Integration of systems of equations in chemical kinetics

Thomas Ernest Michels
Iowa State University

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Integration of systems of equations in chemical kinetics

by

Thomas Ernest Michels

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I. INTRODUCTION

Of the many methods available for the numerical solution of ordinary differential equations or systems of coupled ordinary differential equations, most have specific advantages applicable to special types of problems. Several general methods have become popular, such as Runge-Kutta or predictor-corrector techniques, because of their wide applicability. However, there is a class of problems that arises in fields such as chemical kinetics for which there do not seem to be many accurate and simple methods of solution available.

In particular, there are types of equations in the field of chemical kinetics which describe burning processes and give dynamic concentrations of constituents produced during the burning. These equations are characterized by widely varying time dependent coefficients of the dependent variable and are greatly influenced by the slow or fast intercoupled variations of the dependent variables in the system. These systems are highly nonlinear, and because of the strong interdependence of the components and high values of the derivatives, integration of these systems can be quite time consuming on present day large scale digital computers.

The integration interval of these equations is closely related to the largest coefficient, which represents a rate at which chemical reactions take place, while the region of integration represented in the time domain is determined by
the smallest or slowest reaction rate. Because these re-
action rates have such a wide separation of values within a
given system, they are sometimes referred to as "stiff" equa-
tions, or equations with widely varying time constants.

These dynamic equations which represent the burning
process are referred to as the "kinetic equations". They
are written as a system of nonlinear ordinary differential
equations in the form

$$\frac{dx}{dt} = \mathbf{f}(\mathbf{x}, t)$$

The nonlinear functions \( \mathbf{f}(\mathbf{x}, t) \) contain the widely varying
rate constants, \( k(t) \), and are expressed in the general form

$$f_m(\mathbf{x}, t) = \sum_{i,j} k_{ij}^{(m)}(t)x_j + \sum_{i,j,k} k_{ijk}^{(m)}(t)x_jx_k$$

$$+ \sum_{i,j,k,l} k_{ijkl}^{(m)}(t)x_jx_kx_l + \ldots$$

This paper is concerned with the study of numerical
methods of solution of these equations and in this study
the rate constants, \( k(t) \), are written as implicit functions
of time, \( t \). They enter into the equations with temperature,
\( T \), which is assumed to have some predetermined profile varying with time. The rate constants are of the form

$$k_i(t) = A_i \exp\left(-\frac{B_i}{RT(t)}\right)$$

where \( A_i \) and \( B_i \) are constants which have been determined
experimentally. \( R \) is the ideal gas constant.

Analytical solutions of the kinetic equations have been obtained by a number of researchers (44, 45, 15, 29, 67) with varied success, but as Mah et al. (36, p. 620) states, "The principal drawbacks of the analytical approach is the oversimplification of the situation and the sensitivity of the form of the solution to the exact simplifying assumptions made."

Another approach to the solution of the kinetic equations is discussed in a paper by Mah et al. (36). He describes the work of several authors to obtain solutions by the use of analog computers. Although it is possible to simulate nonlinear systems on these computers, he maintains that, in general, it is prohibitively expensive to study large systems since they require a large number of nonlinear function generators. Mah also mentions the loss of accuracy which arises in the use of analog techniques.

Attempts have also been made by a number of researchers to efficiently and accurately integrate the kinetic equations by using numerical techniques on large scale digital computers. The early investigators (58, 42, 43, 17, 35, 13, 62, 63, 41, 33) found the requirement of excessive computer time prohibitive in performing extensive study of the behavior of various burning processes. Integration time steps need to be so small for general Runge-Kutta and predictor-corrector methods that computer times of 10-100 hours on
large scale computers are required for their successful solution.

Various implicit and explicit schemes (63, 41, 17, 33) have been tried, but savings of only a factor of 10 in computer time have been exhibited. Lomax and Bailey (33) give a good résumé of various techniques for the integration of equations in chemical nonequilibrium. They analyze various Runge-Kutta, predictor-corrector, and implicit techniques which other authors have tried, and point out particular problem areas. Seinfeld et al. (57) also give a résumé of existing methods.

Moretti (41) gives calculations for the combustion of hydrogen and air at a constant pressure. He uses a truncated Taylor's series expansion to linearize the system and reforms the equations, using a product form similar to that used by Tannehill and McMillen (60) for the quadratic terms. He then solves an eigenvalue problem. De Groat and Abbett (17) discuss a method which assumes a solution of the form

\[ x_i = \sum_{k=0}^{2} \hat{d}_{ik} \xi^k \]

which is substituted into the equations to form residues which he requires to go to zero. His method is an order of magnitude faster than a fourth order Runge-Kutta method. He mentions Moretti's method and states that it is not useful for large systems (>9 x 9).
Magnus and Schechter (35) have studied a method which shows saving of a factor of 10 or 20 in computer time over a fourth order Runge-Kutta method. They integrate a system of hydrogen-air chemistry by using a Padé approximation to obtain various integration formulas. Gear (19, 20) gives an efficient scheme for the solution of stiff equations which uses a predictor and corrector form. He first linearizes the right hand sides of the equations and then performs an iteration.

Liniger and Willoughby (32) give a wide range of techniques that employ various linearizations and iteration methods for nonlinear stiff equations which seem to be worthwhile, but most have not been tried on the kinetic equations in the literature.

Opsahl and Seagrave (44, 45) are the first to give a simplified method for nonequilibrium calculations in oscillatory combustion based on the chemical knowledge of the reactions. They also draw conclusions on a method based on Bellman's (5) matrix methods, and give a detailed summary of reaction coefficient expressions.

Recently, Tannehill and McMillen (60) have devised a scheme employing a combination of a linearization method and improved Euler technique which gives good results in the problems he has investigated in rocket reaction.

The purpose of the research described in this paper
was to determine an efficient and accurate numerical method for the solution of kinetic equations that is applicable to oscillatory combustion. This study therefore represents an extension of the work of Opsahl and Seagrave (45). The problems investigated represent the dynamic production (or depletion) of various components that react in a controlled burning process where reaction rate data has already been established. Problems which contain the well known reactions in the burning of carbon monoxide and oxygen (CO–O₂) are discussed, and the results of oscillatory combustion in the methane-air system defined by Opsahl and Seagrave are presented.

Several linearization methods were investigated by the author and one method was found to be superior for the oscillatory study. This method was found to be applicable to a new approach in solving the reduced canonical forms of the equations which for large systems showed considerable saving in computer time requirements over integrations of the full system. Increases of integration step sizes of up to 10⁵ over Runge-Kutta methods have been realized.

One of the objectives of this paper is to formalize the problem in chemical kinetics for the numerical analyst, and in this light, Chapter II is devoted to deriving the general diffusion equation that is basic in a dynamic burning process. In Chapter III, existence and uniqueness
conditions are established and comparison of various linearization methods are presented and compared with one another and with the fourth order Runge-Kutta method.
II. DEVELOPMENT OF DIFFUSION AND KINETIC EQUATIONS

The purpose of this chapter is to trace the development of the general mass transport or diffusion equations that arise in chemical transport processes. This is done not as a tutorial for the chemist or chemical engineer, but more to provide a background for the researcher working in the field of numerical analysis. It is believed that an understanding of the physical processes which a set of equations represent can provide added insights into the solution of those equations.

This chapter therefore is aimed primarily at the numerical analyst, and concerns itself with the development of a few of the basic theories of mass transport or diffusion processes. The general diffusion equation is developed following Bird et al. (9), and the various assumptions and approximations are made to the equations to arrive at the kinetic equations which are the subject of this paper.

A. The General Problem

Consider a burning process, such as the burning of coal in a cylinder open at one end. Assume that we are interested in determining the amounts of various materials produced at each instant of time as a function of the temperature or pressure inside the cylinder. Schematically, the process can be illustrated as shown in Figure 1. The cylinder is divided
Figure 1. Model combustor representing the burning process into the flame, cooling, and exhaust sections and represents a model combustor.

The problem involves a certain amount of coal heated or burned in the flame section at a temperature, $T$. We wish to measure the various amounts of materials produced as they travel up through the combustor in the cooling section, and finally through a section near the top called the exhaust section and out into the open air. This is the model considered by Opsahl (44) in his dynamic calculations investigation.

The investigation can be made by assuming a particular temperature profile through the combustor or by calculating
it, employing various chemical processes well known in the field of chemical engineering. The problems investigated in this paper all assume a precalculated temperature profile and are described in detail later. A temperature profile may look like that shown in Figure 2.

Thus we have a high temperature of approximately $3000^\circ$K applied in the flame section by some type of burner. The resulting gaseous mixture flowing up through the burner experiences a temperature in the cooling section which slowly decreases until the exhaust section is reached, where the temperature is approximately $500^\circ$K.

The lengths of each section in the combustor considered by Opsahl (44) are as follows:

<table>
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<tr>
<td>Flame section</td>
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</tr>
<tr>
<td>Cooling section</td>
<td>10.0 feet</td>
</tr>
<tr>
<td>Exhaust section</td>
<td>0.1 feet</td>
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If we consider a particle of mass inside the gaseous mixture that is flowing up through the model combustor at a constant rate of ten feet per second, the total time the particle is in the combustor is approximately one second. The problem is therefore to calculate the amount of mass of a particular resultant compound or species produced in the burning process as it travels up through the combustor as a function of time. Other models can be proposed which may require longer burning times of course.

B. Equation of Continuity and Mass Balance

To study the rate of change of material at a particular position within the combustor, we look at an infinitesimal region and apply the statement of conservation of mass. That is, for a pure gas flowing through a cylinder such as our model combustor, the time rate of change of material accumulating in this microscopic region can be written as the difference between the mass flowing in and the mass flowing out in an infinitesimal amount of time.

The infinitesimal region is defined in Euclidian three space as a box of dimension $\Delta x, \Delta y, \Delta z$ as shown in Figure 3.

The problem is to determine the total amount of material flowing into the box minus the total amount flowing out. The amount of difference is the accumulation (production) or depletion as the case may be. The equation of mass balance is
Thus the time rate of change of mass within the element of volume $\Delta x, \Delta y, \Delta z$ can be written as

$$\frac{\partial \rho}{\partial t} \Delta x \Delta y \Delta z$$

where $\rho$ is the density of material (mass/unit volume).

The time rate of change across the $\Delta x, \Delta z$ face can be written as the amount flowing in at $y$ minus the amount flowing out at $y + \Delta y$. The amount at $y$ is $(\rho v_y) |_{y} \Delta x \Delta z$ where $v_y$ is the $y$ component of velocity in feet/second. The amount flowing out at $y + \Delta y$ is then $(\rho v_y) |_{y+\Delta y} \Delta x \Delta z$. Similar
expressions can be written for the flow of mass across the other faces of the volume element.

The time rate of change of mass for this infinitesimal region is then

\[
\frac{\partial \rho}{\partial t} \Delta x \Delta y \Delta z = (\rho v_x|_{x} - \rho v_x|_{x+\Delta x}) \Delta y \Delta z + (\rho v_y|_{y} - \rho v_y|_{y+\Delta y}) \Delta x \Delta z + (\rho v_z|_{z} - \rho v_z|_{z+\Delta z}) \Delta x \Delta y
\]  

(2.1)

If we divide Equation 2.1 by \( \Delta x \Delta y \Delta z \) we have

\[
\frac{\partial \rho}{\partial t} = \frac{(\rho v_x|_{x} - \rho v_x|_{x+\Delta x})}{\Delta x} + \frac{(\rho v_y|_{y} - \rho v_y|_{y+\Delta y})}{\Delta y} + \frac{(\rho v_z|_{z} - \rho v_z|_{z+\Delta z})}{\Delta z}
\]  

(2.2)

and in the limiting process Equation 2.2 becomes

\[
\frac{\partial \rho}{\partial t} = -\left(\frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z)\right)
\]  

(2.3)

Equation 2.3 is defined as the "equation of continuity" and describes the time rate of change of density at a fixed point in Euclidean three space that results from the changes in the mass velocity vector \( \overline{\rho v} \) where \( \overline{v} \) is composed of the components \( v_x, v_y, v_z \). Equation 2.3 can also be recognized as the divergence of \( \overline{\rho v} \) or

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot \overline{\rho v} = -\text{div} \overline{\rho v}
\]  

(2.4)
If Equation 2.3 is differentiated and the derivatives of $\rho$ are placed on the left hand side we have

$$\frac{\partial \rho}{\partial t} + v_x \frac{\partial \rho}{\partial x} + v_y \frac{\partial \rho}{\partial y} + v_z \frac{\partial \rho}{\partial z} = -\rho \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) . \quad (2.5)$$

The substantial time derivative $\frac{D \rho}{D t}$ is defined by

$$\frac{D \rho}{D t} = \frac{\partial \rho}{\partial t} + v_x \frac{\partial \rho}{\partial x} + v_y \frac{\partial \rho}{\partial y} + v_z \frac{\partial \rho}{\partial z}$$

and represents the time rate of change of density as seen by an observer floating along with it in space. Thus Equation 2.5 can be written as

$$\frac{D \rho}{D t} = -\rho (\nabla \cdot v) .$$

It should be noted here that in an incompressible mixture the density, $\rho$, is constant and therefore

$$\nabla \cdot v = 0 . \quad (2.6)$$

In determining the true rate of change of mass flowing in the mixture, we also note that Equations 2.3 or 2.4 do not have strict equality for a particular component, but rather that the mass balance equation must be satisfied. That is,

$$\text{ACCUMULATION} = \text{INPUT} - \text{OUTPUT} + \text{PRODUCTION}$$

Thus Equation 2.4 becomes, for a particular species $i$

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i v) = \text{rate of production} = r_i \quad (2.7)$$
where \( r \) is the mass rate of production per unit volume and is dependent upon the chemical reactions considered in the process.

Equation 2.7 represents the mass transport process for a single particle traveling at any velocity through the combustor. In reality we must consider a multicomponent system of many different particles all traveling at different velocities and therefore the problem can become quite complex. In the problems considered in this paper, molar concentrations, \( c \), are used which are analogous to density, and are defined by a mass in units called "moles". The term, \( c_i \), therefore refers to moles of component \( i \) per unit volume.

Furthermore, we define an average velocity \( \omega \) for the mixture, called the molar average velocity, as

\[
\omega = \frac{\sum_i c_i u_i}{\sum_i c_i}
\]

where \( u_i \) is the velocity of a particular component in the gaseous mixture, and the summation is over all components considered.

Normally, in flow of gaseous systems, we are interested in the velocity of a component with respect to the molar velocity. This velocity is called the diffusion velocity and is defined for the \( i^{\text{th}} \) component in the mixture by
The diffusion process is a rate of transport due to a concentration gradient of component \( i \) in which each component in the mixture diffuses at different and widely varying rates. As will be shown, this presents an enormous problem in the calculation of these components.

Normally, Equation 2.7 is written in terms of fluxes of materials (mass/area-time) or a mass flux vector, \( \eta \), given by
\[
\eta_i = \rho \omega_i
\]
Thus, Equation 2.7, representing the diffusion process for component \( i \) is
\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot \eta_i = r_i
\] (2.8)

It is not the intent or within the scope of this paper to derive Fick's Law of Diffusion. We will only state that the flux density \( \eta_i \) can be written as
\[
\eta_i = \rho_i \vec{v} - \rho \mathcal{D}_{ij} \nabla \cdot \omega_i
\]
where \( \omega_i \) is the mass fraction of component \( i \) and is equal to \( \rho_i / \rho \). \( \mathcal{D}_{ij} \) is the diffusivity constant of proportionality that represents the transport of component \( i \) from a diffusion process which involves components \( i \) and \( j \). The total
mass density of the mixture is \( \rho \) and the density of component \( i \) is \( \rho_i \). Thus Equation 2.8 becomes

\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \vec{v} - \nabla \cdot \rho_i \mathcal{D}_{ij} \nabla \cdot \omega_i = r_i
\]  

(2.9)

One normal starting point in studying diffusion problems is to assume constant total mass density, \( \rho \), and diffusivity \( \mathcal{D}_{ij} \). In this case, Equation 2.9 becomes

\[
\frac{\partial \rho_i}{\partial t} + \rho_i \nabla \cdot \vec{v} + (\vec{v} \cdot \nabla) \rho_i - \mathcal{D}_{ij} \nabla^2 \rho_i = r_i
\]  

(2.10)

But from Equation 2.6, when \( \rho \) is a constant, \( \nabla \cdot \vec{v} = 0 \), and therefore Equation 2.10 becomes

\[
\frac{\partial \rho_i}{\partial t} + (\vec{v} \cdot \nabla) \rho_i - \mathcal{D}_{ij} \nabla^2 \rho_i = r_i
\]  

(2.11)

If Equation 2.11 is divided by the molecular weight, \( m_i \), of component \( i \), and since \( c_i \) is the number of moles of component \( i \) per unit volume, then

\[
c_i = \frac{\rho_i}{m_i}
\]

and Equation 2.11 becomes

\[
\frac{\partial c_i}{\partial t} + (\vec{v} \cdot \nabla) c_i - \mathcal{D}_{ij} \nabla^2 c_i = R_i
\]  

(2.12)

\( R_i \) is defined as the molar rate of production of component \( i \) per unit volume that results from the reactions in the
burning process and is equal to \( r_i/m_i \).

