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Abstract

We now focus on chemical reactions, and the coupling between chemical reactions and diffusion—molecular or turbulent. My main message is that chemical reactions and diffusion are strongly coupled. You can't divide your research team into two groups, one in charge of chemistry and one in charge of diffusion, and expect the computer codes that calls subroutines from these two autonomous groups—that did not talk to each other—to give correct answers. This week we set the stage. The details of the punch line will come next week.

1 Reacting Flows

When we have a N-component mixture, the state of the mixture can be represented by two thermodynamic variables (*e.g.* temperature T and pressure p—or density etc.) plus the concentrations (*e.g.* X_n, the mole fractions) of the components.

The conventional "we shall assume thermodynamic equilibrium" assumption is valid when the all relevant "residence times" are very long in comparison to the characteristic chemistry time so that all elementary chemistry reactions are very near equilibrium. Remember that the chemical potentials of all the components are then (approximately) equal. When this condition prevails, the mixture has equations of state that which be derived from chemical thermodynamics:

$$X_n = X_n(T, p; \ldots) \tag{1}$$

The ... represent relevant parameters such as the amount of all the atomic elements in the mixture (how much oxygen, nitrogen, carbon, hydrogen, etc., atoms). The bottom line is that—in the absence of diffusion—we would have access to a mixture equation of state (which can be computed once and for all and stored in some database), and the extra term brought in by Duham-Gibb's does not bother anybody because it is negligible.

What happens if some of the relevant residence times are not long enough? We now have a reacting flow problem. We have to find the X_n's.

1.1 Issues on computing

The computing power available to researcher continues to increase. Many reacting flow problems that are now routinely done were considered impossible to do a decade ago. More progress can be expected.

In CFD dealing with flows under the chemical equilibrium assumption, the number of dependent variables are two thermodynamic variables (T and ρ) and the velocity vector $\mathbf{V}$. The equation of state to get pressure p enthalpy h and the X_n's are subroutines. So the storage requirement for each grid point is quite modest.

Now we have a reacting flow problem, and the number of species is N. The number of dependent variables thus increases by N. It is clear that when N is a big number, the computational resources required to do CFD is an important issue.

When there are N chemically active components, there are R relevant elementary reactions between them, and in general R is greater than N. For each elementary reaction, the reaction rate obeys the Law of Mass Action, and the formula usually contains three parameters. Thus, the chemical kinetics is specified by $3R$ parameters. Our chemical kinetics friends will readily admit that many of these parameters are not known with great certainty. So another important issue is: which of the $3R$ parameters used in the CFD calculation are mostly responsible for the interesting behaviors observed in the computed results?

2 Governing equations for the X_n's

The generic governing equations for the X_n's are:

$$\frac{DX_n}{Dt} = \mathcal{W}_n + \nabla \cdot (\sum_{n'=1}^{N} \mathcal{D}_{nn'} \nabla X_{n'}), \quad n = 1, \dots, N, \tag{2}$$

where $\mathcal{W}_n(X_1, \dots, X_N; T, \rho)$ represents chemical reactions, and $\mathcal{D}_{nn'}$ is the diffusion transports (molecular or turbulent) matrix, often assumed diagonal.

The chemistry term is usually the sum of contributions from all the relevent elementary reactions:

$$\mathcal{W}_n = \sum_{r=1}^{R} s_{nr} W_r, \quad n = 1, \dots, N, \tag{3}$$

where s_{nr} is the *stoichiometric vector* of the r-th elementary reaction, and $W_r(X_1, \dots, X_N; T, \rho)$ is its net reaction rate (respecting the Law of Mass Action).

For example, let reaction #51 be:

$$[X_1] + 2[X_2] \rightleftharpoons [X_3] + [X_4]. \tag{4}$$

Then we have (when the X_n's are mole fractions):[1]

$$s_{n51} = \begin{bmatrix} -1 \\ -2 \\ 1 \\ 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix}, \quad \mathcal{W}_{51} = k_{51}^{+}(X_1 X_2^2) - k_{51}^{-}(X_3 X_4) \tag{5}$$

where k_{51}^{+} and k_{51}^{-} are the *forward* and *backward* rate coefficients, and their ratio K_{51}

$$K_{51} = \frac{k_{51}^{-}}{k_{51}^{+}} \tag{6}$$

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[1] When the X_n's are not mole fractions, the stoichiometric vector no longer consists of integers or rational (dimensionless) numbers. The important point is: you must work out what your stoichiometric vectors are under your chosen formulation.

