Extraction of Chemical Kinetics Insights with Special CSP Data

S. H. Lam∗
Department of Mechanical and Aerospace Engineering
Princeton University, Princeton, NJ 08544, U. S. A.

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Abstract

The following are interesting questions for any chemical reaction system of interest: in any time epoch, which reactions are already exhausted, and which reactions are currently dormant? Which reactions are currently rate-controlling? For each reaction, which chemical species are the major participants and which are the minor participants? Are there chain-branching processes going on? What happens if some of the kinetic rate parameters were wrong? We shall show how insightful answers to these and other questions can be obtained by inspection of CSP-derived equations and analytical formulas.

1 Introduction

The following is a general initial-value problem:

\[ \frac{dy}{dt} = g(y; \kappa), \]
\[ y(t = 0) = y_0, \]  \hspace{1cm} (1)

∗Professor emeritus. Email: lam@princeton.edu. The materials here will be presented at the 15th Numerical Combustion Conference, Avignon, France, April 20-22, 2015.
where both $\mathbf{y}$ and $\mathbf{g}$ are $N$-dimensional column vectors, and $t$ is time. On Eq.(1)’s right hand side, $\mathbf{g}(\mathbf{y}; \kappa)$ is some explicitly given (non-linear) algebraic function of $\mathbf{y}$ and $\kappa$—the latter represents the collection of modeling parameters of the physical problem. The initial vector $\mathbf{y}_o$ is arbitrary.

In principle, once the finite values of $\kappa$ and $\mathbf{y}_o$ are specified, numerical solutions to this initial-value problem can be computed directly—no matter how nonlinear and complicated the given $\mathbf{g}(\mathbf{y}; \kappa)$ may be. However, an inherent weakness of numerical solutions is that they do not provide insights on the problem of interest. For example, insights on $\mathbf{y}$’s dependence on any modeling parameters can only be obtained by skillful examinations of the numbers generated by many computed solutions.

When some of the modeling parameters take on extreme values, the governing ODE system can become "stiff." Such stiffness must be dealt with properly by the numerical algorithms used. It is well known in the chemical kinetics community that such stiffness can be gainfully exploited—by the use of singular perturbation (SP) methodologies—to derive approximate (non-stiff) reduced models [1]. The main virtue of approximate reduced models is that valuable insights can be obtained by inspection of the derived analytical formulas. However, such paper/pencil methodologies are difficult to do when $N$ is large and $\mathbf{g}(\mathbf{y}; \kappa)$ is nonlinear and completely general.

The goal of computational singular perturbation (CSP) methodology, developed by this author and D. A. Goussis some years ago [2, 3], has been to make the classical paper/pencil SP methodologies programmable. Prior to 2013, the early CSP papers dealt with a general $\mathbf{g}(\mathbf{y}; \kappa)$, and advocated a numerical iterative "refinement" procedure [4, 5, 6, 7, 8]. The 2013 version [9] focused on chemical kinetics problems, and took full advantage of certain special properties of chemical kinetics’ $\mathbf{g}(\mathbf{y}; \kappa)$. This class of initial-value problems was analytically reformulated in terms of a number of special CSP data.

This is a follow-up paper which, in addition to providing a recapitulation of the new approach, shows how chemical kinetics insights can be extracted by inspection of the CSP-reformulated equations.

2 Chemical Kinetics

For chemical kinetics, the $N$ components of $\mathbf{y}$ are concentrations of chemical species and temperature. The reaction system includes $R$ elementary reac-
tions, and each reaction makes a contribution to the reaction rate vector, \( \mathbf{g}(\mathbf{y}; \kappa) \):

\[
\mathbf{g}(\mathbf{y}; \kappa) = \sum_{r=1}^{R} \alpha_r \Omega^r(\mathbf{y}; k_r, K_r). \tag{2}
\]

Here \( \alpha_r \) and \( \Omega^r(\mathbf{y}; k_r, K_r) \) are the \( r \)-th reaction's stoichiometric column vector and the net reaction rate, respectively. The direction of the \( r \)-th reaction is given by \( \alpha_r \), and its amplitude is given by \( \Omega^r \). The physical dimension of all the \( \Omega^r \)'s is concentration per unit time. The form of the \( \Omega^r(\mathbf{y}; k_r, K_r) \) formula for elementary reactions is given by the Law of Mass Action. The forward kinetic rate of the \( r \)-th reaction is denoted by \( k_r \), and its equilibrium constant (i.e. ratio of backward to forward kinetic rates) is denoted by \( K_r \). Both are temperature (and pressure) dependent positive dimensional entities. All reactions are allowed to be reversible. The forward reaction direction is chosen so that for problems of interest the \( K_r \)'s do not take on extreme values. Thus, the problem can become stiff only when some of the \( k_r \)'s (and/or some components of \( \mathbf{y}_0 \)) take on extreme values. Note that the physical dimensions of the \( k_r \)'s (and also the \( K_r \)'s) of different reactions are usually different—because the molecularities of different reactions may be different. Thus the relative extremeness of the \( k_r \)'s cannot be appraised by comparing their dimensional numerical values.

For most realistic reaction systems, \( R \) is usually larger than \( N \) [10]. Thus usually the given set of \( \alpha_r \)'s has many linear dependencies. While linear dependencies can always be straightforwardly removed, the physical meanings of the resulting set of tampered reactions are less obvious. We thus choose to deal with the original set of reactions because their physical meanings are more obvious. Additional comments on this point will be presented in §9 later.