Equation 2.12 is the basic equation representing the diffusion process for burning in the model combustor, assuming constant density \( \rho \) and diffusivity \( \mathcal{D}_{ij} \) for a single component \( i \). If there are \( N \) components considered in the burning process, there results a system of \( N \) equations, one for each type of component or species considered.

C. Approximations to Obtain the Kinetic Equations

When written in rectangular coordinates, the diffusion equation representing the burning process is

\[
\frac{\partial c_i}{\partial t} + \left( v_x \frac{\partial c_i}{\partial x} + v_y \frac{\partial c_i}{\partial y} + v_z \frac{\partial c_i}{\partial z} \right) - \mathcal{D}_{ij} \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2} \right) = R_i \quad .
\]

(2.13)

From the geometry of our model combustor, the diffusion equation is more usable in the form of cylindrical coordinates. If we apply the usual transformation, Equation 2.13 becomes

\[
\frac{\partial c_i}{\partial t} + \left( v_r \frac{\partial c_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial c_i}{\partial \theta} + v_z \frac{\partial c_i}{\partial z} \right) - \mathcal{D}_{ij} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_i}{\partial \theta^2} + \frac{\partial^2 c_i}{\partial z^2} \right) = R_i \quad .
\]

(2.14)

The coordinate system for the combustor is shown in Figure 4.
If we follow the assumptions made by Opsahl (44), the combustor is modeled as a flow reactor which assumes angular symmetry ($\frac{\partial c_i}{\partial \theta} = 0$) and a one dimensional velocity profile ($v_\theta, v_r = 0$). The diffusion Equation 2.14 then becomes

$$\frac{\partial c_i}{\partial t} + v_z \frac{\partial c_i}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right) + \frac{\partial^2 c_i}{\partial z^2} = R_i.$$  

If steady state conditions are assumed, that is

$$\frac{\partial c_i}{\partial t} = 0,$$

and integration over the radius, $r$, is performed from 0 to
R, where R is the radius of the cylinder, then

\[
\int_{0}^{R} v_z \frac{\partial c_i}{\partial z} r dr - \oint_{ij} \int_{0}^{R} \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right) dr + \int_{0}^{R} \frac{\partial^2 c_i}{\partial z^2} r dr
\]

\[
= \int_{0}^{R} r R_1 dr .
\]

Under the assumption of plug flow such that a disc perpendicular to the z axis is flowing upward along the z axis, then \( \frac{\partial c_i}{\partial r} = 0 \), and we have

\[
v_z \frac{\partial c_i}{\partial z} \left( \frac{R^2}{2} \right) - \oint_{ij} \int_{0}^{R} \frac{\partial^2 c_i}{\partial z^2} r dr = R_i \left( \frac{R^2}{2} \right) .
\]

Because of high velocities and corresponding Reynolds numbers encountered in the combustor considered, the Peclet number for mass transfer is high. Since the Peclet number is related to the ratio of the convective mass transfer over the mass transfer by diffusion, the remaining integral, which represents the increase of component i due to diffusion is small and can be omitted (Opsahl, 44, p. 26).

Thus under this assumption, we have

\[
v_z \frac{\partial c_i}{\partial z} \left( \frac{R^2}{2} \right) = R_i \left( \frac{R^2}{2} \right) .
\]

The velocity of gaseous flow, \( v_z = \frac{dz}{dt} \), and the kinetic equation for mass flow for component i is
\[
\frac{dc_i}{dt} = R_i \quad \text{(2.15)}
\]

Equation 2.15 is the kinetic equation which when solved gives the varying amount of component \(i\) considered in the burning process represented by our model combustor. There is one equation for each component in the system, and therefore the total burning process is represented by the system of equations

\[
\frac{dc_i}{dt} = R_i \quad i=1,2,\ldots,n
\]

when \(n\) components are considered. This is a fairly simple looking set of equations; however, as has been stated, there are many problems encountered in its solution. The molar rate of production of compound \(i\) per unit volume, \(R_i\), becomes highly nonlinear and intercoupled as more reactions are introduced and this, coupled with the widely varying reaction rates, makes its solution by usual integration techniques extremely difficult.

As an example of the system of equations arising from the kinetic equations consider a combustion process of carbon monoxide in oxygen, labeled the CO-O\(_2\) system. From the chemistry involved, five reactions are important (44, p. 79). They are:

1. \(\text{CO} + \text{O} \xrightarrow{k_1} \text{CO}_2\)
In reaction 1, CO (carbon monoxide) and O (atomic oxygen) combine at a reaction rate $k_1$ to produce CO$_2$ (carbon dioxide). O (atomic oxygen) combines with O$_3$ (ozone) at a reaction rate $k_2$ to form two molecules of oxygen (O$_2$) and so on. The reaction rates, $k_i$, are usually written as implicit functions of time for an assumed time variant temperature profile.

For simplicity, we will rewrite the kinetic expressions in terms of moles rather than concentrations, using $x_i = c_i V$, where $V$ is the volume of the mixture. Then $x_1$ = moles of CO, $x_2$ = moles of O$_2$, $x_3$ = moles of CO$_2$, $x_4$ = moles of O and $x_5$ = moles of O$_3$. Here $k'_i = k_i / V$ and the primes will be suppressed in the material that follows. The kinetic equations become

$$\frac{dx_1}{dt} = -k'_1 x_1 x_4 + k_4 x_3$$

$$\frac{dx_2}{dt} = -k'_3 x_2 x_4 - k_5 x_2 + 2k'_2 x_4 x_5$$

$$\frac{dx_3}{dt} = -k_4 x_3 + k'_1 x_1 x_4$$
Many researchers have published reaction coefficient data (see Opsahl for an extensive bibliography). These data are expressed in the form

\[ k_i = A_i \exp\left(-\frac{B_i}{RT}\right) \]

where \( A_i \) and \( B_i \) are constant coefficients dependent upon the reaction involved and \( T \) is the temperature applied. \( R \) is the ideal gas constant. These reaction coefficients must be determined at each step in the integration as Equations 2.16 are solved.

Equations 2.16 are listed in the usual form for calculation and as was stated earlier, many difficulties arise in their solution. They are a system of coupled nonlinear ordinary differential equations which require very small time steps to perform accurate integrations when using Runge-Kutta or predictor-corrector methods.

A three dimensional phase plane plot of a typical variable is shown in Figure 5.

With the integration performed over time and a constant temperature, very large slopes are encountered (of order \( 10^4 \) moles/sec) for high temperatures. Since the components react
Figure 5. Phase plane plot of the concentration of CO in CO-O$_2$ system at varying rates, depending upon the temperature, each may experience large slopes at various times. Solutions are also dependent upon initial conditions. Figure 5 is obtained by using initial conditions of the equilibrium values at 1000°K.

Figure 5 also suggests, as pointed out by Maple (37), that some advantage may be realized if integration is performed over temperature rather than time and that this may be a possible method of attacking the problem. If one solution is known for a given temperature, then integration can be performed. We may also think of making the set of
equations into a boundary value problem if a set of solutions is known for two lines of constant temperature, where one set can be the equilibrium values. These equilibrium values represent a solution to the problem when \( \frac{dx_i}{dt} \), \( i=1,2,...,5 \) equals zero. If we assume some profile of temperature \( T \) as a function of time \( t \) then the transformation can be made in the following way.

Let

\[ T = f(t) \]

and

\[ \frac{dT}{dt} = \frac{df(t)}{dt} \]

Then for

\[ \frac{dx_i}{dt} = R_i(x_1,x_2,...,x_n,t) \]

we divide by \( \frac{dT}{dt} \) to obtain

\[ \frac{dx_i}{dT} = R_i(x_1,x_2,...,x_n,T) \]

For oscillatory combustion, \( T \) assumes a wave form of varying amplitude, \( A \), oscillating at a frequency, \( \omega \), with mean at \( T_0 \). Then we have

\[ T = T_0 + A \sin(2\pi \omega t) \]

and
\[ \frac{dT}{dt} = 2\pi \omega A \cos(2\pi \omega t) . \]

The equations can then be integrated over a constant time by varying temperature in the form

\[ \frac{dx_i}{dT} = \frac{R_i(x_1, \ldots, x_n, T)}{2\pi \omega A \cos(2\pi \omega t)} . \]

Again, there may be some advantage to this in the numerical integration; however this has not been tried and remains a good problem for future consideration.
III. SOLUTION OF THE KINETIC EQUATIONS

The system of Equation 2.15 is written for equation i as

\[
\frac{dx_i(t)}{dt} = f_i(x_1, x_2, \ldots, x_n, t), \quad i=1,2,\ldots,n
\]

or more compactly as

\[
\frac{d\vec{x}(t)}{dt} = \vec{f}(\vec{x}, t) \quad (3.1)
\]

To obtain a solution to the kinetic equations we then solve the initial value problem

\[
\frac{d\vec{x}(t)}{dt} = \vec{f}(\vec{x}, t)
\]

\[
\vec{x}(0) = \vec{a} \quad (3.2)
\]

where \( \vec{f}(.) \) is defined in \( \mathbb{R}^{n+1} \) and \( \vec{a} \) is a vector of constants representing initial concentrations of \( x_i \) at time zero. The vector of concentrations \( \vec{x}(t) \) is a solution to the initial value problem in the time interval \( 0 \leq t \leq t_{\text{max}} \) if the point \( \vec{x}(t) \) satisfies the system

\[
\frac{d\vec{x}(t)}{dt} = \vec{f}(\vec{x}, t)
\]

such that it is contained in \( \mathbb{R}^{n+1} \) for all \( t \) in \( 0 \leq t \leq t_{\text{max}} \).

System 3.1 is nonlinear if any of its dependent variables or their derivatives appear to some power other than one, or any term is represented as a product of dependent
variables. Necessarily, we hope that the system possesses a unique solution for a given set of initial conditions to make the problem practical in chemical kinetics. Normally, it is not an easy task to show uniqueness in nonlinear systems; however it can be done for the kinetic equations in general as follows.

A. Existence and Uniqueness

By making use of a simplified system of equations which contains types of terms realized in kinetic equations, we can write

\[
\frac{dx_1(t)}{dt} = k_1(t)x_1(t) + k_2(t)x_2(t)^2 + k_3(t)x_1(t)x_2(t)
\]

\[
\frac{dx_2(t)}{dt} = k_4(t)x_1(t)^2x_2(t)
\]

(3.3)

with initial conditions

\[ x_1(0) = \eta_1 \]

\[ x_2(0) = \eta_2 \]

representing the initial value problem

\[
\frac{dx_i(t)}{dt} = f_i(x, t) , \quad x_i(0) = a_i \quad i=1,2 . \quad (3.4)
\]

If we assume that the functions \( f(x, t) \) satisfy the two conditions:
i) \( f(\mathbf{x}, t) \) is defined and continuous in the region 
\[ 0 \leq t \leq t_{\text{max}}, \quad -\infty < x_i < \infty, \quad l=1,2. \]

ii) There exists a Lipschitz constant, \( L \), for arbitrary \( t \) in the interval \([0, t_{\text{max}}]\) and for any two vectors \( \mathbf{x}(t) \) and \( \mathbf{x}^*(t) \) in 
\[ \| f(\mathbf{x}, t) - f(\mathbf{x}^*, t) \| \leq L \| \mathbf{x} - \mathbf{x}^* \| \]
where \( \| \cdot \| \) is the vector norm, then the existence and uniqueness theorem can be expressed as follows:

**THEOREM I.** For the initial value problem 3.4, if \( f(\mathbf{x}, t) \) satisfies conditions i) and ii) for a given vector, \( \mathbf{a} \), then there exists exactly one solution, \( \mathbf{x}(t) \), with the following properties:

a) \( \mathbf{x}(t) \) is continuous and continuously differentiable for \( t \) in the interval \( 0 \leq t \leq t_{\text{max}} \)

b) \( \frac{d\mathbf{x}}{dt} = f(\mathbf{x}, t) \) for \( 0 \leq t \leq t_{\text{max}} \)

c) \( \mathbf{x}(0) = \mathbf{a} \).

Proofs of Theorem I are given by Henrici (23, p. 113), Struble (59, p. 43) and others.

Returning to our simplified problem in Equations 3.3, we note that condition i) must be satisfied by the physical constraints of the problem and that no singularities exist or else the physical situation could not exist. Condition ii) can be shown as follows. We use the first norm
\[ \|x\|_1 = \sum_{i=1}^{2} |x_i| \]

and write,

\[
\| \bar{f}(\bar{x}, t) - \bar{f}(\bar{x}^*, t) \| = |f_1(\bar{x}, t) - f_1(\bar{x}^*, t)| + |f_2(\bar{x}, t) - f_2(\bar{x}^*, t)|
\]

\[
= |k_1x_1 + k_2x_2^2 + k_3x_1x_2 - k_1^*x_1^* - k_2^*x_2^2 - k_3^*x_1^*x_2^*|
+ |k_4x_1^2x_2 - k_4x_1^*x_2^*|
\]

\[
= |k_1(x_1 - x_1^*) + k_2(x_2 - x_2^*)(x_2^* + x_2) + k_3x_1(x_2 - x_2^*)|
+ k_3x_2^*(x_1 - x_1^*)| + |k_4x_1^2(x_2 - x_2^*) + k_4x_2^*(x_1^2 - x_1^*2)|
\]

\[
= |(k_1 + k_3x_2^*)(x_1 - x_1^*) + (k_2(x_2^* + x_2) + k_3x_1)(x_2 - x_2^*)|
+ |k_4x_1^2(x_2 - x_2^*) + k_4x_2^*(x_1 + x_1^*)(x_1 - x_1^*)|
\]

By making use of the triangle inequality and by collecting terms, we have

\[
\| \bar{f}(\bar{x}, t) - \bar{f}(\bar{x}^*, t) \| \leq (|k_1 + k_3x_2^*| + |k_4x_2^*(x_1 + x_1^*)|)(|x_1 - x_1^*|)
+ (|k_2(x_2 + x_2^*) + k_3x_1| + |k_4x_2^*|)(|x_2 - x_2^*|)
\]

If the following two assumptions are made,
1) \( k_i(t), i=1,2, \) is continuous and bounded for \( t \in [0, t_{\text{max}}] \)
2) \( x_i(t), i=1,2, \) is continuous for \( t \in [0,t_{\text{max}}] \)

and if

\[
M \geq \sup_{t \in [0,t_{\text{max}}]} (|k_1 + k_3 x_2^*| + |k_4 x_2^*(x_1 + x_1^*)|)
\]

\[
N \geq \sup_{t \in [0,t_{\text{max}}]} (|k_2 (x_2^* + x_2) + k_3 x_1| + |k_4 x_1^2|)
\]

then

\[
||\tilde{f}(\vec{x}, t) - \tilde{f}(\vec{x}^*, t)|| \leq L ||\vec{x} - \vec{x}^*||
\]

if \( L \geq M + N. \)

This shows existence and uniqueness of the solution of the simplified kinetic equations for a given set of initial conditions.

The above assumptions are readily accepted if the physical problem is understood. The reaction coefficients are derived as continuous functions and are given in exponential form by

\[
k_i = A_i \exp(-B_i/RT(t))
\]

where \( A_i, B_i, \) and \( R \) are constants and \( T(t) \) is a continuous temperature function of time. The concentrations \( x_i(t), \) \( i=1,2 \) must increase or decrease continuously and must necessarily be bounded by the mass balance constraints.

The above analysis showing existence and uniqueness
also applies to the general problem encountered in chemical kinetics since the only difference is that more terms of the same type are added to the right hand sides of the equations as the system becomes larger.

B. Behavior of Solution

Although it is impossible to show the behavior of every type of problem that may be studied with the kinetic equations, a few general remarks can be made on the basis of problems investigated by this author. From these, along with the general physical knowledge of the problem, conclusions can be made about the solutions of these types of problems in several aspects.

When the kinetic equations are integrated with any initial conditions, \( \bar{\mathbf{x}}(0) \), given at time zero and a constant temperature, equilibrium conditions will be reached \( (d\bar{\mathbf{x}}/dt = 0) \) at some later time in the integration. These equilibrium values represent the state at which the concentrations or relative amounts of constituents in the system remain constant when subjected to a constant temperature. If the temperature changes, the concentrations do also.

If we use the CO-\( \text{O}_2 \) system of equations which represents the burning of carbon monoxide in oxygen, a problem to consider may be stated as follows: "Given the CO-\( \text{O}_2 \) system with equilibrium concentrations at temperature \( T_{\text{ic}} \) at time
zero, what are the concentrations at some later time, \( t \), when the system is subjected, instantaneously, to a different constant temperature, \( T \)?