is usually called the *equilibrium constant* of the reaction (a thermodynamically calculable number, independent of kinetic rates), and usually replaces k_r^-. Both k_r^+ and K_r are, of course, functions of T. Usually, k_r^+ is represented by the following formula:

$$k_r^+ = \mathcal{A}_r T^{d_r} \exp(-\frac{\mathcal{E}_r}{kT}) \tag{7}$$

where d_r is dimensionless, $\mathcal{A}_r$ and $\mathcal{E}_r$ (activation energy) are dimensional constants of the r-th elementary reaction, and k is the Boltzmann's constant.

How fast is reaction #51? From dimensional analysis, we can come up with four (reciprocal of) "chemical reaction time scales":

$$k_{51}^+ X_2^2, \quad 2k_{51}^+ X_1 X_2, \quad k_{51}^- X_4, \quad k_{51}^- X_3,$$

which are relevant to X_1, X_2, X_3, X_4, respectively. Somehow, we need to deal with the issue of how to identify fast and slow reactions (when a single reaction has more than one speed).

2.1 Reduced chemistry modelling

There is a significant literature out there to do *reduced chemistry modelling*. The goal is very simple: how to reduce the messy $\mathcal{W}_n$ term to something much simpler, and yet the reduced model can still generate good answers. Frequently, this effort is done in the absence of diffusion—in time dependent homogeneous reaction systems.

When one deals with a reactive-diffusion multi-component flow problem, it is highly tempting to use the reduced chemistry modelling results obtained in the absence of diffusion, and simply keep the diffusion terms in the computer simulations. As we shall show in our sessions on this topic, this is a bad idea in general.

3 The mathematical issue

Keeping in mind that it is a bad idea, we ignore diffusion and consider the following set of first order ODEs:

$$\frac{DX_n}{Dt} = \mathcal{W}_n \tag{8}$$

where the right hand side is a messy, nonlinear function of the X_n's. The question is: do we really need all the stuff on the right hand side when our *time interval of interest* $t_1 \leq t \leq t_2$ is limited and specified. When the question is asked this way, it is purely an issue in mathematics. Chemistry or thermodynamics are not relevant here.

If $\mathcal{W}$ is a linear (and time-invariant) function of its arguments, the answer to this mathematical question can be straightforwardly given mathematically: find the eigenvalues λ_n's of the Jacobian of $\mathcal{W}_n$ (with respect to X_n), and order them in descending magnitudes. Eigenmodes with $|\lambda_m t_1| >> 1$ are *fast* modes ($m = 1, \ldots, M$), and if these λ_m's all have negative real parts then these modes will be exhausted in the time interval of interest. Eigenmodes with $|\lambda_k t_2| << 1$ are *dormant* modes ($k = N - K, \ldots, N$), and can be freely ignored in the time interval of interest. Thus in the time interval of interest, the system behavior is dominated only by those eigenmodes with $\lambda_j t = O(1)$ ($j = M + 1, \ldots, N - K - 1$).

But the governing equations for chemical kinetics are not linear. So the above simple strategy is not immediately applicable.

4 The classical approaches

4.1 Conserved scalars

For chemistry problems, Eq.(8) always has one useful property: the total amount of any atomic element (*e.g.* oxygen, nitrogen, carbon, hydrogen, etc.) is conserved. So if there are A distinct atomic elements in the reaction system, there are A "conserved scalars" in the problem:

$$Z_a = \sum_{n=1}^{N} \alpha_{an} X_n, \quad a = 1, \ldots, A. \tag{9}$$

where α_{an} are integers and denote the number of a atomic elements in species X_n. The α_{an}'s are simply vectors which are orthogonal to *all* the stoichiometric vectors:

$$\sum_{n=1}^{N} \alpha_{an} s_{nr} = 0, \quad r = 1, \ldots, R. \tag{10}$$

The values of the Z_a's are set by initial conditions of the problem. Hence, the number of dependent variables of the problems can immediately be reduced by A via Eq.(9)—we can pick A species from the mixture, and solve for them in terms of the remaining $N - A$

species using Eq.(9) and straightforward linear algebra. The ODE's for these selected A species can now be ignored and removed from the computational code.