An important observation is that the \( \alpha_r \)'s of chemical kinetics do not contain parameters which could take on extreme values. Thus the \( \alpha_r \)'s—which are usually constant vectors—are not responsible for the stiffness issue. This seemingly benign observation is fully exploited here [9].

Since the physical meanings of the \( \alpha_r \)'s and the \( \Omega^r(\mathbf{y}; k_r, K_r) \)'s discussed above are clear and obvious, Eq.(2) is called the physical representation of \( \mathbf{g}(\mathbf{y}; \kappa) \) [4].
2.1 Conserved Scalars

For chemical kinetics, the number of linearly independent $\alpha_r$’s is always less than $N$—even when $R$ is larger than $N$. This is because the given set of $\alpha_r$’s always has $J > 0$ linearly independent left null (row) vectors—which shall be denoted by $\sigma^j$’s here:

$$\sigma^j \odot \alpha_r = 0, \quad j = 1, \ldots, J, \quad r = 1, \ldots, R.$$  \hspace{1cm} (3)

When all the $\alpha_r$’s are constant vectors, then all these $\sigma^j$’s are also constant vectors—they can be found using standard linear algebra tools. Taking the inner product of each of these constant $\sigma^j$’s with Eq.(2) and using Eq.(3), the resulting trivial differential equations can be integrated to obtain:

$$\sigma^j \odot y(t) = \sigma^j \odot y_o, \quad j = 1, \ldots, J.$$  \hspace{1cm} (4)

For chemical kinetics, Eq.(4) is usually interpreted as manifestations of some physically meaningful conservation laws, such as the total amount of atomic elements in the reaction system and/or other interesting entities which are conserved by chemical reactions. We shall refer to Eq.(4) as the conserved-scalar equations of the reaction system.

2.2 Reacting Flows

For reacting flows, the governing equations are partial differential equations. The time derivative on the left hand side of Eq.(1) is replaced by the Lagrangian derivative, and some (laminar or turbulent) diffusion terms are added to the right hand side. The conserved scalars discussed in the previous section are no longer conserved when diffusion is included. To perform numerical computations, a spatial grid must somehow be chosen. Some additional comments on how to deal with the diffusion terms will be given in §7.4 later.

3 CSP Data

The following special CSP data are defined in terms of the given information on the $\alpha_r$’s and the $\Omega^r(y; k_r, K_r)$’s [9].
3.1 Reaction-specific CSP Data

The reaction-specific scalar $\tau^r$—the intrinsic time scale of the $r$-th reaction—is defined by:

$$\tau^r \equiv \frac{1}{\partial \Omega^r / \partial y} \odot \alpha_r = \tau^r(y; k_r, K_r), \quad r = 1, \ldots, R, \quad (5a)$$

where $\partial \Omega^r / \partial y$ is a row vector and $\odot$ is the $N$-dimensional inner product operator. The physical dimension of $\tau^r$ is time, and it is usually a finite negative number. However, it can become positive when the $r$-th reaction involves chain-branching. Note that $|\tau^r|$ is inversely proportional to $k_r$, and that $\Omega^r$ is dimensionless and is independent of $k_r$. Intuitively, the reciprocal of $|\tau^r|$ is a better measure of the intrinsic speed of the $r$-th reaction than $\Omega^r$.

The reaction-specific row vector $\beta^r$ is defined by:

$$\beta^r \equiv \tau^r \frac{\partial \Omega^r}{\partial y} = \beta^r(y; K_r), \quad r = 1, \ldots, R, \quad (5b)$$

It is easy to show that $\beta^r$ as defined above does not depend on the magnitude of $k_r$. Thus the right hand side of Eq.(5b) above deliberately omits the $k_r$ dependence to emphasize this observation.

Since the physical dimensions of different components of $\alpha_r$ may be different, then the physical dimensions of different components of $\beta^r$ can also be different. However, so long as $\tau^r$ is finite, Eq.(5a) guarantees that:

$$\beta^r \odot \alpha_r = 1, \quad r = 1, \ldots, R. \quad (6)$$

We now define $\Gamma^r_{r'}$, a $R \times R$ dimensionless matrix, to be the inner product of $\beta^r$ with $\alpha_{r'}$:

$$\Gamma^r_{r'} \equiv \beta^r \odot \alpha_{r'} = \Gamma^r_{r'}(y; K_r), \quad r, r' = 1, \ldots, R. \quad (7)$$

Note that all elements of $\Gamma^r_{r'}$ are independent of the magnitude of $k_r$.

The left hand side of Eq.(6) is a sum of $N$ dimensionless numbers. Let us denote these numbers by $\Phi^n_r$, and call them the participant pointers of the $r$-th reaction. When $\Phi^n_r$ is an $O(1)$ number, the $n$-th component of $y$ is a major participant of the $r$-th reaction. When $\Phi^n_r$ is non-zero but small compared to unity, that component of $y$ is a minor participant. When $\Phi^n_r$ is zero, that component of $y$ is a non-participant—unless it is a catalyst.
When $\Phi^n_r$ of a chemical species is negative, that species is a chain carrier of a chain-branching process. Since Eq.(6) says the sum of $\Phi^n_r$ over all $N$ participants is unity, then every reaction has at least one major participant.

