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Approximate Solutions to Explosion Kinetics

R. C. AIKEN

Department of Chemical Engineering
University of Utah
Salt Lake City, Utah 84112

Stiffness in combustion models is quite different from that in more conventional kinetic descriptions. The steady-state approximation, so useful in other contexts, cannot be applied in the usual *ad hoc* manner but can be applied with attention to its origins in singular perturbation analysis. The magnitude and time scaling on the equations representing the isothermal kinetics of hydrogen combustion reveal distinct regions of the transient to which this approximation may naturally and successfully be made to reduce computation time. The steady-state approximation is found to apply to some free radicals, but not all, and these can change between regions. An analytical solution to an important section of the transient is found and illustrates dramatically the power of the approach. The analysis may be applied *a priori* and leads to a stagewise efficient numerical solution.

SCOPE

Great strides have been made in the development of fast methods for the numerical solution of stiff differential equations. These methods for the most part certainly apply to mass action kinetics with its simple nonlinearitives and sparse structure. They are not always sufficient, however, for mass action kinetics modeling combustion processes in which there is an explosion. (See Aiken, 1981c, for a definition of an explosion.) One reason for this is the severe efficiency demands placed on the kinetics integration routine when included in a much larger program that models a real non-homogeneous combustor; the kinetics set must be solved many times for each spacial grid. Another and more fundamental reason for the special computational problems for combustion kinetics is associated with the fact that the narrow region of the domain containing the fast dynamics is often of interest, unlike for most kinetic descriptions. This "flamezone" does not occur initially in the solution as the more common "boundary layer" but internal to the time domain (or space if this is the independent variable). Thus, we want to take large steps before and after the flame heart but not within, and this is not necessarily compatible with stiff software designed to cover the domain with nothing but big steps. Recognition of time scales and examination of the solution behavior therein is performed nicely by *singular perturbation analysis* used here. In particular, the power of the steady-state approximation may be used to significantly reduce computation time while preserving all required solution information.

CONCLUSIONS AND SIGNIFICANCE

Combustion kinetic data is becoming more readily available with much improved experimental technique and funding encouraged by the energy crisis. Optimal design and operation of real combustors can undoubtedly be better approached with analysis as has their simpler chemical reactor counterparts. Because of the model complexity required, however, improvements in computation speed must be found first. Even a small improvement in the efficiency of calculating the kinetic step is significant in this regard. A very significant simplification for stiff dynamic systems is found in the steady-state approximation. This approximation has not heretofore been successfully applied to combustion systems; the reasons for this are examined here. Chemical knowledge may be used through these approximations to arrive at a simpler model that is not stiff and thus does not have the associated computational problems. The analysis presented here for the hydrogen-oxygen reaction is completely applicable to other, larger problems where its effect should be more dramatic. The insights obtained through this technique also provide fundamental modeling information useful in parameter estimation and planning of experiments.

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STIFFNESS IN COMBUSTION KINETICS

There is a fundamental difference in the problem of stiffness in combustion kinetics compared to the typical stiff mass action chemical application. This difference is associated with the branching nature of the combustion reaction system that has the fast free radicals dictating the dynamics of the entire reaction set over some small interval, the flame zone. Also unlike the more typical situation in stiff kinetics, we are often *primarily* interested in this narrow interval of radical dominance, analogous to the initial boundary layer in stiff non-combustion kinetics. If only this interval was to be computed, the problem would not be nearly as stiff, since the time scale of interest would correspond to a fast acting radical. It is the situation where a solution is to be found over a time interval (or space) much greater than the "explosion"—but including it—that we address here. There are three main time frames involved, roughly corresponding to initiation, propagation and branching, and termination. Within the propagation and branching zone, there can be several sub-domains where various reactions predominate.

We consider only isothermal pure chemical kinetics of the mass form. There has been only a few studies of numerical integration routines geared to this form (Edsberg, 1974; Pratt, 1979). Much can be done to improve efficiency by, for example, making use of the special and simple equation structure in the Jacobian evaluation. While packages such as Gear can often solve combustion kinetic models, the time required can be excessive if many repeated solutions are to be obtained, as would occur if the kinetics were included in a mixing model or for parameter estimation purposes. Selection of the necessary input parameters for use of stiff packages may be difficult if many automatic calls under differing circumstances must be made; for example, the flame region can be jumped over without report of accuracy loss by the numerical routine.

Another interesting aspect of the stiff combustion kinetic system is the existence of positive *and* negative eigenvalues. Thus integration in forward or reverse time is inherently unstable. This also arises, for example, in interactive counter-diffusion (Aiken, 1981a). A method must be used that has a small or zero stability region in the right-half plane. Very little guidance is offered in the literature for such systems. Because the positive eigenvalues contain the information of interest during an explosion, focusing on them can provide a unique numerical approach (Hoppensteadt et al., 1981).

STEADY-STATE APPROXIMATION

This is probably the most useful approximation for the solution of differential equation models as it transforms an ordinary differential equation to an algebraic equation or a partial differential equation to an ordinary differential equation. Its basis for arbitrary stiff systems was explored by Aiken and Lapidus (1975). Guidelines were given there concerning:

1. The accuracy of the approximation
2. Time domain region of applicability
3. Selection of stable roots

A distinction should be made among the several situations where a derivative is zero: the steady-state approximation (ssa), the pseudo-steady state approximation (pssa), maxima and minima with respect to time, and the true steady-state. Consider a single equation from a scaled set modeling mass action kinetics:

$$\frac{dy}{dt} = w(x,y) \qquad (1)$$

If y is to have fast dynamics relative to the t time scale, there then must exist a small parameter ϵ such that

$$\epsilon\frac{dy}{dt} = g(x,y,\epsilon) \qquad (2)$$

where, for example, g could equal $w\epsilon$. We recognize in Eq. 2 that ϵ may appear in the function as well as multiplying the derivative. The ssa consists of mechanically setting ϵ to zero (zeroth-order outer singular perturbation):

$$0 = g(x,y,0), \qquad (3)$$

while the pssa sets the derivative itself to zero:

$$0 = g(x,y,\epsilon) \qquad (4)$$

while Eq. 3 has a basis in perturbation theory (Aiken and Lapidus, 1974), Eq. 4 does not at present. We shall show later in this paper an example of a system where the pssa (or the ssa, the two being equivalent in the example) can not be used although a fast variable attains a derivative of zero at a point, corresponding to a maximum. Finally note in a true steady-state the value of a variable cannot change, while for a ssa or pssa, the value of y in Eq. 3 or 4 may change with time as the solution of these algebraic equations involves x which has a non-zero time derivative.

