Inverse Problems in Chemical Kinetics

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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 study non-linear, coupled kinetics models. This paper is a preliminary report on our findings.

1. Introduction and Problem Formulation

The problem considered in this talk lies in a very active area of research known as inverse problems. All inverse problems are associated with a forward problem, which is often much easier to solve. For example, consider a simple system studied by Euler and Bernoulli: given the density, length and tension of a plucked string, determine the tones produced. An associated inverse problem is to determine the density of the string from its tones, length and tension [D]. Inverse problems appear in a wide range of scientific areas which include: the reconstruction of images in X-ray tomography, the determination of the shape of flaws or cavities in metal castings, the modelling of groundwater, the study of potential flows and heat conduction, the determination of material properties of a beam from its vibrational modes, the recovery of a cross-sectional area of the vocal tract from measured data, the determination of the density inside the earth from seismographic data, scattering problems in physics, and mathematical inverse problems [IP],[K],[T].

The main topic of this talk is inverse problems in chemical kinetics. Chemical kinetics systems are often described by evolution-type equations of the form:

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

$$u = u_0 \qquad \text{for} \qquad t = 0\,, \tag{2}$$

where u is a vector representing the concentration of chemical species and V describes other parameters, e.g. diffusion and kinetics rate constants [A]. The standard textbook

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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:

$$L_j(u, V) = f_j(d_j, u) \; ; \qquad j = 1, 2, \ldots, m \; , \tag{3}$$

where each $L_j(u, V)$ is a, possibly non-linear, operator acting on u and V.

The remainder of this paper is organized as follows. An algorithm for determining a numerical solution to the inverse problem described above is given in the next section. Implementations of the algorithm to study a simple explosive kinetics model and a non-linear, coupled 28-step reaction model are discussed in the final section. This paper is a preliminary report.

2. An Algorithm for Direct Inversion

An algorithm proposed by Caudill, Rabitz and Askar [CRA] to solve the inverse problem given in the previous section 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:

$$V = \nu[d, u] \; . \tag{4}$$

(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.

Since the algorithm is based on system identities, it should be of no surprise if it yields excellent results for fairly nice, clean and complete data sets. Through implementation studies, we seek to determine its ability to reconstruct desired parameters from ideal as well as incomplete or noisy laboratory data.

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 applications: heat conduction, age-structured population dynamics, and molecular dynamics are discussed in [CRA]. Computer experiments with chemical kinetics models are described in the next section.

3. Numerical Experiments

In this section we describe results from the implemention of the algorithm from the previous section to solve the inverse problem for recovery of kinetics parameters. 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. 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 [YDR] is examined in our second set of numerical experiments. We use real laboratory data whenever it is available.

An Explosive Kinetics Model: Consider the simple explosive reaction model:

$$A + 2X \rightleftharpoons 3X \qquad (\text{ propagation })$$

$$X \rightleftharpoons B \qquad (\text{ termination }),$$

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:

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

For propagation to occur at a reasonable rate, $[A] \gg [X] > 0$ 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 $0 = t_0 < t_1 < \ldots < t_n$.
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 the forward Euler method to compute the concentrations of X, A and B. 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:

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

using a simple forward difference scheme:

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

where the subindex i indicates the concentration of reagents at time $t = t_i$, the i^{th} time step in the simulation. 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 B 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, $k3-1$, $k3-2$, $k3-4$, $k3-8$ in figure 2. Figure 1 shows that the recovery of $[X]$ is good, 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.

A 28-step CO-Hydrogen-Oxygen Reaction Mechanism: In our second set of numerical experiments, we study a 28-step CO-hydrogen-oxygen reaction mechanism proposed by Yetter, Dryer and Rabitz [YDR], given below. Although the mechanism has been validated for a wide range of conditions, the regions of calibration differ for each of the reactions. One of the motivations for our work is to examine the reaction mechanism under a range of conditions, some of which may not be experimentally validated. A second motivation is the study of the sensitivities of the reagents and rate constants to changes in experimental conditions.

