A comparison of the Bader–Deuflhard and the Cash–Karp Runge–Kutta integrators for the GRI-MECH 3.0 model based on the chemical kinetics code Kintecus

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Abstract

The chemical kinetics and associated thermodynamics of the GRI-MECH 3.0 model is described and modeled with the Bader–Deuflhard and the Cash–Karp Runge–Kutta Integrators as implemented by W.T. Vetterling et al. in Kintecus V3.0. Comparisons are made to verify the mathematical correctness of the chemical kinetic model against those already published models and the experimental data in the literature. For the simple H_2–O_2 combustion model, the Cash–Karp Runge–Kutta integrator outperforms the Bader–Deuflhard method in speed and accuracy, but for combustions involving the GRI-MECH model the situation is reversed. The Bader–Deuflhard integrator is selected for the GRI-MECH runs and the selected published GRI-MECH runs in the literature. The comparisons of the Bader–Deuflhard integrator's results and the published results from the GRI-MECH model and experimental results are in excellent agreement.

Keywords: Combustion modeling; Chemical kinetics; The Cash–Karp Runge–Kutta; GRI-MECH; Bader–Deuflhard; Integrator; Kintecus

1. Introduction

The GRI-MECH general gas model has been around the combustion community for quite some time. The latest version of GRI-MECH is GRI-MECH 3.0 [1]. Most modeling groups use the standard Chemkin-II [2] or Chemkin-III [3] package to perform the various types of gas combustion GRI-MECH allows. The present paper focuses on the integration procedures, which are used in solving the chemical kinetic system. In Chemkin-II, the LSODE [4] solver is used, while Chemkin-III employs the VODE solver [5]. In the present paper, two alternative solvers, namely those of the Bader–Deufelhart [6] and the Cash–Karp [7] are applied to solve the ODE of the chemical kinetic system, and their performance is assessed.

2. Governing equations

This section will describe the equations required to solve general chemical kinetics with thermodynamics and then suggest two numerical methods to solve the system, which are different from the numerical method implemented in Chemkin-II or Chemkin-III.

To describe the temperature evolution of the system an ordinary differential equation (ODE) can be written as

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\left(\frac{1}{C_\mathrm{p}(T)}\right) \sum_{i=1}^{N_\mathrm{s}} \left(\frac{\mathrm{d}c}{\mathrm{d}t}\right) H_i(T) \tag{1}$$

Where T is the temperature of the system, N_s is the total number of species present in the system, $C_\mathrm{p}(T)$, $H_I(T)$ and $\mathrm{d}c/\mathrm{d}t$ are equations representing, respectively, the heat capacity of the entire system, enthalpy for a species and the rate of change of a species' concentration:

$$C_\mathrm{p}(T) = \sum_{i=1}^{N_\mathrm{s}} c_i C_{\mathrm{p},i} \tag{2}$$

for which $C_{p,I}$ is a split function

$$\begin{aligned}
C_{\mathrm{p},i} &= R\left(la_{1,i} + la_{2,i}T + la_{3,i}T^2 + la_{4,i}T^3 + la_{5,i}T^4\right), \\
&\quad \text{if } T_L \leq T < T_C \\
C_{\mathrm{p},i} &= R\left(ha_{1,i} + ha_{2,i}T + ha_{3,i}T^2 + ha_{4,i}T^3 + ha_{5,i}T^4\right), \\
&\quad \text{if } T_C \leq T < T_H
\end{aligned} \tag{3}$$

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and $H_i(T)$ is also a split function

$$H_i(T) = RT\left(la_{1,i} + \frac{la_{2,i}}{2}T + \frac{la_{3,i}}{3}T^2 + \frac{la_{4,i}}{4}T^3 + \frac{la_{5,i}}{5}T^4\right),$$

$$\text{if } T_L \leq T < T_C$$

$$H_i(T) = RT\left(ha_{1,i} + \frac{ha_{2,i}}{2}T + \frac{ha_{3,i}}{3}T^2 + \frac{ha_{4,i}}{4}T^3 + \frac{ha_{5,i}}{5}T^4\right),$$

$$\text{if } T_C \leq T < T_H \tag{4}$$

Eqs. (3) and (4) use the coefficients of la_{1-6} for the low temperature range, T_L to T_C, and the coefficients ha_{1-6} for the higher temperature range, T_C to T_H, are taken from the thermodynamic databases described in reference 1 above. As mentioned above, dc/dt is required in Eq. (1) and it also describes the time evolution of the concentrations of the species present in the system:

$$\left(\frac{dc}{dt}\right) = \sum_{j}^{\text{products}} k_j(T,P)n_{i,j} \prod_{k}^{\text{reactants}} A_k^{n_k}$$

$$- \sum_{j}^{\text{reactants}} k_j(T,P)n_{i,j} \prod_{k}^{\text{reactants}} A_k^{n_k} \tag{5}$$

where i is each species present in the system with j reactions, A_k is the kth species' concentration present in reaction j raised to its stoichiometric coefficient n_k. $k_j(T,P)$ represents the forward rate constant evaluated using the expanded Arrhenius equation at the current temperature and pressure. Some forward rate constants might also involve third-body and pressure fall-off reactions involving [M], Lindemann or Troe type reactions. The reverse rate constants are calculated through the equilibrium constant at the current temperature,

$$k_r = \frac{k_j(P,T)}{\left(\frac{1}{RT}\right)^{\Delta n_\ell\left(-\frac{\Delta H(T)_r - T\Delta S(T)_r}{RT}\right)}} \tag{6}$$

where $\Delta H(T)_r$ and $\Delta S(T)_r$ are changes in the enthalpies and entropies of that particular reaction r

$$\Delta H(T)_r = \sum_{i=1}^{\text{products}} n_{r,i} H_i(T) - \sum_{i=1}^{\text{reactants}} n_{r,i} H_i(T) \tag{7}$$

$$\Delta S(T)_r = \sum_{i=1}^{\text{products}} n_{r,i} S_i(T) - \sum_{i=1}^{\text{reactants}} n_{r,i} S_i(T) \tag{8}$$

where the $H_i(T)$ is from Eq. 3 and the $S_i(T)$ is obtained from the split function

$$S_i(T) = R\left(la_{1,i}\ln(T) + la_{2,i}T + \frac{la_{3,i}}{3}T^2 \right.$$
$$\left. + \frac{la_{4,i}}{4}T^3 + \frac{la_{5,i}}{5}T^4 + la_{7,i}\right), \quad \text{if } T_L \leq T < T_C$$

$$\tag{9}$$

$$S_i(T) = R\left(ha_{1,i}\ln(T) + ha_{2,i}T + \frac{ha_{3,i}}{3}T^2 \right.$$
$$\left. + \frac{ha_{4,i}}{4}T^3 + \frac{ha_{5,i}}{5}T^4 + ha_{7,i}\right), \quad \text{if } T_C \leq T < T_H$$

3. Results

To solve the above described chemical kinetic system, the Chemkin-II package uses the LSODE [4] ODE solver while Chemkin-III employs the VODE solver [5]. In this paper the above ODE system can be solved by the Bader–Deuflhard method of integration [6] or the Cash–Karp Runge–Kutta integrator [7] as implemented in Vetterling et al. [8] in Kintecus V3.0 [9]. The size of the GRI-MECH model prevents most authors from displaying all the numeric output from their simulations. Most overlay the plots of their model runs with their experimental runs, so a direct numerical comparison with the many of the GRI-MECH models present in the literature is not possible. To prove first the numerical stability and robustness of the Bader–Deuflhard integrator or the Cash–Karp Runge–Kutta integrator a direct numerical comparison is performed with the 23 reversible reactions of the H_2–O_2 combustion run that is shown in the Chemkin-II manual. Table 1 shows the output from the Chemkin-II program and the output from the Cash–Karp Runge–Kutta integrator at an numerical accuracy of 1×10^{-4}.

The Cash–Karp Runge–Kutta integrator clearly matches the Chemkin-II output to several decimal places. There is one small exception in that the final concentration of OH_2 differs from the Bader–Deuflhard model by about 10%. This could be attributed to the older thermodynamic database used in the manual. The NASA thermodynamic database used here for the H_2–O_2 combustion run is from 1995 while that used in the Chemkin-II run is from 1989. The Bader–Deuflhard method can also replicate the output from the Cash–Karp Runge–Kutta integrator, but only when the numerical accuracy reaches about 1×10^{-14}. Figs. 1 and 2 show the percent differences between the integrators and the output from Chemkin-II at different numerical integrator accuracies.