The advantage of the use of the ssa or the pssa in the numerical solution of stiff kinetic systems manifests itself in several ways. These include: the elimination of the fast dynamics that constrain the stability of integration routines, order-reduction, and simplification of functions. There is a further advantage to parameter estimation (Aiken, 1981b).

COMBUSTION OF HYDROGEN EXAMPLE

An important, yet simple example for illustrative purposes is the combustion of hydrogen. The reaction scheme considered will be:

$$\begin{array}{lll}
H_2 + O_2 \xrightarrow{k_0} H\cdot + HO_2 & \text{initiation} & (5a)\\
H_2 + OH\cdot \xrightarrow{k_1} H\cdot + H_2O & \left.\right\} \text{propagation} & (5b)\\
O_2 + H\cdot \xrightarrow{k_2} OH\cdot + O\cdot & \text{branching, propagation} & (5c)\\
H_2 + O\cdot \xrightarrow{k_3} H\cdot + OH\cdot & \text{branching, propagation} & (5d)\\
OH\cdot \xrightarrow{a_1} & \text{termination} & (5e)\\
H\cdot \xrightarrow{a_2} & \text{termination} & (5f)\\
C\cdot \xrightarrow{a_3} & \text{termination} & (5g)
\end{array}$$

with rate constants (Semenov, 1959):

$$\begin{array}{l}
k_0 = 60\ \text{cm}^3/\text{mol}\cdot\text{s}\\
k_1 = 2.3\text{E}11\ \text{cm}^3/\text{mol}\cdot\text{s}\\
k_2 = 4.02\text{E}9\ \text{cm}^3/\text{mol}\cdot\text{s}\\
k_3 = 2.82\text{E}12\ \text{cm}^3/\text{mol}\cdot\text{s}\\
a_1 = 92/\text{s}\\
a_2 = 8/\text{s}\\
a_3 = 92/\text{s}
\end{array} \qquad (6)$$

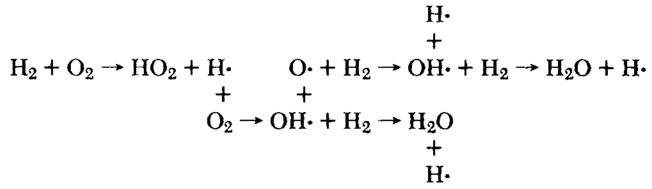
A typical initial condition, say in an experimental bomb, might be

$$\begin{array}{l}
H_2 = 1.\text{E-}7\ \text{mol/cm}^3\\
O_2 = 0.5\text{E-}7\ \text{mol/cm}^3\\
H\cdot = 0\\
OH\cdot = 0\\
O\cdot = 0
\end{array} \qquad (7)$$

Note that the initiation reaction, Eq. 5a, is very slow compared with the propagation reactions, Eq. 5b–d. The three propagation reactions include two reactions, Eq. 5c and Eq. 5d, in which two radicals are produced for every one consumed; this auto-catalytic behavior is termed *branching.* The character of this branching can be seen from the following sequence of reactions:

TABLE 1. ENTIRE ACCURATE NUMERICAL SOLUTION (EQ. 9)

Time, s	Concentration, mol/cm^3				
	H_2	O_2	$H\cdot$	$OH\cdot$	$O\cdot$
.001	.1000E-6	.5000E-7	.4794E-15	.7984E-17	.3404E-18
.002	.1000E-6	.5000E-7	.1259E-14	.2131E-16	.8950E-18
.003	.1000E-6	.5000E-7	.2527E-14	.4300E-16	.1797E-17
0.010	.1000E-6	.5000E-7	.6239E-13	.1067E-14	.4440E-16
0.020	.1000E-6	.5000E-7	.3123E-11	.5344E-13	.2223E-14
0.030	.9977E-7	.4992E-7	.1470E-9	.2517E-11	.1047E-12
0.035	.9846E-7	.4948E-7	.9994E-9	.1718E-10	.7147E-12
0.040	.9005E-7	.4663E-7	.6445E-8	.1140E-9	.4749E-11
0.042	.8010E-7	.4326E-7	.1287E-7	.2369E-9	.9888E-11
0.044	.6299E-7	.3745E-7	.2388E-7	.4809E-9	.2018E-10
0.045	.5153E-7	.3353E-7	.3121E-7	.6831E-9	.2886E-10
0.046	.3865E-7	.2910E-7	.3938E-7	.9823E-9	.4208E-10
0.048	.1279E-7	.1985E-7	.5522E-7	.2419E-8	.1193E-9
0.050	.6562E-10	.1234E-7	.5949E-7	.7787E-8	.1795E-8
0.055	0.0	.4207E-8	.4928E-7	.1115E-7	.7316E-8
0.060	0.0	.1641E-8	.4484E-7	.9017E-8	.6596E-8
0.070	0.0	.3002E-9	.4012E-7	.4359E-8	.3394E-8
0.080	0.0	.6409E-10	.3681E-7	.1874E-8	.1489E-8
0.090	0.0	.1547E-10	.3393E-7	.7751E-9	.6218E-9



$$\begin{array}{rcclcll} & & & & H\cdot & & \\ & & & & + & & \\ H_2 + O_2 \rightarrow HO_2 + & H\cdot & \quad & O\cdot + H_2 \rightarrow & OH\cdot & + H_2 \rightarrow H_2O + H\cdot & \\ & + & & + & & & \\ & O_2 \rightarrow & & OH\cdot + H_2 \rightarrow & H_2O & & \\ & & & & + & & \\ & & & & H\cdot & & \end{array}$$