When $y$ has some small uncertainties, the value of $\Omega^r$ evaluated using the given $\Omega^r(y; k_r, K_r)$ formula would also have uncertainties. Denoting the $y$ uncertainties by $\delta y$, we have

$$\Omega^r(y \pm \delta y; k_r, K_r) = \Omega^r(y; k_r, K_r) \pm \frac{\beta^r \odot \delta y}{\tau^r} + \ldots$$

Thus the evaluated value of $\Omega^r(y \pm \delta y; k_r, K_r)$ is very sensitive to $\delta y$ when $\tau^r$—the $r$-th reaction’s intrinsic time scale—is a very small number.

Summarizing, once $\alpha^r$ and $\Omega^r(y; k_r, K_r)$ for all $R$ reactions are given, explicit analytical formulas are available for the following reaction-specific special CSP data: $\tau^r, \beta^r, \Gamma^r_r$, and $\Phi^n_r$.

### 3.1.1 Example

Consider a reaction system with species concentrations $A, B, C, D, \ldots$ and temperature $T$. All are positive numbers. The $y$ column vector is:

$$y = \begin{pmatrix} A \\ B \\ C \\ D \\ \vdots \\ T \end{pmatrix}.$$  

Note that the physical dimension of the last component of $y$ is different from all others.

The reaction system has $R$ elementary reactions. Suppose the $r_s$-th reaction is:

$$2A + B + D \iff C + D,$$

where $D$ is a catalyst. Then the following information on the $r_s$-th reaction
are given:

\[
\alpha_r = \begin{pmatrix}
-2 \\
-1 \\
+1 \\
0 \\
\vdots \\
\Delta h^o_r
\end{pmatrix}, \quad \Omega^r(y; k_r, K_r) = k_r D (A^2 B - K_r C).
\] (11)

The Law of Mass Action was used for the above \(\Omega^r(y; k_r, K_r)\) formula. Note that the physical dimension of \(\Delta h^o_r\), the heat of reaction of the \(r\)-th reaction, is temperature per concentration. The parameters \(k_r, K_r\) are (temperature and pressure dependent) forward kinetic rate and the equilibrium constant of this reaction, respectively. All are positive dimensional entities.

Differentiating \(\Omega^r\) with respect to \(y\), a row vector is obtained:

\[
\frac{\partial \Omega^r}{\partial y} = \begin{bmatrix}
\frac{\partial \Omega^r}{\partial A} & \frac{\partial \Omega^r}{\partial B} & \frac{\partial \Omega^r}{\partial C} & \frac{\partial \Omega^r}{\partial D} & \cdots & \frac{\partial \Omega^r}{\partial T}
\end{bmatrix}
\]

\[
= k_r D \left[ 2 AB, A^2, -K_r, \frac{A^2 B - K_r C}{D}, 0, \cdots, \left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) \right].
\]

Using it in Eq.(5a) and Eq.(5b), we have:

\[
\tau^r = -\frac{1}{k_r D (4AB + A^2 + K_r - \Delta h^o_r \left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) )},
\]

\[
\beta^r = \frac{\left[ -2 AB, -A^2, K_r, -\frac{A^2 B - K_r C}{D}, 0, \cdots, -\left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) \right]}{4AB + A^2 + K_r - \Delta h^o_r \left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) }.
\]

Note that \(\tau^r\) is inversely proportional to \(k_r D\), and \(\beta^r(y; K_r)\) indeed does not depend on the magnitude of \(k_r\). Note also that the physical dimension of the last component of \(\beta^r\) is different from the others.

The \(r\)-th reaction’s participant pointers are:

\[
\Phi^r_n = \frac{\left\{ 4AB, A^2, K_r, 0, 0, \cdots, -\Delta h^o_r \left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) \right\}}{4AB + A^2 + K_r - \Delta h^o_r \left( \frac{d \ln k_r}{dT} \frac{A^2 B}{dt} - \frac{d \ln (k_r K_r)}{dT} K_r C \right) }.
\]
The participant pointer of \( D \), the catalyst, is zero. If \( K_{\text{rs}} \) is much smaller than \( 4AB \) and/or \( A^2 \), then \( \Phi^3_{\text{rs}} << 1 \) and \( C \) is a minor participant of this reaction. If in addition \( A/B = O(1) \), then both \( A \) and \( B \) are major participants.

### 3.2 Fast Reaction Group CSP Data

At any point in time, the \( R \) reactions can be rank-ordered in ascending values of their \( |\tau^r| \)'s. We assume this is done on the fly. See §7.2 later.

Let \( \Delta t \) denote the current integration time step which had somehow been chosen. Then the \( M \) reactions (with linearly independent \( \alpha_m \)'s) which satisfy the following inequality are considered fast reactions:

\[
|\tau^m| < \Delta t, \quad m = 1, \ldots, M.
\]  

(13)

Obviously, the chosen \( \Delta t \) is too coarse to resolve the progress of these fast reactions. This is the stiffness problem.

Only negative \( \tau^m \)'s are acceptable to be included in the fast reaction group. Once a fast reaction group is identified, the \( M \times M \) dimensionless matrix \( \Gamma^m_{\alpha} \), as defined by Eq.(7) can be computed. Note that usually many reactions which satisfy Eq.(13) are excluded from the group if their \( \alpha^r \)'s are linearly dependent on the selected \( \alpha^m \)'s already in the group. We assume the inverse of \( \Gamma^m_{\alpha} \) exists and denote it by \( \Theta^m_{\alpha} \):

\[
\Theta^m_{\alpha} \equiv [\Gamma^m_{\alpha}]^{-1} = \Theta^m_{\alpha}(y; M; K_m), \quad m, m'' = 1, \ldots, M.
\]  

(14)

The existence of an inverse means \( \Gamma^m_{\alpha} \) must be non-singular. Thus we expect all elements of \( \Theta^m_{\alpha} \) to be order-unity numbers. See §7.2. Note that neither \( \Theta^m_{\alpha} \) nor \( \Gamma^m_{\alpha} \) depends on the magnitude of the fast \( k^m \)'s.

