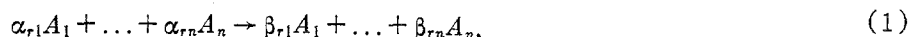


It is well known [1-4] that the rate constants of different elementary reactions are often interdependent. Relationships determined by the principle of detailed balancing exist between them [1-5] when microreversibility is valid and by the generalizations of that principle [5-8] when it is not (for example, in magnetic fields, during macroscopic rotations, etc.). Nevertheless, in practice the verification of consistency in the kinetic constants for complicated transformation schemes involves a certain amount of technical difficulty.

The problem of consistency in the kinetic constants arises especially sharply in connection with the creation of kinetic data banks intended for widespread use [9-11]. Here it is impossible to avoid solving that problem or examining each multistage reaction separately, without leaving the user with the burden of finding a way to carry out this analysis. Thus, the methods for establishing the consistency of these constants, along with the conditions under which this consistency may fail, must be analyzed and suitable algorithms and programs have to be developed.

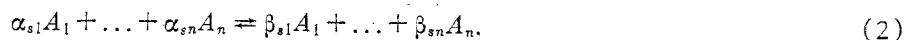
#### RELATIONSHIPS AMONG THE CONSTANTS

In order to describe a complex chemical reaction, one must specify a list of substances and the mechanism of the reaction, i.e., a list of the constituent elementary reactions. We denote the substances by  $A_1, \dots, A_n$ . An elementary reaction is specified by its stoichiometric equation



where  $r$  is the number of the elementary reaction and the stoichiometric coefficients  $\alpha_{ri}$  and  $\beta_{ri}$  are nonnegative whole numbers.

We have written Eq. (1) in a form where different numbers correspond to the forward and reverse reactions. This is convenient for examining systems in the absence of microreversibility. In the other form, the forward and reverse reactions are combined under a single number  $s$ :



Each elementary reaction is associated with a nonnegative intensive [12] quantity  $w_r$  (the reaction rate). The equations of chemical kinetics in a uniform closed chemical system, for example, have the form

$$\dot{N} = V \sum_r \gamma_r w_r. \quad (3)$$

Here  $\gamma_r$  is the stoichiometric vector of the  $r$ -th reaction ( $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$ ),  $V$  is the volume of the system,  $N$  is the composition vector, and  $N_i$  is the amount of  $A_i$  (mole).

The elementary reactions (2) are written down in pairs with the aid of the quantity  $w_s = w_s^+ - w_s^-$ , where the superscripts  $+$  and  $-$  denote quantities that refer to the forward and reverse reactions, respectively. The form of the equations is analogous to Eq. (3) with the indices  $r$  replaced by  $s$ . These equations for heterogeneous and nonuniform systems are given elsewhere [4-6]. It is important to emphasize that, although the reaction rate is most often calculated using equations for closed mixed systems, the quantities  $w_r$  at every point in space are determined by the state of the medium at that point. These functions of state do not change when the system is opened, so that the relationships among them should also be preserved.

$w_r$  can be obtained as a function of other intensive variables (the temperature  $T$  and concentrations  $c_i$  or chemical potentials  $\mu_i$ ) by two approaches. The results of these two approaches are not necessarily different, but the methods for verifying consistency depend substantially on which approach is chosen.

In the approach that proceeds from a kinetic law (most often the law of mass action) one starts by writing down formulas for the  $w_r(c, T)$ , which include a set of parameters, the "constants". Then consistency conditions are imposed on these parameters. If, on the other hand, one proceeds from thermodynamics, then it is possible at once to write down a wide class of consistent formulas which can be made more specific. For the law of mass action one sets

$$w_r = k_r(T) \prod_i c_i^{\alpha_{ri}}, \quad (4)$$

where  $c_i$  is the concentration of  $A_i$ .