After the initial production of a H· through Eq. 5a, three more H· are produced in this sequence which can be repeated at a sharply increasing rate, until fuel is consumed or the termination reactions become dominant. This single cycle can be written as

$$H\cdot + O_2 \xrightarrow{k_2} OH\cdot + O\cdot$$

$$O\cdot + H_2 \xrightarrow{k_3} OH\cdot + H\cdot$$

$$2(OH\cdot + H_2 \xrightarrow{k_1} H_2O + H\cdot)$$

$$\text{or} \quad H\cdot + O_2 + 3H_2 \rightarrow 3H\cdot + 2H_2O \tag{8}$$

as the overall reaction of this cycle. Thus stoichiometrically, three hydrogen radicals are produced for every one consumed and three hydrogen fuel molecules are used for every oxygen consumed.

The termination reactions given as Eq. 5e–g are heterogeneous wall-capture type adsorption reactions; the rates for such reaction can vary significantly for various reactor constructions. We shall only consider here termination by wall capture and thus only the first explosion limit.

The elementary reactions of Eq. 5 can be modelled by the law of mass action as:

$$\frac{d[H_2]}{dt} = -(k_1[OH\cdot] + k_3[O\cdot])[H_2] - k_0[H_2][O_2] \tag{9a}$$

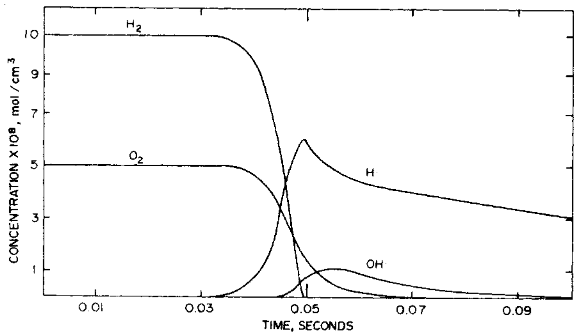


Figure 1. Full solution of hydrogen combustion scheme.

$$\frac{d[O_2]}{dt} = -k_2[H\cdot][O_2] - k_0[H_2][O_2] \tag{9b}$$

$$\frac{d[H\cdot]}{dt} = -(k_2[O_2] + a_2)[H\cdot] + k_1[H_2][OH\cdot] + k_3[H_2][O\cdot] + k_0[H_2][O_2] \tag{9c}$$

$$\frac{d[OH\cdot]}{dt} = k_2[O_2][H\cdot] - (k_1[H_2] + a_1)[OH\cdot] + k_3[H_2][O\cdot] \tag{9d}$$

$$\frac{d[O\cdot]}{dt} = k_2[O_2][H\cdot] - (k_3[H_2] + a_3)[O\cdot] \tag{9e}$$

These equations, with the parameters of Eq. 6 and the initial conditions of Eq. 7, produce the numerical solution shown in Figure 1 and tabulated in Table 1. We define three regions where different chemical mechanisms are dominant: Region I, the initial region where initiation of the hydrogen radical is dominant; Region II, where the branching cycle is most important; and Region III, in which the termination reactions become important. We shall consider these regions each in turn in the next section.

The usual implementation technique for the steady-state approximation would set the derivatives of the fast free radicals (H·, OH·, and O·) to zero and solve the resulting two differential and three algebraic equations. It should be obvious from Eq. 9, that if Eq. 9c–9e are set to zero and solved for [H·], [OH·], and [O·], respectively, that the system may change with time only from the very slow initiation reaction. Thus, for the parameters of Eq. 6 over 0.1 s O_2 and H_2 do not change from their initial conditions, while H·, OH·, and O· instantly attain and hold constant at 0.37E-13, 0.71E-24, and 0.26E-16 mol/cm^3, respectively.

PERTURBATION ANALYSIS

Region I

Without any hydrogen radicals present, the branching cycle cannot go; there is in fact a critical minimum concentration below which the initiation reaction

$$H_2 + O_2 \xrightarrow{k_0} H\cdot + HO_2$$

with H· production rate

$$\frac{d[H\cdot]}{dt} = k_0[H_2][O_2] \tag{10}$$

is faster than the rate at which H· is being used in the cycle, the maximum rate which it can be used being

$$\frac{d[\mathrm{H}\cdot]}{dt} = -k_2[\mathrm{H}\cdot][\mathrm{O}_2] \tag{11}$$

For example, if $[\mathrm{H}_2] = 1.0\mathrm{E}\text{-}7$, $[\mathrm{O}\cdot] = 0.5\mathrm{E}\text{-}7$, $k_0 = 60$, Eq. 10 gives

$$\frac{d[\mathrm{H}\cdot]}{dt} = 3\mathrm{E}\text{-}13 \tag{12}$$

which, to match Eq. 11, would require $[\mathrm{H}\cdot] = 1.5\mathrm{E}\text{-}15$ ($k_2 = 4\mathrm{E}9$, $[\mathrm{O}_2] = 0.5\mathrm{E}\text{-}7$).

