified. For consistency with earlier works, reference quantities are chosen as 298.15 K for temperature, heat of formation at 298.15 K for enthalpy, and low temperature entropy (at 0 K) for the remaining thermodynamic variable.

To better fit the heat capacity equation to the JANAF data, linear regression has been performed on two temperature ranges. They are from 300 K to 1000 K and from 1000 K to 5000 K. The two sets of coefficients are constrained so as to yield the same heat capacity at the common temperature.

3. CHEMICAL REACTION KINETICS

3.1 Rate Equations

In many engineering problems, equilibrium conditions may not be reached because the characteristic time for transport is short compared to that for equilibrium attainment. Therefore, we must utilize a kinetic formulation which makes use of the detailed reaction mechanisms to construct rate expressions for reactants and products. To simplify the notations, we shall represent chemical reactions of a system in a compact form as,

$$\sum_{i=1}^{N_j} \nu_{ij} A_i \underset{k_j'}{\overset{k_j}{\rightleftharpoons}} 0 \tag{32}$$

where

ν_{ij} = stoichiometric number of species i in reaction j

k,k′ = rate constants of the forward and backward reactions, respectively.

In representing chemical reactions by Equation (32), the coefficients ν_{ij}'s are negative for reactants, positive for products, and zero for species that do not take part in the reaction.

By defining ω_{ij} to be the net rate of formation/destruction of species i in reaction j, the time rate of change of component i concentration is given by

$$\frac{dC_i}{dt} = \sum_{j=1}^{NR} \omega_{ij} \tag{33}$$
$$= F_i(\text{state of the system}) \quad .$$

Since the rate expression is a function of state of the system only, the variables temperature, pressure, and composition are not entirely independent. Therefore, specifying temperature and concentration allows the pressure to be calculated from an equation of state. In effect, Equation (33) may be rewritten without loss of generality as

$$\frac{dC_i}{dt} = F_i(T, C_1, \ldots, C_N) \tag{34}$$

In elementary reactions, the results of the transition-state theory (occasionally referred to as theory of absolute reaction rates) indicates that the functional dependencies in Equation (34) can be separated into two distinct functions. One is dependent on temperature, and the other on composition. Thus,

$$F_i(T, C) = k_i(T)\ F_i(C_1, C_2, \ldots, C_N) \quad . \tag{35}$$

The coefficient k_i may be identified as a rate constant. Although several theoretical models have been developed to characterize the temperature dependency in the rate constant, they are all based on the form

$$k_j(T) = \beta_j T^{\alpha_j} e^{-\frac{U_j}{RT}} \tag{36}$$

where

β_j = a preexponential factor

U_j [≡] dimension of energy.

The exponent α_j can have any value. However, it normally ranges between zero and one. In theory, the value may be derived to be either 0, 0.5, or 1.0 depending on the model used. These numbers are in correspondence with the Arrhenius, collision dynamics, and activated complex theories respectively[8].

Even though such theoretical pred'ctions are useful in the absence of actual data and are of great value in correlating experimental observations, they are only rough estimates and correlated values are normally required and used in practice.

3.2 Numerical Integration

The discussion above convinces that at a given temperature, the concentrations of reactants and products in time domain are governed by a system of ordinary differential equations,

$$\frac{dC_i}{dt} = F_i(C_1, C_2, \ldots, C_N) , \qquad i=1,2,\ldots,N \ . \tag{37}$$

In developing an algorithm for integrating Equation (37), we expand C_i^n and C_i^{n-1} about the time level n+1 in the form of Taylor series as

$$C_i^n = C_i^{n+1} - \left.\frac{dC_i}{dt}\right|^{n+1} \frac{(t_{n+1}-t_n)}{1!} + \left.\frac{d^2C_i}{dt^2}\right|^{n+1} \frac{(t_{n+1}-t_n)^2}{2!} - \left.\frac{d^3C_i}{dt^3}\right|^{n+1} \frac{(t_{n+1}-t_n)^3}{3!} + \ldots \tag{38}$$

$$C_i^{n-1} = C_i^{n+1} - \left.\frac{dC_i}{dt}\right|^{n+1} \frac{(t_{n+1}-t_{n-1})}{1!} + \left.\frac{d^2C_i}{dt^2}\right|^{n+1} \frac{(t_{n+1}-t_{n-1})^2}{2!} - \left.\frac{d^3C_i}{dt^3}\right|^{n+1} \frac{(t_{n+1}-t_{n-1})^3}{3!} + \ldots \tag{39}$$