In this case the principle of detailed balancing can be formulated as follows: for any  $T$  there exists a point  $c^*$  with positive coordinates  $c_i^* > 0$  such that at this point each forward reaction is balanced by its reverse

$$w_s^+(T, c^*) = w_s^-(T, c^*) \quad (5)$$

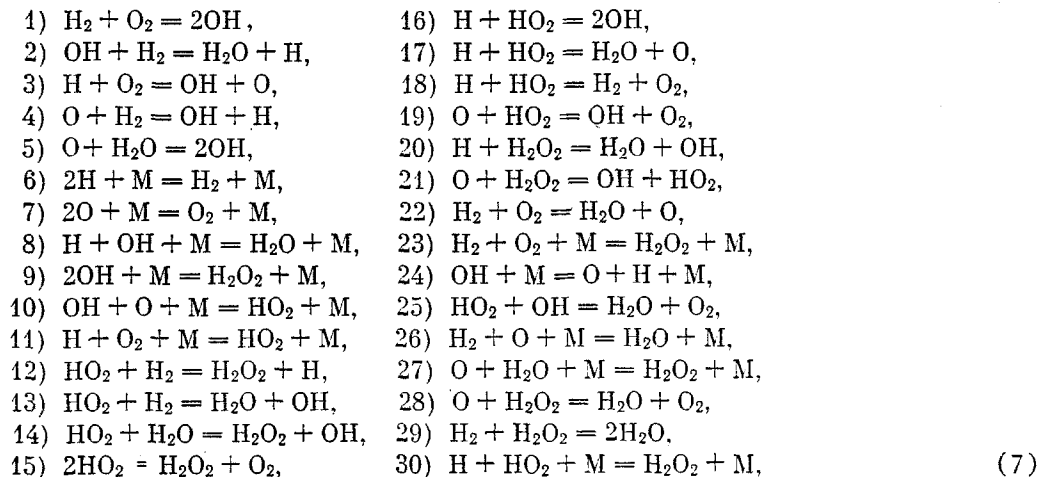
for all  $s$ . (Here the form (2) with a pairwise combination of reactions is more convenient. If there are no reverse reactions in (1) for the transformation to Eq. (2), then they can be written down with constants equal to zero.) This involves a number of important dynamic consequences: in particular, every equilibrium point is a point at which detailed balancing occurs [3, 4].

The condition that a point  $c^*$  exist can be written in the form of a linear relationship among the logarithms of the constants. It is sufficient to take the logarithm and write down the condition for solvability of the resulting system of linear equations in  $\ln c^*$  [4, 6].

In the following discussion we shall use two examples: the simplest reversible cycle



and the most general mechanism for the combustion of an  $H_2 + O_2$  mixture:



where  $M$  is a third particle. The cycle (6) has been studied in detail as a model of the isomerization of the butenes [13]. The rate constants for reactions (7) have been collected by Dimitrov [14-16].

The condition for the existence of a detailed balancing point  $c^*$  for the system (6) takes the form

$$\ln k_1 + \ln k_2 + \ln k_3 = \ln k_{-1} + \ln k_{-2} + \ln k_{-3} \quad (8)$$

or  $k_1 k_2 k_3 = k_{-1} k_{-2} k_{-3}$ .

For the mechanism (7) there are 24 relations analogous to Eq. (8) [24 = 30 reactions - 6 independent = 30 reactions - (8 substances - 2 linear balance equations)]:

