RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM APPROACH TO COMPLEX KINETICS. A REDUCTION SCHEME TO MAKE MODELING ACCESSIBLE TO ENGINEERS UNSPECIALIZED IN CHEMICAL KINETICS

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ABSTRACT

The Rate-Controlled Constrained-Equilibrium (RCCE) model reduction scheme for chemical kinetics provides acceptable accuracies with a number of differential equations much lower than the number of species in the underlying Detailed Kinetic Model (DKM). It was originally proposed by James C. Keck (see [1-3] and references therein). To yield good approximations the method requires accurate identification of the rate controlling constraints. Until recently, a drawback of the RCCE scheme has been the absence of a fully automatable and systematic procedure to identify the most effective constraints for a given range of thermodynamic conditions and a required level of approximation. In a recent paper [4], we have proposed a new methodology for such identification based on a simple algebraic analysis of the results of a preliminary simulation that probes the underlying DKM, focusing on the behavior of the degrees of disequilibrium (DoD) of the individual chemical reactions. The new methodology is based on computing an Approximate Singular Value Decomposition of the Actual Degrees of Disequilibrium (ASVDADD) obtained as functions of time in the probe DKM simulation. The procedure identifies a low dimensional subspace in DoD space, from which the actual DoD traces do not depart beyond a fixed distance related to the first neglected singular value of the matrix of DoD traces. The effectiveness and robustness of the method has been demonstrated [4-6] for various cases of a very rapid supersonic nozzle expansion of the products of hydrogen and methane oxycombustion and for the case of methane/oxygen ignition.

The general idea behind the RCCE method is that for each particular problem, set of conditions, and acceptable degree of approximation there is a threshold time scale which essentially separates the “relatively fast” equilibrating kinetic mechanisms from those that slow down and control the spontaneous relaxation towards equilibrium. The “relatively slow” mechanisms control the interesting part of the non-equilibrium dynamics in that they effectively identify a low dimensional manifold in composition space, where, for the chosen level of approximation, the dynamics can be assumed to take place. In general, the rate controlling mechanisms are slow because they have to go through one or more bottlenecks. For example, the three-body reactions are slow because they require three-body collisions which occur much less frequently than two-body collisions. As a result, the bottleneck mechanism is that of three-body collisions and the associated rate-limiting constraint is the total number of moles, which would not change if all three-body reactions were frozen. The “narrowness” of each bottleneck can be measured by the characteristic time with which the associated constraint would relax towards its equilibrium value in the absence of interactions sustaining the non-equilibrium state. As emphasized for example in Ref. [3], the RCCE method enjoys a very appealing built-in general feature of strong thermodynamic consistency. However, the main difficulties in its practical use have been: (a) identifying the kinetic bottlenecks and (b) constructing an efficient set of constraints implied by them. Several efforts have addressed these problems with varying degrees of success (see [4] for references).

The RCCE method models the local non-equilibrium states as partially equilibrated states with the local composition $\boldsymbol{X}^{\rm CE} = N_j / \sum_{k=1}^{n_{\rm sp}} N_k$ (where of course N_j represents the molar amount of species j) that minimizes the Gibbs free energy subject to the local values of temperature T, pressure p, molar amounts of elements $N_i^{\rm EL} = \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm EL} N_j$ (where of course $a_{ij}^{\rm EL}$ represents the number of atoms of element i in a molecule of species j) and the local values of a set of n_c slowly varying and, hence, rate-controlling (RC) constraints given by linear combinations of the molar amounts, $c_i(\boldsymbol{N}) = \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm RC} N_j$, where the matrix $a_{ij}^{\rm RC}$ is the heart of the model in that it is assumed to fully characterize the rate-controlling bottleneck kinetic mechanisms. For ideal gas behavior, $\mu_j(T,p,\boldsymbol{X}) = g_{j,\rm pure}(T,p) + RT \ln X_j$, the constrained maximization yields the composition

$$\ln X_j^{\rm CE} = -g_{j,\rm pure}(T,p)/RT - \sum_{i=1}^{n_{\rm el}} \gamma_i^{\rm EL} a_{ij}^{\rm EL} - \sum_{i=1}^{n_{\rm c}} \gamma_i^{\rm RC} a_{ij}^{\rm RC} \qquad \text{that is} \qquad -\mu_j(T,p,\boldsymbol{X}^{\rm CE})/RT = \sum_{i=1}^{n_{\rm el}} \gamma_i^{\rm EL} a_{ij}^{\rm EL} + \sum_{i=1}^{n_{\rm c}} \gamma_i^{\rm RC} a_{ij}^{\rm RC} \tag{1}$$