It is useful to point out that there are intelligent picks and there are dumb picks for the species to be removed from further considerations. Suppose you are working on a pollution problem and are interested in NO_x—which is a trace species in comparision to N_2. You know nitrogen atomic elements is conserved. You have to choose whether to remove NO_x or N_2 from your formulation. One choice is dumb. Very dumb. The other choice is smart.

4.2 The QSSA approximation

QSSA is shorthand for *quasi-steady state approximation.* The investigator studies the list of species in the mixture, and selects M of them and calls them "radicals" or "intermediaries." These are species with very low mole fractions and are participants in some very fast reactions.

The lefthand side of Eq.(8) for these chosen species are neglected by the QSSA—this is the rationale for the name of the approximation. The assumption is *not* that the time derivative of these species are zero; the assumption is that the time derivative of these species are small (thus negligible) in comparison to the dominant term on the right hand side. Once the time derivative is dropped, the relevant ODE for these M species becomes algebraic equations. Unlike Eq.(9) (which is linear), they are usually nonlinear algebraic equations.

The follow up steps are obvious. The M algebraic equations can be used to solve for the M radicals (or intermediaries).[2] Together with the conserved scalars[3], the total number of dependent variables remaining is now $N-A-M$. The resulting *reduced chemistry* model is called a $N-A-M$ step simplified model of the original problem. For example, if $N-A-M=1$, we have obtained a "one-step" simplified model—the holy grail in this business.

By far, this is the dominant approach in reduced chemistry modelling for many years. The weakness of the approach is that the selection of the M radicals or intermediaries is mostly based on experience and intuition. Experienced chemical kineticists know to pick them, and papers are published when the results come out good.

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[2] Note that the initial conditions for these M species are ignored.

[3] which respects initial conditions of all species.

4.3 The PE approximation

But the QSSA approximation does not always work. It is easy to concoct a toy problem for which the QSSA approximation gives the wrong answer.

Another useful approximation is the PE approximation—shorthand for *partial equilibrium approximation.* The investigator studies the list of R elementary reactions, and selects M of them and calls them *fast reactions.* The net reaction rate of these M reactions are set to zero—each forward rate is balanced by each reverse rate—yielding M algebraic equations. Then M of the participating species among the fast reactions are selected and solved for from these M algebraic equations.[4] At this point, the number of dependent variables has been reduced from N to $N - A - M$.

Now, what $N - A - M$ ODE's do we use to march forward in time to find the time evolution of our reaction system? Unlike the QSSA approximation where it is intuitively obvious which ODE's to ignore, here we need some rationalizations.

The recommended procedure is as follows. Manipulate the original system of ODEs, Eq.(8), such that the M selected fast reactions do not appear in $N - A - M$ of them. Now solve this reduced system for the $N - A - M$ remaining unknowns.

As you can see, this last step requires some skills in equation manipulations, and is the reason why the PE approximation is much less popular. It is relatively easy to show that the PE approximation can handle QSSA problems, but not *vice versa.*. Of course, the PE approximation shares with the QSSA approximation the weakness that it takes experience and intuition to pick the right fast reactions (or the right radicals).

4.4 Comments on the classical approach

The classical approach as described above has been very successful. The main short coming of this approach is that it depends on experience and intuition. An experience and competent chemical kineticist will always outperform a novice. In addition, the algebra involved is such that the methodology is primarily useful for "tractable problems." If $N = 30$ and $R = 120$, then the pen-and-paper approach is simply not viable. The theory of thermodynamic equilibrium emerges

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[4] The initial conditions of these M species are ignored.

regardless of the value of N abd R whenever $N = A + M$ (and the solution is then independent of all the k_r^+'s—only the K_r's).

For real life problems, it is often more convenient to deal with dimensional formulations—particularly when numerical solutions are involved. When dimensional numbers are involved, the question of what is big and what is small cannot be answered by looking at the numbers. In theoretical modelling, however, dimensionless and "properly nondimensionalized" dependent and independent variables are used and they are said to be "of order unity." When this can be assured, then the magnitude of dimensionless parameters in the problem are mathematically meaningful. The problem is, of course, the procedure to "properly nondimensionalizing" a theoretical model is still an art form. It takes experience and intuition. But once a problem is casted in dimensionless formulation, and a small (or large) dimensionless parameter is found, then the mathematics to exploit the smallness or largeness of that dimensionless parameter is relatively straightforward. Straightforward exploitation is called *regular perturbation.* When it is not too straightforward (by some vague subjective standard), the procedure is called *singular perturbation.*

5 Sensitivity analysis

In general, the solution of Eq.(8) requires a large number (*e.g.* $3R$) of parameters in the specification of the kinetic rates (k_n), many of which are known only with considerable uncertainties.