$$\begin{aligned}
 K_{p1} &= K_{p3}K_{p4}, & K_{p2}K_{p5} &= K_{p4}, & K_{p4}K_{p6} &= K_{p3}K_{p7}, & K_{p12} &= K_{p2}K_{p14}, \\
 K_{p3}K_{p4}K_{p9} &= K_{p2}K_{p11}K_{p14}, & K_{p11} &= K_{p3}K_{p10}, & K_{p13}K_{p11} &= K_{p2}K_{p3}^2K_{p7}, \\
 K_{p15}K_{p11}K_{p4} &= K_{p2}K_{p14}K_{p7}K_{p3}, & K_{p16}K_{p11} &= K_{p3}^2K_{p7}, & K_{p24}K_{p3}K_{p7} &= 1, \\
 K_{p21}K_{p14}K_{p2} &= K_{p4}, & K_{p17}K_{p11}K_{p4} &= K_{p2}K_{p3}^2K_{p7}, & K_{p19}K_{p11} &= K_{p3}\sqrt{K_{p7}}, \\
 K_{p20}K_{p14}K_{p11} &= K_{p3}^2K_{p7}, & K_{p18}K_{p11}K_{p4} &= K_{p3}K_{p7}, & K_{p22} &= K_{p2}K_{p3}, \\
 K_{p23} &= K_{p14}K_{p11}K_{p2}\sqrt{K_{p7}}, & K_{p25}K_{p11}K_{p4} &= K_{p2}K_{p3}K_{p7}, & K_{p26} &= K_{p2}K_{p3}K_{p7}, \\
 K_{p27}K_{p3} &= K_{p14}K_{p11}, & K_{p28}K_{p14}K_{p11} &= K_{p3}K_{p7}, & K_{p30}K_{p4} &= K_{p2}K_{p14}K_{p3}K_{p7}, \\
 K_{p29}K_{p11}K_{p14} &= K_{p2}K_{p3}^2K_{p7}.
 \end{aligned} \tag{9}$$

In the thermodynamic approach, the  $w_r$  can immediately be written down in the special form [5, 6, 17, 18]

$$w_r = \varphi_r \exp\left(\sum_i \alpha_{ri} \mu_i / RT\right), \tag{10}$$

where  $\varphi_r$  is a new nonnegative intensive quantity. Representing the rate of an elementary reaction in terms of this new quantity and the chemical potentials  $\mu_i$  introduces no new restrictions except that, because of the logarithmic singularity of  $\mu_i$  when  $c_i \rightarrow 0$  and  $\alpha_{ri} \neq 0$ , the exponential in Eq. (10) and, thus,  $w_r$  approach zero. (The rate of consumption of the material approaches zero when its concentration is reduced to zero.)

The principle of detailed balancing in this case becomes the identity

$$\varphi_s^+ = \varphi_s^- (= \varphi_s). \tag{11}$$

When microreversibility exists this identity is assumed to be satisfied in all states.

The advantage of this approach is its automatic transferability to nonideal systems, where the ideal expression for the chemical potentials

$$\mu_i = RT \ln c_i + \mu_{i0} \tag{12}$$

can no longer be used and the law of mass action may not be valid. The disadvantage (more appropriately, the imperfection) is the absence of rules for constructing the functions  $\varphi_r(T, c)$  or  $\varphi_r(T, \mu)$ .

Assuming that  $\varphi_r$  is a function of only one variable (T) and using the principle of detailed balancing in the form (11), we arrive at the Marcelin-de Donde kinetic law [19-20]:

$$w_s = w_s^+ - w_s^- = \varphi_s(T) \left[ \exp\left(\sum_i \alpha_{ri} \mu_i / RT\right) - \exp\left(\sum_i \beta_{ri} \mu_i / RT\right) \right]. \tag{13}$$

This simplification, however, is still unrealistic and contradicts the expressions obtained for a number of nonideal systems in the theory of absolute reaction rates [19-21]. (Of course, neither Eq. (10) nor Eq. (11) can contradict this theory.) In general, the  $\varphi_r$  must depend on  $c$  (or  $\mu$ ).

There is an intermediate approach in which the rates of the forward reactions are determined from the law of mass action (4), and the formula

$$w_s^- = w_s^+ \exp\left(\sum_i \gamma_{si} \mu_i / RT\right) = w_s^+ \exp(A_s / RT), \tag{14}$$

where  $A_s = \sum_i \gamma_{si} \mu_i$  is the affinity, is used for the reverse reactions [22]. It can, in principle, be used without contradiction for ideal as well as nonideal systems, although in the latter case it is difficult to justify using the law of mass action for the forward reactions since it will not be satisfied for the reverse reactions. Equation (14) contains the principle of detailed balancing (11) and using the law of mass action for the forward reactions can be regarded as a method for constructing the  $\varphi_s$ .

