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ON ONE MODEL OF CHEMICAL KINETICS[1)]

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The present work deals with the properties of a mathematical model of the chemical kinetics of gases, especially with the problem of model adequacy. It is shown that almost all the qualitative features of the model can be derived from model equations without having to solve these equations explicitly. Included in the considerations are possible model applications in computing the equilibrium composition of a chemical system.

I. INTRODUCTION

The work is, on the one hand, devoted to the analysis of one out of many mathematical models of chemical kinetics (as used in [1]) for the modelling of time-dependent processes taking place in low-temperature plasma resulting from the action of the electric arc on SF_6 (sulphur hexafluoride), on the other hand it points to an interesting possible application of this model in computing the equilibrium composition of a chemical system.

The first part is understood as an attempt at filling the gap between experimental results, i.e. the measurement of the values of quantities characterizing a specific physical model of a system, and the "computer-aided" solution of the model adopted.

The justification of examining the qualitative properties of a model follows, for example, from the fact that a characteristic feature of contemporary physics and chemistry is the interest in non-linear processes, for which it is, of course, difficult to establish whether the numerical results obtained by solving our model are correct or not. The usual way of checking this is to have a large number of computations. It is considerably more convincing to derive the fundamental properties of a model than to solve it for a specific (and thus finite) set of input data - parameters.

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Our aim will be: a) to show that at a suitable level the adopted model is adequate, i.e. it is not in contradiction with the intuitively expected behaviour of a real phenomenon and, moreover, it can, at least in principle, be solved by means of numerical mathematics; b) to point to the interesting possibility of applying this model to the computation of equilibrium composition.

2. DESCRIPTION OF THE ADOPTED MODEL OF CHEMICAL KINETICS

Let there be a chemical system S with the components $S_1, \ldots, S_n$, the concentration of which will be denoted $y_1, \ldots, y_n$. Each component S_i is a linear combination of the base elements $P_1, \ldots, P_d$, where the base element is understood to be a substance which in system S does not decompose into simple substances. (Let it be added that the base elements P_i need not of necessity occur among the elements S_i.) The coefficients of these linear combinations, usually expressed by integers, form the lines of formula matrix U.

Assuming that taking place in S are m reactions described by stoichiometric equations

$$c_{1j}S_1 + \ldots + c_{nj}S_n \overset{r_j}{\underset{d_j}{\rightleftarrows}} c'_{1j}S_1 + \ldots + c'_{nj}S_n$$
$$c_{ij}, c'_{ij} \in \{0,1,2,\ldots\}, \quad i = 1,\ldots,n; \quad j = 1,\ldots,m, \tag{2.1}$$

where c_{ij}, c'_{ij} is the stoichiometric coefficient of the ith component in the jth reaction, and r_j, d_j are non-negative functions of temperature T called rate constants, and assuming further that every reaction (2.1) leads to a time variation in the concentration of the ith component

$$\dot{y}_i = (c_{ij} - c'_{ij})\left[-r_j(T)\prod_{k=1}^{n} y_k^{c_{kj}} + d_j(T)\prod_{k=1}^{n} y_k^{c'_{kj}}\right] =: a_{ij}G_j(T,y), \tag{2.2}$$
$$i = 1,\ldots,n,$$

the resultant time variation in the system composition is the sum of all variations and it can be written in the form

$$\dot{y} = AG(T,y), \tag{2.3}$$

where $A = [a_{ij}]$ is the stoichiometric matrix of the system.

Assuming further that the temperature of S is a known time function $T = T(t)$ and that the rate constants are of Arrhenius' form

$$a\exp(-b/T), \qquad a,b \geq 0, \tag{2.4}$$

and neglecting the effect of the other phenomena, let us pose the question whether this model meets any of the requirements of adequancy.

3. DISCUSSION OF PROBLEMS OF MODEL ADEQUACY

In the following we shall deal with these problems of model adequacy (2.3):

a) the existence and uniqueness of solution for any time $t \geq t_0$. There is no doubt that a model is not admissible whose solution expressing the time composition of the system would only be defined on a bounded time interval. Similarly it is not suitable (from the viewpoint of possible numerical solution) that for a given initial composition of the system S there should be more than one solution.
b) the existence of non-negative solutions, i.e. if the solution of the model (vector of molar concentration) y is at the time t_0 non-negative, it is non-negative at any time $t \geq t_0$ in which it is defined.
c) the existence of stationary solutions of the model in the case of constant temperature, i.e. the existence of solutions corresponding to steady or equilibrium states.

The adopted model (2.3) is formed by a system of ordinary differential equations solved with respect to the derivative whose right-hand side is continous in all the variables and has partial derivatives with respect to the variables y. Hence ([2]) the existence and uniqueness of the solution of the model on a certain interval $\langle t_0, t_0 + \epsilon), \epsilon > 0$, and this solution is a continuous function of the initial system composition.