CO, H_2, O_2 Reaction Mechanism

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 and backward rate constants for the reaction were computed using data from [HH],[J],[YDR] 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 a power index, E_a the *activation energy*, and R the *gas constant*. For reactions 4 and 22, we use 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 in table III of [YDR] in lieu of the values for A, n and E_a [4] Even when temperatures selected for study do not necessarily fall within the calibration range given in the table, we use them as a best estimate.

We follow step 1 of the procedure outlined for the study of the explosive kinetics model and simulate the forward problem. Since this system is very stiff, a simple finite difference scheme will lead to poor results [HW]; the LSODE package of Hindmarsh [H] yields good results for small temporal meshsizes. We are currently investigating formulations of solvable inverse problems. Both noisy and incomplete data will be considered.

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[4] There are different ways to compute backward rate constants, but the method given above appears to be the best. Another method, which relies on the thermodynamic equations $\Delta H(T) = \Delta H(298.15) + \int_{298.15}^{T} c_p(\tau)d\tau$; $\Delta S(T) = \Delta S(298.15) + \int_{298.15}^{T}(c_p(\tau)/\tau)d\tau$; $\Delta G(T) = \Delta H(T) - T\Delta S(T)$; and $k_r = k_f \exp(-\Delta G/RT)$, yields considerably different rate constants, which lead to poor simulation results. Errors from computation of the exponential term may be the cause.

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References

[A] P.W. Atkins, *Physical Chemistry*, Oxford 1978.

[CRA] L.F. Caudill, H. Rabitz, A. Askar, *A Direct Method for the Inversion of Physical Systems*, preprint.

[D] D.R. Durran, *The Inverse Liouville Transformation*, M.A. Thesis, Mathematics, U.C. Berkeley, 1975.

[H] A.C. Hindmarsh, *ODEPACK, A Systematized Collection of ODE Solvers*, Scientific Computing, R. Steplenman et al. (eds.), IMACS/North-Holland, 1983, pp. 55-64.

[HH] A.J. Hills, C.J. Howard, *Rate Coefficient Temperature Dependence and Branching Rates for the OH + ClO Reaction*, J. Chem. Phys., 81, 1984, p. 4458.

[HW] E. Hairer, G. Wanner, *Solving Ordinary Differential Equations II*, Springer, 1980.

[IP] *Inverse Problems* (journal), Inst. of Physics, Pub. Ltd..

[J] JANAF Thermochemical Tables (1971), U.S. Nat'l Bureau of Standards Publication NARDS-NBS 37 and supplements (D.R. Stull, H. Prophet eds.), NBS, Washington, DC, M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Fulrip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical tables, third ed., J. Phys. Chem. Ref. Data., 14, Supplement 1, 1985.

[K] M. Kobayashi, *Discontinuous Inverse Sturm-Liouville Problems with Symmetric Potentials*, Ph.D. Thesis, Mathematics, U.C. Berkeley, 1975.

[RD] A.A. Rigos, J.M. Deutsch, *A Simple Model for the Influence of Fluctuations on Explosive Reactions.* J. Chem. Phys. 76(10), 15 May 1982, pp. 5180-1.

[T] A. Tarantola, *Inverse Problem Theory*, Elsevier, 1987.

[YDR] R.A. Yetter, F.L. Dryer, H. Rabitz, *A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics*, Combus. Sci. and Tech., 1991, Vol. 79, pp. 97-128.