Let us form a general set of scaled equations by use of

$$u = [\mathrm{H}_2]/u_0, v = [\mathrm{O}_2]/v_0, x = [\mathrm{H}\cdot]/x_0,$$
$$y = [\mathrm{OH}\cdot]/y_0, z = [\mathrm{O}\cdot]/z_0, \tau = t/t_0$$

where u_0, v_0, x_0, y_0, z_0, and t_0 are magnitude scaling factors, and choose scales as dictated by the particular chemical knowledge in each region. Eq. 9 becomes

$$\frac{u_0}{t_0}\dot{u} = -(k_1 y_0 y + k_3 z_0 z)u_0 u - k_0 u_0 v_0 u v \tag{13a}$$

$$\frac{v_0}{t_0}\dot{v} = -(k_2 x_0 x)v_0 v - k_0 u_0 v_0 u v \tag{13b}$$

$$\frac{x_0}{t_0}\dot{x} = -(k_2 v_0 v + a_2)x_0 x + (k_1 u_0 u)y_0 y$$
$$+ (k_3 u_0 u)z_0 z + k_0 u_0 v_0 u v \tag{13c}$$

$$\frac{y_0}{t_0}\dot{y} = (k_2 v_0 v)x_0 x - (k_1 u u_0 + a_1)y_0 y + (k_3 u u_0)z_0 z \tag{13d}$$

$$\frac{z_0}{t_0}\dot{z} = (k_2 v_0 v)x_0 x - (k_3 u_0 u + a_3)z_0 z \tag{13e}$$

A pertinent scale for x in this initial region would be obtained by setting rates (Eqs. 10 and 11) equal:

$$k_0 u_0 v_0 = k_2 v_0 x_0$$

or

$$x_0 = \frac{k_0 u_0}{k_2} \ll 1 \tag{14}$$

Thus x starts from zero in this region and reaches a maximum on the order of $k_0 u_0/k_2$. Let us choose the time scale as

$$t_0 = 1/k_2 v_0 \ll 1$$

so that we are stretching time and looking close to the beginning of the reactions. We expect u and v to change very little over this region so that $u_0 = v_0 = \mathrm{H}_2(0)$.

Finally, since H· has not reached a concentration to allow reaction 5c to really get started, certainly reactions 5b and 5d, whose rates depend on the products from Eq. 5c will be negligible, and will be omitted. Equation 13 thus becomes

$$\dot{u} = \frac{k_0}{k_2} u v \tag{15a}$$

$$\dot{v} = \frac{k_0}{k_2}(-vx - uv) \tag{15b}$$

$$\dot{x} = -ux + uv \tag{15c}$$

This makes obvious the small changes in O_2 and H_2 over this region for a significant increase in the concentration of H·, as the right hand sides of Eqs. 15a and 15b are multiplied by small numbers.

Region II

Now allow x to attain a value of the order of u and v as the cycle Eq. 8 becomes the dominant mode for chemical change and significant amounts of u and v are used to produce x. Note also from Eq. 8 that no net y or z radicals are produced so that their characteristic scales (y_0 and z_0, respectively) should be smaller than for x. For extensive branching, however, at any instant there could be quite a significant number of these short-lived radicals.

Let us again take

$$t_0 = 1/k_2 v_0$$

to stretch time for this fast reaction sequence. Take

$$u_0 = v_0 = x_0 = \mathrm{H}_2(0)$$

and

$$y_0 = \frac{k_2 \mathrm{H}_2(0)}{k_1}, \frac{k_2}{k_1} \ll 1$$

$$z_0 = \frac{k_2}{k_3}\mathrm{H}_2(0), \frac{k_2}{k_3} \ll 1$$

These choices lead to

$$\dot{u} = -uy - uz \tag{16a}$$

$$\dot{v} = -vx \tag{16b}$$

$$\dot{x} = -vx + uy + uz \tag{16c}$$

$$\frac{k_2}{k_1}\dot{y} = vx - uy + uz \tag{16d}$$

$$\frac{k_2}{k_3}\dot{z} = vx - uz \tag{16e}$$

where terms for initiation and termination have been omitted because very small numbers multiply them. For example, we have dropped from the right hand side of Eq. 16c $-a_2 x/k_2 \mathrm{H}_2(0)$, since $a_2/k_2\mathrm{H}_2(0) \ll 1$. Thus we have only the cycle Eq. 8 in the model for this region. Since we have just those three reactions, two of the five equations in Eq. 16 must be redundant. In fact,

$$\dot{u} + \dot{x} = \dot{v} \tag{17a}$$

$$\dot{u} = \frac{k_2}{k_1}\dot{y} + 2\frac{k_2}{k_3}\dot{z} + 3\dot{v} \tag{17b}$$

so that (for example)

$$x = v - u + (u(0) - v(0)) + x(0)$$

$$y = \frac{k_1}{k_2}[u - u(0)] - 2\frac{k_1}{k_3}[z - z(0)] - 3\frac{k_1}{k_2}[v - v(0)] + y(0)$$

and Eq. 16 reduce to

$$\dot{u} = -u\left\{\frac{k_1}{k_2}[u - u(0)] - 2\frac{k_1}{k_3}[z - z(0)]\right.$$
$$\left. - \frac{3k_1}{k_2}[v - v(0)] + y_{(0)}\right\} - uz \tag{18a}$$

$$\dot{v} = -v[v - u + (u(0) - v(0)) + x(0)] \tag{18b}$$

$$\frac{k_2}{k_3}\dot{z} = v[v - u + (u(0) - v(0)) + x(0)] - uz \tag{18c}$$

Since $k_2/k_3 \ll 1$, a ssa for Eq. 18c would reduce the system to:

$$z = \frac{v}{u}[v - u + (u(0) - v(0)) + x(0)] \tag{19a}$$

$$\dot{u} = -u\left\{\frac{k_1}{k_2}[u - u(0)] - 2\frac{k_1}{k_3}[z - z(0)]\right.$$
$$\left. - \frac{3k_1}{k_2}[v - v(0)] + y(0)\right\} - uz \tag{19b}$$