If \( T_{ic} = T \), the concentrations do not change during any length of time of integration. If \( T_{ic} \) is very close to \( T \), then we do not expect the relative amounts to change greatly, but still at some later time the concentrations will tend to the equilibrium values at the new temperature, \( T \).

For a problem in which equilibrium values at a temperature \( T_{ic} = 1900^0 \text{K} \) are given as initial conditions and the integration is performed at a temperature \( T = 2200^0 \text{K} \), values very close to the equilibrium values at \( 2200^0 \text{K} \) are reached in less than three milliseconds of burning time. Equilibrium values are reached after approximately 100 minutes of burning time. Figure 6 shows the relative shapes of concentrations of the constituents as a function of time for this case.

For a problem in which equilibrium values are given as initial conditions for a temperature quite different from the constant integration temperature, the relative amounts change greatly and take a shorter burning time to reach near equilibrium values at the new temperature. If the \( \text{CO-}O_2 \) system is integrated at \( T = 2200^0 \text{K} \) using initial equilibrium values at \( T_{ic} = 1000^0 \text{K} \), near equilibrium values are reached in less than a millisecond of burning time. Again,
Figure 6. CO-O₂ system, $T_{ic} = 1900^\circ K$ (integration at a constant temperature of $2200^\circ K$)

Figure 7. CO-O₂ system, $T_{ic} = 1000^\circ K$ (integration at a constant temperature of $2200^\circ K$)
equilibrium values are reached after approximately 100 minutes of burning time. Figure 7 shows the behavior of the system in this problem.

Thus, for the CO-O₂ system, when integrations are performed at a constant temperature close to the equilibrium concentrations that are given as initial conditions, the change in concentration is relatively slow and near equilibrium conditions are reached in a longer burning time. This represents an "easier" problem computationally than one in which integration is performed with a constant temperature that is much different from the temperature at which equilibrium values are given for initial conditions. In this case the slopes \((\frac{\mathrm{d}x}{\mathrm{d}t})\) at the beginning of the burning process are much less, and longer burning times are necessary to reach near equilibrium values. Slopes for this problem \((T_{ic} = 1900\,^\circ\text{K})\) have magnitudes of 20 or less, whereas slopes of \(10^3\) or more are encountered for the problem when \(T_{ic} = 1000\,^\circ\text{K}\).

For the more practical problem physically, in which the temperature is time variant, insight can be gained into the behavior of the concentrations from a three dimensional phase plane plot. Figure 8 represents the concentration of CO in the CO-O₂ system that results when several problems are solved with a constant temperature integration. The initial conditions to the problems are equilibrium values.
Figure 8. Phase plant plot of CO in CO-O₂ system
\( (T_{ic} = 1000^\circ K) \)

at \( T_{ic} = 1000^\circ K \), and integrations are made in the temperature range 2600\(^\circ\)K to 1000\(^\circ\)K in steps of 100\(^\circ\)K.

One aspect was presented in Chapter II which discussed the possibility of transforming the kinetic equations so that integration can be made over temperature. Another aspect can be seen when investigating the behavior of CO in
several different temperature profiles by making the appropriate cut in the T,t plane. For example, if the temperature varies as shown in Figure 9, the shape of the concentration of CO appears close to that shown in Figure 10. This can be an important aspect to the researcher.

![Figure 9. T vs t profile](image)

![Figure 10. Concentration of CO in the CO-O$_2$ system (for the temperature profile in Figure 9)](image)
studying a system such as the CO-O₂ system if he is interested in profiles of the burning constituents as they appear in the time domain rather than particular number concentrations.

Although the previous discussion represents practical problems physically important, other problems were solved to study the behavior of the kinetic equations in general. Their behavior was found to be inherently the same even under widely different initial conditions. If integrations were performed with constant temperature, each component in the system tended toward its equilibrium value at that temperature, given any concentration as initial conditions. If the initial value of one of the variables was close to equilibrium, it "lazily" proceeded toward equilibrium. If it was far from equilibrium initially, that variable experienced a rapid increase or decrease then slowly tended toward its equilibrium value.

The values of the concentrations usually have a wide range in any given problem. They normally range from ten to zero and of course would not be less than zero. In a given problem magnitudes from 10⁰ to 10⁻²¹ or so can exist and therefore care must be taken during the computation to assure accuracy. These problems are discussed in a later section.

The temperature variant problems can be quite complex
during the burning phase and it is difficult to draw conclusions about their behavior. However, as we stated, the three dimensional phase plane plots can be used to give insight into these problems.

An arbitrary temperature variant problem was solved with the CO-O₂ system to study its behavior with a temperature profile representing oscillatory combustion as shown in Figure 11.

The burning began with only CO and O₂ present as shown by the initial concentration vector below.

\[
\begin{align*}
    x_1 &= \text{CO} = 1 \quad \text{(moles)} \\
    x_2 &= 0 \quad = 1/2 \\
    x_3 &= \text{CO}_2 = 0 \\
    x_4 &= 0 \quad = 0 \\
    x_5 &= \text{O}_3 = 0
\end{align*}
\]

The results are shown in Figure 12. This problem was also run without oscillations. In this case variables tended toward a value approximately at a mean between oscillations of the variables shown in Figure 12.

A larger Methane-Air system that has twenty-four reactions and thirteen variables was solved and the results are presented in Chapter VII. These larger systems become much more complex in the burning process, particularly in
Figure 11. $T$ vs $t$ for oscillatory combustion (in the CO-O$_2$ system)

Figure 12. CO-O$_2$ system concentrating with CO=1, O$_2$=1/2 initially
the temperature variant problems, but their general behavior is the same.

C. Numerical Problems in Solution

The investigators working on numerical solution of the kinetic equations have experienced problems in several areas, the most important of which arises in the instability exhibited by the numerical method.

The Euler, Runge-Kutta, and predictor-corrector methods all exhibit a discretization error of the order of a term in the Taylor's Series expansion of the solution. A fourth order Runge-Kutta is a single step method which corresponds to using the first four terms of a Taylor's expansion and has an absolute error of the order of the next term in the expansion. This is true if values of the integration increment are small enough, which implies that the series must be convergent or term by term decreasing. If the next term or terms are larger in absolute value, the method does not provide a good estimate. For the kinetic equations, the higher order derivatives can be quite large unless a very small time increment is used.

This problem can effectively be illustrated by the following example using the CO-O₂ system rewritten below.

\[
\frac{dx_1}{dt} = -k_1 x_4 x_1 + k_4 x_3
\]

\[
\frac{dx_2}{dt} = -(k_3 x_4 + k_5) x_2 + 2k_2 x_4 x_5
\]
\[ dx_3/dt = -k_4 x_3 + k_1 x_1 x_4 \]
\[ dx_4/dt = -(k_1 x_1 + k_2 x_5 + k_3 x_2) x_4 + k_4 x_3 + 2k_5 x_2 \]
\[ dx_5/dt = -k_2 x_4 x_5 + k_3 x_2 x_4 . \]

The orders of magnitude of \( k_i \) for a temperature of 2200°K are

\[ k_1 = 3 \times 10^5 \]
\[ k_2 = 3 \times 10^7 \]
\[ k_3 = 10 \]
\[ k_4 = 10^{-2} \]
\[ k_5 = 10^{-4} . \]

If we use initial conditions of \((1, 1/2, 0, 0, 0)\) for \( x_i \), \( i=1,\ldots,5 \) and "a posteriori" knowledge of the results, we can show that the expansion of \( x_1 \) around time \( t \) can be written approximately as

\[ x_1(t+\Delta t) = x_1(t) + \sum_{n=1}^{\infty} \frac{f_1(t)}{k_1} \frac{(\Delta t \cdot k_1)^n (-1)^{n-1}}{n!} \quad (3.5) \]

where \( f_1(t) \) is the right hand side of the first equation and

\[ f_1(t) = df_1(t)/dt = dx_1^2(t)/dt^2 . \]

From the ratio test we find that convergence is rapid only if \( \Delta t < nk_1^{-1} \).

Since \( k_1 \) is of the order of \( 10^5 \) and \( n \) of order one, \( \Delta t \)
must be less than $10^{-5}$ to make the numerical method practical. In actual test cases run by this author on the computer, $f_1'(t)$ was of the order of $k_1$ thus making $f_1'/k_1$ of the order of unity. This of course is not true in general. Thus we see from the expansion that stability for this problem with any of the previously mentioned numerical methods can be obtained only if $\Delta t$ is extremely small.

This is further exemplified by the following. The expression representing the local discretization error for a fourth order Runge-Kutta method is

$$
\varepsilon_{rk} = \frac{(\Delta t)^4}{5!} \frac{d^4 f_1}{dt^4} + O(\Delta t^5),
$$

which is quite large unless very small time increments are used. Table 1 shows numerical results that are obtained by using a fourth order Runge-Kutta method for the CO-O$_2$ system when using various step sizes. The initial conditions are $(1,1/2,0,0,0)$ for $x_i(0)$, $i=1,2,...,5$ and integration is made with a constant temperature of 2200°K. As can be seen by the magnitudes, instability is realized on the first step for $\Delta t = 10^{-3}$ and the second for $\Delta t = 10^{-5}$; however the integration proceeds smoothly for $\Delta t = 10^{-6}$ and $10^{-8}$. Results are presented with the power of ten as an exponent by which it should be multiplied, and times are presented in seconds.
Table 1. Fourth order Runge-Kutta results for the CO-O\textsubscript{2} system (using various step sizes for integration $T_{ic}=2200^\circ K$ and $x(0) = (1,1/2,0,0,0)$)

<table>
<thead>
<tr>
<th>$t$</th>
<th>time step</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>$x_4$</th>
<th>$x_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>0.001</td>
<td>-1.69\textsuperscript{9}</td>
<td>-1.22\textsuperscript{5}</td>
<td>1.61\textsuperscript{9}</td>
<td>-1.61\textsuperscript{9}</td>
<td>6.12\textsuperscript{4}</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>1x$10^{-5}$</td>
<td>9.56\textsuperscript{-1}</td>
<td>5.00\textsuperscript{-1}</td>
<td>4.37\textsuperscript{-2}</td>
<td>-4.37\textsuperscript{-2}</td>
<td>3.59\textsuperscript{-8}</td>
</tr>
<tr>
<td></td>
<td>2x$10^{-5}$</td>
<td>-3.2\textsuperscript{27}</td>
<td>2.30\textsuperscript{28}</td>
<td>3.20\textsuperscript{27}</td>
<td>-1.47\textsuperscript{28}</td>
<td>-1.15\textsuperscript{28}</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>5x$10^{-4}$</td>
<td>1.0</td>
<td>.5</td>
<td>1.44\textsuperscript{-7}</td>
<td>7.51\textsuperscript{-10}</td>
<td>1.14\textsuperscript{-13}</td>
</tr>
<tr>
<td></td>
<td>5x$10^{-3}$</td>
<td>1.0</td>
<td>.5</td>
<td>1.45\textsuperscript{-6}</td>
<td>7.78\textsuperscript{-10}</td>
<td>1.17\textsuperscript{-12}</td>
</tr>
<tr>
<td></td>
<td>1x$10^{-2}$</td>
<td>1.0</td>
<td>.5</td>
<td>2.89\textsuperscript{-6}</td>
<td>8.08\textsuperscript{-10}</td>
<td>2.38\textsuperscript{-12}</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>1x$10^{-8}$</td>
<td>1.0</td>
<td>.5</td>
<td>8.31\textsuperscript{-13}</td>
<td>2.06\textsuperscript{-12}</td>
<td>6.57\textsuperscript{-19}</td>
</tr>
<tr>
<td></td>
<td>5x$10^{-8}$</td>
<td>1.0</td>
<td>.5</td>
<td>1.05\textsuperscript{-11}</td>
<td>3.93\textsuperscript{-12}</td>
<td>8.33\textsuperscript{-18}</td>
</tr>
<tr>
<td></td>
<td>1x$10^{-7}$</td>
<td>1.0</td>
<td>.5</td>
<td>2.49\textsuperscript{-11}</td>
<td>4.04\textsuperscript{-12}</td>
<td>1.97\textsuperscript{-17}</td>
</tr>
</tbody>
</table>

The above analysis is based on "a posteriori" knowledge of the results and is dependent upon the initial conditions. No easy way has been found to obtain "a priori" discretization error forms in general for these equations since the expressions for each term in the expansion can become quite cumbersome in length. Opsahl (44), however, states that his
experience has shown that errors are kept small if the product of the time increment of integration and the largest derivative is less than one. This is not proved in general however.

D. Reduction to Canonical Form

Other problems occur in the numerical integration of the kinetic equations. In large systems, the nonlinear coupling effect is greatly enhanced but can be reduced. These effects can be reduced by a method Ames (1,2) uses to solve for rate constants in some processes. Effectively, it is a process of writing the system in matrix form and performing elementary row transformations on the coefficient matrix to reduce it to canonical form. This leaves the system with more derivatives per equation but fewer nonlinear terms on the right hand sides. Benson (8) states that there are always redundancies in the kinetic equations and as will be shown, these redundant variables (referred to as "dead end" variables by Ames) can be eliminated from the system to yield a somewhat smaller system to solve.

There may seem to be no advantage to reducing the equations to canonical form; but for the method which proved to be the best for solving the equations studied by this author, there can be a definite saving in computer time requirements.

We use the CO-O₂ system as an example and write the
system in matrix form as

\[
\begin{bmatrix}
  x_1 \\
  x_2 \\
  x_3 \\
  x_4 \\
  x_5 \\
\end{bmatrix}
= 
\begin{bmatrix}
  -1 & 0 & 0 & 1 & 0 \\
  0 & 2 & -1 & 0 & -1 \\
  1 & 0 & 0 & -1 & 0 \\
 -1 & -1 & -1 & 1 & 2 \\
  0 & -1 & 1 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
  k_1 x_1 x_4 \\
  k_2 x_4 x_5 \\
  k_3 x_2 x_4 \\
  k_4 x_3 \\
  k_5 x_2 \\
\end{bmatrix}
\]

or more compactly as

\[
\frac{dx}{dt} = A \bar{y}
\]

where \( \bar{x} \) is the vector of concentrations and \( A \) is the coefficient matrix of the term types vector \( \bar{y} \).

After judiciously applying elementary row operations on the matrix \( A \), one obtains

\[
\frac{dx}{dt} = \begin{bmatrix}
  x_1 \\
  x_1 - x_2 - x_4 - 2x_5 \\
  x_2 + 2x_5 \\
  x_1 + x_3 \\
  x_1 - 2x_2 - x_4 - 3x_5 \\
\end{bmatrix}
= 
\begin{bmatrix}
  -1 & 0 & 0 & 1 & 0 \\
  0 & 1 & 0 & 0 & -1 \\
  0 & 0 & 1 & 0 & -1 \\
  0 & 0 & 0 & 0 & 0 \\
  0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
  k_1 x_1 x_4 \\
  k_2 x_4 x_5 \\
  k_3 x_2 x_4 \\
  k_4 x_3 \\
  k_5 x_2 \\
\end{bmatrix}
\]

which is written as a new system:

\[
\frac{dx^*}{dt} = A \bar{y}^* \quad .
\]
The auxiliary equations containing the "dead end" variables

\[
\frac{d}{dt}(x_1 + x_3) = 0 \tag{3.7}
\]

and

\[
\frac{d}{dt}(x_1 - 2x_2 - x_4 - 3x_5) = 0 \tag{3.8}
\]

can be integrated in closed form.

We integrate Equation 3.7 in the time interval \([0, t]\) and obtain

\[
x_1(t) + x_3(t) = C_1 \tag{3.9}
\]

where \(C_1\) is a constant given by

\[
C_1 = x_1(0) + x_3(0)
\]

Equation 3.7 can then be used to eliminate \(x_3\) or \(x_1\) from the calculation.

Equation 3.8 is integrated similarly to yield

\[
x_1(t) - 2x_2(t) - x_4(t) - 3x_5(t) = C_2 \tag{3.10}
\]

where \(C_2\) is given by

\[
C_2 = x_1(0) - 2x_2(0) - x_4(0) - 3x_5(0)
\]

If \(x_3\) and \(x_5\) are eliminated from the system of Equations 3.6, a new system of equations results. This system can then be integrated to yield the equivalent canonical
problem

\[ \frac{d}{dt}(x_1) = -(k_1x_4 + k_4)x_1 + k_4 C_1 \]

\[ \frac{d}{dt}(2x_1 - x_2 - 2x_4) = 3(k_3x_4 - k_5)x_2 \]

\[ \frac{d}{dt}(x_1 + x_2 - x_4) = (x_1 - 2x_2 - x_4 + C_2)k_2x_4 - 3k_5x_2 \]  

(3.11)

where \( C_1 \) and \( C_2 \) are determined from the initial conditions at time zero.

The "dead end" variables are carried along in the calculation and determined from

\[ x_3(t) = C_1 - x_1(t) \]

\[ x_5(t) = (x_1(t) - 2x_2(t) - x_4(t) - C_2)/3 \]  

(3.12)

Equations 3.11 and 3.12 now form the basic system to solve to yield a complete solution to the CO-\( O_2 \) system.

