

## PHENOMENOLOGICAL DERIVATION OF THE MASS ACTION LAW OF HOMOGENEOUS CHEMICAL KINETICS

I.SAMOHÝL and A.MALIJEVSKÝ

*Department of Physical Chemistry,  
Institute of Chemical Technology, 166 28 Prague 6*

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From the definition of an equilibrium and the phenomenological constitutive equation for the reaction rate in fluids approximated by a polynomial, expressions are derived for the rates of chemical transformations which have the form of the mass action law of homogeneous kinetics in terms of activities or concentrations. These expressions derived for a multicomponent system with more reactions include back reactions, autocatalysis, and catalysis; their practical construction is described in two ways and exemplified. Empirical mass action laws and expressions for the reaction rate following from irreversible thermodynamics are discussed.

The empirical law of mass action in homogeneous chemical kinetics is traditionally motivated by molecular concepts. Their phenomenological reasoning must be sought on the basis of thermomechanical continuum theories, which do not make use of the molecular concept. Classical irreversible thermodynamics (*e.g.*, ref.<sup>1</sup>, chapter 2.5) does not lead to the mass action law; in the linear region of this theory we obtain correct results only very close to the equilibrium. However, we shall show that the mass action law follows as an approximation from phenomenological equations that can be derived by the methods of nonlinear thermomechanics (rational thermodynamics)<sup>2</sup> applied to a special material model<sup>3,4</sup>. As to this model (a reacting fluid mixture with linear transport properties), it can be assumed that it describes well the material discussed, as a rule, in connexion with the mass action law. This procedure was formulated elsewhere<sup>5</sup> only by examples. It is the aim of the present work to gain general formulas for a multicomponent mixture with more reactions. At first, we shall formulate three starting assumptions with the aid of rational thermodynamics, derive a general expression for the reaction rate, and show two alternatives of its practical construction. This process will be exemplified and the relation of the results to empirical mass action laws and linear expressions for the reaction rate which follow from irreversible thermodynamics will be mentioned in the discussion.

### *Starting Assumptions*

We shall consider a fluid mixture of  $n$  constituents (substances), among which chemi-

cal reactions proceed:

$$\sum_{\alpha=1}^n p_{i\alpha} B_{\alpha} = 0, \quad (1)$$

where  $B_{\alpha}$  stands for the constituent  $\alpha$  and  $p_{i\alpha}$  is its stoichiometrical coefficient in the  $i$ -th reaction. In further text, we shall assume that Eq. (1) represents a set of all possible reactions for which  $p_{i\alpha}$  are whole numbers ( $p_{i\alpha} > 0$  for products,  $p_{i\alpha} < 0$  for starting substances,  $p_{i\alpha} = 0$  for nonreacting substances in the  $i$ -th reaction; the latter condition is fulfilled in any reaction for substances that do not react chemically) and we have

$$\sum_{\alpha=1}^n p_{i\alpha} H(p_{i\alpha}) \geq \sum_{\alpha=1}^n p_{i\alpha} [H(p_{i\alpha}) - 1] \quad (2)$$

where  $H$  denotes Heaviside function ( $H(x) = 1$  for  $x > 0$ ,  $H(x) = 0$  for  $x \leq 0$ ). Such a restriction is possible, since it follows from stoichiometry that for a phenomenological description of chemical changes even an arbitrary system of  $r$  independent chemical reactions is sufficient to choose these  $r$  independent reactions from an infinite set (1).

In rational thermodynamics, the chemical changes are expressed by a reaction rate vector,  $\mathbf{J}$ , which can be equivalently represented in two ways<sup>2,4,6</sup>: Either by its components  $J_{\alpha}$  ( $\alpha = 1, 2, \dots, n$ ), which represent the rates of chemical changes of individual substances (in mol of substance  $\alpha$  per time unit in a unit volume), or by its components  $J_i$  ( $i = 1, 2, \dots, r$ ), which represent the rates of  $r$  independent chemical reactions chosen in the description of chemical changes. These quantities are mutually connected by the relations (ref.<sup>4</sup>, Eqs (37), (40), (43), (46), and (47)):

$$J_i = \sum_{\alpha=1}^n \sum_{j=1}^r J_{\alpha} p_{j\alpha} g_{ji}, \quad (3)$$