For ideal systems Eq. (14) becomes the equation

$$k_s^+ / k_s^- = K_{ps}, \tag{15}$$

where the ratio of the kinetic constants is on the left and the equilibrium constant calculated on the basis of thermodynamic data is on the right. In the absence of microreversibility for multistage reactions, Eq. (15) may obviously fail. Only the condition that the thermodynamic equilibrium point is unmoved for the kinetic equations remains unconditionally true and the right hand side of Eq. (3) goes to zero for that point.

In the absence of microreversibility, when detailed balancing can no longer be used (for example, in magnetic fields), the conditions for consistency among the kinetic parameters have a more general form [8]. They have been obtained from the microscopic condition of unitarity (conservation of the total probability) and are written as an equality between different combinations of kinetic factors  $\varphi_r$ . These can have many consequences, ranging from failure of uniqueness to relaxation oscillations.

In order to demonstrate the qualitative consequences to which an inconsistency in the rate constants may lead even in the simplest cases, let us examine the mechanism of reaction (6) in a closed system. When detailed balancing exists in this system and imposes the limitations (8) on the rate constants, the equilibrium point is a stable node and the approach to equilibrium proceeds without damped oscillations.

Let us write Eq. (3) in the standard way for the system (6) under isothermal conditions and solve the problem for the eigenvalues of this system. We find (without using the consistency condition (8)) that

$$2\lambda_{+,-} = -\sum_r k_r \pm \sqrt{D}, \quad (16)$$

where

$$D = \left(\sum_r k_r\right)^2 - 4(k_3 - k_{-1})(k_1 - k_{-2}) - 4(k_1 + k_3 + k_{-3})(k_2 + k_{-2} + k_{-1}). \quad (17)$$

The equilibrium of the system is stable for arbitrary  $k_r$ , since  $D \leq \left(\sum_r k_r\right)^2$ . The requirement that it be a node, however, is satisfied only for  $D \geq 0$ ; otherwise the equilibrium would be a stable focus. The condition (8) implies that  $D \geq 0$ ; however, even small violations of (8) can lead to a change in the sign of the inequality, so that  $D < 0$ . In order to illustrate the mutual positions of the region  $D \geq 0$  and the manifold of consistent sets of constants, let us set  $k_1 = k_2 = \nu$ ,  $k_3 = k_{-2} = \mu$ , and  $k_{-1} = k_{-3} = \tau$ . After substituting the new variables in the formula for the discriminant (17), we obtain  $D = 4(\tau - \mu)(\nu - \mu)$  and, in place of Eq. (8),  $\tau = \nu$ . Figure 1 shows the intersection of the regions where  $D$  has a constant sign and the consistency manifold in the plane  $\mu = \mu_0$ . It is easy to see that in an arbitrarily small neighborhood of the point  $\tau = \mu_0 = \nu$ , points corresponding to sets of constants with focal-type equilibria do exist.

This example shows that even a small deviation of this set of rate constants for the elementary reactions from the consistency manifold can lead to false qualitative effects. Other examples of this sort can be found in [23].

#### CONSISTENCY OF KINETIC AND THERMODYNAMIC DATA

The data used to construct kinetic models can be divided into two large groups: thermodynamic and inherently kinetic. The two are obtained by different methods, ranging from direct experiment to semiempirical or theoretical calculations. The consistency problem can be regarded as intrinsic to both groups of data or as a question of consistency between kinetic and thermodynamic data.

The condition that the kinetic data should be internally consistent makes it possible, in particular, to narrow the arbitrariness in the determination of the constants. Let us consider the example of a system obtained from the law of mass action with an Arrhenius temperature dependence for the rate constants,

$$k_s^\pm(T) = A_s^\pm T^{l_s^\pm} \exp(-E_s^\pm/RT). \quad (18)$$

We shall use the principle of detailed balancing (under the assumption of microreversibility) as a basis for establishing consistency. The consistency condition for each reaction mechanism is written as a system of linear homogeneous equations in  $k_s^\pm$ , which must be satisfied for any  $T$  [4, 6] (for example, the identities (8) and (9)).