The Lagrange multipliers $\gamma_i^{\rm EL}$ and $\gamma_i^{\rm RC}$ are called elemental and constraint potentials, respectively. For the ℓ-th chemical reaction $\sum_{j=1}^{n_{\rm sp}} \nu_{j\ell} A_j = 0$, the stoichiometric balance requires that $b_{i\ell}^{\rm EL} = \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm EL} \nu_{j\ell} = 0$. The advantage of the RCCE approximation is that the composition depends only on the $n_{\rm el} + n_{\rm c}$ parameters $\gamma_i^{\rm EL}$ and $\gamma_i^{\rm RC}$, instead of the $n_{\rm sp}$ molar amounts of species which can be many more. In the CFD modeling context, this means that in addition to the continuity, Navier-Stokes, and energy balance equations, the $n_{\rm sp}$ species balance equations can be effectively substituted by the $n_{\rm el} + n_{\rm c}$ balance equations for the elemental and constraint potentials, thus achieving a substantial model reduction that has a built-in strong thermodynamic consistency and does not require to cut the number of species nor the number of reactions to be taken into account. The method has been used with excellent results. For example (see e.g. [4; 5]) for the ignition delay of hydrogen-oxygen mixtures ($n_{\rm sp} = 8$, $n_{\rm el} = 2$), the RCCE methods yields excellent agreement with a fully detailed model predictions by using only $n_{\rm c} = 2$ constraints, with a savings of $8 - (2+2) = 4$ differential equations. The computational savings is much more important for higher hydrocarbons, for example, for methane-oxygen ignition ($n_{\rm sp} = 29$, $n_{\rm el} = 3$) excellent results [4; 5] are obtained with $n_{\rm c} = 13$, with a savings of $29 - (3+13) = 13$ differential equations and without giving up the ability of predicting fine details such as the typical temperature and composition overshoots occurring immediately following ignition.

The recently proposed ASVDADD algorithm [4] allows the identification of optimal sets of constraints with no need for deep knowledge and understanding of chemical kinetics fundamentals such as chain branching, radical formation, etc., thus making the RCCE method accessible to a broad range of scientists and engineers. The algorithm is based on the following basic observation. The degree of disequilibrium (DoD) of reaction

ℓ, defined by $\phi_\ell = \ln r_\ell^+/r_\ell^-$ where $r_\ell^\pm$ are the forward and reverse rates of reaction ℓ, is given in general by

$$\phi_\ell = \ln\frac{r_\ell^+}{r_\ell^-} = -\frac{1}{RT}\sum_{j=1}^{n_{\rm sp}}\mu_j\nu_{j\ell} = \sum_{j=1}^{n_{\rm sp}}\Lambda_j\nu_{j\ell} \qquad \text{where} \qquad \Lambda_j = -\frac{\mu_j}{RT} \tag{2}$$