where  $g_{ji}$  are elements of the matrix  $\|\mathbf{g}_{ji}\| = \|\mathbf{g}^{ji}\|^{-1}$  and  $\mathbf{g}^{ji} = \sum_{\alpha=1}^n p_{j\alpha} p_{i\alpha}$  ( $i, j = 1, 2, \dots, r$ ); further

$$J_{\alpha} = \sum_{i=1}^r J_i p_{i\alpha}, \quad \alpha = 1, 2, \dots, n; \quad \sum_{\alpha=1}^n J_{\alpha} M_{\alpha} = 0. \quad (4), (5)$$

It follows from the last formula representing the mass conservation law in chemical conversions ( $M_{\alpha}$  are molecular masses of species  $B_{\alpha}$ ) that only  $n - 1$  quantities  $J_{\alpha}$  are independent. Substances which are not chemically converted have, of course,  $J_{\alpha}$  identically equal to zero.

From rational thermodynamics of a reacting fluid mixture with linear transport properties (*i.e.*, with linear laws of viscosity, heat conduction, and diffusion)<sup>3,4</sup>

it follows that the reaction rate  $J$  depends in such a material only on the temperature,  $T$ , and molar concentrations of all mixture constituents,  $\mathbf{C} = (c_1, c_2, \dots, c_n)$  (ref.<sup>3</sup>, Eq. (40) in specific variables)

$$J = J(T, \mathbf{c}). \quad (6)$$

We note that the independent variables in this constitutive equation are only positive<sup>3,4</sup> and that this equation applies for all processes, *e.g.*, locally in nonequilibrium processes of an open system. In chemical kinetics, we often envisage a special case of a closed homogeneous system, in which  $J_i$  represent the time changes of the degrees of conversion of independent reactions<sup>2</sup>. In the general case, the degrees of conversion cannot be introduced and  $J_i$  is obtained from Eq. (3) with the aid of  $n - 1$  independent components  $J_\alpha$ . Similarly the thermodynamic quantities such as molar chemical potential  $\mu = (\mu_1, \mu_2, \dots, \mu_n)$ , are also functions of  $T$  and  $\mathbf{C}$  in all processes (the validity of the local equilibrium principle in such a material has been proved)<sup>3,4</sup>. Assuming the existence of an inversion of the latter relations with respect to the concentrations and using (6) we obtain the dependence

$$J = J(T, \mu). \quad (7)$$

We define the activities of the mixture constituents  $a_\alpha = a_\alpha(T, \mathbf{c})$  as

$$\mu_\alpha = \mu_\alpha^0 + RT \ln a_\alpha, \quad \alpha = 1, 2, \dots, n, \quad (8)$$

where  $\mu_\alpha^0$  is the chemical potential of substance  $\alpha$  in a chosen standard state. Further we shall restrict ourselves to standard states that depend only on the temperature  $T$  (and not on the concentrations  $\mathbf{c}$ ), *i.e.*,  $\mu_\alpha^0 = \mu_\alpha^0(T)$  are chosen functions of the temperature for all mixture constituents  $\alpha = 1, 2, \dots, n$ .

By introducing Eq. (8) into (7) we obtain the first starting assumption of the present work: The reaction rate  $J$  depends only on the temperature  $T$  and on the activities  $\mathbf{a} = (a_1, a_2, \dots, a_n)$  in all processes in this material:

$$J = J(T, \mathbf{a}). \quad (9)$$

The independent variables are again positive quantities; the functional form of Eq. (9) depends, of course, now on the choice of the standard state.

For any reaction of the type (1) we now define the following polynomial in activities  $\mathbf{a}$ :

$$R_i(T, \mathbf{a}) = \prod_{\alpha=1}^n a_\alpha^{p_{i\alpha} H(p_{i\alpha})} - K_i(T) \prod_{\alpha=1}^n a_\alpha^{p_{i\alpha} [H(p_{i\alpha}) - 1]}, \quad (10)$$

where  $K_i$ , the equilibrium constant of the  $i$ -th reaction, is defined by the relation

$$-RT \ln K_i = \sum_{\alpha=1}^n p_{i\alpha} \mu_{\alpha}^0 \quad (11)$$

The equilibrium constants are positive quantities dependent on the choice of the standard states and therefore only on the temperature  $T$ . It follows from the definition (11) that the knowledge of only  $r$  equilibrium constants of some system of independent reactions from (1) is sufficient to determine all others.