By eliminating the second derivative terms, it follows that

$$\frac{2h_{n+1}+h_n}{h_{n+1}(h_{n+1}+h_n)}\,K_i^{n+1} - F_i(C_1^{n+1},\ldots,C_N^{n+1}) = \frac{h_{n+1}}{h_n(h_{n+1}-h_n)}\,K_i^n + E_{n+1} \tag{40}$$

where we have utilized the definitions

$$K_i^{n+1} \equiv C_i^{n+1} - C_i^n, \qquad h_{n+1} \equiv t_{n+1} - t_n \ . \tag{41}$$

The truncation error term in Equation (40) is, for a uniform time increment, on the order of h^2. To be exact, E_{n+1} (due to the alternation in signs), may be given by the leading term of the truncation as

$$|E_{n+1}| \leq \left|\frac{d^3C_i}{dt^3}\right|^{n+1} \frac{h_{n+1}(h_{n+1}+h_n)}{3!} \ . \tag{42}$$

Equation (42) is very useful in that one can control the propagation of error by appropriate adjustment of step size. For a user-supplied tolerance, the time increment is first determined from Equation (42), then Equation (40) is solved for composition. Often, rate expressions are nonlinear, hence, Equation (40) and an iterative solution scheme, such as the Newton-Raphson technique discussed in the preceding section must be used. However, that method usually results in a Jacobian matrix which must be inverted many times

at each time level. And because matrix inversion oftentimes accounts for a large fraction of execution time in a practical problem, the function F_i is linearized as follows:

$$F_i(C_1^{n+1}, \ldots, C_N^{n+1}) = F_i(C_1^n, \ldots, C_N^n) + \sum_{j=1}^{N} \left.\frac{\partial F_i}{\partial C_j}\right|^n K_j^{n+1} + \left.\frac{d^3 C_i}{dt^3}\right|^n \frac{h_{n+1}^2}{2!} + \ldots \tag{43}$$

in which we have assumed that all kinetic parameters are not time-dependent, otherwise a time derivative term must be included in the right hand side of Equation (43). Combining Equations (40) and (43) yields

$$\frac{2h_{n+1} + h_n}{h_{n+1}(h_{n+1} + h_n)} K_i^{n+1} - \sum_{j=1}^{N} \left.\frac{\partial F_i}{\partial C_j}\right|^n K_j^{n+1} = F_i(C_1^n, \ldots, C_N^n) + \frac{h_{n+1}}{h_n(h_{n+1} + h_n)} K_i^n + E'_{n+1} \tag{44}$$

which is now a linear system of equations, and a matrix inversion needs to be computed once for each time step. The system can be solved by any existing well-tested solver. Equation (42) is, as a consequence of the linearization of the rate expressions, now modified to the following:

$$\left|E'_{n+1}\right| = \left|\frac{d^3 C_i}{dt^3}\right|^n \frac{h_{n+1}(2h_{n+1} - h_n)}{3!} \tag{45}$$

It should be noted that the error expressions derived thus far are due to the truncations of the corresponding equations. Errors associated with the concentrations are one order higher for all species. It is also beneficial at this point to emphasize that the scheme is not self-generating, therefore, an alternative must be chosen for the first two time levels. As an example, the following equation may be used for the first two time levels.

$$K_i^{n+1} - \frac{h}{2} \sum_{j=1}^{N} \left. \frac{\partial F_i}{\partial C_j} \right|^n K_j^{n+1} = h F_i(C_1^n, \ldots, C_N^n) \qquad (46)$$

The previous equation was deduced from general Equation (44). Other choices are possible. However, if a low order scheme is used, the time increment must be kept small so that inaccuracy introduced by the time differencing is not excessive.

4. PROGRAM VALIDATION

Before APOLLO is used for applications, it is necessary to ensure that the computer code is free of errors, as well as any unexpected behavior due to inappropriate coding. For the purpose of providing confidence, APOLLO is now tested with problems, for which existing solutions are available. Both equilibrium and nonequilibrium applications are presented.

4.1 Equilibrium Tests

In this section, we wish to calculate the equilibrium composition for three sample problems. First, we shall consider a mixture initially composed of 2 g mol of methane and 3 g mol of water in the unreacted state and would like to know the final composition at 1000 K with the pressure held constant at 1 atm. Input data for this problem include the total mass of each element, and the Gibbs free energy of formation of all compounds under consideration. For the sake of convenience, this information is documented in Tables 1 and 2.