It does not readily appear that Equations 3.11 represent any advantage to the integration for this relatively small system; however a definite advantage in computer time requirements is realized when the matrix of coefficients, \( A \), becomes quite large. It should be pointed out that a disadvantage can also arise in some problems that use the canonical form if the difference in magnitudes of resulting concentrations that appear in computing the "dead end" variables is larger than the word size in the computer.
This may or may not be important since judicious choosing of the "dead end" variables can eliminate the problem. Double or extended precision should always be used with the canonical forms.
IV. INVESTIGATION OF LINEARIZATION AND ITERATION TECHNIQUES

As we have shown, Euler, Runge-Kutta, and predictor-corrector techniques require very small step sizes for stability in the integration of the kinetic equations. Various other methods were investigated to find a practical method for integration and they are discussed in this chapter.

Normally when we wish to solve a nonlinear algebraic equation, \( g(x) = 0 \), the idea of trying some iterative technique comes to mind. To show that a sequence of iterates converges to a solution of the equation, we show that the sequence forms a Cauchy Sequence such that the error at iteration, \( k \), defined by

\[
    e_k = |x^k - x|
\]

is reduced at each step. Here \( x^k \) is the iterates and \( x \) is the true solution to \( g(x) = 0 \). If

\[
    \lim_{{k \to \infty}} e_k = 0
\]

we say that the method converges to the true solution, or

\[
    \lim_{{k \to \infty}} x^k = x
\]

Analogously, in systems of equations the test for convergence of an iteration is done by replacing the absolute value in Equation 4.1 by a norm. That is, the vector of
iterates, $x^k$, for the system of equations

$$g_i(x_1, x_2, \ldots, x_n) = 0, \quad i=1, 2, \ldots, n$$

converges to a solution of the system if the error, $e^k$, at iteration $k$ defined by

$$e^k = ||x^k - x||$$

is reduced at each step. If

$$\lim_{k \to \infty} e^k = 0$$

then

$$\lim_{k \to \infty} x^k = \bar{x}$$

where $\bar{x}$ is a true solution to the system.

For systems of equations containing a derivative, as do the kinetic equations, we write the system as

$$g(x, \frac{dx}{dt}, t) = 0$$

and convergence of iterative methods for solving this type of system is similar.

Several linearization and iteration techniques were investigated for the kinetic equations and are discussed on the following pages. A detailed comparison of usable methods is given later in Chapter VI.
A. Cauchy-Picard Method

One of the best known and widely used iterative methods is the Cauchy-Picard Method. If we write the system of kinetic equations as

$$\frac{dx_i}{dt} = f_i(x_1, x_2, \ldots, x_n, t) \quad i=1,2,\ldots,n$$

with initial conditions

$$x_i(t_0) = \eta_i \quad i=1,2,\ldots,n$$

the solution in the interval \([t_0, t]\) is

$$x_i(t) = x_i(t_0) + \int_{t_0}^{t} f_i(x_1, \ldots, x_n, t) dt , \quad i=1,2,\ldots,n .$$

The Cauchy-Picard iteration process begins with initial guesses, \(x_i(t_0)\), and proceeds according to the scheme

$$x_i^{k+1}(t) = x_i(t_0) + \int_{t_0}^{t} f_i(x_1^k, \ldots, x_n^k, t) dt , \quad i=1,\ldots,n$$

(4.2)

where \(k\) represents the iteration step.

This method always converges to the solution if \(f_i(x_1, \ldots, x_n, t)\) satisfies the existence and uniqueness conditions in Theorem 1. Davies and James (16) give a detailed convergence proof for this method and it will not be repeated here.
The CO-O₂ system was solved by this author with this method using constant reaction coefficients at a temperature of 2200°K. Although the method converged to the solution, stability criteria were the same as in the Runge-Kutta and predictor-corrector methods. That is, the same time increments were required (less than 10⁻⁶) for the method to converge. This method was programmed in both a Jacobi type iteration as signified by Equation 4.2 and a Gauss-Seidel type, in which the updated values were used as they were computed. The Gauss-Seidel method is represented at iteration k for equation i by

\[ x_{i}^{k+1}(t) = x_{i}(t_{0}) + \int_{t_{0}}^{t} f_{i}(x_{1}^{k+1}, \ldots, x_{i-1}^{k+1}, x_{i}^{k}, \ldots, x_{n}^{k}, t) dt. \]

Although convergence was relatively slow, usually 10 to 50 iterations for seven significant digits, the Gauss-Seidel iteration always converged faster than the Jacobi iteration for the given problem. Since no saving in computer times is realized over present methods, the Cauchy-Picard method is not considered practical.

B. Exponential Method

The exponential method linearizes the right hand side of equation i with respect to the i_th variable and is iterated as follows:
For the kinetic equations, this can always be written in the form

\[
\frac{dx_i^{k+1}}{dt} = f_i(x^k, t) + (x_i^{k+1} - x_i^k) \frac{\partial f_i}{\partial x_i}(x^k, t)
\]

Equation 4.3 is a linear equation which can be integrated in the interval \([t_0, t]\) to give

\[
x_i^{k+1}(t) = (x_i(t_0) - \frac{B_i^k}{A_i^k}) \exp(-A_i^k \Delta t) + \frac{B_i^k}{A_i^k}
\]

where \(A_i^k\) and \(B_i^k\) are functions evaluated with components from the previous iteration \(k\).

A method due to Pope (48) which in turn is similar to some of Bellman's (4) methods for autonomous systems uses an exponential solution to a fully linearized system which is similar to but not the same as this method. It may be of interest to the reader to investigate Pope's method, but results from this method imply that it is not practical for large systems.

Equation 4.4 can then be used to obtain a sequence of iterates for any given time step by using initial guesses of the accepted values obtained from the previous time step.
The iteration starts at the first time step by using the initial conditions at time zero.

Both a Jacobi type iteration, as denoted by Equation 4.4, and a Gauss-Seidel type in which $A_i^k$ and $B_i^k$ are re-evaluated as new iterates, $x_i^{k+1}$, are calculated, were tried with this method. As in the Picard method, the Gauss-Seidel type was always faster.

The exponential method has been found to be quite good for smaller systems of equations. Although it is not possible to converge to a solution using as large a time step as that enabled by some succeeding methods, the time per iteration is sufficiently less and the method is simple enough to warrant it as being acceptable for solving the kinetic equations when smaller systems (five equations or less) are studied. The larger systems are solvable by this method but normally a very small time step is required.

C. Finite Replacements Method

This method linearizes the system as does the exponential method but instead of integrating the linearized system in closed form, a finite difference is substituted for the derivative and is algebraically solved for $x_i(t)$.

We write

$$\frac{dx_i}{dt} = -A_i x_i + B_i, \quad i=1,2,\ldots,n$$
and substitute a forward difference in the interval \([t_0, t]\). We then perform an iteration as shown in Equation 4.5.

\[
\frac{x_i^{k+1}(t) - x_i(t_0)}{\Delta t} = -A_i x_i^{k+1} + B_i^k.
\]  

Equation 4.5 can then be solved for \(x_i^{k+1}\) to give

\[
x_i^{k+1}(t) = \frac{x_i(t_0) + \Delta t B_i^k}{1 + \Delta t A_i^k}.
\]

This method was iterated using both a Jacobi and Gauss-Seidel type iteration and, in general, convergence was quite good with both methods for fairly large time increments. The Gauss-Seidel type of iteration was always faster, however. This method usually required less iterations per time step than the Exponential method.

It should be noted that this method is similar to the method of Accelerated Successive Replacements used to solve nonlinear systems of algebraic equations first discussed by Lieberstein (31, p. 113).

In general, both the Exponential and Finite Replacements Methods proved to be acceptable methods for integrating the smaller five component system of CO-O2. Time increments as large as 0.1 seconds can be used on some problems; however, if calculations are begun for conditions not near equilibrium,
small time steps are necessary and convergence is quite slow. For a larger system of CO-Air which has nine equations, time increments of $10^{-4}$ seconds or smaller are required and it is necessary to use 30 to 50 iterations per time step. For the larger Methane-Air system given in the Appendix which has thirteen equations, time increments of $10^{-5}$ or smaller are required.

D. Variable Linear Method

Since most of the kinetic equations contain one or more linear terms of the form $k_i x_j$ another linearization method is suggested. The technique is to linearize the equations by taking the higher order terms as constants at each step, and evaluating them with the iterated values obtained from the previous step. The iteration is denoted for equation $i$ and iteration $k+1$ by

$$\frac{d x_i^{k+1}}{dt} = L_i^{k+1} + H_i^k$$

where $L_i^{k+1}$ is composed of the linear forms at step $k+1$, and $H_i^k$ contains the higher order terms evaluated from results of the previous step, $k$. This method can be used primarily when the linear terms are predominant in the system.

As an example, one of the equations in the CO-$O_2$ system is
\[ \frac{dx_2^{k+1}}{dt} = -k_5 x_2^{k+1} - k_3 x_4^{k+1} + 2k_3 x_4 x_5 \]

The expressions for \( L_i^{k+1} \) and \( H_i^{k+1} \) are then

\[ L_2^{k+1} = -k_5 x_2^{k+1} \]

and

\[ H_2^k = -k_3 x_4 x_2^k + 2k_2 x_4 x_5 \]

This equation can then be integrated in closed form in the interval \([t_0, t]\) to give

\[ x_2^{k+1}(t) = \left( x_2(t_0) - \frac{H_2^k(t)}{k_5} \right) \exp(-k_5\Delta t) + H_2^k(t) \]

Similar expressions can be obtained for the other variables in the system either by direct integration or by first substituting expressions already derived and then integrating. We can also solve the system by transforming it into one containing higher order derivatives. The integrated system is then iterated either in a Jacobi or Gauss-Seidel fashion.

As an example this method is applied to the CO-O\(_2\) system. We write, using operator notation, the linearized system already transformed to equations of higher order for \( x_1(t) \) and \( x_4(t) \) as
\[(D^2 + k^4 D)x_1^{k+1} = k_4 (H_1^k + H_3^k)\]

\[(D + k_5)x_2^{k+1} = H_2^k\]

\[(D + k_4)x_3^{k+1} = H_3^k\]

\[(D^3 + (k_4 + k_5)D^2 + k_5 k_4 D)x_4^{k+1} = k_4 k_5 (H_3^k + 2H_2^k + H_4^k)\]

\[Dx_5^{k+1} = H_5^k\]

where the operator notation, \(D\), means

\[D^n = \frac{d^n}{dt^n}\]

and

\[D = \frac{d}{dt}\]

By integrating Equations 4.6 in closed form in the interval \([t_0, t]\) we get

\[x_1^{k+1}(t) = x_1(t_0) + [H_3^k(t) + H_1^k(t)]\Delta t - [x_3(t_0) - \frac{H_3^k(t)}{k_4}]\]

\[[\exp(-k_4\Delta t) - 1]\]

\[x_2^{k+1}(t) = [x_2(t_0) - \frac{H_2^k(t)}{k_5}]\exp(-k_5\Delta t) + \frac{H_2^k(t)}{k_5}\]
\[x_{3}^{k+1}(t) = [x_{3}(t_{0}) - \frac{H_{3}^{k}(t)}{k_{4}}] \exp(-k_{4}\Delta t) + \frac{H_{3}^{k}(t)}{k_{4}}\]

\[x_{4}^{k+1}(t) = x_{4}(t_{0}) + [H_{3}(t) + 2H_{2}(t) + H_{4}(t)]\Delta t - [x_{3}(t_{0}) - \frac{H_{3}^{k}(t)}{k_{4}}][\exp(-k_{4}\Delta t) - 1]\]

\[-2[x_{2}(t_{0}) - \frac{H_{2}^{k}(t)}{k_{5}}][\exp(-k_{5}\Delta t) - 1]\]

\[x_{5}^{k+1}(t) = x_{5}(t_{0}) + \frac{H_{5}^{k}(t)}{k_{5}}\Delta t\]

where \(\Delta t = t - t_{0}\). \(H_{i}^{k}(t)\) implies \(H_{i}(t)\) evaluated at time \(t\), using results, \(x_{i}^{k}\), obtained from the previous step.

When the CO-O\(_{2}\) system was solved this method converged to the solution; however stability conditions were essentially the same as for Runge-Kutta methods. The same problem as that previously discussed for the Runge-Kutta method (see Table 1) was solved and time increments less than \(10^{-6}\) seconds were required. Convergence was quite slow, of the order of 100 iterations. To obtain desired accuracy, time increments of the order of \(10^{-7}\) seconds were required and 30 to 35 iterations were necessary so no change was noted in the seventh significant digit in any component. Thus this method was not further considered for solution to the problem.
E. The NRK Method

A method similar to the Newton-Raphson-Kantorovich method (henceforth referred to as the NRK method) for solving algebraic equations was also tried and was found to work quite well for the kinetic equations. It is similar, but not the same as, the method of quasilinearization described by Bellman and Kalaba (6) and many others (47, 1, 49). The NRK method gives very satisfactory results when relatively large step sizes are used and it is also applicable to the reduced canonical forms of the kinetic equations.

This method is applied by substituting a forward difference for the time derivative and solving the equations as an algebraic system.

We begin by substituting a forward difference for the time derivative for the interval \([t_o, t]\)

\[
\frac{dx_i(t)}{dt} = \frac{x_i(t) - x_i(t_o)}{\Delta t}, \quad i=1,2,\ldots,n
\]

where, for convenience, we use the notation

\[
\frac{dx_i}{dt} = \frac{x_i - x_{i0}}{\Delta t}.
\]

The system then becomes

\[
F_i(\bar{x}, t, \frac{x_i - x_{i0}}{\Delta t}) = 0, \quad i=1,2,\ldots,n \quad (4.7)
\]
The NRK method is then applied to Equation 4.7 in iterative form as shown below.

\[-F_i(x^k, t, \frac{x_i^k - x_{i0}}{\Delta t}) = \sum_{j=1}^{n} F_{ij}(x^k, t, \frac{x_i^k - x_{i0}}{\Delta t}) \Delta x_{j}^{k+1}, \]

where \( F_{ij}(x^k, t, \frac{x_i^k - x_{i0}}{t}) \) is the partial of \( F_i \) with respect to \( x_j \) as shown by

\[ F_{ij} = \frac{\partial F_i}{\partial x_j}, \]

and \( \Delta x_{j}^{k+1} \) represents the change in \( x_j \) at the present step as expressed by

\[ \Delta x_{j}^{k+1} = (x_{j}^{k+1} - x_{j}^{k}). \]

The CO-O_2 system which required a stepsize of less than \( 10^{-6} \) seconds with Runge-Kutta methods can be integrated with the NRK method by using time increments of up to \( 10^{-1} \) seconds. Past the critical areas where stiffness is important even larger steps can be used. Chapter V has been devoted to explaining this method in more detail. The important property of this method which reduces the stiffness encountered in these equations is also discussed.
V. THE NRK METHOD

A. General Discussion

Given the system of \( n \) nonlinear algebraic equations

\[
f_i(x_1, \ldots, x_n) = 0, \quad i=1, 2, \ldots, n
\]

the Newton-Raphson-Kantorovich Method of solution first linearizes the system by expanding it in a Taylor's expansion about a true solution, \( \bar{x} \), at some close point, \( \bar{a} \), represented by

\[
f_i(x_1, x_2, \ldots, x_n) = f_i(a_1, a_2, \ldots, a_n) + \sum_{j=1}^{n} f_{ij}(a_1, \ldots, a_n) (x_j - a_j)
\]

\[
+ \frac{1}{2} \sum_{j=1}^{n} \sum_{k=1}^{n} f_{ijk}(a_1 + \theta(x_1 - a_1), \ldots, a_n)
\]

\[
+ \theta(x_n - a_n)(x_j - a_j)(x_k - a_k)
\]

\[
i=1, 2, \ldots, n \quad (5.1)
\]

where

\[
f_{ij} = \frac{\partial f_i}{\partial x_j}, \quad f_{ijk} = \frac{\partial^2 f_i}{\partial x_j \partial x_k},
\]

and \( 0 < \theta < 1 \).

If we write Equations 5.1 in matrix form with

\[
f_i(x_1, \ldots, x_n) = 0,
\]

we have
\[ 0 = \vec{f}(\vec{a}) + J(\vec{a})\Delta \vec{x} + T(\vec{a}) \]

where \( \vec{f}(\vec{a}) \) and \( \Delta \vec{x} \) are vectors given below

\[
\vec{f}(\vec{a}) = \begin{bmatrix}
  f_1(\alpha_1, \ldots, \alpha_n) \\
  \vdots \\
  f_n(\alpha_1, \ldots, \alpha_n)
\end{bmatrix}, \quad \Delta \vec{x} = \begin{bmatrix}
  \alpha_1 - x_1 \\
  \vdots \\
  \alpha_n - x_n
\end{bmatrix},
\]

\( J(\vec{a}) \) is the matrix of partials

\[
J(\vec{a}) = \begin{bmatrix}
  f_{11} & f_{12} & \cdots & f_{1n} \\
  \vdots & \vdots & \ddots & \vdots \\
  f_{n1} & f_{n2} & \cdots & f_{nn}
\end{bmatrix},
\]

referred to as the Jacobian matrix, and \( T(\vec{a}) \) is a matrix containing the second partials, \( f_{ijk} \).

