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Note

First Integral Method for Evaluation of the Relations Between Components of Bray-Liebhafsky Models

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The first integral method is used for transformation of the set of non-linear differential equations for the time evolution of components in Bray-Liebhafsky models.

The capabilities for the method are demonstrated on the models proposed by Schmitz and Furrow.

The method gives us time invariant relations between the components during the course of the process. They correspond to the conservation laws.

The relations developed are allways linear; more precisely, we obtain all linearly independent relations.

As the result of the proposed transformations, the starting system is simplified to one with fewer number of non-linear differential equations and with complementary number of linear relations. In order to perform simplification, linear relations could be explicitly solved and substituted to the system.

The method can be applied to any complex reaction model without any additional difficulty.

INTRODUCTION

The first integral method is one of the usable mathematical methods[1] for the simplification of the complex systems of non-linear differential equations which arise in different fields of science. We applied this methodology for the case of kinetic systems, specifically, for hydrogen-peroxide decompositions in the presence of the pottasium iodate and sylphuric accide known as Bray-Liebhafsky reaction.[2,3] This complex process exibits an oscillatory behaviour in the certain domain of the initial concentrations.

There exists a number of models for this process,[4–7] and we restrict us on two of them with the main goal to make the corresponding systems which describe the time evolution of the components concentrations simpler, and thus obtain deeper insight into the process.

In order to do so, we used the first integral method which gives us certain number of relations between the components concentrations invariant in time. These relations can be viewed as the surfaces in the space of components over which the solutions are moving in the time.

One first integral allows us to express any of its components as the function of the remaining components. Substituting into the starting system of differential equations leads to the system with one component less.

If there exist more then one first integral then the previous procedure can be applied equally well for every of them and, thus, reduce the number of unknown concentrations.

CHEMICAL INTERPRETATION

Chemical equivalent of first integrals are conservation laws. There exist number of them. Clarke[8] p. 18–20 in his theoretical presentation avoid to mention any of them. We find a lot of similarities between his theoretical and our practical approach.

Each mass conservation law is linear combination of species involved in process, corresponding to the particular atom. Evidently, they are linearly independent.

Also electro-neutrality is a suitable conservation law. This law exibits the same features as previous ones.

Our proposed procedure is based on finding all linearly independent solutions; so, we are finding all linear conservation laws which exist for particular model. For some models the number of first integrals is equal to the number of conservation laws; for some other this is not the case.

Here, we present the calculations for Schmitz's model from the first group of models and Furrow's model which belongs to the second group of models.

Obviously, it is possible to recalculate first integrals from conservation laws, and vice versa, if there is equal number of them. In the opposite case, which we have with Furrow's model, the number of first integrals is higher, and it is necessary to use some new conservation law which is valid for that model.

The examples which we present bellow will clarify the whole procedure.

MODEL PROPOSED BY SCHMITZ

The model proposed by Schmitz[7] of hydrogen peroxide decomposition in the presence of the potassium iodate and sulphuric acid, i.e. the Bray-Liebhafsky reaction is:

$$A_1 + A_2 + 2A_3 \Leftrightarrow A_4 + A_5 \tag{1.1}$$

$$A_2 + A_3 + A_4 \Leftrightarrow A_7 + A_{10} \tag{1.2}$$

$$A_7 + A_{10} \Leftrightarrow 2A_5 \tag{1.3}$$

$$A_2 + A_3 + A_5 \Leftrightarrow A_7 + A_9 \tag{1.4}$$

$$A_5 + A_6 \Leftrightarrow A_2 + A_3 + A_7 + A_8 \tag{1.5}$$

$$A_6 + A_{10} \Leftrightarrow A_4 + A_5 \tag{1.6}$$

$$2A_2 + 2A_3 + A_8 \Leftrightarrow 2A_5 \tag{1.7}$$

where A_i, $i = 1,\ldots, 10$ corresponds to the components of the system:

$A_1 \Leftrightarrow IO_3^-$, $A_2 \Leftrightarrow I^-$, $A_3 \Leftrightarrow H^+$, $A_4 \Leftrightarrow HIO_2$, $A_5 \Leftrightarrow HIO$,

$A_6 \Leftrightarrow H_2O_2$, $A_7 \Leftrightarrow H_2O$, $A_8 \Leftrightarrow O_2$, $A_9 \Leftrightarrow I_2$, $A_{10} \Leftrightarrow I_2O$,

Here, all steps are reversibile although in the original Schmitz's model[7] last three steps are irreversible. This generalisation don't make any inconveniences in mathematical treatment.

Denoting by x_i, $i = 1,\ldots, 10$ the concentrations of the mentioned species, the time evolution of system is given by set of differential equations,

$$\frac{dx_1}{dt} = -V_1 \tag{2.1}$$

$$\frac{dx_2}{dt} = -V_1 - V_2 - V_4 + V_5 - 2V_7 \tag{2.2}$$

$$\frac{dx_3}{dt} = -2V_1 - V_2 - V_4 + V_5 - 2V_7 \tag{2.3}$$

$$\frac{dx_4}{dt} = V_1 - V_2 + V_6 \tag{2.4}$$

$$\frac{dx_5}{dt} = V_1 + 2V_3 - V_4 - V_5 + V_6 + 2V_7 \tag{2.5}$$

$$\frac{dx_6}{dt} = -V_5 - V_6 \tag{2.6}$$

$$\frac{dx_7}{dt} = V_2 - V_3 + V_4 + V_5 \tag{2.7}$$

$$\frac{dx_8}{dt} = V_5 - V_7 \tag{2.8}$$

$$\frac{dx_9}{dt} = V_4 \tag{2.9}$$

$$\frac{dx_{10}}{dt} = V_2 - V_3 - V_6 \tag{2.10}$$

where the following notation is used

$$V_1 = k_1\, x_1\, x_2\, x_3^2 - k_{-1} x_4\, x_5 \tag{3.1}$$

$$V_2 = k_2\, x_2\, x_3\, x_4 - k_{-2}\, x_7\, x_{10} \tag{3.2}$$

$$V_3 = k_3\, x_7 x_{10} - k_{-3}\, x_5^2 \tag{3.3}$$

$$V_4 = k_4 x_2 x_3 x_5 - k_{-4} x_7 x_9 \tag{3.4}$$

$$V_5 = k_5 x_5 x_6 - k_{-5} x_2 x_3 x_7 x_8 \tag{3.5}$$

$$V_6 = k_6 x_6 x_{10} - k_{-6} x_4 x_5 \tag{3.6}$$

$$V_7 = k_7 x_2^2 x_3^2 x_8 - k_{-7} x_5^2 \tag{3.7}$$

Obviously, V_i, $i = 1,...,7$ denotes the rates of particular steps in which k_i and k_{-i} are forward and reversal rate constants for the step i, $i = 1,...,7$.

This set, non-linear in respect with concentrations of special but linear in respect with rates of particular steps, $V_1,...,V_7$ can be transformed into the set of four first integrals - relations between components

$$2\frac{dx_1}{dt} - \frac{dx_2}{dt} + \frac{dx_4}{dt} + \frac{dx_6}{dt} + 2\frac{dx_8}{dt} - \frac{dx_9}{dt} = 0 \tag{4.1}$$

$$5\frac{dx_1}{dt} - \frac{dx_2}{dt} + 3\frac{dx_4}{dt} + \frac{dx_5}{dt} + 2\frac{dx_6}{dt} + 4\frac{dx_8}{dt} + 2\frac{dx_{10}}{dt} = 0 \tag{4.2}$$

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} - \frac{dx_3}{dt} = 0 \tag{4.3}$$

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} + \frac{dx_4}{dt} + \frac{dx_5}{dt} + 2\frac{dx_6}{dt} + 2\frac{dx_7}{dt} = 0 \tag{4.4}$$