The dimensionless entropic chemical potentials Λ_j can be viewed as the components of the $n_{\rm sp}$-vector $\boldsymbol{\Lambda}$. Also the $n_{\rm el}$ rows of the elemental composition matrix $a_{ij}^{\rm EL}$ can be viewed as the components of the $n_{\rm sp}$-vectors $\boldsymbol{a}_i^{\rm EL}$. Due to relation $\sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm EL}\nu_{j\ell} = 0$, the $n_{\rm el}$-dimensional linear span of vectors $\boldsymbol{a}_i^{\rm EL}$ is the left null space of the matrix $\nu_{j\ell}$ of stoichiometric coefficients, often called the inert subspace. The projection of vector $\boldsymbol{\Lambda}$ onto the inert subspace can be written as $\boldsymbol{\Lambda}_{{\rm span}(\{\boldsymbol{a}_i^{\rm EL}\})} = \sum_{i=1}^{n_{\rm el}}\gamma_i^{\rm EL}\boldsymbol{a}_i^{\rm EL}$ where the coefficients $\gamma_i^{\rm EL}$ can be readily computed (see, e.g., the appendix of Ref. [7]). Since $\boldsymbol{\Lambda}_{{\rm span}(\{\boldsymbol{a}_i^{\rm EL}\})}$ does not contribute to the DoD of any reaction (in fact, $\sum_{j=1}^{n_{\rm sp}}\sum_{i=1}^{n_{\rm el}}\gamma_i^{\rm EL}a_{ij}^{\rm EL}\nu_{j\ell} = \sum_{i=1}^{n_{\rm el}}\gamma_i^{\rm EL}b_{i\ell}^{\rm EL} = 0$), we call the vector

$$\boldsymbol{\Lambda}_{\rm DoD} = \boldsymbol{\Lambda} - \boldsymbol{\Lambda}_{{\rm span}(\{\boldsymbol{a}_i^{\rm EL}\})} = \boldsymbol{\Lambda} - \sum_{i=1}^{n_{\rm el}}\gamma_i^{\rm EL}\boldsymbol{a}_i^{\rm EL} \qquad \text{or, equivalently,} \qquad \Lambda_{{\rm DoD},j} = \Lambda_j - \sum_{i=1}^{n_{\rm el}}\gamma_i^{\rm EL}a_{ij}^{\rm EL} \tag{3}$$

the "overall DoD vector." In fact, it contains the information about the DoD's ϕ_ℓ of all the reactions, $\phi_\ell = \sum_{j=1}^{n_{\rm sp}}\Lambda_{{\rm DoD},j}\nu_{j\ell}$, and it is the null vector if and only if all reactions are equilibrated, in the sense that their DoD's are all zero. Notice than within the RCCE model, from Eq. (1), we have

$$\boldsymbol{\Lambda}_{\rm DoD}^{\rm RCCE} = \sum_{i=1}^{n_{\rm c}}\gamma_i^{\rm RC}\boldsymbol{a}_i^{\rm RC} \qquad \text{or, equivalently,} \qquad \Lambda_{{\rm DoD},j}^{\rm RCCE} = \sum_{i=1}^{n_{\rm c}}\gamma_i^{\rm RC}a_{ij}^{\rm RC} \tag{4}$$

Now let us consider a CFD numerical simulation in which the index $z = 1,\dots,Z$ labels the space-time discretization (i.e., z labels both the finite volumes or elements of the mesh as well as the time grid). If we adopt the full DKM and solve the full set of balance equations including those for all the species, the resulting overall DoD vectors form an $n_{\rm sp}\times Z$ matrix $\Lambda_{{\rm DoD},jz}^{\rm DKM} = \Lambda_{{\rm DoD},j}(z)$ that has rank $r = n_{\rm sp} - n_{\rm el}$. If instead the local states are described according to the RCCE assumption defined above, the $n_{\rm sp}\times Z$ matrix $\Lambda_{{\rm DoD},jz}^{\rm RCCE} = \Lambda_{{\rm DoD},j}^{\rm RCCE}(z) = \sum_{i=1}^{n_{\rm c}}\gamma_i^{\rm RC}(z)a_{ij}^{\rm RC}$ has rank equal to the (typically much smaller) number $n_{\rm c}$ of constraints. In other words, even if the number $n_{\rm sp}$ of chemical reactions in the underlying DKM is in the hundreds and therefore the $n_{\rm sp}\times Z$ matrix $\Lambda_{{\rm DoD},jz}^{\rm DKM}$ has hundreds of rows and rank $n_{\rm sp} - n_{\rm el}$, its approximation within the RCCE model, $\Lambda_{{\rm DoD},jz}^{\rm RCCE}$, is of much lower rank $n_{\rm c}$.