The system is then linearized by dropping the matrix of second partials, \( T(\vec{a}) \), to obtain

\[
J(\vec{a})\Delta \vec{x} = -\vec{f}(\vec{a}) \quad (5.2)
\]

If \( J(\vec{a}) \) is nonsingular the linear system 5.2 can be solved for \( \Delta \vec{x} \) and can effectively be written in vector form below as

\[
\Delta \vec{x} = \vec{a} - J^{-1}(\vec{a}) \vec{f}(\vec{a}) \quad (5.3a)
\]
where $J^{-1}(\alpha)$ is the inverse of the Jacobian matrix.

The error in solution is given by

$$\epsilon(\alpha) = -J^{-1}(\alpha)^T \pi(\alpha).$$

For a vector, $\alpha$, close to $\bar{x}$ one would expect $\epsilon(\alpha)$ to be small and Equation 5.3a would be expected to yield a solution to the system. However, it is rarely the case that vectors, $\alpha$, close to the true solution are known and the usual practice is to write Equation 5.3a in an iterative fashion and iterate the system of equations to obtain a solution. Equation 5.3a is then written as

$$x^{k+1} = x^k - J^{-1}(x^k) f(x^k)$$

for iteration $k+1$. The iteration begins by making an initial guess, $x^0$, and when the norm of successive iterates becomes less than some predetermined amount, the vector $x^{k+1}$ is accepted as the desired solution. That is, if

$$\lim_{k \to \infty} ||x^{k+1} - x^k|| = 0$$

then

$$x^{k+1} = \bar{x}.$$  

When this method converges, it converges quadratically, which is an important property computationally. Quadratic convergence is asserted if
\[ \| \overline{x}^{k+1} - \overline{x} \| \leq \eta \| \overline{x}^k - \overline{x} \|^2 \]

where \( \overline{x} \) is a true solution, \( x^k \) and \( x^{k+1} \) are the iterates at step \( k \) and \( k+1 \) respectively, and \( \eta \) is independent of \( k \). Quadratic convergence can be shown for this method by the following. We write an equivalent form of Equation 5.3b in vector form as

\[ \overline{x}^{k+1} - \overline{x} = \overline{x}^k - J^{-1}( \overline{x}^k ) \overline{f}( \overline{x}^k ) - \overline{x} \]

Since \( \overline{x} = \overline{x} - J^{-1}( \overline{x} ) \overline{f}( \overline{x} ) \), we have

\[ \overline{x}^{k+1} - \overline{x} = \overline{x}^k - J^{-1}( \overline{x}^k ) \overline{f}( \overline{x}^k ) - ( \overline{x} - J^{-1}( \overline{x} ) \overline{f}( \overline{x} ) ) \]

\[ = \overline{g}( \overline{x}^k ) - \overline{g}( \overline{x} ) \]

where

\[ \overline{g}( \overline{r} ) = \overline{r} - J^{-1}( \overline{r} ) \overline{f}( \overline{r} ) \]

By making use of the first three terms of the Taylor's series with a remainder, we obtain

\[ \overline{x}^{k+1} - \overline{x} = ( \overline{x}^k - \overline{x} ) \overline{Q}'( \overline{x} ) + \frac{( \overline{x}^k - \overline{x} )^2}{2} \overline{Q}''( \overline{\theta} ) \]

where \( \overline{x}^0 \leq \overline{x}^k \leq \overline{\theta} \leq \overline{x} \). Since

\[ \overline{Q}'( \overline{r} ) = ( J^{-1}( \overline{r} )' \overline{f}( \overline{r} ) \]

then
\( \bar{Q}'(\bar{x}) = 0 \)

and

\[
\|x^{k+1} - x^k\| \leq \eta \|x^k - \bar{x}\|^2
\]

where \( \eta = \max_{0 \leq \theta \leq x} 1/2 \|Q''(\theta)\| \).

Similarly, it can be shown that

\[
\|x^{k+1} - x^k\| \leq \eta \|x^k - x^{k-1}\|^2.
\]

Thus, if the NRK method converges, and if we are close to the desired solution, an enormous acceleration of convergence is experienced. As will be shown, this is one of the important advantages of using this method for the kinetic equations.

Convergence of this method is insured by the following theorem.

**THEOREM II.** If \( f_i(x_1, \ldots, x_n) = 0, i=1,2,\ldots,n \) satisfies the following conditions:

a) \( \max_i |f_i(x_1, \ldots, x_n)| \leq A, \quad i=1,\ldots,n \)

b) the Jacobian, \( J(x^0) \), is nonsingular and

\[
\|J^{-1}(x^0)\| \leq B
\]

c) \( \max_{i,j,k} |f_{ijk}(x^*)| \leq G, \text{ for } x^* \text{ in the region defined by} \)

...
where \( c_o \) is defined by and satisfies
\[
\frac{1-\sqrt{1-c_o}}{c_o} \leq \frac{1}{\sqrt{1-c_o}} - 1
\]
then the system \( f_i(x_1, \ldots, x_n) = 0 \) has a unique solution obtainable by the NRK method.

Proof of this theorem is usually first attributed to Kantorovich (25) but is also effectively shown by Ortega (46), Saaty and Bram (54) and many others (47, 61).

B. Application to the Kinetic Equations

If we write the kinetic equations below as
\[
\frac{dx_i(t)}{dt} = f_i(\vec{x}, t), \quad i=1,2,\ldots,n \quad (5.4)
\]
the first step of the NRK method is to replace the derivative with a forward difference and treat the resulting system as a system of nonlinear algebraic equations which is solved at each time step. When the canonically reduced system is solved, several derivatives can appear in each equation and in this case each derivative is replaced by a forward difference.

The forward difference for the time interval \([t_0, t]\) is written
\[
\frac{dx_i(t)}{dt} = \frac{x_i(t) - x_i(t_0)}{t - t_0},
\]

and for convenience we write
\[
\frac{dx_i(t)}{dt} = \frac{x_i - x_{i0}}{\Delta t}.
\]

Then we solve the algebraic system
\[
F_i(\bar{x}, t, \frac{x_i - x_{i0}}{\Delta t}) = f_i(\bar{x}, t) - \frac{x_i - x_{i0}}{\Delta t} = 0, \quad i=1,2,...,n
\]

using the Newton method. The iteration is written
\[
-F_i(x^k, t, \frac{x_i - x_{i0}}{\Delta t}) = \sum_{j=1}^{n} F_{ij}(x^k, t, \frac{x_i - x_{i0}}{\Delta t}) \Delta x_{j}^{k+1} \tag{5.5}
\]

in each time interval \([t_0, t]\).

\[
F_{ij} = \frac{\partial F_i}{\partial x_j}, \quad \text{and} \quad \Delta x_{j}^{k+1} = x_{j}^{k+1} - x_{j}^{k}.
\]

The initial guesses are \(\bar{x}_{i0}\) and are replaced at the beginning of each time step by the iterated values obtained from the previous time step. At the beginning of the integration initial guesses are the initial conditions.

The iteration continues until the norm of \(\Delta x^{k+1}\) is reduced to less than some predetermined quantity. New iterates are determined from
\[
x_i^{k+1} = x_i^k + \Delta x_i^{k+1}, \quad i=1,2,...,n.
\]
The test for convergence must be a normalized norm and is discussed in more detail later on. The test is

\[ \sum_{i=1}^{n} \frac{\Delta x_{i}^{k+1} + x_{i}^{k}}{\Delta x_{i}^{k+1} + x_{i}^{k}} < \varepsilon. \]

For small \( \Delta t \), we assume that the initial guesses are close enough to the new solution to insure convergence of the iteration, and for the cases tested this was true. It was also found that even when relatively large time increments are chosen appropriate accuracy in the solution can still be obtained.

C. Example Using the CO-O\(_2\) System

As we have mentioned previously, the rate equations in the CO-O\(_2\) system are

\[
\begin{align*}
\frac{dx_1}{dt} &= -k_1 x_1 x_4 + k_4 x_3 \\
\frac{dx_2}{dt} &= -k_2 x_2 x_5 - k_5 x_2 + 2k_2 x_4 x_5 \\
\frac{dx_3}{dt} &= -k_4 x_3 + k_1 x_1 x_4 \\
\frac{dx_4}{dt} &= -(k_1 x_1 + k_2 x_5 + k_3 x_2) x_4 + k_4 x_3 + 2k_5 x_2 \\
\frac{dx_5}{dt} &= -k_2 x_4 x_5 + k_3 x_2 x_4.
\end{align*}
\]
The rate constants for this system are given by Opsahl (44, p. 80) and are listed as follows:

\[ k_1 = 2 \times 10^8 \exp(-4500/RT) \text{ liters/mole-sec} \]
\[ k_2 = 3 \times 10^{10} \exp(-6000/RT) \]
\[ k_3 = 1.1585 \times 10^8 \exp(-60500/RT) \]
\[ k_4 = 3.928 \times 10^{13} \exp(-127700/RT) \text{ sec}^{-1} \]
\[ k_5 = 7.47 \times 10^9 \exp(-135000/RT) \]

We write the equations as

\[ \frac{dx_i}{dt} = f_i(x,t) \quad i=1,2,\ldots,5 \]

and substitute a forward difference for the derivative. The system then becomes, for iteration \( k+1 \),

\[ -F_i(x^k,t,\frac{x^k_i-x_{i0}}{\Delta t}) = \sum_{j=1}^{5} F_{ij}(x^k,t,\frac{x^k_j-x_{j0}}{\Delta t}) \Delta x_j^{k+1} \quad i=1,\ldots,5, \]

(5.6)

where \( \Delta t = t-t_0 \). Equations 5.6 are solved at each iteration by using Gauss Elimination with back substitution.

It should be noted that we should not solve these equations by taking inverses since it is more time consuming particularly in larger systems. Care must also be taken in the calculation since loss of accuracy can occur because
of the extreme difference in magnitudes of the partials in $F_{ij}$.

At the first time step $[t_0, t]$

$$x_i^1 = x_{i0} = \text{initial conditions},$$

and for succeeding time steps $[t, t + \Delta t]$

$$x_i^1(t + \Delta t) = x_{i0} = x_i(t)$$

where $x_i(t)$ is obtained from the final iteration at the previous time step. $x_{i0}$ remains constant over the time step.

Equations 5.6 in vector form are

$$-F^k = J^k \Delta x^{k+1}$$

and the expressions for $F^k$, $J^k$, and $\Delta x^{k+1}$ are

$$\Delta x^{k+1} = \begin{bmatrix}
    x_1^{k+1} - x_1^k \\
    x_2^{k+1} - x_2^k \\
    \vdots \\
    x_5^{k+1} - x_5^k
\end{bmatrix}$$

and
The components in $F^k$ are evaluated at iteration $k$. The matrix of partials $J^k$ has the components $j_{ik}$ below, where $i$ and $k$ are the row and column respectively and are also evaluated with components at iteration $k$.

$$
\begin{bmatrix}
\frac{x_1-x_{10}}{\Delta t} + k_1 x_1 x_4 - k_4 x_3 \\
\frac{x_2-x_{20}}{\Delta t} + k_3 x_2 x_4 + k_5 x_2 - 2k_2 x_4 x_5 \\
\frac{x_3-x_{30}}{\Delta t} + k_4 x_3 - k_1 x_1 x_4 \\
\frac{x_4-x_{40}}{\Delta t} + (k_1 x_1 + k_2 x_5 + k_3 x_2) x_4 - k_4 x_3 - 2k_5 x_2 \\
\frac{x_5-x_{50}}{\Delta t} + k_2 x_4 x_5 - k_3 x_2 x_4
\end{bmatrix}
$$

The components in $F^k$ are evaluated at iteration $k$. The matrix of partials $J^k$ has the components $j_{ik}$ below, where $i$ and $k$ are the row and column respectively and are also evaluated with components at iteration $k$.

$$
\begin{align*}
    j_{11} &= \frac{1}{\Delta t} + k_1 x_4 & j_{25} &= -2k_2 x_4 & j_{44} &= \frac{1}{\Delta t} + k_1 x_1 \\
    j_{12} &= 0 & j_{31} &= -k_1 x_4 + k_2 x_5 + k_3 x_2 \\
    j_{13} &= -k_4 & j_{32} &= 0 & j_{45} &= k_2 x_4 \\
    j_{14} &= k_1 x_1 & j_{33} &= k_4 + \frac{1}{\Delta t} & j_{51} &= 0 \\
    j_{15} &= 0 & j_{34} &= -k_1 x_1 & j_{52} &= -k_3 x_4 \\
    j_{21} &= 0 & j_{35} &= 0 & j_{53} &= 0 \\
    j_{22} &= \frac{1}{\Delta t} + k_3 x_4 + k_5 & j_{41} &= k_1 x_4 & j_{54} &= k_2 x_5 - k_3 x_2 \\
    j_{23} &= 0 & j_{42} &= k_3 x_4 - 2k_5 & j_{55} &= \frac{1}{\Delta t} + k_2 x_5 \\
    j_{24} &= k_3 x_2 - 2k_2 x_5 & j_{43} &= -k_4
\end{align*}
$$
Reduction of the CO-O$_2$ system to canonical form in Chapter III gives the following equivalent system below:

$$\frac{d(x_1)}{dt} = -k_1 x_1 x_4 - k_4 x_1 + k_4 C_1$$

$$\frac{d}{dt}(2x_1 - x_2 - 2x_4) = 3(k_3 x_4 - k_5)x_2$$

$$\frac{d}{dt}(x_1 + x_2 - x_4) = k_2(x_1 - 2x_2 - x_4 + C_2)x_4 - 3k_5 x_2$$

The constants $C_1$ and $C_2$ are derived from the initial conditions of the problem and are given below.

$$C_1 = x_{10} + x_{30}$$

$$C_3 = -x_{10} + 2x_{20} + x_{40} + 3x_{50}$$

The "dead end" variables $x_3$ and $x_5$ are determined from

$$x_3(t) = C_1 - x_1(t)$$

$$x_5(t) = (C_3 - x_1(t) - 2x_2(t) - x_4(t) - 3x_5(t))/3$$

Expressions for $F^k$ and $\Delta x^{k+1}$ for the reduced system are
\[ f^k = - \begin{bmatrix} \frac{x_1 - x_{10}}{\Delta t} + k_1 x_1 x_4 + k_4 c_1 \\ \frac{2(x_1 - x_{10}) - (x_2 - x_{20}) - 2(x_4 - x_{40})}{\Delta t} - 3k_3 x_2 x_4 - 3k_5 x_2 \\ \frac{x_1 - x_{10} + x_2 - x_{20} - (x_4 - x_{40})}{\Delta t} - k_2 x_4 (x_1 - 2x_2 - x_4 + c_3) - 3k_5 x_2 \end{bmatrix} \]

and

\[ \Delta x^{k+1} = \begin{bmatrix} x_1^{k+1} - x_1^k \\ x_2^{k+1} - x_2^k \\ x_4^{k+1} - x_4^k \end{bmatrix} \]

and the components for the Jacobian for the reduced system are

\[ j_{11} = \frac{1}{\Delta t} + k_1 x_4 \quad j_{21} = \frac{2}{\Delta t} \quad j_{31} = \frac{1}{\Delta t} - k_2 x_4 \]

\[ j_{12} = 0 \quad j_{22} = -\frac{1}{\Delta t} - 3k_3 x_4 - 3k_5 \quad j_{32} = \frac{1}{\Delta t} - 2k_2 x_4 - 3k_5 \]

\[ j_{13} = k_1 x_4 \quad j_{23} = -\frac{2}{\Delta t} - 3k_3 x_2 \quad j_{33} = \frac{1}{\Delta t} - k_2 (x_1 - 2x_2 - 2x_4 + c_3) \]
D. Error and Reduction of the Stiffness

Instead of solving the kinetic equations

\[ \frac{dx_i}{dt} = f_i(\bar{x}, t), \quad i=1,2,...,n \]

exactly in the interval \([t_o, t]\), the quantities computed, \(\bar{x}(t)\), possess a discretization error due to the numerical method. Inherent in this error is the problem associated with the stiffness in the kinetic equations which can effectively be shown to be reduced by applying the NRK method.