Table 1. Input elemental mass for pyrolysis example (units in atomic weight)

Element	i	b_i
Carbon	1	2.0
Hydrogen	2	14.0
Oxygen	3	3.0

Table 2. Input free energy of formation of pyrolysis example (units in K cal/g mol)

	H_2	CH_4	H_2O	CO	CO_2
i	1	2	3	4	5
Δg_f	0.0	4.61	-46.03	-47.94	-94.61

Upon entering these data to APOLLO and setting the convergence criteria at 10^{-4}, five iterations were required for the equilibrium composition to be numerically accurate to four decimal places. These results are given in Table 3 in which the mole fractions compare favorably well with those of Smith and Van Ness[9]. As indicated from the table, the predicted composition is in agreement with the published results of up to four digits, except hydrogen, which differs by 0.0001.

Table 3. Equilibrium composition of pyrolysis problem (units in g mol)

Iteration	H_2	CH_4	H_2O	CO	CO_2
1	14.7781	0.6942	1.5766	3.4597	0.5055
2	8.1498	0.2801	0.9696	2.0230	0.3322
3	6.1132	0.1872	0.8652	1.5814	0.3089
4	5.8037	0.1724	0.8609	1.5186	0.3109
5	5.7951	0.1720	0.8610	1.5170	0.3110
6	5.7951	0.1720	0.8610	1.5170	0.3110
Mole fract.	0.6695	0.0199	0.0995	0.1753	0.0359
Reference 9	0.6694	0.0199	0.0995	0.1753	0.0359

Next, we will look at a Claus oxidation process, which has been proposed to burn hydrogen sulfide (a noxious pollutant) released from refineries to less hazardous chemicals. Here, the process is carried out at 2200°F and 1 atm, in which hydrogen sulfide residing in the inlet stream is removed by the partial oxidation of sulfides to SO_2, followed by a catalytic reaction between SO_2 and the remaining H_2S. The feed gas consists of 12 species with specific flow rates given in Table 4, and the air (assuming a mole proportion of 79% for nitrogen and 21% for oxygen) is supplied at the rate of 275 lb mol/h.

Table 4. Inlet gas composition for claus oxidation (units are in lb mol/h)

Components	Flow Rate
H_2S	31.60
CO_2	8.29
CH_4	0.50
C_2H_6	0.33
C_3H_8	0.38
C_3H_6	3.58
C_4H_{10}	0.13
C_5H_{12}	0.70
CH_3SH	5.17
C_2H_5SH	0.69
H_2O	12.97
NH_3	8.68

From Table 4, the total number of atomic weight for each element comprising the compounds can be computed, and those values are listed in Table 5.

Taking advantage of the perfect behavior established for ideal gas, along with the properties of ideal mixture, and the fact that the standard chemical potential can be replaced by the free energy of formation, computation begins with initial guess arbitrary taken as 2 lb mol/h. For a tolerance of 0.01, 0.001, and 0.0001, the number of iterations necessary for convergence are observed to be seven, eight, and 10, respectively. For the purpose of illustration, the convergence process corresponding to tolerance of 0.01 is presented in Table 6.

Table 5. Constraints on mass of elements (air supply included)

Element	i	b_i No. of AW
Nitrogen	1	443.18
Oxygen	2	145.05
Sulfur	3	37.46
Carbon	4	31.90
Hydrogen	5	178.40

Table 6. Computer output showing convergence of equilibrium composition of claus oxidation process (units in lb mol/h)

	Iteration Number						
Species	1	2	3	4	5	6	7
N_2	14.778	109.196	281.258	227.495	221.666	221.590	221.590
H_2	2.537	10.159	19.026	10.793	9.162	9.025	9.024
S_2	2.110	3.126	20.630	13.538	11.499	11.329	11.327
CO_2	2.427	8.421	48.043	29.273	24.420	23.971	23.967
SO_2	2.344	6.419	16.650	9.391	7.970	7.851	7.850
CO	2.281	5.303	16.090	9.419	7.824	7.673	7.671
COS	2.083	2.506	0.648	0.317	0.266	0.262	0.261
H_2O	2.746	18.776	138.735	87.431	74.539	73.490	73.483
H_2S	2.450	7.822	13.521	7.915	6.782	6.693	6.693
CS_2	1.725	0.545	0.001	0.000	0.000	0.000	0.000

To compare the results of this calculation with those reported in Reference 10, the converged mole numbers (last column) are converted to mole percent, and those values are compared in Table 7. As seen from this table, the Apollo calculations agree well for the equilibrium condition. The agreement is consistently good for all species, and the discrepancy between the two results is considered negligible.

