

A Direct Inversion of Chemical Kinetics Problems

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Abstract

A general algorithm for the direct inversion of data to yield unknown functions was recently developed by Caudill, Rabitz and Askar. We apply the technique to non-linear, coupled kinetics models to simulate the experimental inversion of kinetics parameters and to analyze the stability of the algorithm. This paper is a preliminary report on our findings.

0. Introduction

This paper presents results from the implementation of an algorithm developed by Caudill, Rabitz and Askar [2] to solve inverse problems in the field of chemical kinetics. In section 1 we describe the class of chemical inverse problems which are considered. The algorithm and applications are given in section 2. We discuss specific examples and results from computer experiments in the final section.

1. Problem Formulation

Chemical kinetics systems are often described by evolution-type equations of the form:

$$\frac{\partial u}{\partial t} = T(V, u(V)) \quad \text{for } t > 0, \quad (1)$$

$$u = u_0 \quad \text{for } t = 0, \quad (2)$$

where u is a vector representing the concentration of chemical species and V describes other parameters, e.g. diffusion and kinetics rate constants [1]. The standard textbook or *forward* problem consists of determining u for a choice of V . In actual laboratory situations some of the V_i may not be measurable, even though we would like accurate approximations of their values under various conditions, e.g. temperature, pressure. This quandary may be formulated as a mathematical *inverse* problem; determine V , given a set of data measurements $d = \{d_j\}$, which are related to V through equations of the form:

$$L_j(u, V) = f_j(d_j, u); \quad j = 1, 2, \dots, m, \quad (3)$$

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where each $L_j(u, V)$ is a, possibly non-linear, operator acting on u and V . An algorithm for determining a numerical solution to this problem is given in the next section.

2. Algorithm and Examples

The algorithm proposed by Caudill, Rabitz and Askar in [2] consists of three steps:

- (i) Formally invert the system (3) to express the unknown V in terms of the data d and the (unknown) forward solution u :

$$V = \nu[d, u] . \quad (4)$$

- (ii) Input (4) into equation (1) and solve the resulting system for u .
 (iii) Substitute the solution u obtained in step (ii) into the right-hand-side of (4) to determine V explicitly in terms of the data d .

The algorithm is attractive as it is based on system identities. Through implementation studies, we seek to determine its ability to reconstruct desired parameters from ideal as well as incomplete or noisy laboratory data.

In particular, we implement the algorithm to recover parameters, such as rate constants or species concentrations, in a chemical kinetics system (1) – (3). The set of data, given by equation (3), are typically sets of measurements of several species under various conditions. We consider the problem of recovering one or a few of the rate constants and some of the chemical species concentrations. Follow step (i) of the algorithm, and use the data measurements (3) in discretized versions of the rate equations from (1) to derive expressions of the form (4) for unknown rate constants. As step (ii), use (4) in place of the rate constants to solve system (1) for u . Finally, this computed solution for u is substituted back into (4) to recover unknown rate constants. Quite often, the system of M differential equations is coupled and very stiff. Solution of the forward problem requires use of techniques such as the backward Euler.

Finally, we remark that this algorithm can be used to solve a variety of inverse problems, which can be mathematically modeled by equations of the form (1) – (2) with measurable laboratory data (3). Three other types of applications: heat conduction, age-structured population dynamics and molecular dynamics are discussed in [2].

3. Numerical Experiments

In this section we describe results from the implementation of the algorithm from the previous section to solve the inverse problem for recovery of kinetics rate constants for two chemical systems. In our first set of experiments, a simple explosive reaction model is investigated. The model is based on the assumption that an infinite reservoir of the principal reagent is available, and no or negligible back reactions take place. The analytic solution to the forward problem was first derived by Rigos and Deutsch [4]. We examine the associated inverse problem. A more sophisticated non-linear, highly coupled 28-step reaction mechanism for the oxidation of carbon monoxide in the presence of hydrogen proposed by Yetter, Dryer and Rabitz [5] is studied in our second set of numerical experiments. We use real laboratory data whenever it is available in our simulations.

3a. An explosive kinetics model

Consider the simple explosive reaction model:



where the forward and backward rate constants for the propagation and termination reactions are k_1 , k_2 , k_3 , and k_4 respectively. The rate equations for the system are:

$$\frac{\partial[X]}{\partial t} = k_1[A][X]^2 - k_2[X]^3 - k_3[X] + k_4[B]$$

$$\frac{\partial[A]}{\partial t} = -k_1[A][X]^2 + k_2[X]^3$$

$$\frac{\partial[B]}{\partial t} = k_3[X] - k_4[B]$$

For propagation to occur at a reasonable rate, we must have $[A] \gg [X] > 0$ for $t > 0$ and $k_1 \gg k_2$. Termination occurs if $k_3 \gg k_4$. All of our numerical experiments consist of 4 steps:

1. Given all rate constants and initial concentrations of all reagents, solve the forward problem, i.e. determine concentrations of all reagents for finite times $t : 0 \leq t < \infty$.