Suppose you want to find out how sensitive is a solution of Eq.(8) to a particular parameter, say k_o. We write down:

$$\begin{aligned} k_o &= k_o^o + k_o', \qquad (11) \\ X_n &= X_n^o + X_n', \qquad (12) \end{aligned}$$

where $X_n^o(t)$ is an exact solution with $k_o = k_o^o$. The question of sensitivity now reduces to: what is the perturbation $X_n'(t)$ in response to some small k_o'?

The procedure to answer this question is obvious. We linearize to find the ODE for X_n':

$$\frac{dX_n'}{dt} = \sum_{n'=1}^{N} J_{nn'} X_{n'}' + k_o' \frac{\partial \mathcal{W}_n}{\partial k_o} \qquad (13)$$

where $J_{nn'}$ is the Jacobian of $\mathcal{W}$ with respect to X_n (and partial derivative of $\mathcal{W}$ with respect to k_o indicates that $\mathcal{W}$ has many parameters in addition to k_o). This is a simple linear (time-dependent) ODE for $X'_n(t)$. After the solution is found, the interesting thing to look at is:

$$\sigma_n(t) = \frac{k_o^o}{X_n^o}\frac{X'_n}{k'_o}. \tag{14}$$

In plain English, σ_n represents the percentage change of $X_n(t)$ in response to a percentage change of k_o. Inspite of the clarity of this interpretation, it is nevertheless not straightforward to interpret this data. Note: if we have $3R$ parameters, we need to look at $3R \times N$ number of σ_n vs. t graphs.

Homeworks

1. Consider the linear ODE system for $\mathbf{X} = (X_1, X_2, X_3, X_4, X_5)$:

$$\frac{d\mathbf{X}}{dt} = \mathbf{L}\mathbf{X} \tag{15}$$

where

$$\mathbf{L} = \begin{bmatrix} -560800 & -560000 & -39200 & -599200 & 40000 \\ -219600 & -220001 & 19600 & -200399 & -20000 \\ -340200 & -340000 & -59800 & -399800 & 60000 \\ -219600 & -220000 & 19600 & -200400 & -20000 \\ 340200 & 340000 & 59800 & 399800 & -60000 \end{bmatrix} \tag{16}$$

and the initial conditions (at $t = 0$) are $X_1 = X_2 = X_3 = X_4 = X_5 = 1$.

(a) Try to get a numerical solution using your favorite software for $0 \leq t \leq 100$. If you have no experience with stiff ODEs, then just play around to see how far you can get.

(b) You are mainly interested in the milli-second time range. Find a simple mathematical model for this time range.

(c) You are mainly interested in the time range between fractions of seconds to hundreds of seconds. Find a simple mathematical model for this time range.

(d) Discuss the impact of (different) initial conditions on (b) and (c).

(e) Discribe (very briefly) what you need to do if a constant vector is added to the righthand side (a forcing term).

2. Consider the following toy problem (it makes no chemistry sense) with $N = 2$ and $R = 3$. The following are the stoichimetric vectors and the reaction rates:

$$\begin{aligned} s_{n1} &= \left|\begin{array}{c} 1 \\ -1 \end{array}\right|, \quad s_{n2} = \left|\begin{array}{c} 1 \\ 0 \end{array}\right|, \quad s_{n3} = \left|\begin{array}{c} 0 \\ 1 \end{array}\right|, \qquad (17) \\ W_1 &= \frac{X_2^2 - X_1}{\epsilon}, \quad W_2 = 1 - X_1, \quad W_3 = -X_2. \qquad (18) \end{aligned}$$

with initial conditions

$$X_1(0) = 0, \quad X_2(0) = 1. \tag{19}$$

Compute the numerical solutions for some relatively small $\epsilon > 0$ for $0 \leq t \leq 10$, and plot $W_1(t)$ and $\mathcal{W}_1(t) - 2X_2(t)\mathcal{W}_2(t)$ in addition to the solutions $X_n(t)$. How sensitive is the solution when ϵ is changed from one small ϵ to another?

This is an easy problem to do pen-and-pencil singular perturbation. We will do that in class.