To solve the problem of the existence of non-negative solutions, let us write (2.2) in the form

$$\dot{y}_i = -|a_{ij}| P_{ij}(t, y)\ y_i + |a_{ij}| Q_j(t, y)$$
$$i = 1, \ldots, n; \quad j = 1, \ldots, m,$$

where P_{ij}, Q_{ij} are monoms of y such that if $y \geq 0$, then also $P_{ij} \geq 0$, $Q_{ij} \geq 0$.

If at time $t_1 \geq t_0$ the concentration y_i of a component S_i is zero, its time derivative will be

$$\dot{y}_i(t_1) = |a_{ij}| Q_{ij}(t_1, y(t_1)) \geq 0,$$

and thus the given component of the vector field (2.3) cannot point out of the region of non-negative values.

If we start from the physically reasonable assumption of non-negativeness of the vector of initial concentrations, the concentration vector components will be non-negative for any time $t \geq t_0$ at which the solution is defined.

It remains to be added that this result can be enhanced considerably if all the reactions in the system S are assumed to be reversible and all constants a in (2.4) are positive. Under this conditions, depending on the stoichiometric matrix, the components y_i of the vector of concentrations y fall into three classes:

a) constantly positive components, b) constantly positive components with the exception of the initial time t_0, c) identically zero components.

The assumption of the reversibility of all reactions is not at all unnatural, it corresponds to the dynamic understanding of the chemical equilibrium as a state of a system when the rates of forward and back reactions become equal. Identically zero components are easy to eliminate from (2.3).

In the following, the term "solution" will always refer to non-negative solutions only - it is only these that carry any physical meaning.

While the local existence of solution (2.3) was the trivial consequence of the Picard-Lindelöf theorem, the global existence is not exactly so selfevident. For its proof it is of advantage to use the formula matrix $U = [u_{ij}]$. From the law of conservation of mass and charge it follows that this matrix forms d time-invariant functionally independent first integrals of (2.3) in the form

$$u_{i1} y_1 + \ldots + u_{in} y_n = b_i \qquad i = 1, \ldots, d. \tag{3.1}$$

For the sake of simplicity, let us first assume that the system does not contain any ions. Then the number of base components $d \geq 1$ and there is no electron among the base components. This, of course, means that all coefficients u_{ij} can be chosen such that

a) $u_{ij} \in \{0, 1, 2, \ldots\}, \qquad i = 1, \ldots, d; \quad j = 1, \ldots, n$
b) rank $(U) = d$
c) $\sum_{i=1}^{d} u_{ij} > 0 \quad j = 1, \ldots, n,$

whence it follows directly that the components y_i of the solution y of (2.3) are bounded and thus the solution y is bounded in the norm and hence it exists at any time $t \geq t_0$.

If S contains any ions, then an electron can be choosen as the base component P_d so that the first d-1 lines of formula matrix U are formed by non-negative integers. Hence it is easy to find that d-1 components are bounded i.e. the remaining component must also be bounded.

In the conclusion of this Chapter let us suggest a proof of the existence of a steady state of system S in the case of constant temperature, i.e. a proof of the existence of a stationary solution of the system

$$\dot{y} = AG(y), \qquad Uy(0) = b, \tag{3.2}$$

where the initial condition specifies from what substances the system S was formed during the preceding development (we put t_0:=0).

The trajectories of (3.2) lie in the intersection of subspaces (3.1) with the positive cone of the phase space of concentrations $\Omega : \langle 0, \infty) \times \langle 0, \infty) \times \ldots \times \langle 0, \infty)$. The set Ω_0 determined in this way is convex and compact. Let us consider the

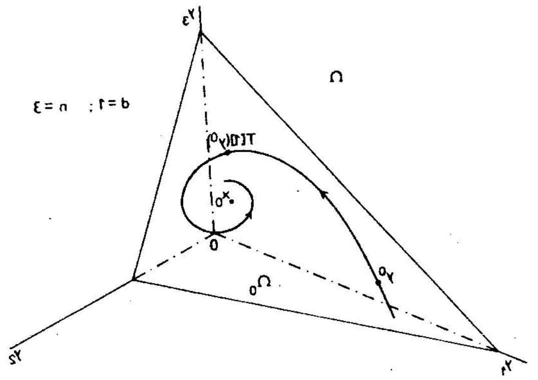

Fig. 1. Effect of mapping T on phase space.

mapping (phase shift) $T[1]$: $\Omega_0 \to \Omega_0$ of this set onto itself, which to any point $y^0 \in \Omega_0$ will assign a point $y(1) \in \Omega_0$, where $y(t)$ is such a solution of (3.2) that $y(0) = y^0$; see Figure 1.