2. Select data for concentrations of reagents at various times
 $0 = t_0 < t_1 < \dots < t_n$.
3. Formulate the inverse problem and apply the algorithm from section 2.
4. Compare the computed algorithm from step 3 with the actual solution from step 1.

To solve the forward problem, we use a simple forward Euler, finite difference scheme to compute the concentrations of X , A and B :

$$\begin{aligned} X_{i+1} &= \{ [(-k_2 X_i + k_1 A_i) X_i - k_3] \Delta t + 1 \} X_i + k_4 \Delta t B_i, \\ A_{i+1} &= (k_2 X_i - k_1 A_i) \Delta t X_i^2 + A_i, \\ B_{i+1} &= (k_3 X_i - k_4 B_i) \Delta t + B_i, \end{aligned}$$

where X_i , A_i and B_i denote the concentrations of the chemical species at the i^{th} time step. A subset of the data generated from the forward solver will be used to solve an inverse problem. We consider the following inverse problem, which can be "solved" using the algorithm described in the previous section: Given the rate constants k_1 , k_2 , k_4 and the concentrations of A and B , determine the concentration of X and the rate constant k_3 . First determine X , numerically, from:

$$\frac{\partial[X]}{\partial t} = -\frac{\partial[B]}{\partial t} + k_1[A][X]^2 - k_2[X]^3,$$

i.e.

$$\frac{X_{i+1} - X_i}{\Delta t} = \frac{-B_{i+1} + B_i}{\Delta t} + k_1 A_i X_i^2 - k_2 X_i^3.$$

Re-arranging terms yields:

$$X_{i+1} = + X_i - B_{i+1} + B_i + k_1 \Delta t A_i X_i^2 - k_2 \Delta t X_i^3.$$

The rate equation for k_3 :

$$k_3 = \frac{1}{[X]} \left(\frac{\partial[B]}{\partial t} + k_4[B] \right),$$

is discretized using the simple difference scheme:

$$k_3 = \frac{1}{X_i} \left(\frac{B_{i+1} - B_i}{\Delta t} + k_4 B_i \right).$$

The values for X_i computed above are used to evaluate k_3 .

We simulated an infinite reservoir system by taking $[B] = 0$, $[X] = 0.1$, $k_1 = 2$, $k_3 = 1$, $k_2 = k_4 = 0$ at time $t = 0$, the concentration of A to be constant at $[A] = 500$,

and $dt = 0.00001$. As A and X react, the concentration of X and, consequently, D, take off. We consider the associated inverse problem and implement the algorithm described above to recover the concentration of X for $0 < t < 0.005$ and the rate constant k_3 . Not surprisingly, recovery of $[X]$ and k_3 is near perfect when k_1, k_2, k_4 and $[A]$ are known and all of the data generated in the forward solver for $[B]$ is used. We next consider the inverse recovery problem using partial data. Results from experiments using all points for $[B]$, every other point, every fourth point and every eighth point are denoted by X1, X2, X4, X8, respectively in figure 1, and $k_3 - 1, k_3 - 2, k_3 - 4, k_3 - 8$ in figure 2. The figures show that the recovery of $[X]$ is excellent, i.e. less than 10% relative error for $t < 0.004$, before the explosion begins to take off. For times $0.004 \leq t < 0.005$, the relative error remains below 100%. A more sophisticated scheme or finer mesh would decrease the error associated with a linear discretization of the derivative terms.

3b. A 28-step CO-hydrogen-oxygen reaction mechanism

In our second set of numerical experiments, we examine a 28-step CO-Hydrogen-Oxygen reaction mechanism proposed by Yetter, Dryer and Rabitz [5] (given below). Although the mechanism has been validated for a wide range of conditions, the regions of calibration may differ quite a bit from step to step. The motivation for our work is to recover unmeasurable kinetics data, e.g. rate constants and reagent concentrations for a given set of experimental conditions.