$$\dot{v} = -uz \tag{19c}$$

It may in fact be true that the ssa is adequate to apply to Eqs. 16d and 16e directly to give

$$\begin{aligned}\dot{u} &= -3vx\\ \dot{v} &= -vx\\ \dot{x} &= 2vx\end{aligned} \tag{20}$$

or since here $\dot{x} = -2/3\,\dot{u}$, $\dot{v} = 1/3\,\dot{u}$, then

$$\dot{v} = -v[1 - 2v - x(0)] \tag{21}$$

as the single equation! This can be solved analytically from t_0 to t:

$$v = \frac{(1 - x(0))}{2 - \phi} \tag{22}$$

where

$$\phi = \mathrm{EXP}\left[(x(0) - 1)(t - t_0) - ln\,\frac{(x(0) - 1) + 2v(0)}{v(0)}\right]$$

This is likely not to be as accurate as Eq. 19 since we use here both $k_2/k_1 \ll 1$ *and* $k_2/k_3 \ll 1$ while Eq. 19 uses only $k_2/k_3 \ll 1$; also $k_2/k_3 < k_2/k_1$ by about an order of magnitude. However neither Eq. 22 nor Eq. 19 will strictly apply near to the point of maximum $x(\dot{x} = 0)$. This can be seen by examining Eq. 17b which, upon elimination of $\dot{v}$, gives

$$\dot{u} = -\frac{k_2}{2k_1}\dot{y} - \frac{k_2}{k_1}\dot{z} - \frac{3}{2}\dot{x} \tag{23}$$

Now, near to the maximum in x (where $\dot{x} = 0$), the rate of using x (reaction 5c) is the same as the rate of its creation (reactions 5b and 5d). At this point, $\dot{x}$ is zero but H_2 is still being used (although now in small concentrations) and thus $\dot{y}$ and $\dot{z}$ may not be zero. The degree of error incurred from setting them to zero is parameter dependent but definitely less error would result from setting only one of the two derivations to zero, as is done in the scheme resulting in Eq. 10. Away from the maximum, however, when $3/2\dot{x} \gg k_2\dot{y}/2k_1, k_2\dot{z}/k_1$, the approximations $k_2\dot{y}/2k_1 = k_2\dot{z}/k_1 = 0$ can be used. Therefore, in Region II, the ssa is not recommended in general on $\dot{x}$ at all and can be used for $\dot{z}$ and $\dot{y}$ everywhere except near the maximum in $\dot{x}$. Let us call the approach using Eq. 19 the *partial steady-state* and that for Eq. 22 the *complete steady-state* approach.

Once past the maximum in H·, fuel has been depleted and thus reactions 5b and 5d are no longer important; reaction 5c, in which O_2 and H· form OH· and O·, is now of major importance. As such, these radicals reach substantial concentrations. We must therefore re-scale concentrations. Let:

$$v_0 = x_0 = y_0 = z_0 = H_2(0);\ u_0 = \frac{k_2H_2(0)}{k_3}$$

while keeping the cycle time scale $t_0 = 1/k_2H_2(0)$. This gives:

$$\frac{k_2}{k_3}\dot{u} = -\frac{k_1}{k_3}uy - uz \tag{24a}$$

$$\dot{v} = -xv \tag{24b}$$

$$\dot{x} = -xv + \frac{k_1}{k_3}uy + uz - \frac{a_2x}{k_2H_2(0)} \tag{24c}$$

$$\dot{y} = xv - \frac{k_1}{k_3}uy + uz - \frac{a_1y}{k_2H_2(0)} \tag{24d}$$

$$\dot{z} = xv - uz - \frac{a_3z}{k_2H_2(0)} \tag{24e}$$

where initiation terms have again been omitted but termination terms have been allowed in now since they will come into importance sometime after the H· maximum, when depending on the values of the a's. For the values specified in Eq. 6, they in fact do not immediately come into importance here and some additional saving in computation could be gained by their omission until later.

Now let us apply the steady-state approximation to Eq. 24a:

$$u\left(\frac{k_1}{k_3}y + z\right) = 0$$

Since neither y nor z may be zero, we take $u = 0$ as the root. Thus we may simplify:

$$\dot{v} = -xv \tag{25a}$$

$$\dot{x} = -xv - \frac{a_2x}{k_2H_2(0)} \tag{25b}$$

$$\dot{y} = xv - \frac{a_1y}{k_2H_2(0)} \tag{25c}$$

$$\dot{z} = xv - uz - \frac{a_3z}{k_2H_2(0)} \tag{25d}$$

The advantage of omitting the termination terms until v has decayed sufficiently to make their presence felt is more obvious here as an analytical formulation would be possible. If this is performed, a periodic test for the importance of the termination term could be made and included when important.

Region III

Now let's slow down our time scale to $t_0 = 1/a_3$ (assuming relatively slow termination) and examine the situation where H_2 and O_2 are low in concentration, having gone into the production of radicals, whose concentrations are of the order of $H_2(0)$. Thus take

$$u_0 = \frac{a_3}{k_3},\quad v_0 = \frac{a_3}{k_2}$$

$$x_0 = y_0 = z_0 = H_2(0)$$

then

$$\frac{a_3}{k_3H_2(0)}\dot{u} = -uy - uz \tag{26a}$$

$$\frac{a_3}{k_3H_2(0)}\dot{v} = -vx \tag{26b}$$

$$\dot{x} = -vx - \frac{a_2}{a_3}x + \frac{k_1}{k_3}uy + uz \tag{26c}$$

$$\dot{y} = vx - \frac{k_1}{k_3}uy - y + uz \tag{26d}$$

$$\dot{z} = vx - uz - z \tag{26e}$$

where

$$\frac{a_3}{k_3H_2(0)} \ll 1, \frac{a_3}{k_3H_2(0)} \ll 1, \frac{a_2}{a_3} < 1, \frac{k_1}{k_3} < 1$$

The ssa may apply to Eqs. 26a and 26b and, if so, would give $y = z, u = v = 0$

leading to

$$\dot{z} = -z \tag{27a}$$

$$\dot{y} = -y \tag{27b}$$

$$\dot{x} = -\frac{a_2}{a_3}x \tag{27c}$$

which is obviously the correct limit of simple decay for each species.