The \( \Theta^m_{\alpha} \) matrix is the center piece of the fast reaction group’s special CSP data. For \( M \) larger than two or three, there are no simple analytical formula for \( \Theta^m_{\alpha} \). Thus information on \( \Theta^m_{\alpha} \) is only available as arrays of time-dependent numbers.

#### 3.2.1 Fast and Slow Subspaces

A non-singular \( \Gamma^m_{\alpha} \) means that the set of fast \( \alpha_m \)'s and the set of fast \( \beta^m \)'s are both linearly independent sets. Together, they can serve as basis vectors to span the \( M \)-dimensional fast subspace of the \( N \)-dimensional \( y \) vector space.
The $N \times N$ fast subspace projection matrix is [9]:

$$Q^{fast} = \sum_{m,m'=1}^{M} \alpha_m \Theta_{m/m'} \beta_{m'} = Q^{fast}(y; K_m; M). \quad (15)$$

The $N - M$ dimensional subspace complementary to this $M$-dimensional fast subspace is called the slow subspace.

### 3.2.2 CSP Radicals

All major participants of the fast reaction group are referred to as CSP radicals [4]. The total number of CSP radicals is always larger than (or equal to $M$. The rapid initial transients of the CSP radicals are too fast to be resolved by the current $\Delta t$ which is too coarse. However, these initial transients are expected be already over at the first $\Delta t$ time step.

When a fast reaction has only one major participant, then the quasi-steady approximation is applicable to this participant. When a fast reaction has more than one major participants, then the partial equilibrium approximation is applicable to this fast reaction.

### 4 Differential Equations for the fast $\Omega^m$’s

It was shown in Eq.(8) that direct evaluation of $\Omega^m(y + \delta y; k_m, K_m)$ was problematic in the small $|\tau^m|$ limit. How should the $\Omega^m$’s be evaluated when the $|\tau^m|$’s are very small?

Let us formally differentiate each of the $M$ given $\Omega^m(y; k_m, K_m)$ formulas with respect to time (using the chain-rule). The following $M$ exact differential equations for the $\Omega^m$’s are obtained:

$$\frac{d\Omega^m}{dt} = \frac{\partial \Omega^m}{\partial y} \circ \frac{dy}{dt} = \frac{1}{\tau^m} \beta^m \circ g$$

$$= \frac{1}{\tau^m} \left( \sum_{m'=1}^{M} \sum_{m'=1}^{M} \Gamma_{m'}^m \Omega^m + \sum_{k=1}^{R-M} \Gamma_{M+k}^m \Omega^{M+k} \right),$$

$$= \frac{1}{\tau^m} \sum_{m'=1}^{M} \Gamma_{m'}^m \left( \Omega^m - \Omega^m_\infty \right), \quad m = 1, \ldots, M, \quad (16)$$
where

\[
\Omega_{\infty}' \equiv - \sum_{k=1}^{R-M} \left( \sum_{m=1}^{M} \Theta_{m}^{m'} \Gamma_{M+k}^{m} \right) \Omega^{M+k}
\]

\[
= \Omega_{\infty}'(y; K_m; K_{M+k}, K_{M+k}), \quad m' = 1, \ldots, M.
\]

Multiplying Eq.(16) on its left by the matrix \( \Theta_{m}^{m'} \Gamma_{m}^{m} \) and summing over all \( m \) (and taking advantage of Eq.(14), we obtain the following equations:

\[
\Omega_{\infty}' = \Omega_{\infty} + \omega_{\text{fast}}, \quad m = 1, \ldots, M,
\]

where

\[
\omega_{\text{fast}} \equiv \sum_{m=1}^{M} \Theta_{m}^{m'} \Gamma_{m}^{m} \frac{d\Omega^{m}}{dt} = \omega_{\text{fast}}(y; k_{m'}, K_{m'}),
\]

\[
m = 1, \ldots, M.
\]

Both Eq.(16) and Eq.(18a) are differential equations—the latter is just an alternative representation of the former. No assumption on the \( \alpha_{m} \)'s had been made.

The mathematical implications of small \( \tau_{m} \)'s are now clear. When all the \( \tau_{m} \)'s are negative and small (in comparison to the current \( \Delta t \)), Eq.(16) and Eq.(18a) are stable and stiff differential equations. Thus the fast \( \Omega_{m} \)'s are expected to rapidly decay toward the slower evolving \( \Omega_{\infty}(y; K_m; K_{M+k}, K_{M+k}) \)'s. After the initial transient, the \( \omega_{\text{fast}} \) term on the right hand side of Eq.(18a) is expected to be a small “correction” term. Unlike the originally given analytical \( \Omega^{m}(y; k_{m}, K_{m}) \) formulas (which are exact solutions of Eq.(16) and Eq.(18a)), evaluation of \( \Omega^{m} \) using Eq.(18) is not problematic when all the fast \( \tau_{m} \)'s are negative and asymptotically small in comparison to \( \Delta t \).