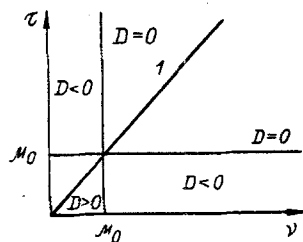


Fig. 1

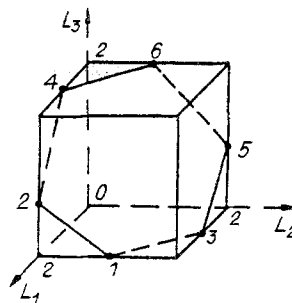


Fig. 2

Fig. 1. The intersection of the manifold of consistent sets of constants for the example of reaction (6) in the plane  $\mu = \mu_0$ . 1 denotes the consistency condition.

Fig. 2. The consistency polyhedron for the reaction mechanism (6).

The primary stages of the consistency algorithm are as follows: according to the principle of detailed balancing, a point  $c^*$  where Eq. (5) is satisfied must exist. Using Eq. (4) and (5), we can write

$$k_r^+ \prod_i c_i^{\alpha_{ri}} = k_r^- \prod_i c_i^{\beta_{ri}}. \quad (19)$$

Taking the logarithm of this expression and using Eq. (15), we obtain

$$\ln K_{pr} = \sum_i (\beta_{ri} - \alpha_{ri}) \ln c_i^*$$

or, in matrix form,

$$\ln K_p = \Gamma \ln c^*, \quad (20)$$

where  $\Gamma$  is the stoichiometric matrix. Since as long as  $c^*$  covers the set of positive vectors,  $\ln c^*$  will cover all of  $n$ -dimensional space, the only restriction on  $K_p$  imposed by the principle of detailed balancing is

$$\ln K_p \in \text{Im } \Gamma. \quad (21)$$

In order to write this restriction in explicit form, we must find all linearly independent solutions of the system of equations

$$y\Gamma = 0 \quad (22)$$

(where  $y$  is a row vector). Let  $y^1, \dots, y^q$  be the solutions of Eq. (22); then the restriction (21) takes the form

$$y^j \ln K_p = 0, \quad j = \overline{1, q}. \quad (23)$$

For the Arrhenius dependence (18), Eqs. (23) reduce to three systems of linear homogeneous equations with respect to  $\{E_S^\pm\}$ ,  $\{\ell_S^\pm\}$ , and  $\{\ln A_S^\pm\}$ . These systems determine linear subspaces within the spaces with coordinates  $\{E_S^\pm\}$ ,  $\{\ell_S^\pm\}$ , and  $\{A_S^\pm\}$ . We shall denote these subspaces by  $W_E$ ,  $W_\ell$ , and  $W_{\ln A}$ , respectively.

The parameters  $E_S^\pm$ ,  $\ell_S^\pm$ , and  $A_S^\pm$  are always given, with a certain amount of error, in the form of an interval. Thus, the vectors of the parameters  $E$ ,  $\ell$ , and  $A$  belong to multidimensional intervals (rectangular parallelepipeds). Not all of these intervals satisfy the restrictions, but only those which lie within the region where they intersect  $W_E$ ,  $W_\ell$ , or  $W_{\ln A}$ , respectively. These intersections are the consistency polyhedra for the kinetic parameters.

The problem of internal consistency (self-consistency) of the kinetic data involves describing these consistency polyhedra. The simplest approach is to find all their vertices.