Since T [1] is continuous, there must necessarily be (see [3] T.2.2.4) at least one fixed point $x_1 \in \Omega_0$ of the mapping $T[1]$, i.e. such a point that $x_1 = T[1](x_1)$. This means that for the solution y starting at time $t_0 = 0$ from point x_1 it holds that

$$y(0) = x_1 = T[1](x_1) = y(1),$$

or, in other words, that this solution is periodic with the smallest period not exceeding 1. Similarly, we can consider the mapping T [2] and show thus the existence of point x_2, from which the solution with a period not exceeding $\frac{1}{2}$ starts. From the group property of mapping T it follows that

$$x_2 = T\left[\frac{1}{2}\right](x_2) = T\left[\frac{1}{2}\right](T\left[\frac{1}{2}\right](x_2)) = T\left[\frac{1}{2} + \frac{1}{2}\right](x_2) = T[1](x_2),$$

i.e. x_2 is also a fixed point of $T[1]$. In this way a sequence of fixed points $\{x_1, x_2, x_4, x_8, ...\}$ of the mapping T [1] can be obtained from which a subsequence convergent to the point $x_0 \in \Omega_0$ can be choosen. Since the solution starting from point x_{2^n} is periodic with the smallest period less than or equal to 2^{-n}, it can be seen that starting from point x_0 the required stationary solution is $y(t) \equiv x_0$.

A detailed analysis which, however, is beyond the scope of this work, can be used to show that among the possible steady states there is only one state which is globally asymptotically stable on Ω_0 (in the Lyapunov sense). This state can be identified with the state of thermodynamic equilibrium.

4. USING THE MODEL OF CHEMICAL KINETICS FOR THE COMPUTATION OF EQUILIBRIUM COMPOSITION OF A CHEMICAL SYSTEM

The above knowledge can also be made use of in the computation of an equilibrium composition of homogenous gaseous systems, which is a task equivalent to finding the only globally asymptotically stable solution y^* of system (3.2). Then the following procedure may be choosen for the computations:

a) solving (2.3) at the required temperature $T = T_0$ with an arbitrary initial condition satisfying the element-abundance equations

$$Uy(t_0) = b \tag{4.1}$$

over a "suffieciently long" time interval $\langle t_0, t_1 \rangle$, with the value t_1 being obtained as soon as the solution with an accuracy chosen in advance behaves like a constant with respect to time t. Now we can either write directly $y^* := y(t_1)$, or

b) regard $y(t_1)$ as the first approximation of y^*. The exact value of y^* is then obtained by solving the system of nonlinear algebraic equations

$$AG(T_0, y) = 0 \tag{4.2}$$

for example by the Newton-Raphson iteration method with first approximation $y(t_1)$.

5. DISCUSSION OF RESULTS

The above mentioned method was used to compute equilibrium composition for the SF_6 system with the components SF, S_2, F_2, S, S^+, F, F^-, e^- at a temperature of 10 000 K. The computations were carried out at a constant volume corresponding to the initial pressure of 1 MPa. Rate constants were obtained from [4].

The results were compared with the equilibrium composition of this system as computed by the method of minimizing the Gibbs function (determined on the basis of [5]). It turned out that to obtain an agreement in the order of per cent it was not necessary in this case to solve the system (4.2). A typical result can be found in the Table 1.

Table 1

The composition of the SF_6 system at temperature 10 000 K

	y^0	y^*	y^g
SF	0.1	4.3282−4	4.3288−4
S_2	0.1	8.0188−5	8.0389−5
F_2	0.4	3.9617−5	3.9517−5
S	0.4	8.8790−1	8.8746−1
S^+	0.3	1.1151−1	1.1194−1
F	5.0	5.9981+0	5.9982+0
F^-	0.1	1.3235−3	1.3243−3
e^-	0.2	1.1016−1	1.1062−1

y^0 - the vector of randomly chosen initial composition satisfying element-abundance equations (4.1), y^* - the equilibrium composition determined as given in a) of the method presented, y^g - the equilibrium composition as determined on the basis of [5] by the method of minimizing the Gibbs function, $a \pm b$ denotes $a \times 10^{\pm b}$. The composition is given in moles per one mole of source compound.

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ОБ ОДНОЙ МОДЕЛИ ХИМИЧЕСКОЙ КИНЕТИКИ

Работа описывает некоторые свойства математической модели химической кинетики газов с упором на ее соответствие. Показано, что большинство качественных свойств модели можно вывести из уравнений модели без их непосредственного решения. Внимание уделено также применению вычислительных методов и возможность применения модели при вычислении равновесного состава химической системы.