5 Exact CSP Reformulation

Instead of using the original given analytical \( \Omega^{m}(y, k_{m}, K_{m}) \) algebraic formulas to evaluate the \( \Omega^{m} \)'s, we now use Eq.(18a), \( \Omega^{m} \)'s own differential equations.

We first rewrite Eq.(2), the physical representation of \( g(y; \kappa) \), as follows:

\[
g(y; \kappa) = \sum_{m=1}^{M} \alpha_{m} \Omega^{m} + \sum_{k=1}^{R-M} \alpha_{M+k} \Omega^{M+k}(y; k_{M+k}, K_{M+k}).
\]

(19)
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Eliminating $\Omega^m$ from the fast reaction group term using the exact Eq.(18a), and absorbing all the newcomer $\Omega_{\infty}^{M+k}$’s by the slow reaction group term, the following alternative representation of $g(y;\kappa)$ is obtained:

$$g(y;\kappa) = g^{\text{fast}} + g^{\text{slow}},$$  

(20)

where

$$g^{\text{fast}} \equiv \sum_{m=1}^{M} \alpha_m \omega_m^{\text{fast}}(y; k_m, K_m),$$  

(21a)

$$g^{\text{slow}} \equiv \sum_{m=1}^{M} \alpha_m \Omega_{\infty}^m(y; \kappa) + \sum_{k=1}^{R-M} \alpha_{M+k} \Omega^{M+k}(y; k_{M+k}, K_{M+k})$$

$$= \sum_{k=1}^{R-M} \alpha_{M+k} \Omega^{M+k}(y; k_{M+k}, K_{M+k}),$$  

(21b)

$$\alpha_{slow}_{M+k} \equiv \alpha_{M+k} - \sum_{m',m''=1}^{M} \alpha_{m'} \Theta_{m''}^{m'} \Gamma_{M+k}^{m''}, \quad k = 1, \ldots, R - M. \quad (21c)$$

Eq.(20) is the CSP-reformulated representation of $g(y;\kappa)$ [9] It is important to emphasize here that all the above derivations are exact.

Note that $g^{\text{fast}}$ depends on the original fast $\alpha_m$’s and the new $\omega_m^{\text{fast}}$’s, while $g^{\text{slow}}$ depends on the new slow $\alpha_{M+k}$’s and the original given analytical $\Omega^{M+k}(y; k_{M+k}, K_{M+k})$ formulas. Both $\omega_m^{\text{fast}}$ and $\alpha_{M+k}$ depend on special CSP data, particularly the $\Theta_{m''}^{m'}$ matrix. Eq.(18b) says the new $\omega_m^{\text{fast}}$’s are some linear combinations of the time derivatives of the fast $\Omega^m$’s, while Eq.(21c) says the new $\alpha_{M+k}$’s are the projection of the original $\alpha_{M+k}$’s in the slow subspace. Thus if $\alpha_{M+k'}$ is completely linearly dependent on the set of $M$ fast $\alpha_m$’s (and therefore was excluded from the fast reaction group regardless of the value of $\tau^{M+k'}$), then $\alpha_{slow}_{M+k'}$ is a null vector.

We now need to decide how to evaluate $\omega_m^{\text{fast}}$, knowing full well that it is an important term only during the rapid initial transient, and is a small correction term in comparison to $\Omega_{\infty}^m$ after the initial transient.

6 Paper/pencil Exploitation of Stiffness

For the CSP-reformulated problem, it is no longer necessary to decide which species/reactions would accept the quasi-steady/partial equilibrium approx-
The Rapid Initial Transient

During the brief but rapid initial transient, Eq.(20) is dominated by $\mathbf{g}^{\text{fast}}$. Neglecting $\mathbf{g}^{\text{slow}}$, we have:

$$
\frac{dy}{dt} \approx \sum_{m=1}^{M} \alpha_{m} \omega_{m}^{n} \tau_{m}^{\text{fast}}
$$

$$
= \sum_{m,m'=1}^{M} \alpha_{m} \left( \Theta_{m}^{n} \tau_{m'} \frac{d\Omega_{m'}}{dt} \right). \tag{22}
$$

Since $\mathbf{y}_{0}$, the initial $\mathbf{y}(t = 0)$ vector, is arbitrary, the initial values of all the $\Omega^{r}(\mathbf{y}_{0}, \kappa)$’s are then also arbitrary (and may therefore be huge). Since all the fast $\tau^{m}$’s are negative, all the fast $\Omega^{m}$’s are expected to decay. Let $\mathbf{y}_{+}$ denote the value of $\mathbf{y}$ when this rapid transient is nearly exhausted. If the details of the transient processes are not of interest, then only the value of $\mathbf{y}_{+}$ is needed to serve as the initial condition for the slow epoch afterwards. If one can justifiably approximate the column vector $\sum_{m=1}^{M} \alpha_{m} \Theta_{m}^{n} \tau_{m'}$ by a constant vector during the brief transient period, then Eq.(22) can be analytically integrated to yield $\mathbf{y}_{+}$. This simple procedure was advocated in [4] as the so-called radical correction. Note that the values of $\mathbf{y}_{+}$ and $\mathbf{y}_{0}$ are different only for the CSP-radical components of $\mathbf{y}$.

