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Note

Improved Iteration Scheme for Partial Equilibrium Flow*

A numerical method for partial equilibrium flow [1] was recently described [2]. The heart of the method is a quadratic iteration scheme in which the progress increment for equilibrium reaction s is obtained from the equilibrium constraint for reaction s alone. The scheme therefore converges best when the equilibrium reactions are weakly coupled, which can frequently be achieved by a judicious choice of the independent equilibrium reactions [2].

In the continuing use of this method, situations have been encountered in which no single choice of the equilibrium reactions is weakly coupled over the entire range of parameters that occur in a calculation, and convergence difficulties have then been experienced. We have therefore developed an improved iteration scheme which is considerably more robust than the original one, and which works well even when the equilibrium reactions are not weakly coupled.

The new iteration scheme consists, in essence, of the following ingredients: (a) preconditioning of the equilibrium constraint conditions to make them more nearly linear in the progress variables, (b) application of a one-step Gauss–Seidel–Newton iteration [3] to the preconditioned system, followed by (c) switching to a full Newton–Raphson iteration if the simpler Gauss-Seidel-Newton iteration fails to converge in a specified number of steps. If the equilibrium reactions are weakly coupled, convergence usually occurs before the full Newton–Raphson iteration is called into play. However, if the reactions are not weakly coupled the interaction between them is properly accounted for by the matrix inversion in the Newton–Raphson procedure.

The idea of using a simple fast iteration procedure for a certain number of steps and then switching to a full Newton–Raphson procedure is due to Meintjes and Morgan [4], who utilized a full Newton–Raphson method as a backup to the original quadratic iteration scheme of Ref. [2]. Results were encouraging but not fully satisfactory. The main innovation in the present approach is the preconditioning of the equilibrium constraint conditions, which was not done by Meintjes and Morgan. (Another difference between our scheme and theirs is that we use a one-step Gauss–Seidel–Newton iteration in place of the quadratic iteration of Ref. [2].

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However, this has little effect on the convergence behavior because the nonlinearity is greatly reduced by the preconditioning.)

For present purposes, we may restrict attention to the equilibrium part of the partial equilibrium flow description discussed in Refs. [1, 2]. We have a system of N equilibrium reactions symbolized by

$$\sum_k a_{ks} X_k \rightleftarrows \sum_k b_{ks} X_k, \tag{1}$$

where s ranges from 1 to N, and X_k represents one mole of chemical species k. Each equilibrium reaction imposes a constraint of the form

$$\prod_k (\rho_k / M_k)^{b_{ks} - a_{ks}} = K_c^s(T) \tag{2}$$

on the partial mass densities ρ_k of the species involved in the equilibrium reactions. Here M_k is the molecular weight of species k, and $K_c^s(T)$ is the concentration equilibrium constant for reaction s at temperature T. The starting values of the partial mass densities, which do not satisfy Eq. (2), are denoted by $\tilde{\rho}_k$. For present purposes T and the $\tilde{\rho}_k$ may simply be regarded as given, although they are of course actually determined by other parts of the numerical scheme that are not of concern here. The precise significance of the $\tilde{\rho}_k$ in terms of the remainder of the calculation is given in Ref. [2].

The species densities are related to their starting values by

$$\rho_k = \tilde{\rho}_k + M_k \sum_s (b_{ks} - a_{ks})\, \omega_s, \tag{3}$$

where ω_s is the progress increment for reaction s. Equations (2) and (3) combine to yield a coupled nonlinear system of N equations in the N unknown quantities ω_s. Since these equations will be solved iteratively, we introduce an iteration index v which will be displayed as a superscript. Thus the approximation to ω_s after iteration v is denoted by ω_s^v, and the corresponding approximation to ρ_k is

$$\rho_k^v = \tilde{\rho}_k + M_k \sum_s (b_{ks} - a_{ks})\, \omega_s^v. \tag{4}$$

It is understood that $\omega_s^0 = 0$, so that $\rho_k^0 = \tilde{\rho}_k$. It will also be necessary to refer to intermediate species densities defined by

$$\rho_k(v, s) = \tilde{\rho}_k + M_k \sum_{z=1}^{s-1} (b_{kz} - a_{kz})\, \omega_z^v + M_k \sum_{z=s}^{N} (b_{kz} - a_{kz})\, \omega_z^{v-1}. \tag{5}$$

It is convenient to introduce a vector $\boldsymbol{\rho} = (\rho_1, \rho_2, \ldots)$ whose components are the species densities ρ_k. Functions of the ρ_k can then be compactly written simply as functions of the vector variable $\boldsymbol{\rho}$. The notation $\boldsymbol{\rho}^v$ refers, of course, to the vector whose components are the ρ_k^v, and $\boldsymbol{\rho}(v, s)$ refers to the vector with components $\rho_k(v, s)$.