H_2, O_2 Chain Reactions

1. $H + O_2 \rightleftharpoons O + OH$
2. $O + H_2 \rightleftharpoons H + OH$
3. $OH + H_2 \rightleftharpoons H + H_2O$
4. $OH + OH \rightleftharpoons O + H_2O$

H_2, O_2 Dissociation-Recombination Reactions

- 5a. $H_2 + M \rightleftharpoons H + H + M(N_2)$
- 5b. $H_2 + M \rightleftharpoons H + H + M(Ar)$
- 6a. $O + O + M \rightleftharpoons O_2 + M(N_2)$
- 6b. $O + O + M \rightleftharpoons O_2 + M(Ar)$
7. $O + H + M \rightleftharpoons OH + M$
- 8a. $H + OH + M \rightleftharpoons H_2O + M(N_2)$
- 8b. $H + OH + M \rightleftharpoons H_2O + M(Ar)$

Formation and Consumption of HO_2

- 9a. $H + O_2 + M \rightleftharpoons HO_2 + M(N_2)$
- 9b. $H + O_2 + M \rightleftharpoons HO_2 + M(Ar)$
10. $HO_2 + H \rightleftharpoons H_2 + O_2$

11. $HO_2 + H \rightleftharpoons OH + OH$
12. $HO_2 + O \rightleftharpoons OH + O_2$
13. $HO_2 + OH \rightleftharpoons H_2O + O_2$

Formation and Consumption of H_2O_2

14. $HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$
- 15a. $H_2O_2 + M \rightleftharpoons OH + OH + M(N_2)$
- 15b. $H_2O_2 + M \rightleftharpoons OH + OH + M(Ar)$
16. $H_2O_2 + H \rightleftharpoons H_2O + OH$
17. $H_2O_2 + H \rightleftharpoons H_2 + HO_2$
18. $H_2O_2 + O \rightleftharpoons OH + HO_2$
19. $H_2O_2 + OH \rightleftharpoons H_2O + HO_2$

Oxidation of CO

- 20a. $CO + O + M \rightleftharpoons CO_2 + M(N_2)$
- 20b. $CO + O + M \rightleftharpoons CO_2 + M(Ar)$
21. $CO + O_2 \rightleftharpoons CO_2 + O$
22. $CO + OH \rightleftharpoons CO_2 + H$
23. $CO + HO_2 \rightleftharpoons CO_2 + OH$

Formation and Consumption of HCO

- 24c. $HCO + M \rightleftharpoons H + CO + M(N_2)$
- 24b. $HCO + M \rightleftharpoons H + CO + M(Ar)$
25. $HCO + O_2 \rightleftharpoons CO + HO_2$
26. $HCO + H \rightleftharpoons CO + H_2$
27. $HCO + O \rightleftharpoons CO + OH$
28. $HCO + OH \rightleftharpoons CO + H_2O$

Forward rate constants for the reaction were computed at the seven temperatures: 298.15, 300, 500, 800, 1000, 1500, and 2000 degrees Kelvin using data from Table III in [5] and the Arrhenius rate formula $k = AT^n \exp(-E_a/RT)$, where A is the pre-exponential factor (which is independent of temperature, or nearly so), T is the temperature, n is a power index, E_a the activation energy, and R the gas constant. For reactions 4 and 22, we used the formulae $k_4 = 5.46 \times 10^{11} \exp(0.00149 \times T)$ and $k_{22} = 6.75 \times 10^{10} \exp(0.000907 \times T)$ given in the table in lieu of the values for A , n and E_a . Note that the seven temperatures selected for study do not necessarily fall within the calibration range given in the table, however, we use them as a best estimate. Backward rate constants for the reactions were computed at the same seven temperatures using the thermodynamic equations:

$$\begin{aligned} \Delta H(T) &= \Delta H(298.15) + \int_{298.15}^T c_p(\tau) d\tau , \\ &\approx \Delta H(298.15) + \sum_{i=1}^6 c_p(\tau_{i+1}) \cdot (\tau_{i+1} - \tau_i) , \\ \Delta S(T) &= \Delta S(298.15) + \int_{298.15}^T \frac{c_p(\tau)}{\tau} d\tau , \\ &\approx \Delta S(298.15) + \sum_{i=1}^6 \frac{c_p(\tau_{i+1})}{\tau_{i+1}} \cdot (\tau_{i+1} - \tau_i) , \\ \Delta G(T) &= \Delta H(T) - T\Delta S(T) , \end{aligned}$$

$$k_r = k_f \exp(-\Delta G/RT) ,$$

forward rate constants, enthalpy, entropy and specific heat data given in Table II of [5]. We are using the LSODE package [H] to simulate the forward 28-step reaction. LSODE solves systems of stiff equations, such as the ones which appear in chemical kinetics problems. The sensitivities of various parameters in the 28-step reaction have been studied [5]. We plan to use subsets of the data generated from the simulations to solve associated inverse problems.

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