We shall call the affinity  $A_i$  of  $i$ -th reaction the following quantity:

$$A_i = \sum_{\alpha=1}^n p_{i\alpha} \mu_{\alpha} \quad (12)$$

(this definition<sup>4</sup> differs from the classical one by the sign).

An equilibrium is defined in rational thermodynamics as a certain class from all possible processes<sup>2</sup>. In the case if chemical changes in our fluid mixture, a part of this definition is the condition of zero affinities of independent reactions chosen to describe the chemical changes<sup>4</sup> (this implies obviously that the affinities of all other reactions are also equal to zero). By combining Eqs (12) and (7) it is possible to express  $\mathbf{J}$  as a function of the affinities of independent chemical reactions  $\mathbf{A} = (A_1, A_2, \dots, A_r)$  (Eq. (53) in ref.<sup>4</sup>). With the assumption of continuity of such a function and with the use of the inequality (Eq. (52) in ref.<sup>4</sup>)

$$-\mathbf{J} \cdot \mathbf{A} \geq 0, \quad (13)$$

which implies that the entropy production in chemical conversions is nonnegative, it can be proved<sup>4</sup> that the reaction rate is equal to zero ( $\mathbf{J} = 0$ ) if the affinities are equal to zero ( $\mathbf{A} = 0$ ). As follows from Eqs (8), (10)–(12), (this definition of equilibrium,  $\mathbf{A} = 0$ , is equivalent to setting all polynomials  $R_i$  equal to zero.

The second starting postulate of the present work can hence be formulated as follows: In the equilibrium (defined by setting the affinities of  $r$  independent reactions equal to zero) we have for all reactions (1)

$$R_i(T, \mathbf{a}) = 0 \quad (14)$$

and the rates of chemical conversions are equal to zero

$$\mathbf{J} = 0. \quad (15)$$

Eq. (14) suggests, with respect to (10), the known relations for the equilibrium constants connecting the equilibrium activity values.

The rational thermodynamical concept of an equilibrium as a defined special case among all possible cases leads to the hypothesis that the second starting postulate (14), (15) restricts in some way the form of the function (9), which applies for all processes, hence also in the equilibrium. We shall derive such a restriction assuming that the function (9) can be approximated by a polynomial of a sufficiently high degree in  $\mathbf{a}$  (this is always possible for continuous functions according to the Weierstrass theorem).

Our third starting postulate will hence be: The reaction rates  $\mathbf{J}$  as functions (9) represent polynomials of the degree  $M$  in  $\mathbf{a}$ :

$$\mathbf{J} = \sum_{\nu} \mathbf{k}_{\nu} \prod_{\alpha=0}^n a_{\alpha}^{\nu_{\alpha}}, \quad \sum_{\alpha=1}^n \nu_{\alpha} \leq M, \quad (16)$$

where  $\nu = (\nu_1, \nu_2, \dots, \nu_n)$  and the coefficients  $\mathbf{k}_{\nu}$  depend only on the temperature and on the choice of the standard state. If  $\mathbf{J}$  is represented by  $J_{\alpha}$  or  $J_i$ , the coefficients  $\mathbf{k}_{\nu}$  are represented by the components  $k_{\nu}^{\alpha}$  or  $k_{\nu}^{(i)}$  ( $i = 1, 2, \dots, r$ ;  $\alpha = 1, 2, \dots, n$ ).

#### Derivation of the Equation for the Reaction Rate

From the starting postulate (14), (15) about equilibrium follows a restriction for the reaction rates (16). For  $n$  given substances and degree  $M$  of the polynomial we shall write all the reactions from (1) for which

$$\sum_{\alpha=1}^n p_{i\alpha} H(p_{i\alpha}) \leq M \quad (17)$$

(this can be achieved by trial and error by choosing whole numbers  $p_{i\alpha}$  in accord with stoichiometry, e.g., with Eqs (44) in ref.<sup>4</sup>). The number,  $l$ , of such reactions is obviously finite (for sufficiently small  $M$  it can be even equal to zero) and the polynomials (10) corresponding to them will be with respect to (2) and (17) of the degree at most  $M$ . By using these polynomials  $R_j$ , Eq. (16) can be written in an equivalent form (in the derivation we shall not express the dependence on  $T$ )