Under the hypothesis that the true solution, \(x^*(t)\), satisfies the conditions of existence and uniqueness of Theorem I and possesses continuous derivatives, we may write

\[ x^*_i(t) = x^*_i(t_o) + \Delta t f_i(x^*, t) - \frac{\Delta t^2}{2} \frac{d^2 f_i}{dt^2}(x^*, \gamma) \]  \hspace{1cm} (5.7)

where \(t_o < \gamma < t\) and \(\Delta t = t - t_o\). By replacing the derivative by a forward difference as is done in the NRK method, the computed values satisfy

\[ x_i(t) = x_i(t_o) + \Delta t f_i(x, t) \]  \hspace{1cm} (5.8)

If we define an error in the solution of component \(i\) by

\[ e_i(t) = x_i(t) - x^*_i(t) \]

and subtract Equation 5.7 from 5.8, we have
\[ e_i(t) = e_i(t_0) + \Delta t[f_i(x,t) - f_i(x^*, t)] + \frac{\Delta t^2}{2} \frac{df_i}{dt}(x^*, \gamma) . \]  

(5.9)

From the mean value theorem, the term in brackets becomes

\[ [.] = \sum_{j=1}^{n} f_{ij}(x^{**}, t^{**})(x_j - x_j^*) \]

where \( t^{**} \in [t_0, t] \), \( x^{**} \in [x, x^*] \), and \( f_{ij} = \frac{\partial f_i}{\partial x_j} \). Then Equation 5.9 becomes

\[ e_i(t) = e_i(t_0) + \Delta t[ \sum_{j=1}^{n} f_{ij} e_j(t) ] + \frac{\Delta t^2}{2} \frac{df_i}{dt}(x^*, \gamma) . \]  

(5.10)

If we write Equation 5.10 in vector form we have

\[ \vec{e}(t) = \vec{e}(t_0) + \Delta t J(x^{**}, t^{**}) \vec{e}(t) + \frac{\Delta t^2}{2} \frac{\vec{f}}{dt}(x^*, \gamma) \]

where \( J(x^{**}, t^{**}) \) is the matrix of partials earlier referred to as the Jacobian. We solve for \( \vec{e}(t) \) to obtain

\[ \vec{e}(t) = (I - \Delta t J)^{-1}[\vec{e}(t_0) + \frac{\Delta t^2}{2} \frac{\vec{f}}{dt}(x^*, \gamma) ] . \]  

(5.11)

We then denote the total local discretization error introduced into the system by proceeding from time \( t_0 \) to time \( t \) by \( E(t) \) where
\[ E(t) = \| \tilde{e}(t) \| . \]

From the triangle inequality, we obtain

\[ E(t) \leq \| (I - \Delta t J)^{-1} \{ E(t_0) + \frac{\Delta t^2}{2} \| \frac{df}{dt}(x^*, \gamma) \| \} \]  

(5.12)

We now expand the vector of functions

\[ \frac{df}{dt}(x^*, \gamma) \]

about \( \gamma \) in the interval \([t_0, t]\) to obtain

\[ \frac{d\tilde{f}}{dt}(\tilde{x}^*, \gamma) = \frac{df}{dt}(\tilde{x}, t) + \Delta t \frac{d^2f}{dt^2}(\tilde{x}, t) + \frac{\Delta t^2}{2} \frac{d^3f}{dt^3}(\tilde{x}, t) + ... \]  

(5.13)

The derivative \( d\tilde{f}(\tilde{x}, t)/dt \) is written for component \( i \) as

\[ \frac{df_i}{dt}(\tilde{x}, t) = \sum_{j=1}^{n} \frac{\partial f_i}{\partial x_j} \frac{\Delta x_j}{\Delta t} + \frac{\partial f(\tilde{x}, t)}{\partial t}, \quad i = 1, 2, ..., n \]

and \( d^2\tilde{f}(\tilde{x}, t)/dt^2 \) is given by

\[ \frac{d^2f_i}{dt^2}(\tilde{x}, t) = \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial^2 f_i}{\partial x_j \partial x_k} \frac{\Delta x_j \Delta x_k}{\Delta t^2} + \sum_{j=1}^{n} \frac{\partial^2 f_i(\tilde{x}, t)}{\partial x_j \partial t} \frac{\Delta x_j \Delta t}{\Delta t^2} \]

and so on for the higher order derivatives. If we substitute these into Equation 5.13 and order terms we have
\[
\frac{df}{dt} = \left[ \sum_j \frac{\partial \bar{f}}{\partial x_j} \frac{\Delta x_j}{\Delta t} + \Delta t \sum_j \sum_k \frac{\partial^2 \bar{f}}{\partial x_j \partial x_k} \frac{\Delta x_j \Delta x_k}{\Delta t^2} \right.
\]
\[+ \Delta t \sum_j \frac{\partial^2 \bar{f}}{\partial x_j \partial t} \frac{\Delta x_j \Delta t}{\Delta t^2} + \ldots \] \[+ \left. \left[ \frac{\partial \bar{f}}{\partial t} + \frac{\partial^2 \bar{f}}{\partial t^2} + \ldots \right] \right]
\]

which for convenience is written as

\[
\frac{df(x^*, \tau)}{dt} = [\bar{g}(\Delta x, t)] + \left[ \sum_{j=1}^{\infty} \frac{\partial^j \bar{f}(x, t)}{\partial t^j} \right]. \quad (5.14)
\]

When stiffness is exhibited in the kinetic equations, the term \(\bar{g}(\Delta x, t)\) which contains the partials with respect to the dependent variables, \(x\), is the predominant one in Equation 5.14 and is usually several orders of magnitudes larger than the partials with respect to \(t\). The reason for this is that the derivatives with respect to the dependent variables, \(\bar{x}\), contain rate constants raised to a power equal to the order of the derivative in which they are contained. Since the rate constants can be quite large, of the order \(10^{10}\) or more, these derivatives can be quite large even when small concentrations exist. Thus, \(\bar{g}(\Delta \bar{x}, t)\) is the largest portion of the discretization error seen in Equation 5.12 and is referred to as the "stiff" part of the error.

If we substitute Equation 5.14 into Equation 5.11 we have
\[ \bar{e}(t) = (I - \Delta t J)^{-1} \left[ \bar{e}(t_0) + \frac{\Delta t^2}{2} (\bar{g}(\Delta \bar{x}, t)) + \sum_{j=1}^{\infty} \frac{\partial_j f(x, t)}{\partial t} \right] . \] (5.15)

We now write the error, \( \bar{e}(t) \), in three parts: the error from the previous step, the error due to the integration increment, \( \Delta t \), and the error due to stiffness, respectively, as shown below.

\[ \bar{e}(t) = \bar{B}\bar{e}(t_0) + \Delta t^2 \bar{B}h_t + \frac{\Delta t^2}{2} \bar{B}g(\Delta \bar{x}, t) \] (5.16)

\( B \) is the matrix given by

\[ B = (I - \Delta t J(\bar{x}^{**}, t^{**}))^{-1} \]

and

\[ h_t = \sum_{i=1}^{\infty} \frac{\partial_i f(\bar{x}, t)}{\partial t} . \]

When we use the NRK method to solve the kinetic equations in the interval \([t_0, t]\), \( \bar{e}(t) \) is effectively reduced during the iteration process. This can be seen by the following. After the linearization, the system is written for iteration \( k+1 \) as

\[ \Delta \bar{x}^{k+1} = -J^{-1}(\bar{x}^k, t)f(\bar{x}^k, t) . \]

If the method converges, \( ||\Delta \bar{x}^{k+1}|| \) is reduced at each step during the iteration. It reduces very rapidly since
we have quadratic convergence. The iteration continues until

\[ ||\Delta x^{k+1}|| < \varepsilon , \quad \varepsilon > 0 \]

where \(\varepsilon\) is some predetermined small number.

Before the iteration begins, the error introduced by substituting a forward difference for the derivative is \(\tilde{e}(t)\) as shown in Equation 5.15. During the iteration the stiff term containing \(g(\Delta x, t)\) is reduced and thus \(\tilde{e}(t)\) is reduced for a given \(\Delta t\) during the iteration as well. It is for this reason that relatively larger step sizes can be used with the NRK method to solve the kinetic equations than those required by the Runge-Kutta and predictor-corrector methods.

Let \(||g(\Delta x, t)||\) be denoted by \(g_b\) and \(g_a\) before and after the iteration respectively. Then the total local discretization error in the interval \([t_0, t]\) defined in Equation 5.12 before and after the iteration is

\[ E_b(t) \leq ||B|| \left[ E(t_0) + \Delta t^2 ||h_t|| \right] + \frac{\Delta t^2}{2} ||B|| g_b \]

and

\[ E_a(t) \leq ||B|| \left[ E(t_0) + \Delta t^2 ||h_t|| \right] + \frac{\Delta t^2}{2} ||B|| g_a . \]

But, since \(g(\Delta x, t)\) is reduced in the iteration, \(g_a \leq g_b\) and we have

\[ E_a(t) \leq E_b(t) . \]
Since $g_b$ is by orders of magnitude the largest part of the error, $E_a(t)$ is necessarily much less than $E_b(t)$ when stiffness is encountered during the integration. Thus, desired degrees of accuracy can still be obtained when relatively large step sizes are used in the integration.
VI. COMPARISON OF USABLE METHODS

As we have seen, the three methods which were found to be practical in solving the kinetic equations were the Exponential, the Finite Replacements, and the NRK. The NRK method can be used both on the full system and the reduced canonical form as well, and was considered the best for the kinetic equations in general. The Exponential and Finite Replacement methods worked well on smaller systems, and because of their simplicity were considered worthwhile for these problems. It is our intention in this chapter to compare these three methods in greater detail. In the succeeding discussion the following simplified notations are used:

- **R-K** 4th order Runge-Kutta method
- **EXP** Exponential method
- **FR** Finite Replacement method
- **NRK** Newton Raphson Kantorovich method used on the full system
- **NRKR** NRK method used on the reduced system.

Table 2 summarizes the three methods.

It is difficult to show the behavior of these methods for comparison purposes in general, as their behavior is highly dependent upon both the size of the system being studied and the initial conditions of the problem. Four
Table 2. Summary of usable methods for the solution of the kinetic equations

<table>
<thead>
<tr>
<th>Name</th>
<th>Form</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP</td>
<td>$x^{k+1} = (x_0 - \frac{B^k}{A^k})e^{-A^k \Delta t} + \frac{B^k}{A^k}$</td>
<td>good for smaller systems</td>
</tr>
<tr>
<td>FR</td>
<td>$x^{k+1} = \frac{x_0 + \Delta t B^k}{1 + \Delta t A^k}$</td>
<td>same as EXP but factor of ten increase of $\Delta t$ OK</td>
</tr>
<tr>
<td>NRK</td>
<td>$F^k = F_j^k \cdot \Delta x^{k+1}$</td>
<td>best of three; large time increments and small number of iteration on large or small system</td>
</tr>
</tbody>
</table>

problems are presented in this chapter however, that take into account extreme conditions for a practical problem. They can be used to justify the applicability of these methods and to draw conclusions as to which is best for particular problems.

Timings listed represent the CPU times required per iteration and for the total problem, including I/O, and are differentiated during the discussion. Timings were obtained on the IBM 360/65 computer at Iowa State University, using the Computation Center routine, ALTIME, written by White and Scranton (66). Numerical results showing concentrations
are written in the form \(x \cdot \times_{-n}\). where \(n\) represents the power of ten by which \(x \cdot \times\) should be multiplied.

A. Problem A

Problem A was run with the CO-O\(_2\) system previously discussed which has five reactions and five concentrations. Initial conditions were \((1,1/2,0,0,0)\) and integration was performed at a constant temperature of \(220^\circ\text{K}\).

When a fourth order Runge-Kutta method was used on this problem, a stable solution could be obtained only with \(\Delta t \leq 10^{-6}\) seconds. This method took a total of 120 seconds of CPU time integrating in the interval \([0, .020]\) seconds. With the three usable methods, desirable accuracies were obtained with \(\Delta t \leq .1\) seconds, and although more iterations were required per step for the EXP and FR methods, the total times for these and the NRK method were approximately the same.

Table 3 shows the amount of CPU time required with the four methods in seconds (s) and milliseconds (ms). Also shown are results obtained with the three usable methods when \(\Delta t = .01\) seconds and with the Runge-Kutta method, which required \(\Delta t = 10^{-6}\) seconds. I/O time is not included. As can be seen, the results obtained using the three usable methods agree quite well with the Runge-Kutta, even though a large time increment was used.

Thus, for problem A, we are able to compute concentrations at times .01 and .02 seconds approximately 4000 to
Table 3. Results for Problem A, comparing 4th order R-K with EXP, FR, and NRK methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Iterations</th>
<th>C U</th>
<th>x₁</th>
<th>x₂</th>
<th>x₃</th>
<th>x₄</th>
<th>x₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-K</td>
<td>.01</td>
<td>120(s)</td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>2.89⁻⁶</td>
<td>8.08⁻¹⁰</td>
<td>2.38⁻¹²</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td></td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>5.78⁻⁶</td>
<td>8.68⁻¹⁰</td>
<td>5.12⁻¹²</td>
</tr>
<tr>
<td>EXP</td>
<td>.01</td>
<td>9</td>
<td>35(ms)</td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>2.89⁻⁶</td>
<td>8.08⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>7</td>
<td></td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>5.78⁻⁶</td>
<td>8.68⁻¹⁰</td>
</tr>
<tr>
<td>FR</td>
<td>.01</td>
<td>9</td>
<td>27(ms)</td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>2.89⁻⁶</td>
<td>8.08⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>7</td>
<td></td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>5.78⁻⁶</td>
<td>8.68⁻¹⁰</td>
</tr>
<tr>
<td>NRK</td>
<td>.01</td>
<td>3</td>
<td>24(ms)</td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>2.89⁻⁶</td>
<td>8.08⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>3</td>
<td></td>
<td>9.99⁻¹</td>
<td>4.99⁻¹</td>
<td>5.78⁻⁶</td>
<td>8.68⁻¹⁰</td>
</tr>
</tbody>
</table>

5000 times faster by using the EXP, FR, or NRK methods than by using the fourth order Runge-Kutta method and still retain desirable accuracies. If higher degrees of accuracy are required, smaller time increments can be used.

B. Problem B

Problem B was run on the CO-O₂ system with initial conditions equal to the equilibrium concentrations at \( T_{IC} = 1000^\circ K \). The integration was performed at a constant temperature, \( T = 2200^\circ K \). The EXP, FR, and NRK methods were
used on this problem with the NRK method used both on the full five component system as well as the canonically reduced three component system previously discussed. Table 4 shows the time required per iteration in milliseconds for the particular method and includes the I/O time required to write the five results and the time step.

Table 4. Time required per iteration for Problem B (times are in milliseconds and include I/O)

<table>
<thead>
<tr>
<th>Method</th>
<th>EXP</th>
<th>FR</th>
<th>NRK</th>
<th>NRKR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.4</td>
<td>3.9</td>
<td>4.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 5 shows the number of iterations that were required for this problem at selected time steps using various time increments for the integration. At the end of each set of data for a particular time increment is the total number of iterations required for that problem as well as the total CPU time in milliseconds (including I/O) which is shown in parenthesis. An asterisk (*) indicates that this method did not converge in 200 iterations to the required number of significant digits expected in the answer, which for this problem was seven for each variable. Concentration results
Table 5. Iterations required for Problem B at selected time steps by using various integration increments (total gives number of iterations and time including I/O in milliseconds, shown in parentheses for each problem)

<table>
<thead>
<tr>
<th>$\Delta t$(ms)</th>
<th>$t$(ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>.01</td>
<td>.01</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>.1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>.3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>90</td>
<td>90</td>
<td>90(350)</td>
<td>90(350)</td>
</tr>
<tr>
<td>.1</td>
<td>.1</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>.3</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>1.0</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>142</td>
<td>142</td>
<td>87(340)</td>
<td>88(442)</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>18</td>
<td>17</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>17</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>19</td>
<td>13</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>140</td>
<td>122</td>
<td>72(280)</td>
<td>72(346)</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>*</td>
<td>*</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>*</td>
<td>*</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>*</td>
<td>*</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td>71(276)</td>
<td>71(340)</td>
</tr>
</tbody>
</table>

*Did not converge in 200 iterations.
Table 5 (Continued)

<table>
<thead>
<tr>
<th>$\Delta t$(ms)</th>
<th>t(ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>*</td>
<td>*</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>*</td>
<td>*</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>*</td>
<td>*</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>*</td>
<td>*</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>-</td>
<td>-</td>
<td>31(121)</td>
<td>32(153)</td>
</tr>
</tbody>
</table>

are not shown for this problem; however, agreement was at least to 0.1% in each variable for a given problem.

Although the EXP and FR methods did not converge to the desired accuracy with $\Delta t = 10\text{ms}$ and 100ms, the iteration was slowly tending to the answer. Results were not obtained to determine the number of iterations necessary for convergence for more than 200 iterations for any of the methods.

C. Problem C

Problem C was also run with the CO-$O_2$ systems, using the equilibrium values at 2200°K for initial conditions, and was temperature variant. The temperature profile used is shown below.
Table 6 shows results for the most ill behaving variable (O) in the system, using the EXP, FR, NRK, and NRKR methods. For all time increments shown, the other variables agreed to more significant digits, most out to six significant digits. Also shown in Table 6 are the number of iterations that were necessary for the particular time steps. These appear in parenthesis to the left of the resultant concentration. Results were obtained using a convergence criterion of seven significant digits in the iteration.