The notation adopted here is essentially the same as that of Ref. [2], with the minor exceptions that in Ref. [2] parentheses were placed around the superscript ν, the progress increments ω_s were denoted by $\Delta\omega_s$, the species densities ρ_k satisfying Eq. (2) were denoted by ρ_k^{n+1}, and N was denoted by N_{eq}.

We now proceed to consider how the equilibrium constraints of Eq. (2) might be preconditioned to make them more nearly linear in the ω_s. The first step is to identify the principal or dominant dependence of the left member of Eq. (2) upon the ω_s. The form of this quantity suggests that we determine, for each reaction s, the species k for which the factor $(\rho_k/M_k)^{b_{ks}-a_{ks}}$ depends most sensitively, in some appropriate sense, on the ω_s. Let this be the species with index $k=\kappa(s)$, and denote $b_{\kappa(s),s}-a_{\kappa(s),s}$ by q_s. The species $k=\kappa(s)$ will be referred to as the *reference species* for reaction s. The dominant dependence of the left member of Eq. (2) on the ω_s is now regarded as being contained in the factor $(\rho_{\kappa(s)}/M_{\kappa(s)})^{q_s}$. Since $\rho_{\kappa(s)}$ itself is linear in the ω_s, this dominant dependence can be made to manifest itself linearly by raising both sides of Eq. (2) to the power $p_s\equiv 1/q_s$. We therefore replace the constraint conditions of Eq. (2) by the preconditioned constraint conditions

$$\prod_k (\rho_k/M_k)^{(b_{ks}-a_{ks})p_s}=[K_c^s(T)]^{p_s}. \tag{6}$$

It is convenient to introduce quantities F_s and G_s defined by

$$G_s=K_c^s(T)\prod_k (\rho_k/M_k)^{a_{ks}-b_{ks}}, \tag{7}$$

$$F_s=G_s^{-p_s}-1, \tag{8}$$

in terms of which Eq. (6) becomes simply

$$F_s=0. \tag{9}$$

We have yet to specify how the reference species are to be determined. For simplicity, we shall define the reference species for reaction s as the species for which the factor $(\rho_k/M_k)^{b_{ks}-a_{ks}}$ depends most sensitively on ω_s alone, without regard for the other progress variables. That is, $\kappa(s)$ is the value of k for which the quantity

$$R_{ks}\equiv\left(\frac{\rho_k}{M_k}\right)^{a_{ks}-b_{ks}}\frac{\partial}{\partial\omega_s}\left(\frac{\rho_k}{M_k}\right)^{b_{ks}-a_{ks}} \tag{10}$$

is largest in magnitude. This quantity is easily evaluated from Eq. (3), with the result $R_{ks}=(M_k/\rho_k)(b_{ks}-a_{ks})^2$.

In the subsequent development, we shall require the partial derivatives $\partial F_s/\partial\omega_t$, which are also easily evaluated from Eq. (3). The result is

$$\frac{\partial F_s}{\partial\omega_t}=p_sG_s^{-p_s}A_{st}, \tag{11}$$

where

$$A_{st} = \sum_k (M_k/\rho_k)(b_{ks} - a_{ks})(b_{kt} - a_{kt}). \tag{12}$$

We note that the matrix A_{st} is symmetric and positive definite. We also note that the reference species for reaction s is the species which makes the largest contribution to the diagonal element A_{ss}.

The quantities F_s and G_s have been defined as functions of the species densities, and may therefore be written as $F_s(\boldsymbol{\rho})$ and $G_s(\boldsymbol{\rho})$. Similarly, $A_{st} = A_{st}(\boldsymbol{\rho})$. By virtue of Eq. (3), all of these quantities may alternatively be regarded as functions of the progress variables ω_s, and this will be done without special comment when it is convenient.

Next we must define the two basic iteration procedures that the present method utilizes, namely the Gauss-Seidel-Newton and Newton–Raphson procedures. The one-step Gauss–Seidel–Newton iteration procedure, applied to the system of Eq. (9), takes the form [3]

$$\omega_s^{\nu+1} = \omega_s^{\nu} - \frac{F_s(\omega_1^{\nu+1},\ldots,\omega_{s-1}^{\nu+1},\omega_s^{\nu},\ldots,\omega_N^{\nu})}{\partial F_s(\omega_1^{\nu+1},\ldots,\omega_{s-1}^{\nu+1},\omega_s^{\nu},\ldots,\omega_N^{\nu})/\partial\omega_s^{\nu}}. \tag{13}$$

Equations (5), (8), and (11) allow us to rewrite Eq. (13) in the more useful form

$$\omega_s^{\nu+1} = \omega_s^{\nu} + \frac{q_s}{A_{ss}(\boldsymbol{\rho}(\nu+1,s))}\{[G_s(\boldsymbol{\rho}(\nu+1,s))]^{p_s} - 1\}. \tag{14}$$

As remarked in Ref. [2], it is not necessary to actually evaluate $\boldsymbol{\rho}(\nu+1,s)$ by means of Eq. (5), because if the ρ_k are continually updated as running sums then $\boldsymbol{\rho}(\nu+1,s)$ is simply the "current" value of $\boldsymbol{\rho}$ just prior to the evaluation of $\omega_s^{\nu+1}$.