$$\mathbf{J}(\mathbf{a}) = \sum_{j=1}^l R_j(\mathbf{a}) \mathbf{P}_j(\mathbf{a}) + \mathbf{Q}(\mathbf{a}), \quad (18)$$

where  $\mathbf{P}_j$  are general polynomials of the degree  $M - \sum_{\alpha=1}^n p_{j\alpha} H(p_{j\alpha})$  and  $\mathbf{Q}$  is a polynomial of a degree at most  $M$  defined so that neither of its terms can be written in the form of a product of some  $R_j$  with a polynomial (in the opposite case we carry such a term group into the sum in (18)). The vectorial character of  $\mathbf{P}_j$  and  $\mathbf{Q}$  is related to the fact that these polynomials contain the vectors  $\mathbf{k}_{\nu}$ .

If we now introduce the equilibrium conditions (14) and (15) into (18), we obtain

the result

$$Q(\mathbf{a}) = 0, \quad (19)$$

which applies for the equilibrium values of the activities  $\mathbf{a}$  obeying Eqs (10) and (14). With respect to the definition of the polynomial  $Q$ , all its coefficients must be identically equal to zero, *i.e.*, Eq. (19) holds not only in the equilibrium but also generally. The reaction rate  $J$  has therefore for all processes the form

$$J(\mathbf{a}) = \sum_{j=1}^l R_j(\mathbf{a}) P_j(\mathbf{a}). \quad (20)$$

Some of the coefficients of the general polynomials  $P_j$  are possibly superfluous. Indeed, by performing the multiplication of  $P_j$  in (20) we obtain

$$J(\mathbf{a}) = \sum_h k_h R'_h(\mathbf{a}), \quad (21)$$

where the summation concerns all coefficients  $k_h$  of the polynomials  $P_j$  (these are obviously equal to some of the coefficients  $k_i$  in (16)), and where the terms  $R'_h$  represent products of the expression (10) with various powers of activities. If some of them are linearly dependent on one another (which is possible with respect to their form and to the fact that the equilibrium constants contained in  $R'_h$  can be expressed with the use of the equilibrium constants of only  $r$  independent reactions), then the number of independent coefficients  $k_h$  is equal to the number,  $q$ , of linearly independent  $R'_h$  terms, hence other coefficients (and the corresponding dependent  $R'_h$  terms) can be left out from the sum (21). In general, there exist more ways of the choice of dependent  $R'_h$  terms, *i.e.*, more equivalent forms of Eq. (21) with the same number  $q$  of independent coefficients  $k_h$ . Mutually dependent  $R'_h$  terms can be found, *e.g.*, as follows: We note down various products of powers of the activities from all  $R'_h$  terms in Eq. (21) and we join by a line the pairs which compose each of them. Those  $R'_h$  terms which are dependent form in this scheme a cycle and the number of such cycles gives the number of the coefficients  $k_h$  which can be left out. Now we rearrange the reduced expressions (21) with the aid of (10) again into the form (20), where the polynomials  $P_k$  will be no more general and where the sum is restricted to  $m \leq l$  (the equality occurs if all  $R'_h$  terms in (21) are linearly independent, or if we choose from more equivalent notations that for which  $m = l$ ). In the special case of a single independent reaction ( $r = 1$ ) all reactions (1) are multiples of one of them, hence the resulting form can be rearranged so that  $m = 1$ ). Thus, we arrive at the final equation for the reaction rate  $J$  in fluids with linear transport properties in the form

$$J(T, \mathbf{a}) = \sum_{k=1}^m R_k(T, \mathbf{a}) P_k(T, \mathbf{a}). \quad (22)$$

This result has the form of the mass action law in terms of activities involving back reactions, homogeneous autocatalysis, and catalysis (the activities of the mixture constituents which are chemically inert do not occur in  $R_k$ ). We shall denote the independent coefficients  $\mathbf{k}_h$  (or the components of these vectors) contained in the polynomials  $\mathbf{P}_k$  as rate constants, which, similarly as the equilibrium constants  $K_k$  contained in  $R_k$ , depend only on the temperature and on the choice of the standard state.