TABLE 1

Reaction No.	$A_{ps}$	
	from Table 4 of [16]	from the consistency condition
1	2.97—337,5	13—39,4
5	7.5—16	4,94—25
9	$6.4 \cdot 10^{-6}$ — $8.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$ — $2.4 \cdot 10^{-4}$
8	$0.3 \cdot 10^4$ — $10^4$	0,25—3,1
15	13—40	$5 \cdot 10^{-6}$ — $3 \cdot 10^{-3}$
20	4,66—16,25	$2 \cdot 10^{-4}$ —0,083
26	$10^{-7}$ — $10^{-5}$	$3.4 \cdot 10^{-8}$ — $1 \cdot 10^{-6}$
30	$3.2 \cdot 10^{-5}$ — $6 \cdot 10^{-4}$	$1 \cdot 10^{-8}$ — $2 \cdot 10^{-6}$

Let us consider reaction (6). We can rewrite the consistency condition (8) in the form  $\ln K_{p1} + \ln K_{p2} + \ln K_{p3} = 0$ . Let each of the equilibrium constants be localized within the interval  $\ln K_{pi} \in [-1, 1]$ . We now make the coordinate transformation  $L_i = \ln K_{pi} + 1$ . In these coordinates the consistency polyhedron is described by the system of inequalities  $L_i \geq 0$  and  $L_i \leq 2$  together with the equation  $L_1 + L_2 + L_3 = 3$ . This becomes a linear programming problem, if we add a target function. The first vertex is found by the simplex method by introducing a fictitious basis and the target function  $L_1' + L_2' + L_3' \rightarrow \min$ . After determining the first vertex (2, 1, 0), the search for the remaining vertices is carried out by looking over all the allowable (in the sense of the simplex method) substitutions. This procedure terminates after a finite number of steps since the polyhedron has a finite set of vertices (Fig. 2): (2, 1, 0), (2, 0, 1), (0, 2, 1), (1, 2, 0), (1, 0, 2), (0, 1, 2). After transforming to the coordinates  $\ln K_{pi} = L_i - 1$ , we obtain the vertices of the polyhedron in the original coordinates.

A complete list of the vertices of a consistency polyhedron may be cumbersome and inconvenient to use. It is simpler and more customary to work with points or intervals (even one-dimensional). Thus, besides seeking the consistency polyhedron it is desirable to indicate some set of constants lying within it (e.g., the center of gravity of unit masses located at the vertices), as well as an interval circumscribed around the polyhedron. The latter is easily constructed from a description of the vertices: it is sufficient to find the maximum and minimum of each coordinate in the set of vertices. The product of these intervals (from the maximum to the minimum) will be the desired multidimensional interval.

In the example considered previously, the center of gravity of the polyhedron in the coordinates  $\ln K_p$  will be the point (0, 0, 0), while the interval circumscribed around the polyhedron will coincide with the original.

The mutual consistency of the thermodynamic and kinetic data can also be described in terms of constructing a consistency polyhedron. Here the equations for the law of mass action are simple:

$$\ln k_s^+ - k_s^- = \ln K_s, \quad (24)$$

where  $K_s$  is the equilibrium constant calculated on the basis of thermodynamics.

A basis set of reactions is chosen for which the equilibrium constants are specified by an interval. The remaining equilibrium constants are uniquely expressed in terms of the basis constants. Then, if Eq. (24) is satisfied, the kinetic constants are already consistent and no further verification is needed.

For concreteness let the basis reactions be numbered 1, ..., q and the intervals ( $s = 1, q$ ) be specified as

$$\begin{aligned} K_s^0 - \Delta_s &\leq K_s \leq K_s^0 + \Delta_s, \\ k_s^{0\pm} - \Delta_s^{\pm} &\leq k_s^{\pm} \leq k_s^{0\pm} + \Delta_s^{\pm}. \end{aligned} \quad (25)$$

The polyhedron specified by Eqs. (24), the inequalities (25), and the thermodynamic expressions  $K_s$  ( $s > q$ ) as  $K_1, \dots, K_q$ , can be referred to as a polyhedron of mutually consistent thermodynamic and kinetic data. One of the important problems in analyzing the data is to

find the vertices of this polyhedron. Shorter forms of the answer, namely this interval and an interior point for this polyhedron, are important.