Table 7. Comparison of exit gas composition (mole percent)

Species	Kyle[10]	Present
N_2	61.2	61.24
H_2	2.5	2.49
S_2	3.1	3.13
CO_2	6.6	6.62
SO_2	2.2	2.17
CO	2.1	2.12
COS	0.1	0.07
H_2O	20.3	20.31
H_2S	1.9	1.85
CS_2	<< 0.1	0.0001

All of the species included in both examples conducted so far are either simple molecules or compounds commonly encountered in engineering practice, and therefore the free energy of formation exists. In other applications of interest (such as the oxidation of metals in thermal plasma processing) the molecules are so complex, that the needed thermodynamic data is not readily available. For these cases the JANAF data base is often very useful. To demonstrate the usefulness of the data bank, we predict how the composition of a mixture containing 1 mol of lead, 1 mol of silicon, and 2.5 mol of oxygen shift as the temperature changes. The input data on elemental mass is listed in Table 8.

Table 8. Input elemental mass for metal oxidation (units in mol)

Elements	i	b_i No. of AW
Pb	1	1.0
Si	2	1.0
O	3	5.0

The results of this problem at 3500 K, 4000 K, 4500 K, and 5000 K are summarized in Table 9 along with the values obtained from SOLGAS-MIX. Only converged solutions from APOLLO are shown.

All the calculations presented in Table 9 are initialized with an initial mole number of 0.1 for all compounds, and a total of 1.0 mol for each phase. Despite the encouragement associated with the results, APOLLO could not handle the cases when the temperature is set at a value lower than or equal to 3000 K. At these temperatures, condensed phases co-exist. The problem in the code has been investigated by arbitrarily changing the initial guess. It was learned that APOLLO was able to give a good solution if a reasonable first estimate was given. This behavior can possibly be attributed to the use of $\ln(n_{p,i})$ as the dependent variables. This conclusion comes from the fact that the $\ln(n_{p,i})$'s are very sensitive to even small perturbation. This difficulty needs further study and as a consequence, numerical results as well as discussion on multiphase systems are not included in this report.

Table 9. Variations of equilibrium composition with temperature using JANAF data base (units in mol)

	Temperature							
	3500 K		4000 K		4500 K		5000 K	
Species	APOLLO	SOLGAS	APOLLO	SOLGAS	APOLLO	SOLGAS	APOLLO	SOLGAS
O	1.7143	1.1743	2.6740	2.6740	3.6097	3.6097	3.9361	3.9361
O_2	1.2856	1.2856	0.6161	0.6161	0.1833	0.1833	0.0531	0.0531
O_3	0.152(-5)	0.152(-5)	0.860(-6)	0.860(-6)	0.215(-6)	0.215(-6)	0.483(-7)	0.483(-7)
Pb	0.7878	0.7878	0.9178	0.9178	0.9733	0.9733	0.9908	0.9908
PbO	0.2120	0.2120	0.0820	0.0820	0.0266	0.0266	0.916(-2)	0.916(-2)
Pb_2	0.104(-3)	0.104(-3)	0.770(-4)	0.770(-4)	0.535(-4)	0.535(-4)	0.378(-4)	0.378(-4)
Si	0.269(-4)	0.269(-4)	0.494(-3)	0.494(-3)	0.633(-2)	0.633(-2)	0.0525	0.0525
SiO	0.9575	0.9574	0.9872	0.9872	0.9903	0.9902	0.9464	0.9464
SiO_2	0.0425	0.0425	0.0123	0.0123	0.344(-2)	0.344(-2)	0.106(-2)	0.106(-2)
Si_2	0.13(-10)	0.13(-10)	0.946(-9)	0.946(-9)	0.489(-7)	0.489(-7)	0.138(-5)	0.138(-5)
Si_3	0.11(-16)	0.11(-16)	0.21(-14)	0.21(-14)	0.33(-12)	0.33(-12)	0.25(-10)	0.25(-10)

4.2 Nonequilibrium Tests

To test the integrator routine, consider a simple model which resembles the situation that may be encountered in the system, where consecutive reactions take place, such as the pathway symbolized by the following:

$$A_1 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} A_2 \xrightarrow{k_2} A_3 \quad . \tag{47}$$

Where the first reaction is reversible followed by irreversible transformation from A_2 to A_3. For this system, the concentration of the species at any instant of time is governed by a system of ordinary differential equations

$$\frac{d}{dt}\{C\} = [A]\{C\} \tag{48}$$

where

$\{C\}$ = concentration vector

$[A]$ = matrix containing kinetic information.