Tables 7 and 8 give the results obtained using a convergence criterion of three and seven significant digits at selected time steps, and the number of iterations required for each, respectively. Again the worst behaving variable is presented.

If we compare the results shown in Tables 6, 7, and 8 at various time intervals, several interesting points are apparent. If we use small time increments similar results
Table 6. Resultant concentrations of O in Problem C for various time increments (iterations required are in parentheses for convergence of seven significant digits)

<table>
<thead>
<tr>
<th>Δt (ms)</th>
<th>time (ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>1</td>
<td>(4) 4.52^{-4}</td>
<td>(4) 4.52^{-4}</td>
<td>(2) 4.52^{-4}</td>
<td>(3) 4.52^{-4}</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>(4) 3.91^{-4}</td>
<td>(4) 3.92^{-4}</td>
<td>(2) 3.92^{-4}</td>
<td>(3) 3.92^{-4}</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>(8) 3.91^{-4}</td>
<td>(8) 3.92^{-4}</td>
<td>(4) 3.92^{-4}</td>
<td>(4) 3.92^{-4}</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>(7) 3.32^{-4}</td>
<td>(7) 3.33^{-4}</td>
<td>(3) 3.33^{-4}</td>
<td>(3) 3.33^{-4}</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>(5) 8.53^{-5}</td>
<td>(5) 8.61^{-5}</td>
<td>(3) 8.61^{-5}</td>
<td>(3) 8.61^{-5}</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>(2) 8.57^{-9}</td>
<td>(2) 8.68^{-9}</td>
<td>(3) 8.67^{-9}</td>
<td>(3) 8.68^{-9}</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>(2) 4.28^{-19}</td>
<td>(2) 4.35^{-19}</td>
<td>(3) 4.35^{-19}</td>
<td>(3) 4.35^{-19}</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>(52) 3.91^{-4}</td>
<td>(28) 3.92^{-4}</td>
<td>(3) 3.92^{-4}</td>
<td>(4) 3.92^{-4}</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>(41) 3.32^{-4}</td>
<td>(25) 3.34^{-4}</td>
<td>(3) 3.34^{-4}</td>
<td>(4) 3.34^{-4}</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>(14) 8.53^{-5}</td>
<td>(12) 8.61^{-5}</td>
<td>(3) 8.61^{-5}</td>
<td>(4) 8.61^{-5}</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>(3) 8.57^{-9}</td>
<td>(3) 8.68^{-9}</td>
<td>(2) 8.68^{-9}</td>
<td>(3) 8.68^{-9}</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>(2) 4.28^{-19}</td>
<td>(2) 4.37^{-19}</td>
<td>(2) 4.37^{-19}</td>
<td>(2) 4.37^{-19}</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>*</td>
<td>(63) 8.62^{-4}</td>
<td>(4) 8.62^{-4}</td>
<td>(4) 8.62^{-4}</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>*</td>
<td>(4) 8.74^{-9}</td>
<td>(3) 8.74^{-5}</td>
<td>(4) 8.74^{-5}</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>*</td>
<td>(2) 8.53^{-19}</td>
<td>(3) 8.53^{-19}</td>
<td>(3) 8.53^{-19}</td>
</tr>
</tbody>
</table>

*Did not converge in 200 iterations.
Table 7. Resultant concentrations obtained in Problem C with convergence criteria of 3 and 7 significant digits (results are for most ill behaving component)

<table>
<thead>
<tr>
<th>Δt(ms)</th>
<th>t(ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>.1</td>
<td>1</td>
<td>4.514×10^{-4}</td>
<td>4.514×10^{-4}</td>
<td>4.518×10^{-4}</td>
<td>4.518×10^{-4}</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>3.908×10^{-4}</td>
<td>3.906×10^{-4}</td>
<td>3.918×10^{-4}</td>
<td>3.918×10^{-4}</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>3.911×10^{-4}</td>
<td>3.906×10^{-4}</td>
<td>3.920×10^{-4}</td>
<td>3.917×10^{-4}</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>8.565×10^{-5}</td>
<td>8.527×10^{-5}</td>
<td>8.635×10^{-5}</td>
<td>8.611×10^{-5}</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>*</td>
<td>*</td>
<td>8.637×10^{-5}</td>
<td>8.624×10^{-5}</td>
</tr>
</tbody>
</table>

* Did not converge in 200 iterations.

Table 8. Required number of iterations for Problem C with convergence criteria of 3 and 7 significant digits (for all components)

<table>
<thead>
<tr>
<th>Δt(ms)</th>
<th>t(ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>.1</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>3</td>
<td>8</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>19</td>
<td>52</td>
<td>11</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>6</td>
<td>14</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>*</td>
<td>*</td>
<td>29</td>
<td>63</td>
</tr>
</tbody>
</table>

* Did not converge in 200 iterations.
are obtained for all the methods and approximately the same number of iterations are required. This indicates that the EXP and FR methods are desirable for this system when smaller time increments are desired because of the simplicity of their use. Their behavior is not as good when the time increment is increased. The EXP did not converge in 200 iterations with \( \Delta t = 100 \text{ms} \).

As expected since finite differences were used, the FR, NRK, and NRKR methods gave similar results for all the time increments shown; however, a smaller convergence criterion was necessary for the FR method to attain accuracy. In all cases the number of iterations required for the NRK and NRKR methods was less than or equal to the number required for the FR or EXP methods. When large time increments were used, the number of iterations was much less. For \( \Delta t = 10 \text{ms} \), the EXP, FR, NRKR, and NRK methods required 52, 28, 3, and 4 iterations respectively at 10ms.

In general, all four methods took approximately the same amount of CPU time when a small \( \Delta t \) was used for the CO-O₂ system; however this was not true as the system and the integration increments became larger. This is further exemplified in Problem D.

The NRK and NRKR methods gave the same results in approximately the same number of iterations; however, since a smaller system was solved, the NRKR method was the faster
of the two. As shown by the next problem which solved a larger system, a saving of nearly 2 to 1 was realized in CPU time requirements.

The NRK and NRKR methods gave consistent results for all the time increments shown, and the same results (to four significant digits) were obtained with either a convergence criterion of three or seven significant digits. In general, this was true for both of these methods for all the problems studied by this author. The behavior of these methods was such that in one iteration a result very close to the answer was obtained and by iteration three, a change was not noted in the tenth significant digit in most of the components. This is exemplary of quadratic convergence.

In general it was found that a convergence criterion of three significant digits used with the NRK and NRKR methods was sufficient in the integration. Problems were run with convergence criteria of three, seven, and twelve significant digits and the answers were the same (to three significant digits) for these runs throughout the whole integration interval.

D. Problem D

Problem D was run with the Methane-Air system discussed in Chapter VII. This system is larger than the CO-O\textsubscript{2} system and consists of 24 reactions and 13 species or components.
The problem represents oscillatory combustion with the temperature oscillating at a frequency of 1000 Hz and decreasing from 2600°K to 500°K in a period of 220 milliseconds. Initial conditions were the equilibrium values at 2600°K.

Table 9 shows the time that was required per iteration in milliseconds for each of the EXP, FR, NRKR, and NRK methods but does not include I/O time. Table 10 shows the total time required for the total problem using various integration increments and does not include I/O time.

Concentration results are not presented here as they are discussed in Chapter VII; however acceptable agreement in the results was obtained using time increments of 1/8ms, 1ms, and 5ms.

The FR method did not converge to a solution of this problem within 200 iterations unless an integration increment less than 0.01 milliseconds was used. The problem was not run through to completion using this Δt; however a projected time based on an average number of iterations (30) derived from those actually required at the beginning of the iteration (50) was obtained and appears in parenthesis in Table 10. The EXP method did not converge to a solution in 200 iterations for Δt = 0.01 milliseconds and was no longer considered.

For comparison, projected times are also shown for the NRKR and NRK methods for Δt = 0.01 milliseconds and are based
Table 9. Time per iteration for Problem D (times are in milliseconds and do not include I/O)

<table>
<thead>
<tr>
<th></th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>4.9</td>
<td>21.1</td>
<td>35.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 10. Total time in seconds for Problem D (for integration increments shown—does not include I/O)

<table>
<thead>
<tr>
<th>Δt(ms)</th>
<th>EXP</th>
<th>FR</th>
<th>NRKR</th>
<th>NRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>.01</td>
<td>*</td>
<td>(3800)</td>
<td>(870)</td>
<td>(1470)</td>
</tr>
<tr>
<td>.125</td>
<td>*</td>
<td>*</td>
<td>117</td>
<td>176</td>
</tr>
<tr>
<td>1</td>
<td>*</td>
<td>*</td>
<td>13.4</td>
<td>23.4</td>
</tr>
<tr>
<td>5</td>
<td>*</td>
<td>*</td>
<td>3.5</td>
<td>6.1</td>
</tr>
</tbody>
</table>

* Did not converge in 200 iterations.

on the number of iterations required for actual cases run with larger time increments. The number of iterations required for Δt = 1/8ms was less or equal to three for the whole range and therefore an average of two was used for Δt = .01 milliseconds.

As is pointed out in Tables 9 and 10, the NRK and NRKR
methods required four to five times more time per iteration than the EXP or FR method, however they can be used to integrate the Methane-Air system much faster since less iterations are required. Although the EXP and FR methods were tending to a solution, convergence was not reached in 200 iterations for $\Delta t > 0.01$ ms for either method.

No time estimates were obtained using the Runge-Kutta method on this system; however from times given for similar systems, such as that given by Opsahl (44), it is felt that 30 hours of computer time would be a low estimate. This figure, in comparison to those shown in Table 10, indicates savings of from 1000 to 10000 times in CPU time.

E. Convergence Criterion and Accuracy Problems

In order to test for convergence of the iteration with any of the methods discussed, the usual practice is to use a summation norm such as

$$\|\bar{x}^{k+1} - \bar{x}^{k}\| = \sum_{i=1}^{n} |x_{i}^{k+1} - x_{i}^{k}|$$

which is compared with some predetermined quantity, $\varepsilon > 0$. If the norm is less than this quantity, the iterates $\bar{x}^{k+1}$ are accepted as the solution to the problem.

Care must be taken however when testing for convergence of results obtained in the kinetic equations. These results can have such a wide range in magnitude for a particular
problem that it is possible for a norm to lose the smallest variable completely when the summation is performed in the computer. These smaller components are usually the slowest to converge in the iteration in these problems and therefore the convergence of these variables would not be tested.

A normalized norm can be used to test the convergence of all variables in the system if the following form is used:

$$\|x^{k+1} - x^k\| = \sum_{i=1}^{n} \left| \frac{x_i^{k+1} - x_i^k}{x_i^{k+1}} \right| = \sum_{i=1}^{n} \left| \frac{\Delta x_i^{k+1}}{\Delta x_i^{k+1} + x_i^k} \right| < \varepsilon , \varepsilon > 0 .$$

The quantity $\varepsilon$ is then a measure of the number of significant digits desired such that no change is noted by further iterating any variable.

Another problem can occur in the kinetic equations which can be alleviated by using double or extended precision in the computer. In some problems the right hand sides of the equations can have terms that are of the same magnitude and sometimes the same value to several significant digits. If these terms are of opposite sign and are the largest in magnitude in the equations severe loss of accuracy results. This has been encountered particularly in the auxiliary equations used to calculate the "dead end" variables in the NRKR method. By judiciously choosing variables that are extraneous to the calculation as the "dead end" variables this problem can be lessened however.
VII. OSCILLATORY COMBUSTION IN THE METHANE-AIR SYSTEM

The problems and results presented in this chapter show the effects of oscillatory combustion in the burning of methane in air and have been solved using the NRK and NRKR methods. The important reactions and rate equations in this system are presented in the Appendix for use with the NRK and NRKR methods and will not be repeated here.

Two problems were run to show the resultant effects of oscillations on a given temperature profile. The first problem was solved with the temperature profile shown in Figure 13. The second problem was solved with sixty degree oscillations superimposed on this basic profile which were oscillated at a frequency of 1000 Hz. This profile is shown in Figure 14. The initial concentrations used in this problem were the equilibrium values calculated by Seagrave (56) at $T = 2600^\circ K$.

A great deal of discussion can be made concerning the results of this problem; however it is not the purpose here to do this. We leave this to an interested reader of the paper. The purpose is, however, to show the use of the NRK and NRKR methods on this relatively large system. Results of the two problems are shown in Figures 17 through 26 for important constituents in the system, and equilibrium concentrations are shown in Figures 15 and 16 for the basic
temperature profile shown in Figure 13.

It was found that both the NRK and NRKR methods worked well for these problems. The discussion of Problem D presented in Chapter VI gives more detail of their behavior and includes run times for the total problem for various time increments of integration.
Figure 13. Temperature profile for the Methane-Air problem
Figure 14. Temperature profile for the Methane-Air problem—
60°K peak to peak oscillations superimposed at a
frequency of 1000 Hz
Figure 15. Equilibrium concentrations for CO, NO, and O in the Methane-Air problem (temperature profile given in Figure 13)
Figure 16. Equilibrium concentrations for NO$_2$ and O$_3$ in the Methane-Air problem (temperature profile given in Figure 13)
Figure 17. Dynamic concentration of $O_3$
Figure 18. Dynamic oscillatory concentration of O₃
Figure 19. Dynamic concentration of NO$_2$
Figure 20. Dynamic oscillatory concentration of NO$_2$
Figure 21. Dynamic concentration of NO
Figure 22. Dynamic oscillatory concentration of NO
Figure 23. Dynamic concentration of CO
Figure 24. Dynamic oscillatory concentration of CO
Figure 25. Dynamic concentration of O
Figure 26. Dynamic oscillatory concentration of O
The kinetic equations studied for this paper represent systems of nonlinear ordinary differential equations which approximate burning processes. They are sometimes referred to as "stiff" equations and are characterized by extremely varying rate constants which exhibit instabilities in most general numerical methods.

This was aimed at finding an efficient and accurate numerical method of solution to these equations that is applicable to oscillatory combustion. Attempt was made to bring the problems associated with these equations into perspective for the numerical analyst, hopefully to spur interest for further research in this area.

Problems associated with Runge-Kutta and predictor-corrector solution of the kinetic equations have been brought out. Several linearization and iteration methods of solution were tried on these equations by this author and have also been presented. Of these, three methods were considered to be superior since they allowed increases of $10^5$ in integration step size over the Runge-Kutta and predictor-corrector methods. Two methods were found usable for smaller systems and one, the NRK method, was applicable to large and small systems. A section showing how reduction of error accomplished by the NRK method has also been presented.

Several conclusions can be drawn concerning the
application and usability of the methods considered. They are summarized below.

1. The Exponential and Finite Replacements Methods represent applicable methods of solution on smaller systems (5 components or less) and are particularly appealing because of their simplicity of use. Relatively large step sizes can be used on these systems and desirable accuracy is still attained in few iterations. These methods also work on large systems. However in these cases, the step sizes must be reduced and the number of iterations increased to such an extent that integration times become too large to warrant them being practical.

2. The Newton-Raphson-Kantorovich (NRK) method is applicable to large or small systems of kinetic equations and works well for the problems in oscillatory combustion. Relatively large step sizes can be used and few iterations are required. This method is applicable to the canonically reduced system which makes possible even greater savings in computer times.

3. Relative shapes and behaviors of components are still retained even though extremely large step sizes are used with the Exponential, Finite Replacements and NRK methods. An advantage is realized here for studying the behavior of systems very economically to find near equilibrium times. Problems can be run with desirable accuracy in
less than 10 seconds which previously took 20 to 30 hours using Runge-Kutta methods.

4. There can be a disadvantage realized when solving systems with the canonically reduced form if the "dead end" components are of the same magnitude as the smallest component from which it is computed. Extended precision or judicious choosing of the dead end variables to eliminate from the system can reduce this problem.

5. If integrations are desired at constant times for varying temperatures, T, there may be some advantage to transforming the equations such that the independent variable is temperature, since the slopes \( \frac{dx}{dT} \) were smaller than \( \frac{dx}{dt} \) for the problems investigated.

6. Although the temperature variant problems and those representing oscillatory combustion are extremely complicated in their behavior, it is felt that some relationship could exist for automatic determination of integration step size other than halving the interval techniques. Further work could be done to see if some relation exists between the step size and the size of the derivative or perhaps the size of the largest rate constant.
IX. BIBLIOGRAPHY


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X. ACKNOWLEDGMENTS

It would be difficult to adequately express my sincere appreciation to Professor Clair G. Maple, who directed this research. To detail his many hours of discussion and helpful suggestions needed to research and prepare this thesis would be an impossibility. I am deeply grateful for his guidance and assistance.

I am also greatly indebted to Dr. Richard C. Seagrave, who brought the numerical problem in solving the kinetic equations to my attention. His many hours spend discussing the chemical and physical processes involved have been of invaluable assistance and an integral part of this thesis.