The previous set of first integrals is readily transformed to the four relations between components we are interested in

$$2x_1 - x_2 + x_4 + x_6 + 2x_8 - x_9 = \alpha_1 \tag{5.1}$$

$$5x_1 - x_2 + 3x_4 + x_5 + 2x_6 + 4x_8 + 2x_{10} = \beta_1 \tag{5.2}$$

$$x_1 + x_2 - x_3 = \gamma_1 \tag{5.3}$$

$$x_1 + x_2 + x_4 + x_5 + 2x_6 + 2x_7 = \delta_1 \tag{5.4}$$

Real constant[5] $\alpha_1, \beta_1, \gamma_1, \delta_1,$ are the consequence of initial conditions.
Application of conservation laws leads to the four relations

$$x_1 + x_2 + x_4 + x_5 + 2x_9 + 2x_{10} = \alpha_2 \tag{6.1}$$

$$3x_1 + 2x_4 + x_5 + 2x_6 + x_7 + 2x_8 + x_{10} = \beta_2 \tag{6.2}$$

$$x_3 + x_4 + x_5 + 2x_6 + 2x_7 = \gamma_2 \tag{6.3}$$

$$x_1 + x_2 - x_3 = \delta_2 \tag{6.4}$$

The first three are consequence of mass conservation law and the fourth correspond to electroneutrality.

Equivalence of this relations with the first integral ones is established by multiplying previous set of equations with respectively $(-1, 2, -1, -1)$, $(0, 2, -1, -1)$, $(0, 0, 0, 1)$, $(0, 0, 1, 1)$ to obtain (5.1), ... (5.4).

The matrix formatted with this vectors is non-singular; so, the inverse exist and reverse transformation is also possible.

The previous procedure is applied to the more complex Noyes-Edelson model[5] without problems, and with similar results.

MODEL PROPOSED BY FURROW

The model proposed by Furrow[6] for the Bray-Liebhafsky reaction is:

$$A_1 + A_2 + 2A_3 \Leftrightarrow A_4 + A_5 \tag{7.1}$$

$$A_1 + A_3 + A_6 \Leftrightarrow A_4 + A_7 + A_8 \tag{7.2}$$

$$A_4 + A_6 \Leftrightarrow A_5 + A_7 + A_8 \tag{7.3}$$

$$A_5 + A_6 \Leftrightarrow + A_2 + A_3 + A_7 + A_8 \tag{7.4}$$

$$2A_4 \Leftrightarrow A_1 + A_3 + A_5 \tag{7.5}$$

$$A_2 + A_3 + A_5 \Leftrightarrow A_7 + A_9. \tag{7.6}$$

$$A_2 + A_3 + A_4 \Leftrightarrow 2A_5 \tag{7.7}$$

$$A_1 + A_3 + A_4 \Leftrightarrow A_7 + 2A_{11} \tag{7.8}$$

were A_i, $i = 1,...,9$ corresponds to the same components of the system as in the Schmitz's model.

$A_{11} \Leftrightarrow \cdot IO_2$, is the new one, whereas A_{10} is not present in the model considered.

The time evolution of the system is readily expressible by set of differential equations which gives us the set of five first integrals

$$x_1 + x_2 + x_4 + x_5 + 2x_6 + 2x_7 = \alpha_3 \tag{8.1}$$

$$x_6 + x_8 = \beta_3 \tag{8.2}$$

$$-x_1 + 5x_2 + x_4 + 3x_5 + 2x_6 + 8x_9 = \gamma_3 \tag{8.3}$$

$$-5x_1 + x_2 - 3x_4 - x_5 + 2x_6 - 4x_{11} = \delta_3 \tag{8.4}$$

$$x_1 + x_2 - x_3 = \eta_3. \tag{8.5}$$

Real constant[5] α_3, β_3, γ_3, δ_3, η_3 are obtained from initial conditions.