In order to identify the constraint matrix $a_{ij}^{\rm RC}$ that allows such approximation, the idea behind the ASVDADD algorithm is to run a preliminary full DKM computation, possibly on a submesh of the full problem and for a shorter time so span a limited range of values of temperature, pressure and compositions. From such computation we obtain the $r\times Z$ matrix $\boldsymbol{D}$ with elements $\Lambda_{{\rm DoD},jz}^{\rm DKM}$. Then we compute its singular value decomposition (SVD). As is well known, the result can be written formally in reduced form as $\boldsymbol{D} = \boldsymbol{U}\,{\rm diag}(\boldsymbol{\sigma})\boldsymbol{V}$ where $\boldsymbol{U}$ is an $n_{\rm sp}\times r$ unitary matrix whose r columns represent an orthonormal basis for the column space of $\boldsymbol{D}$, $\boldsymbol{V}$ is an $r\times P$ unitary matrix whose r rows represent an orthonormal basis for the row space of $\boldsymbol{D}$, and $\boldsymbol{\sigma}$ is the r-vector of singular values of $\boldsymbol{D}$ in decreasing order. Explicitly, recalling that $r = {\rm rank}(\boldsymbol{D}) = n_{\rm sp} - n_{\rm el}$, the SVD decomposition of the overall DoD matrix can be written as

$$\Lambda_{{\rm DoD},jz}^{\rm DKM} = \sum_{k=1}^{r}U_{jk}\sigma_k V_{kz} = \sum_{k=1}^{r}U_{jk}\gamma_{kz}^{\rm DKM} \qquad \text{where} \qquad \sigma_1 \ge \sigma_2 \ge \cdots \ge \sigma_r > 0 \qquad \text{and we defined} \qquad \gamma_{kz}^{\rm DKM} = \sigma_k V_{kz} \tag{5}$$

Next, we use the well-known Eckart-Young theorem of linear algebra, whereby if in the SVD of matrix $\boldsymbol{D}$ we set to zero the singular values for $k > n_{\rm c}$ (i.e., we set $\sigma_{n_{\rm c}+1} = \sigma_{n_{\rm c}+2} = \cdots = \sigma_r = 0$) then we obtain the "closest" rank$\le n_{\rm c}$ approximation $\boldsymbol{D}_{\rm approx}$ of the original matrix $\boldsymbol{D}$ in the sense that the Frobenius norm distance $\|\boldsymbol{D}_{\rm approx} - \boldsymbol{D}\|_{\rm Fro}$ between the two matrices is minimal. Such norm distance is equal to $(\sum_{k=n_{\rm c}+1}^{r}\sigma_k^2)^{1/2})$ and can be taken as a measure of the error introduced by the approximation. Therefore, if we accept such level of approximation, we can setup an optimal RCCE model with $n_{\rm c}$ constraints by selecting as our constraint matrix the first $n_{\rm c}$ columns of the matrix $\boldsymbol{U}$. In fact, by setting

$$\text{ASVDADD choice of RCCE constraints:} \quad a_{ij}^{\rm RC} = U_{ji} \quad \text{for} \quad i = 1,\dots,n_{\rm c} \qquad \text{we obtain} \quad \Lambda_{{\rm DoD},jz}^{\rm RCCE} = \sum_{k=1}^{n_{\rm c}}U_{jk}\gamma_{kz}^{\rm RC} = \sum_{i=1}^{n_{\rm c}}\gamma_{iz}^{\rm RC}a_{ij}^{\rm RC} \tag{6}$$

Interestingly, the r columns of the matrix $\boldsymbol{U}$ obtained from the SVD decomposition of the overall DoD matrix $\boldsymbol{D}$ resulting from the preliminary DKM simulation provides at once the entire set of optimal RCCE constraints, already ordered in decreasing order of importance. Essentially, in conclusion, the ASVDADD algorithm identifies all the constraints that characterize the kinetic bottlenecks of the underlying DKM in effect in the chosen range of conditions, and it ranks them in terms of their relative contribution to the overall degree of disequilibrium. These features make the algorithm suitable for adaptive or tabulation strategies and therefore opens up the advantages of the RCCE method to CFD simulation.