To be complete, the matrix [A] is given as

$$[A] = \begin{bmatrix} -k_1 & k_1' & 0 \\ k_1 & -(k_1'+k_2) & 0 \\ 0 & k_2 & 0 \end{bmatrix} \tag{49}$$

For ease of numerical assessment we assign the values 1.0, 0.3, and 0.5 to rate constants k_1, k_1', and k_2 respectively along with the initial condition specified as $C_1(0) = 1.0$, $C_2(0) = 0.0$, and $C_3(0) = 0.0$. Based on

these values, the results of the simulation are shown in Figure 1 where species concentration are normalized by $C_1(0)$. Throughout the process, species 1 is continually diminished without interruption since the combined forward and reverse rates of the first reaction resulted in a net loss of the reactant. During the early period, the concentration of specie 1 is high enough to sustain the production of both intermediate and final products. At a time of approximately 1.5, the concentration of specie 2 starts to fall because the reactant cannot maintain its dominant intensity any longer due to its low concentration. Figure 2 is a plot of the error in our numerical prediction. The agreement is generally excellent in that the error in the solution never exceeds 2×10^{-5}. Most accurate results are seen to be associated with early times at which small time increments are used. However, the accuracy deteriorates quickly to a prescribed level (1×10^{-5}), in an exponential manner. The error tends to die out at a later stage after $t = 5$. Although it is not very clear why the errors behave as they do in Figure 2, it is speculated that such behavior may be linked to the curvature of the concentration curves and the step-size strategy implemented in the computer program.

To further establish the confidence, a more complex system is simulated, which arises from an auto catalytic reaction[11]. Since the detailed kinetics of this reaction is beyond the scope of the present context, we shall omit the derivation leading to a differential system of equations and use only their result. This may be given in the form of Equation (48) with the matrix [A] modified to

$$[A] = \begin{bmatrix} -0.04 & 0 & 10^4 C_2 \\ 0.04 & -3 \times 10^7 C_2 & -10^4 C_2 \\ 0 & 3 \times 10^7 C_2 & 0 \end{bmatrix} \tag{50}$$

There are two apparent difficulties in this problem. First, the matrix [A] is not constant; implying the presence of nonlinearities. Second, the rate constants vary by nine orders of magnitude signifying the existence of a