COMPUTATIONAL SCHEME FROM PERTURBATION ANALYSIS

Let us now use the simple perturbation analysis of the last section to construct a computational scheme that solves the H_2-O_2 reaction set of Eq. 9 as efficiently as possible. We shall again consider each region in turn and the parameters and initial conditions of Eqs. 6 and 7, respectively.

Region I

This region ends with [H·] achieving a magnitude of about 1.5E-15 mol/cm^3, as given by the scale of Eq. 14. From Table 1, it is seen that this occurs after about 0.002 s into the reaction sequence. The full equation set is very stiff, as three time scales are represented: the very slow initiation time scale, the faster termination rate, and the much faster time scale of the cycle reactions (maximum H· changes from these three causes are on the order 10^{-13}, 10^{-7}, 10^{-4} mol/cm^3 · s). This stiffness is eliminated, how-

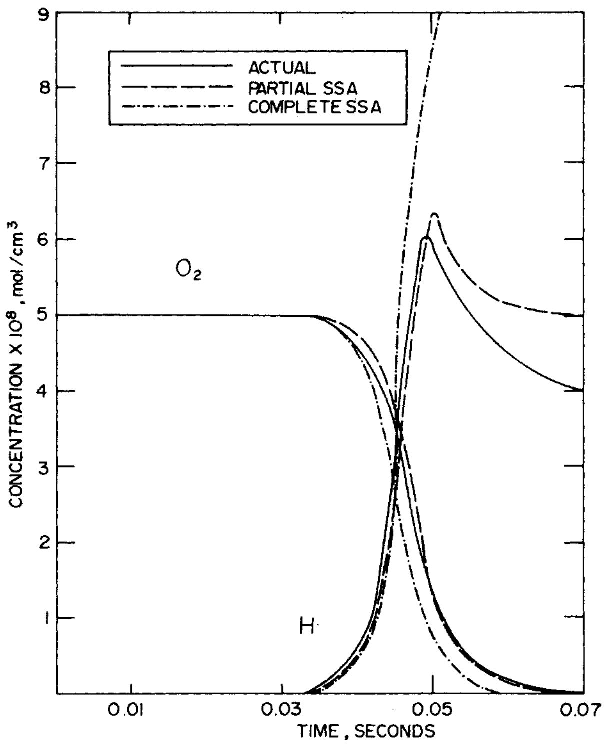


Figure 2. Solutions from use of certain steady-state approximations throughout explosion interval.

ever, through use of Eq. 15; order reductions as well as a simplification of the functions are achieved. Equation 15 may thus be used initially until H· reaches about 1.E-15, at which point we switch to the solution scheme for Region II. As this region lasts for only a very short time, use of Eq. 15 brings minimal returns. There is no reason why this region should not be omitted entirely, and a starting concentration of [H·] = about 1.5E-15 be used immediately in Region II. This can be estimated *a priori*, as above, and the inaccuracy in time is quite small.

Region II

We have two possible equation sets to use initially in this region from our perturbation analysis that resulted from Eq. 16: the *partial steady-state* approach, Eq. 19, that resulted from, first, an elimination of two dependent equations, then an application of the ssa to one equation; and the *complete steady-state* approach, Eq. 21, that resulted from use of the ssa twice, then elimination of two dependent equations. Each of these solutions eliminates the (moderate) stiffness of the cycle equations, reduces the order of the set, and simplifies the functional evaluation. The results of a numerical solution of each approach is shown in Figure 2; with tabulated results in Tables 2 and 3 for the partial and complete steady-state approaches, respectively. Although the partial steady-state method is quite clearly superior over all of Region II shown, either scheme could be considered adequate for most conceivable practical purposes, until the maximum in H· is approached. As was predicted in the perturbation analysis, the time derivatives of OH· and O· may in general not both be taken as zero when H·'s time derivative is also zero.

A time must be determined, near to the point of maximum H·, after which a steady-state may not be applied. A quite adequate measure is provided bythe inflection point in the solution for H·. This can be monitored at no additional expense during the solution. Chemically, this criterion states that H· are being significantly depleted by the cycle reactions (relative to the rate of generation). This switch takes place at about 0.048 s for the partial steady-state approach and at about 0.045 s for the complete steady-state approach. The solution thereafter by use of the equation set (Eqs. 16) is shown in Figure 3 and Tables 4 and 5 for the partial and complete steady-state approaches, respectively. The larger equation set indeed does improve the solution over the H· turning point and after. We seek the most efficient solution however so use Eq. 25 as soon as possible.

We must face the problem, however, of when to make the switch to Eq. 25. The scales for Eq. 24 suggest this to occur when H· is quite small. The maximum in H· in fact happens at about that point, so we should be able to safely use Eq. 25 any time after the maximum. This has been verified computationally. For example, application after t = 0.052 s gives the exact solution.