The Reduced Model in the Slow Epoch

After the rapid initial transient, Eq.(20) will be dominated by $\mathbf{g}^{\text{slow}}$. Neglecting $\mathbf{g}^{\text{fast}}$ in the slow epoch, we obtain:

$$
\frac{dy}{dt} \approx \sum_{k=1}^{R-M} \alpha_{M+k}^{\text{slow}} \Omega_{M+k}^{M+k}(\mathbf{y}; k_{M+k}, K_{M+k}), \tag{23}
$$

$$
\mathbf{y}(t \approx 0) \approx \mathbf{y}_{+},
$$

where $\alpha_{M+k}^{\text{slow}}$ is defined by Eq.(21c). We shall call $\alpha_{M+k}^{\text{slow}}$ the effective stochiometric vector of the $(M+k)$-th slow reaction. On the right hand side
of Eq.(23), the original analytical \( \Omega^{M+k}(y; k_{M+k}, K_{M+k}) \)'s formulas are used. This set of differential equations for \( y \) is the leading order paper/pencil reduced model.

Note that this new \( \alpha_{M+k}^\text{slow} \) and the original \( \Omega^{M+k}(y; k_{M+k}, K_{M+k}) \) together do not respect the Law of Mass Action.

We can define the effective slow time scale of the \((M+k)\)-th reaction—to be denoted by \( \tau_{\text{slow}}^{M+k} \)—also by Eq.(5a) except that \( \alpha_{M+k}^\text{slow} \) is used instead of \( \alpha_{M+k} \). The result is:

\[
\tau_{\text{slow}}^{M+k} = \frac{\tau^{M+k}_{\text{slow}}}{1 - \eta^{M+k}},
\]

where

\[
\eta^{M+k} \equiv \sum_{m,m'=1}^M \Gamma_m^{M+k} \Theta_{m'}^m \Gamma_{m'}^{M+k}, \quad k = 1, \ldots, R - M.
\]

Note that \( \tau_{\text{slow}}^{M+k} \) can be greater or smaller than \( \tau^{M+k} \), and they may even have opposite signs when \( \eta^{M+k} \) goes above positive unity.

Let \( |\tau_{\text{slow}}^{M+k}| \) be the smallest of all the \( |\tau_{\text{slow}}^{M+k}| \)'s, and \( |\tau^{M}| \) be the largest of all the fast \( |\tau^{m}| \)'s. Then the dimensionless ratio \( |\tau^{M}/\tau_{\text{slow}}^{M+k}| \) is the small parameter being exploited by the paper/pencil SP analysis.

### 6.3 Algebraic Equations of State in the Slow Epoch

To the same leading order accuracy as Eq.(23), the second term on the right hand side of Eq.(18a) is a higher order term in comparison to the first term. Neglecting it yields the following approximate algebraic equations:

\[
\Omega^m(y; k_m, K_m) \approx \Omega^m_\infty(y; K_m; k_{M+k}, K_{M+k}), \quad m = 1, \ldots, M.
\]

All solutions of Eq.(23) are automatically consistent with these \( M \) approximate algebraic equations. Hence Eq.(25) is a set of approximate algebraic equations of state in the slow epoch. Mathematically, they can be used to replace the differential equations of \( M \) CSP radicals—one from each of the fast reactions in the current fast reaction group [4]. In paper/pencil SP analysis, this option is nearly always taken.

From the paper/pencil SP point of view, the \( \Omega^m_\infty \) term on the right hand side of Eq.(25) is itself also a higher order term. However, this higher order term is solely responsible for the reformulated new \( \alpha_{M+k}^\text{slow} \)'s to be different from the original \( \alpha_{M+k} \)'s. It is important to note that the CSP-reformulated
Eq.(23) can utilize Eq.(25) \textit{without} its right hand side because its impacts on the slow $\alpha_{M+k}$'s have already been properly accounted for. However, Eq.(2), the original physical representation of $g(y; \kappa)$, \textit{cannot} utilize Eq.(25) without keeping its right hand side.

In addition to Eq.(25), the $J$ algebraic conserved scalar equations in Eq.(4) are also available (when all the $\alpha_r$'s are constant) to replace additional $J$ selected differential equations. So the number of non-stiff $y$ differential equations in the leading order reduced model can be as small as $N - (M + J)$ [11].

7 Computational Exploitation of Stiffness

How to computationally exploit the stiffness of the CSP reformulated initial-value problem? The answer is obvious: use implicit integration algorithms for the stiff equations, and conventional explicit algorithms for the non-stiff equations. For example, backward difference can be used to evaluate the fast time derivatives, and iterations can be used to improve accuracy. Conceptually, \textit{nothing is neglected}—while any inherent weaknesses of the implicit integration algorithms used are conceded.

As mentioned earlier in §6.3, Eq.(18a) can be used to replace $M$ differential equations of the CSP-radicals, and Eq.(4) can be used to replace additional $J$ differential equations. Both of these replacement steps are optional. How to utilize these available options to gain computational advantages should be decided by programming considerations.

7.1 How and Why to Compute the $\omega_{fast}^m$'s

Use Eq.(18a) to eliminate $\Omega^m$ from Eq.(18b) to obtain an equation for $\omega_{fast}^m$:

$$\omega_{fast}^m = \sum_{m'=1}^{M} \Theta_{m'}^m \tau_{m'} \frac{d}{dt} (\Omega_{\infty}^m + \omega_{fast}^m).$$  \hspace{1cm} (26)

This can be used to compute $\omega_{fast}^m$ \textit{iteratively} using the previous iterants to implicitly evaluate the needed time derivatives. For the starting iterant, use Eq.(18b) with backward difference for $d\Omega^m/dt$. We need the values of the $\omega_{fast}^m$'s mainly to decide whether the fast reactions are exhausted. Keeping $\omega_{fast}^m$ (in some approximate manner) in the computations at every time step...
means a CSP radical correction is being executed. Thus no special attention is needed to deal with the initial rapid transient for arbitrary $y_o$—it is being correctly and automatically handled by the implicit iterative algorithm.