Strictly speaking, since p_s is considered constant in evaluating $\partial F_s/\partial\omega_t$, p_s (and therefore q_s) should be held constant and not allowed to vary with ν. However, we have found that convergence is slightly accelerated if p_s and q_s in Eq. (14) are allowed to vary by reevaluating $\kappa(s)$ in terms of the $\rho_k(\nu+1,s)$ on every iteration. Just as in Ref. [2], the value of $\omega_s^{\nu+1} - \omega_s^{\nu}$ given by Eq. (14) is subjected to the restriction

$$0.9\delta\omega_s^{\min} \leqslant \omega_s^{\nu+1} - \omega_s^{\nu} \leqslant 0.9\delta\omega_s^{\max}, \tag{15}$$

where $\delta\omega_s^{\min}$ and $\delta\omega_s^{\max}$ are the minimum and maximum values of $\omega_s^{\nu+1} - \omega_s^{\nu}$ that preserve the nonnegativity of the ρ_k [2].

The second iteration procedure used is a standard Newton–Raphson iteration, which for the system of Eq. (9) becomes

$$\sum_t [\partial F_s(\omega_1^{\nu},\ldots,\omega_N^{\nu})/\partial\omega_t^{\nu}](\omega_t^{\nu+1} - \omega_t^{\nu}) = -F_s(\omega_1^{\nu},\ldots,\omega_N^{\nu}). \tag{16}$$

Using Eqs. (4), (8), (11), and (12), we may rewrite this as

$$\sum_t A_{st}(\boldsymbol{\rho}^\nu)(\omega_t^{\nu+1} - \omega_t^\nu) = q_s\{[G_s(\boldsymbol{\rho}^\nu)]^{p_s} - 1\}. \tag{17}$$

To obtain the $\omega_s^{\nu+1}$, it is necessary to invert the $N \times N$ matrix $A_{st}(\boldsymbol{\rho}^\nu)$. This may be done using any of the standard methods, one or more of which are usually available as modular library subroutines in large computer centers.

Just as before, p_s and q_s should strictly be held constant in Eq. (17). In practice, however, we find it slightly advantageous to allow them to vary with ν by reevaluating the reference species in terms of the ρ_k^ν on every iteration.

In spite of the preconditioning, Eq. (7) occasionally yields values of $\omega_s^{\nu+1}$ that drive one or more of the $\rho_k^{\nu+1}$ negative. (In particular, this may happen when a single trace species of very small concentration is involved in two or more reactions, as the matrix A_{st} then becomes ill-conditioned.) When this occurs, the values of $\omega_s^{\nu+1} - \omega_s^\nu$ given by Eq. (17) are all reduced in magnitude by a factor α $(0 < \alpha < 1)$, and the $\rho_k^{\nu+1}$ are recomputed accordingly. If any of them are still negative, the reduced values of $\omega_s^{\nu+1} - \omega_s^\nu$ are further reduced by another factor of α and the $\rho_k^{\nu+1}$ are recomputed again. If necessary, this procedure is repeated up to N_α times, whereupon if negative values of the $\rho_k^{\nu+1}$ still persist the $\omega_s^{\nu+1}$ given by Eq. (17) are simply discarded. The iteration is then repeated as a Gauss–Seidel–Newton iteration, with the $\omega_s^{\nu+1}$ obtained from Eq. (14). We currently use the values $\alpha = 0.3$ and $N_\alpha = 6$.

The iteration scheme as a whole is structured as follows. The first N_0 iterations are performed with the one-step Gauss–Seidel–Newton algorithm. If convergence has not already occurred, all subsequent iterations are performed with the Newton-Raphson algorithm, except as noted in the preceding paragraph. We currently take $N_0 = 7$. The iteration scheme is considered to have converged when $|G_s - 1| < \varepsilon$ for all s. Currently ε is taken to be 0.02.

In some situations, it may be advantageous to replace the one-step Gauss–Seidel–Newton iteration by the corresponding one-step SOR–Newton iteration [3]. This may be done by the trivial modification of replacing the factor of q_s in the right member of Eq. (14) by Ωq_s, so that the change in ω_s on each iteration is multiplied by the overrelaxation factor Ω $(0 < \Omega \lesssim 2)$.

The improved iteration scheme for partial equilibrium flow described above has been in routine use for more than a year in the CONCHAS-SPRAY [5] and KIVA [6] computer programs. The applications to date have encompassed a variety of different conditions, including rich and lean hydrocarbon combustion and rapid exothermic transients. No convergence failures have yet been experienced, even in situations where the original quadratic scheme of Ref. [2] failed badly. It is therefore our intention and recommendation that the iteration scheme of Ref. [2] be superseded by the improved scheme described above.

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