It is quite clear that the Cash–Karp Runge–Kutta integrator is almost invariant with respect to the numerical accuracy, but the accuracy of Bader–Deuflhard to replicate the Chemkin-II output is dependent upon the numerical integrator accuracy. The major differences between the Cash–Karp Runge–Kutta and the Bader–Deuflhard integrator in modeling the GRI-MECH 3.0 is simulation time. At a numerical integrator accuracy of 1×10^{-4} the Cash–Karp Runge–Kutta method produces a few small negative concentrations and extremely small steps for the independent variable time. These very small time steps force the simulations to take 30–40 times longer to completion than the Bader–Deuflhard method.

Fig. 3 shows four separate runs of the GRI-MECH 3.0 system with different starting conditions.

Each run is from a previous published paper on a kinetic run of the GRI-MECH 3.0 model using Chemkin and experimental verification. The starting conditions, such as the initial temperatures, pressures and concentrations, of

Table 1
Combustion of H_2 and O_2 at constant pressure: comparison of results at 3×10^{-4} s

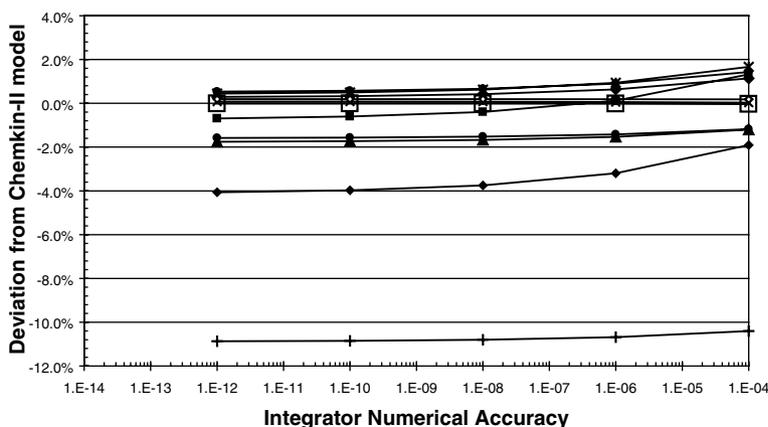|	H_2	O_2	OH	H_2	H	O
Bader–Deuflhard	1.80E−03	6.72E−01	3.02E−02	2.56E−01	1.04E−03	1.15E−02
CHEMKIN-II	1.79E−03	6.72E−01	3.07E−02	2.56E−01	1.03E−03	1.14E−02
Percent difference	0.6%	0.0%	−1.5%	0.1%	0.9%	0.9%
	HO_2	H_2O_2	N_2	NO	N	Temp. (K)
Bader–Deuflhard	5.36E−05	1.50E−06	2.74E−02	2.10E−05	2.41E−09	2.49E−09
CHEMKIN-II	6.00E−05	1.52E−06	2.73E−02	2.17E−05	2.41E−09	2.49E−09
Percent difference	−10.7%	−1.4%	0.2%	−3.2%	0.1%	0.0%

Fig. 1. Comparison of the Cash–Karp Runge–Kutta integrator with the results from the LSODE integrator used in Chemkin-II. Each line represents the percent difference deviation between the species concentration output of the Cash–Karp Runge–Kutta integrator and the output species concentrations of Chemkin-II.
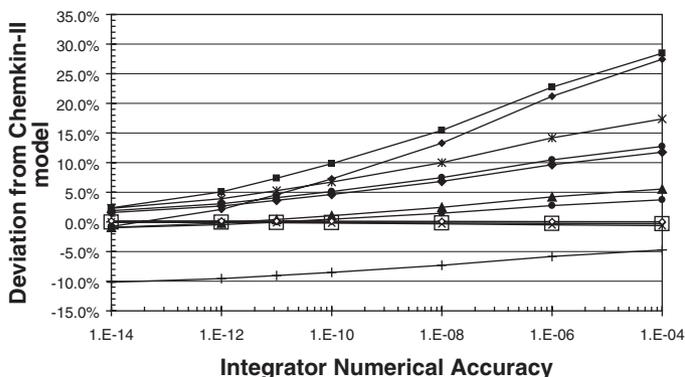

Fig. 2. Comparison of the Bader–Deuflhard integrator with the results from the LSODE integrator used in Chemkin-II. Each line represents the percent difference deviation between the species concentration output of the Bader–Deuflhard integrator and the output species concentrations of Chemkin-II.