7.2 Updating the Fast Subspace

For non-linear problems, all special CSP data are time dependent. Thus the values of the $\tau^r$'s, the identities of the fast reactions, and the value of $M$ can all change with time. From the vantage point of numerical computations, the current integration time step $\Delta t$ should be some fraction of the smallest value of the current $|\tau_{\text{slow}}^{M+k}|$'s. Thus $\Delta t$ also needs to be updated. From the point of view of SP methodology, a good fast subspace should honor the following inequality:

$$|\omega_{\text{fast}}^m| << |\Omega_\infty^m(y;K_m;k_{M+k},K_{M+k})|, \quad m = 1, \ldots, M.$$  \hfill (27)

Since the CSP reformulated problem is exact and nothing is neglected, a conservative approach would be to include all marginally fast reactions in the fast reaction group. The elements of $\Theta_{m'}^m$ of a good fast reactions group should all be numbers of order unity, and the smallest $|\tau_{\text{slow}}^M|$ should be significantly larger than the largest $|\tau^m|$. Thus the competitive merits of candidate fast reaction groups under consideration can be computationally assessed.

7.3 Updating $\Theta_{m'}^m$

The $\Theta_{m'}^m$ matrix is the inverse of $\Gamma_{m'}^m$. It is the most important special CSP data for the current fast reaction group. Calculations of both the $\alpha_{M+k'}$'s and the $\omega_{\text{fast}}^m$'s need it.

When each of the fast reactions has only one major participants and all the $\alpha_r$'s are weakly time dependent, then it can be shown that $\Theta_{m'}^m$ is also weakly time dependent. Hence, it may not be necessary to update $\Theta_{m'}^m$ at every integration time step. In general, inversion of a large matrix is always a computationally intensive task. However, iterative algorithms can be quite efficient [12]. The previous time step's $\Theta_{m'}^m$ is always available to serve as the starting iterant.

Let $\tilde{\Theta}_{m'}^m$ denote an approximation to $\Theta_{m'}^m$:

$$\Theta_{m'}^m = \tilde{\Theta}_{m'}^m + \Delta \Theta_{m'}^m, \quad m, m' = 1, \ldots, M.$$ \hfill (28)
If $\Delta \Theta^m_{n'}$ is ignored in the computations, the errors to $\alpha_{M+k}^{\text{slow}}$ and $\omega_{\text{fast}}^m$ so introduced can be straightforwardly estimated.

### 7.4 Reacting Flows and Diffusion

For reacting flows, we can assign all the diffusion terms to the $R$-th term on the right hand side of Eq.(2). For example, we can set $\Omega^R = 1$ and let $\alpha_R$ represent all the diffusion (and any other non-chemical kinetics) terms. By doing so the row vector $\beta^R$ and the participation pointers $\Phi^R_n$ are now meaningless.

It is reasonable to assume that the $n$-th component’s diffusion term should depend on $D^n$, a characteristic (laminar or turbulent) diffusion coefficient (or matrix), and on $\Delta x$, the local spatial grid size. By dimensional analysis, a credible estimate of $\tau^{R,n}$, the $n$-th species’ diffusion time scale, is then $(\Delta x)^2 / D^n$.

In a reacting flow, the intrinsic time scales of all the reactions in different spatial regions are different. At each spatial grid point, the CSP reformation methodology can be applied provided the local diffusion process is known to be slower than the slowest of the local fast reactions. In other words, $|\tau^{R,n}| >> |\tau^M|$ for $n = 1, \ldots, N$. Thus all diffusion terms are kept inside the $g^{\text{slow}}$ term.

The main consequence of stiffness is that the (laminar or turbulent) diffusion coefficients for all components of $y$ inside the $g^{\text{slow}}$ term are modified in the slow epoch. See §7.6 of [4].

### 8 Insights by Inspections

All the special CSP data, with the exception of the $\Theta^m_m$ matrix, have analytical formulas giving their values in terms of the given chemical kinetics data.

#### 8.1 Impacts of Reactions and Reactants

Let $\Delta y$ denote the user-specified upper bound of tolerable error for each component of $y$. Then $\Delta g = \Delta y / \Delta t$ is the user-specified upper bound of tolerable error for each component of $g$. The impact of any elementary
reaction can now be assessed by comparing its contribution to \( g(y, \kappa) \) against the value of \( \Delta g \).

It is interesting to note that the \( r \)-th reaction’s contribution to \( g \) is not \( \alpha_r \Omega^r \)—whenever currently there is a fast reaction group. We rewrite the CSP-reformulated Eq.(20) as follows:

\[
g(y; \kappa) = \sum_{m=1}^{M} g_{m}^{\text{fast}} + \sum_{k=1}^{R-M} g_{M+k}^{\text{slow}}
\]  

(29)

where the definitions of \( g_{m}^{\text{fast}} \) and \( g_{M+k}^{\text{slow}} \) can be deduced from Eq.(21a) and Eq.(21b). Each term in the summations now represents the effective net contributions to \( g(y; \kappa) \) by each of the fast and slow reactions.