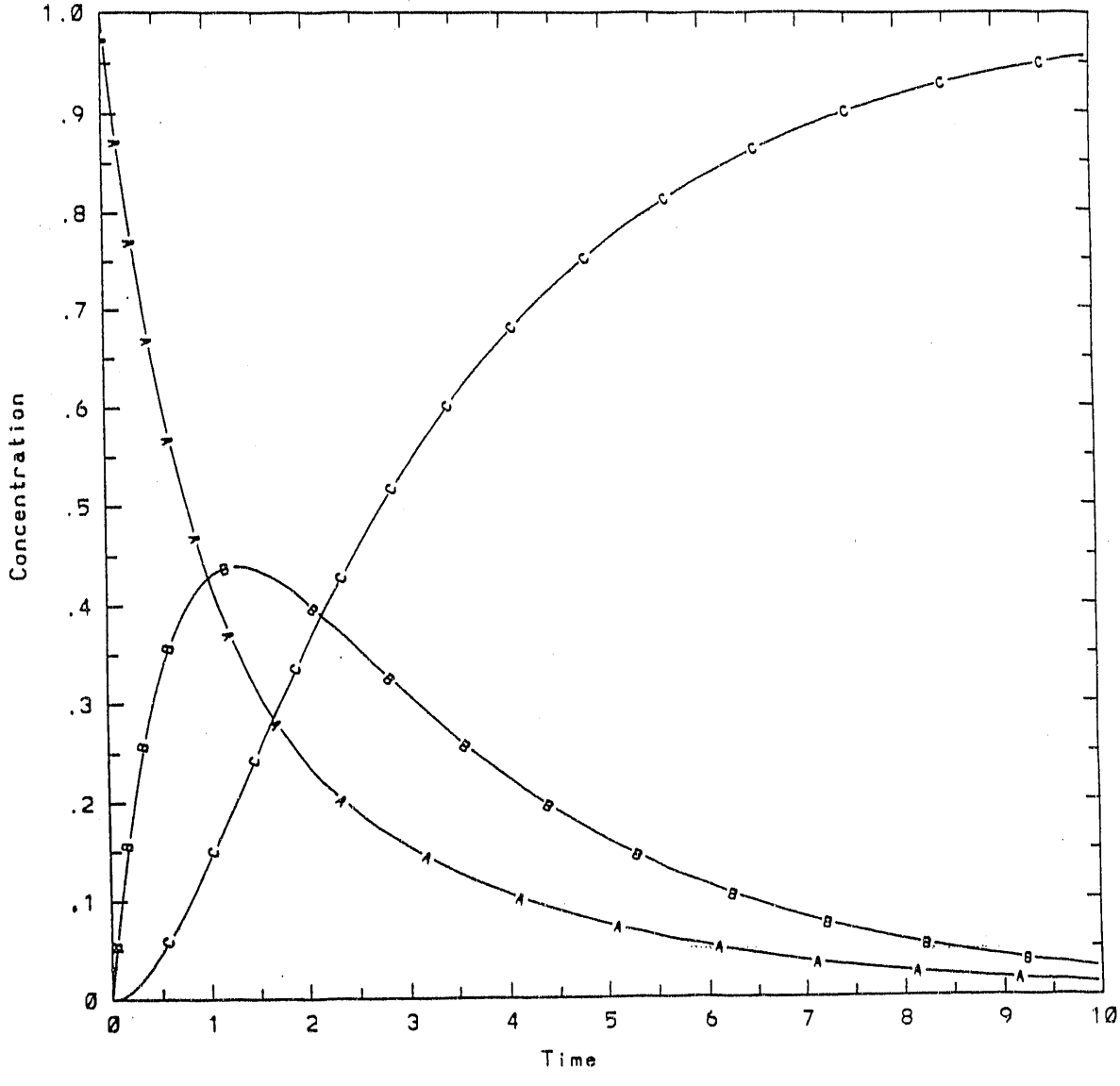

Figure 1. Temporal evolution of chemical species.