TABLE 2. PARTIAL STEADY-STATE SOLUTION TO REGION II

Time,			Concentration, mol/cm^3		
s	H_2	O_2	H·	OH·	O·
0.011	.1000E-6	.5000E-7	.7729E-13	.1096E-14	.1081E-16
0.020	.1000E-6	.5000E-7	.1904E-11	.2974E-13	.1336E-14
0.030	.9985E-7	.4995E-7	.9713E-10	.1664E-11	.7043E-13
0.040	.9278E-7	.4756E-7	.4781E-8	.8392E-10	.3555E-11
0.042	.8500E-7	.4493E-7	.9935E-8	.1796E-9	.7618E-11
0.045	.6028E-7	.3656E-7	.2628E-7	.5411E-9	.2312E-10
0.046	.4799E-7	.3238E-7	.3439E-7	.7812E-9	.3366E-10
0.048	.2054E-7	.2285E-7	.5231E-7	.1816E-8	.8442E-10
0.050	.6171E-9	.1419E-7	.6357E-7	.3811E-8	.2120E-8
0.052	0.0	.8646E-8	.5900E-7	.2787E-7	0.0
0.055	0.0	.4378E-8	.5448E-7	.4378E-7	0.0

TABLE 3. COMPLETE STEADY-STATE SOLUTION TO REGION II

Time,			Concentration, mol/cm^3		
s	H_2	O_2	H·	OH·	O·
0.010	0.1000E-6	.5000E-7	.6239E-13	.1090E-14	.4447E-16
0.020	0.1000E-6	.5000E-7	.3475E-11	.6074E-13	.2477E-14
0.030	.9971E-7	.4990E-7	.1932E-9	.3380E-11	.1378E-12
0.040	.8540E-7	.4513E-7	.9733E-8	.1798E-9	.7333E-11
0.044	.4751E-7	.3250E-7	.3500E-7	.8369E-9	.3413E-10
0.045	.3312E-7	.2771E-7	.4459E-7	.1304E-8	.5318E-10
0.046	.1809E-7	.2270E-7	.5461E-7	.2395E-8	.9766E-10
0.048	−.4326E-8	.1356E-7	.7288E-7	−.3704E-8	−.1510E-9
0.050	−.2859E-7	.7137E-8	.8573E-7	−.7481E-9	−.3051E-10
0.055	−.4673E-7	.1091E-8	.9782E-7	−.7985E-10	−.3256E-11
0.060	−.4955E-7	.1490E-9	.9970E-7	−.1048E-10	−.4274E-12

TABLE 4. FULL EQUATION SET (EQ. 9) WITH INITIAL CONDITIONS FROM TABLE 2 AT t = 0.0455 s

Time, s	Concentration, mol/cm^3 H_2	O_2	H·	OH·	O·
0.0455	.2561E-7	.2520E-7	.4959E-7	.1706E-8	.6958E-10
0.047	.6688E-8	.1802E-7	.6066E-7	.3673E-8	.2184E-9
0.048	.4727E-9	.1404E-7	.6240E-7	.7093E-8	.1083E-8
0.049	.9593E-13	.1099E-7	.5933E-7	.9551E-8	.3589E-8
0.050	0.0	.8705E-8	.5659E-7	.1089E-7	.5449E-8
0.052	0.0	.5618E-8	.5263E-7	.1186E-7	.7332E-8
0.055	0.0	.3052E-8	.4885E-7	.1120E-7	.7770E-8

TABLE 5. FULL EQUATION SET (EQ. 9) WITH INITIAL CONDITIONS FROM TABLE 3 AT t = 0.048 s

Time, s	Concentration, mol/cm^3 H_2	O_2	H·	OH·	O·
0.048	.2054E-7	.2285E-7	.5231E-7	.1816E-8	.8442E-10
0.049	.8485E-8	.1824E-7	.5931E-7	.3167E-8	.1739E-9
0.050	.1099E-8	.1426E-7	.6222E-7	.6167E-8	.7134E-9
0.052	.4559E-16	.8822E-8	.5693E-7	.1034E-7	.4910E-8
0.055	0.0	.4605E-8	.5142E-7	.1147E-7	.7347E-8
0.060	0.0	.1729E-8	.4659E-7	.9451E-8	.6851E-8
0.070	0.0	.2964E-9	.4165E-7	.4580E-8	.3544E-8
0.080	0.0	.5965E-10	.3822E-7	.1962E-8	.1549E-8
0.100	0.0	.3496E-11	.3252E-7	.3282E-9	.2626E-9

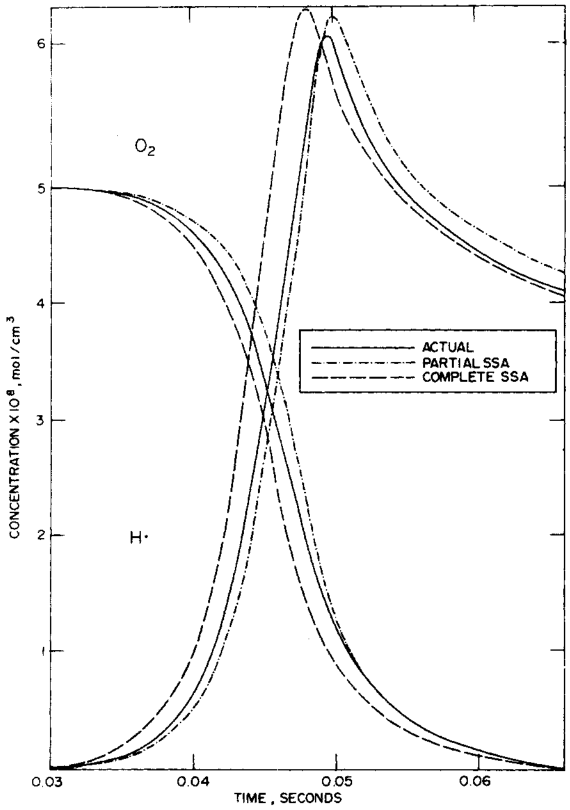


Figure 3. Solutions from use of steady-state approximations with switches to full solution around maximum in H· according to inflection criteria.

Region III

After about 0.08 s, [O_2] has a value <10^{-10} mol/cm^3 and Eq. 27 may then safely be used without any loss in accuracy.