### 8.1.1 Fast Reactions

When \( |g_{m}^{\text{fast}}| < \Delta g \) for all components of \( \Delta g \), the \( m \)-th fast reaction is said to be exhausted. The exhausted value of \( \Omega^m \) is not zero—its leading approximation is \( \Omega^m_{\infty} \). The numerical values of these \( k_m \)'s are irrelevant provided they are big enough. The fast equilibrium constants—the \( K_m \)'s—are always relevant. Major participants to the fast reactions are called CSP-radicals. The ordering of the fast reactions among themselves is not important.

### 8.1.2 Slow Reactions

Note that \( \Omega^{M+k}_{M+k} \) is an order-unity dimensionless number. When some components of \( g_{M+k}^{\text{slow}} \) satisfy \( |g_{M+k}^{\text{slow}}| < \Delta g \), then the \( (M+k) \)-th slow reaction is a dormant reaction for those components. A reaction which is dormant for all species is not an important reaction to the reaction system. When some components of \( g \) satisfy \( |g_{M+k}^{\text{slow}}| = O |g| \), then this \( (M+k) \)-th slow reaction is one of the rate-controlling reactions for those components. All major participants of such important reactions must be properly tracked [8].

The direction of the \( (M+k) \)-th slow reaction is now \( \alpha_{M+k}^{\text{slow}} \) and its effective time scale is now \( \tau_{M+k}^{\text{slow}} \). If \( \tau_{M+k}^{\text{slow}} \) turns positive, something interesting is going on and an ignition or explosion may be imminent.

When \( g_{m}^{\text{fast}} \) is negligible in comparison to \( g_{M+k}^{\text{slow}} \), then \( \Omega^m(y; k_m, K_m) \approx 0 \) is an acceptable approximation to be used by Eq.(29). However, it is not acceptable to be used by Eq.(2) or Eq.(19). For example, if the \( r \)-th reaction in §3.1.1 is one of the current fast reactions, then \( A^2 B - K_r C \approx 0 \) can be freely used by Eq.(29) in the slow epoch, but not by Eq.(2) or Eq.(19).
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The ordering of the slow reactions among themselves is not important.

9 Uniqueness of CSP Reformulation

When the reaction system has \( J \) conserved scalars, then there are \( N - J \) linearly independent \( \alpha_r \)'s in the given set of stoichiometric vectors.

Let us pick \( N - J \) linearly independent reactions from the given set of reactions, and add to them \( J \) linearly independent \textit{fictitious} reactions which can either create or destroy the conserved scalars. Now denote this expanded set of \( N \) stoichiometric vectors by \( \hat{\alpha}_n \), and assign the fictitious reactions (with zero kinetic reaction rates) to be its last \( J \) members. We can now rewrite Eq.(2), the original physical representation of \( g(y;\kappa) \), as follows:

\[
g(y;\kappa) = \sum_{n=1}^{N-J} \hat{\alpha}_n \hat{\Omega}_n^*, \quad (30a)
\]

where

\[
\hat{\Omega}_n^* \equiv \hat{\beta}_n^* \circ g = \hat{\beta}_n^* \circ \sum_{r=1}^{R} \alpha_r \Omega_r, \quad n = 1, \ldots, N - J, \quad (30b)
\]

and the set of \( \hat{\beta}_n^* \)'s and the chosen set of \( \hat{\alpha}_n \)'s are orthonormal to each other:

\[
\hat{\beta}_n^* \circ \hat{\alpha}_{n'} = \delta_{n'n'}, \quad n, n' = 1, \ldots, N. \quad (30c)
\]

All \( N - J \) selected original \( \hat{\alpha}_n \)'s in Eq.(30a) are now guaranteed to be linearly independent. Eq.(30b) says the new \( \hat{\Omega}_n^* \)'s are some linear combinations of the original \( \Omega_r(y;k_r,\hat{K}_r) \)'s.

It is duly noted that Eq.(30a) is non-unique because the set of chosen \( \hat{\alpha}_n \)'s is non-unique. One may now do CSP reformulation on this alternative representation of \( g(y;\kappa) \).

10 Conclusions

The CSP-reformulation methodology is particularly suited for chemical kinetics problems. It is not a general SP methodology. For example, it cannot handle high frequency but weakly-damped WKB type SP problems.
In classical paper/pencil SP analysis, the crucial step is to intelligently estimate the order of magnitudes of the dependent and independent variables so that their dimensionless counterparts can be assumed to be “of order unity.” This step requires good intuition and experience. When some of the dimensionless modeling parameters of the problem take on extreme values, the resulting stiffness is exploited by applying the quasi-steady and/or partial equilibrium approximations.

The main virtue of CSP reformulation is that no non-dimensionalization is required for chemical kinetics problems. Except for $\Theta_{m'}$, analytical formulas for all the special CSP data are available. Some representative data for $\tilde{\Theta}_{m'}$’s should be computed and made available. Then one can discern the major functional dependence of any entities of interest on $y$ and the modeling parameters—with the help of the numerical $\tilde{\Theta}_{m'}$ data—by inspection and examination of the CSP-derived analytical formulas.

Conceptually, there is no reason to “neglect” anything on a computer—except when doing so could significantly reduce the amount of computations. The CSP reformulation identifies all the terms which are considered “higher order terms” in classical SP analysis. Most importantly, inspection and examination of the derived equations and formulas provide analytical insights on who is doing what to whom at any time. Such insights also provide informed guidance on numerical strategies to trade off exactness against computational costs.

References