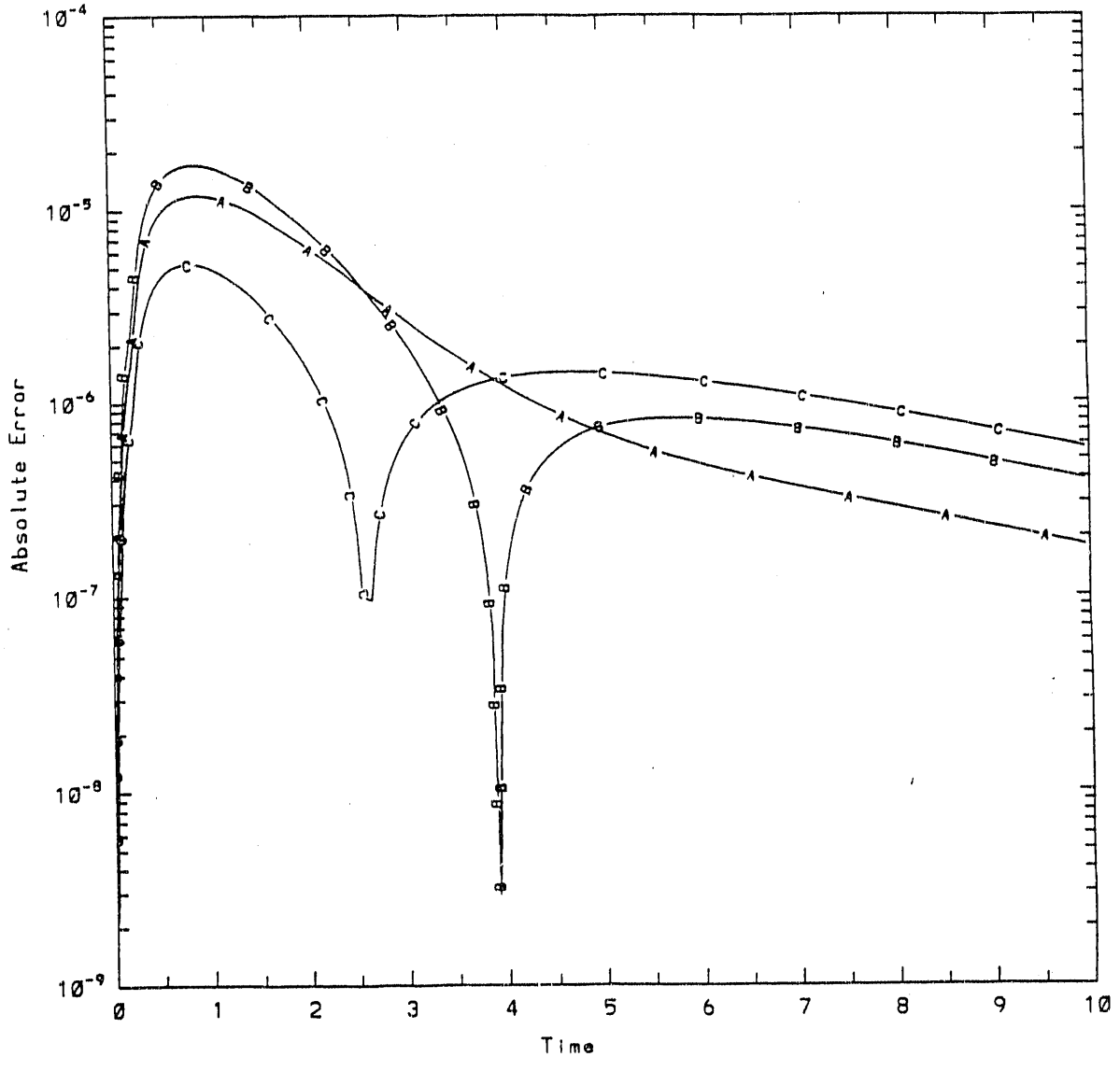

Figure 2. Error propagation.

thin region where concentration of at least one component changes drastically. These two features have been used as key aspects in examining the capability of various software packages. Equations (48) and (50) were subjected to the initial condition $C_1(0) = 1$, $C_2(0) = 0$, and $C_3(0) = 0$. They have been solved using different solvers with the outcomes summarized in Reference 11. We now solve this problem using the APOLLO integrating scheme. The results are presented in Figure 3. Qualitatively, the scheme performed exceptionally well with a peak concentration of species 2 of $.36 \times 10^{-4}$ which is very favorable with the value of $.35 \times 10^{-4}$ obtained by other methods. To illustrate the magnitude of the numerical error, we prepared Table 10 for comparison with other proven computer codes at three different times (i.e., t = 1.0, 4.0, 10.0. at a specified tolerance of 10^{-6}).

From the tabular data above, one may conclude that APOLLO is capable of giving reasonable, if not superior, answers as other software packages predicted. One striking thing is the success of APOLLO in producing a stable solution at a tolerance of 10^{-4} at which, as mentioned in Reference 11, some codes such as DVERK, ODE, DGEAR, LSODE, and EPISODE fail because of the growth of the error due to large tolerances.