Last but not least, I am deeply grateful to my wife, Mary-Ann, and our children, for their forbearance, understanding, and love in supporting me throughout my research.
XI. APPENDIX: THE METHANE-AIR EQUATIONS

A complete set of reactions were found by Opsahl (44, p. 84) for the combustion of methane and air. For the problem presented in Chapter VII, the following reactions were considered:

1. \( \text{NO}_2 + O \rightarrow O_2 + \text{NO} \)
2. \( O + O_2 \rightarrow O_3 \)
3. \( \text{CO} + O \rightarrow \text{CO}_2 \)
4. \( O + O_3 \rightarrow 2O_2 \)
5. \( \text{NO} + N \rightarrow N_2 + O \)
6. \( N + O_2 \rightarrow \text{NO} + O \)
7. \( 2\text{NO} \rightarrow N_2 + O_2 \)
8. \( 2\text{NO} + O_2 \rightarrow 2\text{NO}_2 \)
9. \( \text{NO} + O \rightarrow N + O_2 \)
10. \( N_2 + O \rightarrow \text{NO} + N \)
11. \( \text{CO}_2 \rightarrow \text{CO} + O \)
12. \( N_2 + O_2 \rightarrow 2\text{NO} \)
13. \( O_2 \rightarrow 2O \)
14. \[ \text{NO}_2 + \text{CO}_2 \rightarrow \text{NO} + \text{CO}_2 \]

15. \[ \text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH} \]

16. \[ \text{CO}_2 + \text{H} \rightarrow \text{OH} + \text{CO} \]

17. \[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]

18. \[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]

19. \[ \text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H} \]

22. \[ \text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH} \]

23. \[ \text{H} + \text{OH} \rightarrow \text{H}_2 + \text{O} \]

24. \[ 2\text{HO} \rightarrow \text{H}_2\text{O} + \text{O} \]

27. \[ \text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O} \]

28. \[ \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH} \]

If we set

\[ x_1 = \text{CO} \]
\[ x_2 = \text{O}_2 \]
\[ x_3 = \text{CO}_2 \]
\[ x_4 = \text{O} \]
\[ x_5 = \text{O}_3 \]
\[ x_6 = \text{OH} \]
\[ x_7 = H_2O \]
\[ x_8 = H_2 \]
\[ x_9 = H \]
\[ x_{10} = N \]
\[ x_{11} = N_2 \]
\[ x_{12} = NO_2 \]
\[ x_{13} = NO \]

the reactions yield the following kinetic equations:

\[ \frac{dx_1}{dt} = -k_3 x_1 x_2 - k_{14} x_1 x_{12} - k_{17} x_1 x_6 + k_{11} x_3 - k_{16} x_3 x_9 \]

\[ \frac{dx_2}{dt} = -k_2 x_2 x_4 - k_6 x_2 x_{10} - k_8 x_2 x_{13} - k_{12} x_2 x_{11} - k_{13} x_2 + k_{18} x_2 x_9 + k_4 x_4 x_5 + k_7 x_{13} + k_9 x_4 x_{13} + k_{19} x_4 x_6 \]

\[ \frac{dx_3}{dt} = -k_{11} x_3 - k_{16} x_3 x_9 + k_3 x_1 x_4 + k_{14} x_1 x_{12} + k_{17} x_1 x_6 \]

\[ \frac{dx_4}{dt} = -k_1 x_4 x_{12} - k_2 x_2 x_4 - k_3 x_1 x_4 - k_{14} x_4 x_5 - k_9 x_4 x_{13} - k_{10} x_4 x_{11} - k_{19} x_4 x_6 - k_{22} x_2 x_8 + k_{23} x_6 x_9 + k_{15} x_{10} x_{13} + k_{6} x_{10} x_{13} - k_6 x_2 x_{10} + k_{11} x_3 + 2k_{13} x_2 + k_{18} x_2 x_9 + k_{24} x_6 \]
\[
\begin{align*}
\frac{dx_5}{dt} &= -k_4^2 x_5 + k_2 x_2^2 x_4 \\
\frac{dx_6}{dt} &= -k_{17} x_1 x_6 - k_{19} x_4^2 x_6 - k_{23}^2 x_6^2 x_9 - 2k_{24} x_6^2 - k_{27} x_6^2 x_8 \\
&\quad + k_{15}^2 x_9 x_{12} + k_{16} x_3^2 x_9 + k_{18} x_2^2 x_9 + k_{22} x_4^2 x_8 + k_{28} x_7 x_9 \\
\frac{dx_7}{dt} &= -k_{28} x_7 x_9 + k_{24} x_6^2 + k_{27} x_6^2 x_8 \\
\frac{dx_8}{dt} &= -k_{22} x_4^2 x_8 - k_{27} x_6 x_8 + k_{23} x_6 x_9 + k_{28} x_7 x_9 \\
\frac{dx_9}{dt} &= -k_{15}^2 x_9 x_{12} - k_{16} x_3^2 x_9 - k_{18} x_2^2 x_9 - k_{23} x_6 x_9 - k_{28} x_7 x_9 \\
&\quad + k_{17} x_1 x_6 + k_{19} x_4^2 x_6 + k_{22} x_4^2 x_8 + k_{27} x_6 x_8 \\
\frac{dx_{10}}{dt} &= -k_{5} x_{10} x_{13} - k_{6} x_2 x_{10} + k_{9} x_4 x_{13} + k_{10} x_4 x_{11} \\
\frac{dx_{11}}{dt} &= -k_{10} x_4 x_{11} - k_{12} x_2 x_{11} + k_{5} x_{10} x_{13} + k_{7} x_{13} \\
\frac{dx_{12}}{dt} &= -k_{1} x_4 x_{12} - k_{14} x_1 x_{12} - k_{15} x_9 x_{12} + 2k_{8} x_2 x_{13}^2 \\
\frac{dx_{13}}{dt} &= -k_{5} x_{10} x_{13} - 2k_{7} x_{13}^2 - 2k_{8} x_2 x_{13}^2 + k_{9} x_4 x_{13} + k_{1} x_4 x_{12} \\
&\quad + k_{6} x_2 x_{10} + k_{10} x_4 x_{11} + 2k_{12} x_2 x_{11} + k_{14} x_1 x_{12} \\
&\quad + k_{15} x_9 x_{12}
\end{align*}
\]
The rate constant expressions were obtained from Opsahl (44, p. 82) and from an exponential fit to equilibrium calculations made by Seagrave (56). These are shown below. The units are litters/mole-second.

\[ k_1 = 7.83094 \times 10^{11} \exp(-2500/RT) \]
\[ k_2 = 2.7487 \times 10^7 \exp(-57669.6/RT) \quad 2200K < T \leq 2600K \]
\[ k_3 = 7.52445 \times 10^7 \exp(-62071.7/RT) \quad T \leq 2200K \]
\[ k_4 = 2 \times 10^8 \exp(-4500/RT) \]
\[ k_5 = 3 \times 10^{10} \exp(-6000/RT) \]
\[ k_6 = 3 \times 10^{10} \exp(-200/RT) \]
\[ k_7 = 8.3 \times 10^9 \exp(-7100/RT) \]
\[ k_8 = 1.7 \times 10^{10} \exp(-4800/RT) \]
\[ k_9 = 2.581 \times 10^{12} \exp(-12376.6/RT) \]
\[ 7.91 \times 10^9 \exp(-36538/RT) \quad 2100K < T \leq 2600K \]
\[ k_{10} = 4.33 \times 10^9 \exp(-34027/RT) \quad 1700K < T \leq 2100K \]
\[ 3.365 \times 10^9 \exp(-33173/RT) \quad T \leq 1700K \]
\[ k_{11} = 4.386 \times 10^7 \exp(74000/RT) \]
\[ k_{12} = 3.5087 \times 10^{13} \exp(-127088/RT) \]
\[ k_{13} = 3.26 \times 10^{11} \exp(-47797/RT) \]
\[ k_{14} = 2.5257 \times 10^9 \exp(-8358/RT) \]
\[ k_{14} = 2.96398 \times 10^7 \exp(-23948/RT) \]
\[ k_{15} = 1.24678 \times 10^{12} \exp(-2104/RT) \]
\[ k_{16} = 3.5 \times 10^{12} \exp(-33300/RT) \]
\[ k_{17} = 3.6 \times 10^{10} \exp(-12252/RT) \]
\[ k_{18} = 6 \times 10^{11} \exp(-18000/RT) \]
\[ k_{19} = 4.2018 \times 10^9 \exp(1633/RT) \]
\[ k_{22} = 2.46 \times 10^{10} \exp(-7700/RT) \]
\[ k_{23} = 5.7 \times 10^9 \exp(-5800/RT) \]
\[ k_{24} = \begin{cases} 1.203 \times 10^{28} \exp(-257000/RT) & 2000^\circ K < T \leq 2600^\circ K \\ 0 & T \leq 2000^\circ K \end{cases} \]
\[ k_{27} = 6 \times 10^{10} \exp(-5900/RT) \]
\[ k_{28} = 1 \times 10^{12} \exp(-25500/RT) \]

Reduction to Canonical Form

The full Methane-Air System written in matrix form is

\[ \frac{d\tilde{x}}{dt} = A\tilde{y} \quad (A.1) \]

where the concentration vector is

\[ \tilde{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{13} \end{pmatrix} \]
and the term types vector is

\[ \tilde{y} = \begin{array}{c}
y_1 \\
y_2 \\
\vdots \\
y_{25}
\end{array} \]

with components, \( y_i \), given below:

\[
\begin{align*}
y_1 &= k_1x_4x_{12} & y_{10} &= k_{10}x_4x_{11} & y_{19} &= k_{19}x_4x_6 \\
y_2 &= k_2x_2x_4 & y_{11} &= k_{11}x_3 & y_{20} &= k_{20}x_9 \\
y_3 &= k_3x_1x_4 & y_{12} &= k_{12}x_2x_{11} & y_{21} &= k_{22}x_4x_8 \\
y_4 &= k_4x_4x_5 & y_{13} &= k_{13}x_2 & y_{22} &= k_{23}x_6x_9 \\
y_5 &= k_5x_{10}x_{13} & y_{14} &= k_{14}x_1x_{12} & y_{23} &= k_{24}x_6 \\
y_6 &= k_6x_2x_{10} & y_{15} &= k_{15}x_9x_{12} & y_{24} &= k_{26}x_6x_8 \\
y_7 &= k_7x_{13} & y_{16} &= k_{16}x_3x_9 & y_{25} &= k_{27}x_7x_9 \\
y_8 &= k_8x_2x_{12}^2 & y_{17} &= k_{17}x_1x_6 \\
y_9 &= k_9x_4x_{13} & y_{18} &= k_{18}x_2x_9
\end{align*}
\]

The coefficient matrix, A, for the full Methane-Air System is shown in Figure Al. The nonzero components are included. The left hand column contains the subscript of the components in the concentration vector \( \bar{x} \), and the top row contains the subscript of corresponding rate constants, k.
Figure A1. The coefficient matrix, $A$, for the full Methane-Air system.
Figure A2. The coefficient matrix $A^{**}$ for the reduced canonical form of the Methane-Air system
Table Al. Row operations performed to matrix A to obtain matrix A**

<table>
<thead>
<tr>
<th>Orig. Row of Matrix A</th>
<th>Row operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2 + 5 + 11 + 12 + 13</td>
</tr>
<tr>
<td>3</td>
<td>1 + 3</td>
</tr>
<tr>
<td>4</td>
<td>-1 + 2<em>2 + 4 + 5 + 6 + 7 + 2</em>12 + 13</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>(6-9)/2 + 7</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>(6+9)/2</td>
</tr>
<tr>
<td>9</td>
<td>6 + 2*(7+8) + 9</td>
</tr>
<tr>
<td>10</td>
<td>2*11 + 12 + 13</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td>10 + 2*11 + 12 + 13</td>
</tr>
</tbody>
</table>

By judiciously applying elementary row operations to matrix a, one obtains the equivalent canonical form shown in Figure A2. We call this new matrix A**. The top row of matrix A** contains the subscripts of the rate constants and the left hand column contains the row numbers of the original matrix A. In Table Al we have tabulated the row operations which were necessary to reduce the system. These are used
to write the new components, $\tilde{x}$, for the derivatives.

Note that rows 3, 9, and 13 in matrix $A^{**}$ become zero in the reduction to canonical form, thus the problem of solving a full 13 component system had been reduced to solving a 10 component system. The auxiliary equations are then used to solve for the other three components. The problem of solving Equations A.1 containing a coefficient matrix of size $13 \times 27$ has been reduced to one with a coefficient matrix of size $10 \times 24$. If we write the new system as

$$\frac{dx^*}{dt} = A^* y$$

then $x^*$ is given by

$$x^* = \begin{bmatrix}
    x_1 \\
    x_2 + x_5 + x_{11} + x_{12} + x_{13} \\
    -x_1 + 2x_2 + x_4 + x_5 + x_6 + x_7 + 2x_{12} + x_{13} \\
    x_5 \\
    (x_6 - x_9)/2 + x_7 \\
    x_7 \\
    (x_6 + x_9)/2 \\
    x_{13} + x_{12} + 2x_{11} \\
    x_{11} \\
    x_{12}
\end{bmatrix}$$

and matrix $A^*$ is the same as matrix $A^{**}$ given in Figure A2 with the zero rows removed. The term types vector $y$ remains
the same in the canonically reduced system.

As can be seen by the sparseness of matrix $A^*$, the number of nonlinear terms has been greatly reduced, from 87 in matrix $A$, to 40 in $A^*$ and only a small number of linear ones have been added in $x^*$.

The auxiliary equations are

\[
\begin{align*}
\frac{d}{dt}(x_1 + x_3) &= 0 \\
\frac{d}{dt}(x_9 + x_6 + 2x_8 + 2x_7) &= 0 \\
\frac{d}{dt}(x_{13} + x_{12} + x_{10} + 2x_{11}) &= 0
\end{align*}
\]

These are solved for $x_3$, $x_8$, and $x_{10}$, to yield the following expressions:

\[
\begin{align*}
x_3 &= C_1 - x_1 \\
x_8 &= \frac{1}{2}(C_2 - x_9 - x_6 - 2x_7) \\
x_{10} &= C_3 - x_{13} - x_{12} - 2x_{11}
\end{align*}
\]

The constants $C_1$, $C_2$, and $C_3$ are derived from the initial conditions to the problem, $x_{i0}$, $i=1,2,\ldots,n$ and are given below:

\[
\begin{align*}
C_1 &= x_{10} + x_{30} \\
C_2 &= x_{90} + x_{60} + 2(x_{70} - x_{80}) \\
C_3 &= x_{130} + x_{120} + x_{100} + x_{110}
\end{align*}
\]
The kinetic equations for the reduced Methane-Air System after eliminating \( x_3, x_8, \) and \( x_{10} \) are:

\[
\frac{dx_1}{dt} = -k_3 x_1 x_4 - k_{11} x_1 + k_{11} c_1 - k_{14} x_1 x_{12} - k_{17} x_1 x_6 - k_{16} x_1 x_9 + k_{16} c_1 x_9
\]

\[
\frac{d}{dt}(x_2 + x_5 + x_{11} + x_{12} + x_{13}) = k_1 x_4 x_{12} - k_8 x_2 x_{13} - k_{13} x_2 - k_{18} x_2 x_9 + k_{19} x_4 x_6
\]

\[
\frac{d}{dt}(-x_1 + 2x_2 + x_4 + x_5 + x_6 + x_7 + 2x_{12} + x_{13}) = 2k_2 x_2 x_4
\]

\[
\frac{dx_5}{dt} = -k_4 x_4 x_5 + k_2 x_2 x_4
\]

\[
\frac{d}{dt}(1/2x_6 - 1/2x_9 + x_7) = k_{15} x_9 x_{12} - k_{16} x_1 x_9 - k_{17} x_1 x_6 + k_{18} x_2 x_9 - k_{19} x_4 x_6 + k_{16} x_1 x_9
\]

\[
\frac{dx_7}{dt} = k_{24} x_6^2 + \frac{k_{27}}{2} x_6 (c_2 - x_9 - x_6 - 2x_7) - k_{28} x_7 x_9
\]

\[
\frac{d}{dt}(1/2x_6 + 1/2x_9) = -\frac{k_{22}}{2} x_4 (c_2 - x_9 - x_6 - 2x_7) + k_{23} x_6 x_9 + k_{24} x_6^2
\]
\[ \frac{d}{dt}(x_{13} + x_{12} + 2x_{11}) = - (k_5 x_{13} + k_6 x_2)(c_3 - x_{13} - x_{12} - 2x_{11}) \\
+ k_9 x_4 x_{13} + k_{10} x_4 x_{11} \]

\[ \frac{dx_{11}}{dt} = -k_{10} x_4 x_{11} - k_{12} x_2 x_{11} + k_7 x_{13}^2 + k_5 x_{13}(c_3 - x_{13} - x_{12} - 2x_{11}) \]

\[ \frac{dx_{12}}{dt} = -k_1 x_4 x_{12} - k_{14} x_1 x_{12} - k_{15} x_9 x_{12} + 2k_8 x_2 x_{13}^2 \]