SUMMARY OF MOST EFFICIENT NUMERICAL SCHEME

If the complete steady-state approach gives accuracy adequate for some predictive or design purpose, the following summary in dimensional form may be used:

Step 1

Determine the approximate concentration of H· where the depletion of H_2 by the cycle is comparable to the homogeneous generation; i.e., $k_0[H_2][O_2] \simeq k_2[H\cdot][O_2]$. For the parameters of Eq. 6, this gives [H·] $\simeq$ 1.5E-5 mol/cm^3. We shall start the Region II equations with this value; thus denote it by [H·(0)].

Step 2

$$0_2(t) = \frac{([H_2(0)] - [H\cdot(0)])}{2 - \phi}$$

where

$$\phi = \mathrm{EXP}\left\{[[H\cdot(0)] - [H_2(0)]]k_2 t - ln\frac{([H\cdot(0)] - 1) + 2\left(\frac{O_2(0)}{H_2(0)}\right)}{\frac{O_2(0)}{H_2(0)}}\right\}$$

$$[H\cdot(t)] = [H\cdot(0)] - 2([O_2(t) - O_2(0)])$$

$$[H_2(t)] = [H_2(0)] - 3([O_2(0)] - [O_2(t)])$$

$$[O\cdot(t)] = k_2[O_2(t)][H\cdot(t)]/k_3[H_2(t)]$$

$$[OH\cdot(t)] = \frac{k_2}{k_1}\left\{\frac{[O_2(t)][H\cdot(t)] + [0\cdot(t)][H\cdot]\frac{k_3}{k_2}}{[H_2(t)]}\right\}$$

Step 3

When the inflection point of x has been reached, switch to the full equation set (Eqs. 16). Initiation and termination reaction terms may be omitted. The initial condition for these equations is the concentration of all species at the inflection point of the previous step. Compute until past the maximum in H·.

Step 4

Take [$H_2(t)$] thereafter equal to zero. Solve

$$\frac{d[0_2]}{dt} = -k_2[H\cdot][O_2]$$

$$\frac{d[\mathrm{H}\cdot]}{dt} = -(\mathrm{k}_2[\mathrm{O}_2] + a_2)[\mathrm{H}\cdot] + k_1[\mathrm{H}\cdot][\mathrm{OH}\cdot] + k_3[\mathrm{H}_2][\mathrm{O}\cdot]$$

$$\frac{d[\mathrm{OH}\cdot]}{dt} = k_2[\mathrm{O}_2][\mathrm{H}\cdot] - (k_1[\mathrm{H}_2] + a_1)[\mathrm{OH}\cdot] + k_3[\mathrm{H}_2][\mathrm{O}\cdot]$$

$$\frac{d[\mathrm{O}\cdot]}{dt} = k_2[\mathrm{O}\cdot][\mathrm{H}\cdot] - (k_3[\mathrm{H}\cdot] + a_3)[\mathrm{O}\cdot]$$

until $[\mathrm{O}_2] < k_2\mathrm{H}_2(0)/k_3$, then with those conditions

Step 5

Use

$$\frac{d[\mathrm{OH}\cdot]}{\mathrm{dt}} = -a_1[\mathrm{OH}\cdot]$$

$$\frac{d[\mathrm{H}\cdot]}{dt} = -a_2[\mathrm{H}\cdot]$$

$$\frac{d[\mathrm{O}\cdot]}{dt} = -a_3[\mathrm{O}\cdot]$$

until the desired time interval is completed. Use of such a five step scheme results in a very substantial savings in computation time with a small loss in accuracy.

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Viscoelastic Flow from a Tube into a Radial Slit

The viscoelastic flow from a tube into a radial slit between two parallel disks is investigated numerically by orthogonal collocation. A modified ZFD model and a generalized Newtonian fluid, with identical viscosity functions, are investigated. Results for these models indicate that fluid elasticity alters the velocity profiles significantly, but has little effect on the pressure profile in the radial flow region.

ALBERT CO
Department of Chemical Engineering and
Rheology Research Center
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

W. E. STEWART
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

SCOPE

In steady shear flows, polymeric fluids are satisfactorily described by the Criminale-Ericksen-Filbey equation (Criminale et al., 1958; Ericksen, 1960; Bird et al., 1977), in which the viscometric functions (i.e., the viscosity and the primary and secondary normal stress coefficients) are the only material functions used. Aside from steady shear flows, the questions regarding the "proper" rheological equation of state and the required material functions are still unresolved.

Among the nonviscometric flows, converging-diverging flows are frequently encountered in polymer processing. This investigation focuses on a particular diverging flow, namely, the outward radial flow between two parallel disks, with the fluid introduced through a central tube. We describe the flow system, including the entrance region, by using an "appropriate" rheological model, whose parameters can be determined from available measurements of material functions, and by numerically solving the resulting system of nonlinear partial differential equations.

The principal rheological model used in the study is a modified Zaremba-Fromm-DeWitt (MZFD) model, which has six material parameters. The parameters are obtained from experimental data on the viscosity and primary normal stress coefficient for the given fluid.

In order to obtain a well-posed problem, the entry tube is extended to infinity, at which position the flow is considered to be fully developed. The radii of the disks are assumed equal and infinite, so that the Newtonian creeping-flow solution holds at the system outlet.

The numerical calculations are done by orthogonal collocation, in which the stream function, the shear stress and the two normal-stress differences are approximated by trial functions. Interior collocation points are chosen to be the zeros of the Tschebysheff and related polynomials. The system is divided into three regions, designated as the tube flow, stagnation flow, and radial flow regions. The trial functions are matched, at the junctions of these regions, by mass and momentum conservation conditions. The vorticity equation and the rheological equation of state are solved at the collocation points by a modified Newton method.

Correspondence concerning this paper should be addressed to A. Co, Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706.

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