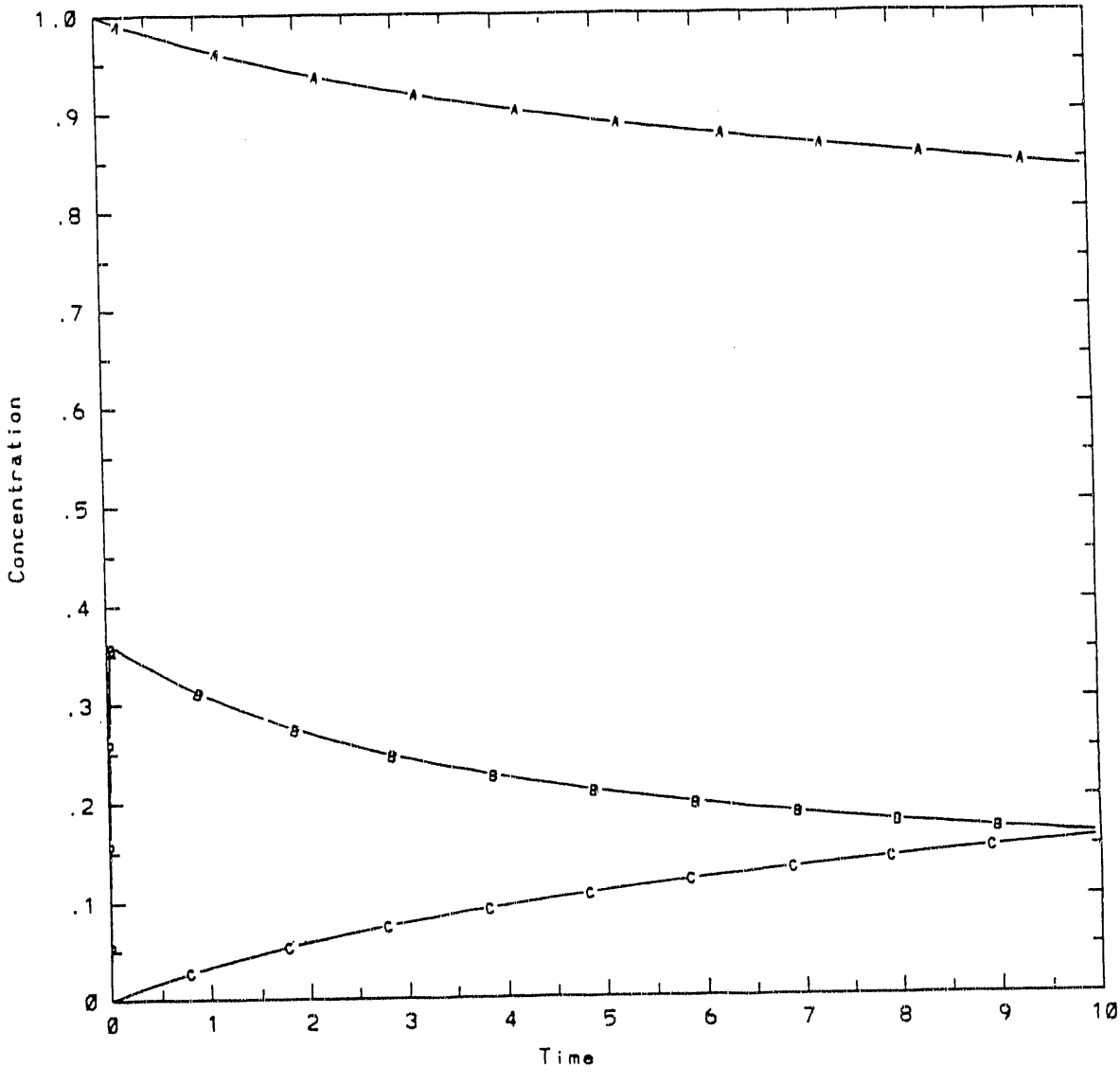

Figure 3. Species evolution.

Table 10. Comparison of normalized concentration of stiff example[11]

Codes	Time	Concentrations C_1	C_2	C_3
EXACT	1.0	0.966	0.307(-4)	0.335(-1)
	4.0	0.906	0.224(-4)	0.944(-1)
	10.0	0.841	0.162(-4)	0.159
APOLLO	1.0	0.966	0.307(-4)	0.335(-1)
	4.0	0.906	0.224(-4)	0.945(-1)
	10.0	0.841	0.162(-4)	0.159
STIFF3	1.0	0.966	0.307(-4)	0.335(-1)
	4.0	0.905	0.224(-4)	0.945(-1)
	10.0	0.841	0.162(-4)	0.159
DGEAR	1.0	0.966	0.309(-4)	0.335(-1)
	4.0	0.905	0.224(-4)	0.944(-1)
	10.0	0.841	0.162(-4)	0.159
EPSIODE	1.0	0.966	0.307(-4)	0.335(-1)
	4.0	0.905	0.224(-4)	0.945(-1)
	10.0	0.841	0.162(-4)	0.159
ODE	1.0	0.966	0.307(-4)	0.335(-1)
	4.0	0.905	0.222(-4)	0.945(-1)
	10.0	0.841	0.159(-4)	0.159

5. SUMMARY AND FUTURE DIRECTION

The APOLLO computer code has been developed for the analysis of complex chemical systems that involve multiple reactions, which can either be at equilibrium or nonequilibrium. Test cases conducted in this study indicated that the code can be used successfully for a wide variety of chemical systems. However, there are two areas that need attention. One of them is the extension of the equilibrium calculation so that it can be usable in condensed multiphase systems, and the other is the modification of the iterative algorithm to make it less susceptible to initial guesses, as well as an ability to self-readjust these values. Such incorporation would make APOLLO adaptable to an even larger variety of applications in chemically reacting flow systems.

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