To reiterate, the ASVDADD algorithm for systematic RCCE constraint identification is based on analyzing how the degrees of disequilibrium (DoD) of the chemical reactions behave in a full DKM test simulation. Geometrically, the procedure identifies a low-dimensional subspace in DoD space from which the actual DoD traces do not depart beyond a fixed distance related to a preset tolerance level.

The effectiveness and robustness of the methodology has already been demonstrated in [4,6] for several test cases of increasing complexity in the framework of oxy-combustion of hydrogen (8 species, 24 reactions) and methane (29 species, 133 reactions) as well as in [5] where a demonstration is given for the even more complex full GRI-Mech 3.0 kinetic scheme (53 species, 325 reactions) for methane/air combustion including nitrogen oxidation.

The excellent performance of the ASVDADD constraints confirm the conclusion that the new algorithm essentially resolves the difficulties that have prevented the RCCE method from a more widespread use in model order reduction of detailed combustion kinetic models of hydrocarbon fuels.

In future work we will show that the same model order reduction logic can find natural extensions also in the more general field of nonequilibrium thermodynamics, in particular in the general frameworks discussed in [8,9].

The RCCE equations can be integrated more efficiently by rewriting them as rate equations for the elemental and constraint potentials. These are obtained by combining the species and energy balance equations, the kinetic equations, the ideal gas equation of state, and the linear combinations $c_i(\boldsymbol{N}) = \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm RC}N_j$ that define the values c_i of the constraints. As shown in Ref. 3, we obtain the following set of rate equations, where for convenience we use $\beta = 1/RT$ instead of the temperature and the notation $N_j = [N_j]V$ for the number of moles of species j, u_{jj} and c_{vjj} for the molar specific internal energy and heat capacity at constant volume of species j, Φ for the viscous dissipation function (usually negligible),

$$\sum_{k=1}^{n_{\rm el}} \dot\gamma_k^{\rm EL} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm EL} N_j a_{ij}^{\rm EL} + \sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm RC} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm RC} N_j a_{ij}^{\rm EL} = -\frac{\dot\beta}{\beta} \sum_{j=1}^{n_{\rm sp}} N_j \beta u_{jj} a_{ij}^{\rm EL} + \frac{\dot V}{V} \sum_{j=1}^{n_{\rm sp}} N_j a_{ij}^{\rm EL} + \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm EL} \dot N_j^{\rightarrow} \qquad \text{for } i = 1,\dots,n_{\rm el} \tag{7}$$

$$\sum_{k=1}^{n_{\rm el}} \dot\gamma_k^{\rm EL} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm EL} N_j a_{ij}^{\rm RC} + \sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm RC} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm RC} N_j a_{ij}^{\rm RC} = -\frac{\dot\beta}{\beta} \sum_{j=1}^{n_{\rm sp}} N_j \beta u_{jj} a_{ij}^{\rm RC} + \frac{\dot V}{V} \sum_{j=1}^{n_{\rm sp}} N_j a_{ij}^{\rm RC} + \sum_{j=1}^{n_{\rm sp}} a_{ij}^{\rm RC} \dot N_j^{\rightarrow} - \dot c_{i,\rm chem}(\beta, p, \boldsymbol{N}) \qquad \text{for } i = 1,\dots,n_{\rm c} \tag{8}$$

$$\sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm EL} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm EL} N_j \beta u_{jj} + \sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm RC} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm RC} N_j \beta u_{jj} = -\frac{\dot\beta}{\beta} \sum_{j=1}^{n_{\rm sp}} N_j \left(\beta^2 u_{jj}^2 + \frac{c_{vjj}}{R}\right) + \frac{\dot V}{V} \sum_{j=1}^{n_{\rm sp}} N_j \beta u_{jj} + \beta \dot E^{\rightarrow} + \beta p \dot V - \beta V \Phi \tag{9}$$

$$\sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm EL} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm EL} N_j + \sum_{k=1}^{n_{\rm c}} \dot\gamma_k^{\rm RC} \sum_{j=1}^{n_{\rm sp}} a_{kj}^{\rm RC} N_j = -\frac{\dot\beta}{\beta} \sum_{j=1}^{n_{\rm sp}} N_j \left(\beta u_{jj} + 1\right) - \frac{\dot p}{p} \sum_{j=1}^{n_{\rm sp}} N_j \tag{10}$$