each run in this paper parallel that of the reference papers [10–12]. In order to simulate the GRI-MECH reaction model runs with the integrators, the Chemkin version of the GRI-MECH 3.0 model was translated to the format used in Kintecus [9] where both integrators have been implemented. The ethane combustion test run 1 shown in Fig. 3 shows the simulated CH_3 profile that equates well with the experimental and simulated results from Chang et al. [10]. The associated methane combustion of test runs 2 and 3 also equally compare well with the carbon
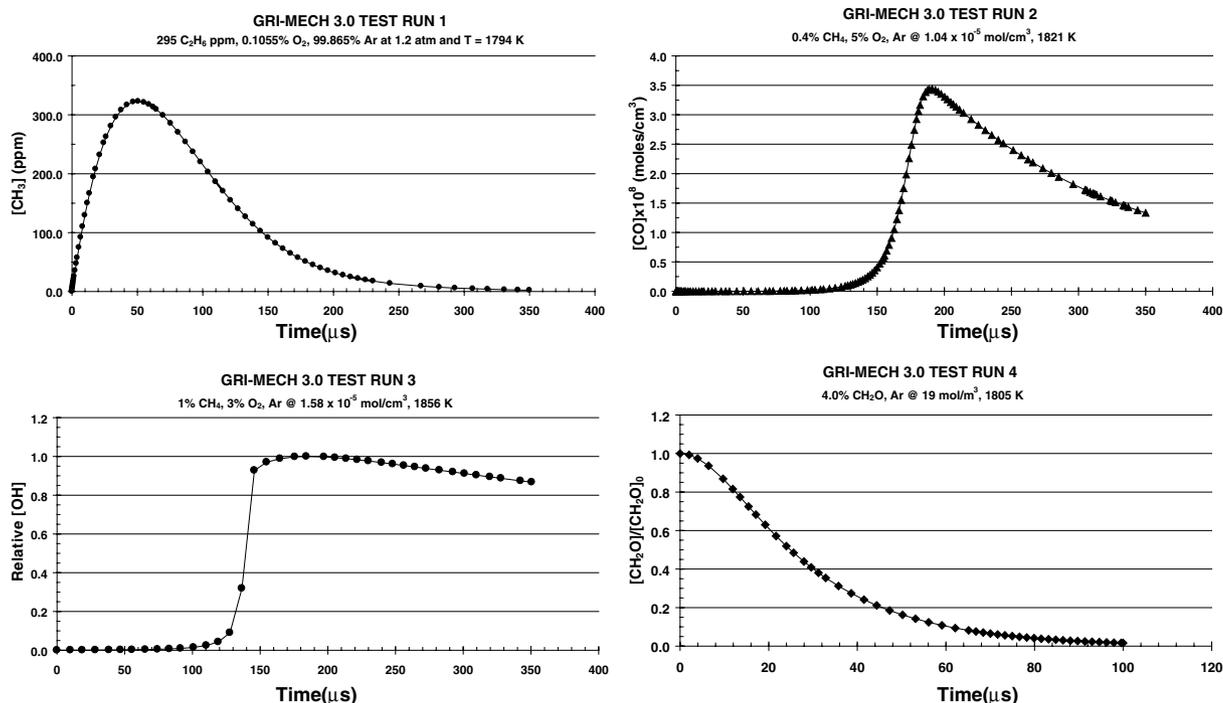
Fig. 3. Output from various combustion runs of the GRI-MECH 3.0 model integrated with the Bader–Deuflhard integrator using the initial conditions specified as the sub-titles.

monoxide and hydroxide free radical experimental and simulated results from Yu et al. [11]. Test run 4 involves the combustion of CH_2O which also agrees with both the experimental and simulated decay profile of CH_2O of Hidaka et al. [12]. Using the equations described above and the Bader–Deuflhard integrator, the GRI-MECH 3.0 model was integrated, and the peak heights, times to the peak height, widths of the peaks and overall peak profile of all four test runs are in excellent agreement with the corresponding runs in the referenced papers.

4. Conclusions

The conclusions are that the Bader-Deuflhard and the Cash–Karp Runge–Kutta integrators can replicate the results from the integrators used in Chemkin-II and Chemkin-III. The Bader–Deuflhard method is recommended over the Cash–Karp Runge–Kutta method simply because it is many orders of magnitude faster.

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