We are able to find, as in the case of Schmitz's model, only four relations from conservation principles.

$$x_1 + x_2 + x_4 + x_5 + 2x_9 + x_{11} = \alpha_4 \tag{9.1}$$

$$3x_1 + 2x_4 + x_5 + 6x_6 + 2x_7 + 2x_8 + 2x_{11} = \beta_4 \tag{9.2}$$

$$x_3 + x_4 + x_5 + 2x_6 + 2x_7 = \gamma_4 \tag{9.3}$$

$$x_1 + x_2 - x_3 = \delta_4. \tag{9.4}$$

Real constant α_4, β_4, γ_4, δ_4, are obtained from initial conditions.

At present time, we are not able to find one additional conservation law which we need in order to have same number of them as the number of first integrals.

CONCLUSION

First integral method is alternative way of obtaining conservation relations between the components of complex chemical models.

Method leads to a maximal number of linearly independent linear relations; so it is more general than the application of mass and electro-neutrality conservation laws.

There exist the similarity with the theoretical Clark's presentation of conservation laws.

These relations allows us to reformulate the model into a smaller one, with smaller number of non-linear differential equations.

By using their linearity, the system of relations could be explicitely solved and the simplification is readily performed.

The advantage of this simplification could be important in computer time necessary for computations of solutions; also, complexity of the computations could be reduced and, consequently, accuracy of the calculated results is higher.

We developed FORTRAN program for previous mentioned calculations. In order to obtain as accurate results as possible, we simulates integer arithmetics troughout the computations. Program is used on PC computers and is avaiable on request.

The obtained relations compared with the ones calculated from experiments can be used for justification of the postulated models.

Obviously, the first integral method can be easily applied to any model of any complex reactions without additional difficulties.

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REFERENCES

1. N. P. Erugin, *Book for Reading on General Course of Differential Equations,* Nauka i Tehnika, Minsk, 1972.
2. W. C. Bray, *J. Am. Chem. Soc.* **43** (1921) 1262.
3. W. C. Bray, and H. A. Liebhafsky, *J. Am. Chem. Soc.* **53** (1931) 38.

4. H. A. Liebhafsky, W. C. McGavock, R. J. Reyes, G. M. Roe, and L. S. Wu. *J. Am. Chem. Soc.* **100** (1978) 87.

5. D. Edelson, R. M. Noyes, *J. Phys. Chem.* **83** (1979 212.

6. S. D. Furrow, *Chemical Oscillators Based on Iodate Ion and Hydrogen Peroxide*, in *Oscillations and Travelling Wawes in Chemical Systems,* eds. R. J. Field, and M. Burger, p.171, J. Willey, New York, 1985.

7. G. Schmitz, *J. Chim. Phys.* **89** (1987) 7023.

8. B. Clarke, *Stability Of Complex Reaction Network,* in *Advances In Chemical Physics,* eds. I. Prigogine, and A. Stuart, A. Rice, p.217, J. Willey, New York, 1980.

SAŽETAK

Metoda prvih integrala za evoluciju Bray-Liebhafsky sistema

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Metoda prvih integrala je korišćena za transformaciju skupa nelinearnih diferencijalnih jednačina koji opisuje vremensku evoluciju komponenata sistema Bray-Liebhafsky.

Mogućnosti metode su prikazane na modelima Schmitz-a i Furrow-a.

Metodom dobijamo vremenski invarijantne veze između komponenata tokom procesa. One odgovaraju konzervacionim zakonima.

Dobijene relacije su uvek linearne; preciznije, dobijamo sve linearno nezavisne relacije.

Kao posledica predloženog postupka, polazni sistem se pojednostavljuje do sistema sa manjim brojem nelinearnih diferencijalnih jednačina i sa komplementarnim brojem linearnih veza. Da bi se izvelo pojednostavljenje, linearne relacije se mogu eksplicitno rešiti i zameniti u sistem.

Metod se može primeniti i na bilo koji drugi složeni model bez dodatnih problema.