where $\dot N_j^{\rightarrow}$ and $\dot E^{\rightarrow}$ denote the species and energy transport rates (positive if outgoing) and the bottleneck source terms are

$$\dot c_{i,\rm chem}(\beta, p, \boldsymbol{N}) = V \sum_{\ell=1}^{n_{\rm r}} \left(\sum_{m=1}^{n_{\rm sp}} a_{im}^{\rm RC} \nu_{m\ell}\right) \left[\frac{k_\ell^+(\beta,p)}{V^{\nu_\ell^+}} \prod_{j=1}^{n_{\rm sp}} (N_j)^{\nu_{j\ell}^+} - \frac{k_\ell^-(\beta,p)}{V^{\nu_\ell^-}} \prod_{j=1}^{n_{\rm sp}} (N_j)^{\nu_{j\ell}^-}\right] \tag{11}$$

and of course the composition is that given by Eq. (1), i.e.,

$$N_j = \beta p V X_j = \exp\left(-g_{j,\rm pure}(\beta,p)\beta - \sum_{i=1}^{n_{\rm el}} \gamma_i^{\rm EL} a_{ij}^{\rm EL} - \sum_{i=1}^{n_{\rm c}} \gamma_i^{\rm RC} a_{ij}^{\rm RC}\right) \qquad \text{for } j = 1,\dots,n_{\rm sp} \tag{12}$$

The above $n_{\rm el} + n_{\rm nc} + 2$ implicit differential equations together with the $n_{\rm sp}$ Eqs. (12) can be solved for given values of $\dot E^{\rightarrow}$, $V(t)$, and the $\dot N_j^{\rightarrow}$, to yield the $n_{\rm sp} + 2$ state variables $\beta(t)$, $p(t)$, and $N_j(t)$, and the $n_{\rm el} + n_{\rm c}$ constraint-potentials $\gamma_i^{\rm EL}(t)$ and $\gamma_i^{\rm RC}(t)$.

It is important to notice that in Eqs. (11) only the chemical reactions that are not equilibrated contribute to $\dot c_{i,\rm chem}$, i.e., only those for which $b_{i\ell}^{\rm RC} = \sum_{m=1}^{n_{\rm sp}} a_{im}^{\rm RC} \nu_{m\ell} \neq 0$. In fact, from Eqs. (2), (14) and (6) we can write

$$\phi_\ell^{\rm DKM} = \sum_{j=1}^{n_{\rm sp}} \Lambda_{{\rm DoD},jz}^{\rm DKM} \nu_{j\ell} = \sum_{j=1}^{n_{\rm sp}} \nu_{j\ell} \sum_{k=1}^{r} U_{jk} \sigma_k V_{kz} = \sum_{k=1}^{r} \left(\sum_{j=1}^{n_{\rm sp}} \nu_{j\ell} U_{jk}\right) \sigma_k V_{kz} = \sum_{i=1}^{r} b_{i\ell} \sigma_i V_{iz} = \sum_{i=1}^{r} b_{i\ell} \sigma_i \gamma_{iz}^{\rm DKM} \qquad \text{where we defined} \quad b_{i\ell} = \sum_{j=1}^{n_{\rm sp}} \nu_{j\ell} U_{ji} \tag{13}$$

which shows that within the RCCE approximation, whereby we set to zero the singular values $\sigma_{n_{\rm c}+1} = \sigma_{n_{\rm c}+2} = \cdots = \sigma_r = 0$ and we set $a_{ij}^{\rm RC} = U_{ji}$ for $i = 1,\dots,n_{\rm c}$, the DoD's are given by

$$\phi_\ell^{\rm RCCE} = \sum_{i=1}^{n_{\rm c}} b_{i\ell}^{\rm RC} \sigma_i V_{iz} = \sum_{i=1}^{n_{\rm c}} b_{i\ell}^{\rm RC} \gamma_{iz}^{\rm RC} \tag{14}$$

and therefore the reactions that contribute to $\dot c_{i,\rm chem}$, those with $b_{i\ell}^{\rm RC} \neq 0$, are those with a nonzero DoD.

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