Thus, in the course of our examination of the data consistency problem, new objects have appeared: the consistency polyhedra. A description of these polyhedra should be a constituent of all banks of kinetic (more precisely, thermodynamic-kinetic) data. One important question is "should the data be kept in a consistent form or should it be made consistent each time anew when it is delivered for use?" Here there is an important distinction from purely thermodynamic data; namely, the consistency of kinetic parameters depends on the reaction mechanism (the list of stages). Furthermore, inconsistent, but in a certain sense correct, data may exist. (This is discussed below.) Thus, we propose that consistency must be imposed when the data are delivered at the service level and that data banks should contain the appropriate service programs. It is better to accumulate bases of kinetic data in a "raw", inconsistent form.

#### PROBLEM OF INCONSISTENT DATA

We now present some results from an analysis of the consistency problem for the kinetic constants of the specific system (7). Taking the basis constants  $A_{ps}$ , corresponding to Eq. (20) and the numbers of the elementary reactions from Eq. (7) 2, 3, 4, 7, 11, and 14, using Eq. (9) and the kinetic data from [16], we have calculated the remaining  $A_{ps}$  for  $s = 1, \dots, 30$  with  $s \neq 2, 3, 4, 7, 11, 14$ . Part of the results are listed in the Table. A comparison of the computed and published data indicates that for  $s = 1, 5, 9$ , and 26 the ranges of variation of the constants derived from Eq. (9) and the Table [16] have a nonempty intersection, while for  $s = 8, 15, 20$ , and 30, they do not overlap. This indicates that self-consistency is lacking in part of the kinetic data given in [16].

The traditional approach to using thermodynamic data in the formulation of kinetic models consists of the following: for all  $s$  the rate constant for the reverse elementary reaction  $k_s^-$  is expressed in terms of  $k_s^+$  and the equilibrium constant  $K_s$ . Here half of the kinetic data are lost; the entire block of  $k_s^-$  is unused, but these parameters could be found in independent experiments. In this approach perhaps, in particular, an important manifestation of the inconsistency of the data may be lost in the framework of the model assumptions that are used.

Examples of differences between  $k_s^+/k_s^-$  and  $K_s$  for experimentally determined constants are well known [24, 25]. The reasons may be many: neglect of some intermediate substances and fast reactions, significant deviations from a Maxwell-Boltzmann velocity distribution for the molecules, etc. Identifying inconsistency among the constants is important information on the system (assuming that the initial data are sound).

Procedures for establishing consistency make it possible to reduce arbitrariness in the initial data and to construct a physically correct kinetic model, as well as to identify cases of inconsistency. The answer to the question of what causes this inconsistency (the physicochemical peculiarities of the system or inaccuracy in evaluating the errors of the methods being used to obtain the constants) must be found in each specific case from additional considerations.

#### LITERATURE CITED

1. E. M. Lifshits and A. P. Pitaevskii, Physical Kinetics [in Russian], Nauka, Moscow (1980).
2. L. Meitis, Introduction to a Course in Chemical Equilibrium and Kinetics [Russian translation], Mir, Moscow (1984).
3. A. I. Vol'pert and S. I. Khudyaev, Analysis in Classes of Discontinuous Functions and Equations of Mathematical Physics [in Russian], Nauka, Moscow (1975).
4. G. S. Yablonskii, V. I. Bykov, and A. N. Gorban', Kinetic Models of Catalytic Reactions [in Russian], Nauka, Novosibirsk (1983).
5. A. N. Gorban', Bypassing Equilibrium. The Equations of Chemical Kinetics and Their Thermodynamic Analysis [in Russian], Nauka, Novosibirsk (1984).
6. A. N. Gorban', V. I. Bykov, and G. S. Yablonskii, Essays on Chemical Relaxation [in Russian], Nauka, Novosibirsk (1986).
7. E. C. G. Stuckelberg, Helv. Phys. Acta, 37, 521 (1964).
8. A. N. Gorban', The Thermodynamics of Irreversible Processes [in Russian], Nauka, Moscow (1987).