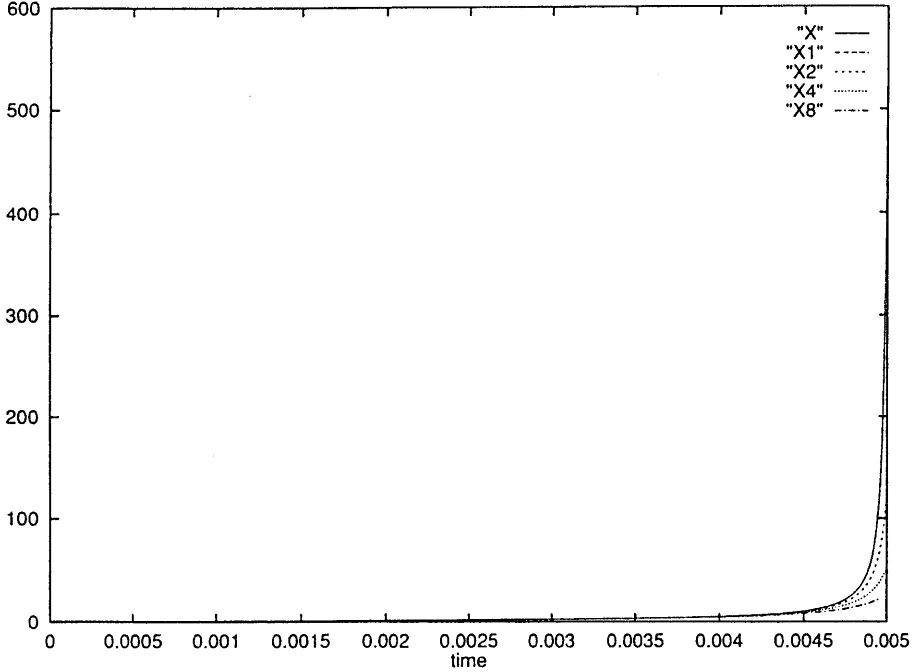
Figure 1: Reconstruction of [X]: B=0, X = 1.015, k1=2, k3=1, k2=k4=0 at t=0, dt=0.00001, A=100

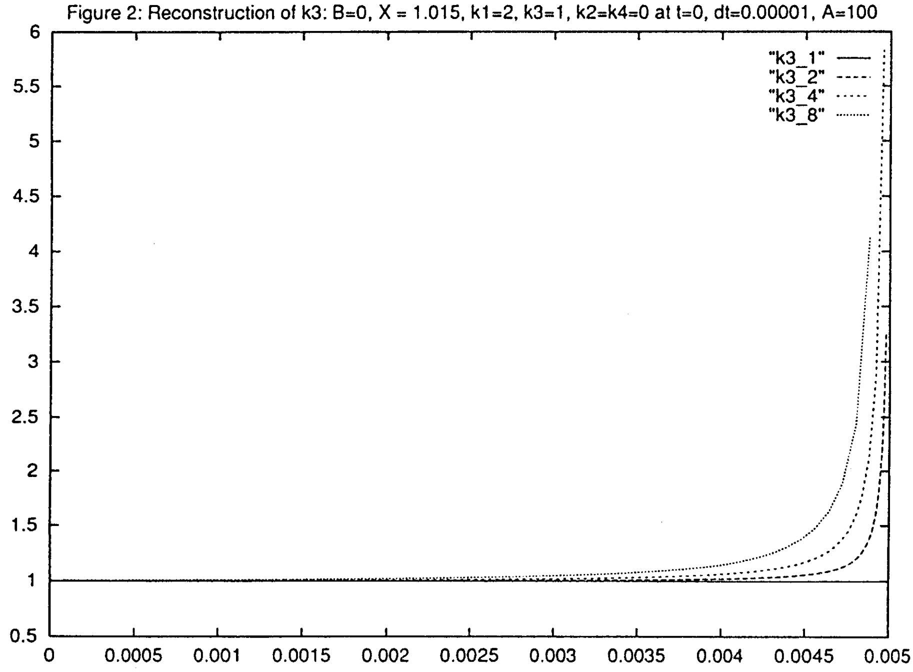
Figure 2: Reconstruction of k3: B=0, X = 1.015, k1=2, k3=1, k2=k4=0 at t=0, dt=0.00001, A=100