9. V. S. Babkin, V. I. Babushok, Yu. P. Drobyshev, et al., Automated Bank of Kinetic Information [in Russian], Preprint, Computer Center, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk (1987).
10. V. I. Kondrat'ev, A. I. Poroikova, and E. T. Denisov, Combustion and Explosions [in Russian], Nauka, Moscow (1972).
11. V. P. Varakin, V. G. Gromov, S. A. Losev, et al., Scientific-Research Information System "AVOGADRO" for Automatic Support of Physico-Chemical Gas Dynamics [in Russian], Deposited in VINITI, No. 2510-85.
12. M. I. Temkin, Theoretical questions in the kinetics of catalytic reactions. in: Material from the International Symp. on the Kinetics of Catalytic Reactions [in Russian], IOKh Akad. Nauk SSSR, Moscow (1982); Chernogolovka (1984).
13. J. Wei and C. Prater, Catalysis. Semifunctional Catalysts and Complex Reactions [Russian translation], Mir, Moscow (1965).
14. V. I. Golovichev and V. I. Dimitrov, Fiz. Goren. Vzryva 8, No. 1, p. 129 (1972).
15. V. I. Dimitrov, React. Kinet. Catal. Lett. 7, No. 1, p. 81 (1977).
16. V. I. Dimitrov, Simple Kinetics [in Russian], Nauka, Novosibirsk (1982).
17. I. F. Bakhareva, Nonlinear Nonequilibrium Thermodynamics [in Russian], Izd. Sarat. Univ., Saratov (1976).
18. O. K. Davtyan, Kinetics and Catalysis of Chemical and Electronic Processes [in Russian], Izd. Akad. Nauk ArmSSR, Erevan (1984).
19. P. van Rysselberg, J. Chem. Phys. 29, No. 3, p. 640 (1958).
20. M. Feinberg, Arch. Rat. Mech. Anal. 46, No. 1, p. 1 (1972).
21. T. A. Akramov, V. I. Bykov, and G. S. Yablonskii, Mathematical Problems in Chemistry [in Russian], Computer Center, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk (1975).
22. T. de Donde and P. van Rysselberg, The Thermodynamic Theory of Affinity [Russian translation], Metallurgiya, Moscow (1984).
23. H. G. Othmer, Chem. Eng. Sci. 36, No. 9, p. 993 (1976).
24. S. W. Benson, F. R. Cruickshank, and R. Shaw, Intern. J. Chem. Kinet., 1, No. 1, p. 29 (1969).
25. B. V. Alekseev, Mathematical Kinetics of Reacting Gases [in Russian], Nauka, Moscow (1982).

#### ELECTRICAL CONTACT PROCEDURE FOR RECORDING $x$ , $t$ -DIAGRAMS

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In performing different gas dynamic studies the problem often arises of measuring the free surface velocity of projected bodies or the shock and detonation wave (SW, DW) velocities. The electrical contact procedure is the most used method for these purposes. With its use a record is made of the instant of closing wire or foil contacts with any surface (body, screen). The value of velocity sought is found as a result of treating  $x$ ,  $t$ -diagrams of movement for the surface or wave being studied. In this work a short description is given of a modified electrical contact procedure developed by the authors for recording detailed  $x$ ,  $t$ -diagrams using a miniature multicontact sensor.

Normally in measuring devices use is made of quite massive tubular sensors with screens protecting the contacts from premature closure by an air SW. Sensors of different levels are placed in different locations beneath the surface of the flying body (e.g., a plate), and therefore the measurement accuracy is affected by the shape of the surface closing the contacts (e.g., deviation of the plate surface from being flat in the measurement zone). Oscillation of the amplitude and duration of electric pulse fronts obtained with closure of contacts also reduces measurement accuracy.

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