Besides the method described above, if the value of  $M$  is not too large, we can proceed in constructing Eq. (22) by the following elimination method<sup>5</sup>: We choose  $r$  independent reactions from (1) and write for them the starting assumptions (14). From them we can express  $r$  equilibrium activities (and this uniquely since  $a_\alpha$  and  $K_i$  are positive), which can be introduced into the polynomials (16) with the use of (15). After rearrangement we obtain a polynomial in the remaining  $n-r$  activities which is identically equal to zero for an infinite number of values of such activities that can be in the equilibrium changed independently on one another. In this way we conclude that some of the coefficients  $\mathbf{k}_v$  must be equal to zero, others are connected through the equilibrium constants  $K_i$  of the chosen system of independent reactions. In view of the identical validity of these results (namely, they contain quantities which depend only on the temperature) they can be introduced into the original Eq. (16) and in this way we obtain the result (22) (such a substitution can be performed in several ways reflected again in several equivalent notations of Eq. (22)).

It should be noted that both mentioned modes of constructing Eq. (22) may be carried out with only one component of the vector  $\mathbf{J}$  since the other expressions are similar and differ only by the values of the components of  $\mathbf{k}_h$ .

The rate constants  $\mathbf{k}_h$  in Eq. (21) represent  $k_h^{(i)}$  or  $k_h^{(\alpha)}$  according to whether the reaction rate  $\mathbf{J}$  is represented by  $J_i$  or  $J_\alpha$  ( $i = 1, 2, \dots, r$ ;  $\alpha = 1, 2, \dots, n$ ;  $h = 1, 2, \dots, q$ ). Their name is motivated by the fact that  $k_h^{(i)}$  represent (regardless to their sign) the classical rate constants of back reactions corresponding to  $R_k$  in Eq. (22), and the rate constants of forward reactions can be obtained by multiplying them with the corresponding constants  $K_k$ , so that the familiar property of the rate constants of opposed reactions is preserved.

Since Eqs (3)–(5) apply for both representations of  $\mathbf{J}$ , it follows from the form of Eq. (22) that analogous relations hold also among the rate constants in both representations

$$k_h^{(i)} = \sum_{\alpha=1}^n \sum_{j=1}^r p_{j\alpha} g_{ji} k_h^{(\alpha)}, \quad k_h^{(\alpha)} = \sum_{i=1}^r k_h^{(i)} p_{i\alpha}, \quad (23), (24)$$

$$\sum_{\alpha=1}^n k_h^{(\alpha)} M_\alpha = 0, \quad i = 1, 2, \dots, r; k = 1, 2, \dots, q; \alpha = 1, 2, \dots, n, \quad (25)$$

where  $g_{ji}$  have the same meaning as in Eq. (3).

If the constants  $k_h^{(i)}$  of one system of  $r$  independent reactions are known (e.g., from

experiments in a homogeneous system), the mentioned relations enable to calculate the constants  $k_h^{(a)}$  and on their basis also the constants  $k_h^{(i)}$  of any other system of  $r$  independent reactions (even of such a system which is not contained in (1), *i.e.*, which does not fulfil the relation (2) and whose stoichiometric coefficients are not whole numbers). Besides that, such a system can be used also in constructing Eq. (22), and in the representation of  $\mathbf{J} = (J_1, J_2, \dots, J_n)$  the result (22) will not depend on the system of  $r$  independent reactions chosen for the description of chemical processes (if we disregard the eventual expressing of  $K_k$  with the aid of the equilibrium constants of independent reactions).

The number of vectors  $\mathbf{k}_h$  is in all equivalent notations equal to  $q$ , therefore the representation by independent reactions  $\mathbf{J} = (J_1, J_2, \dots, J_r)$  gives the number,  $qr$ , of the rate constants  $k_h^{(i)}$ , which fully describe the kinetics of the system of  $n$  components and  $r$  independent reactions when  $\mathbf{J}$  is approximated by the polynomial (16) of  $M$ -th degree. This number is not larger than the number of  $q(n-1)$  independent constants  $k_h^{(a)}$  in the representation by the conversion rates  $\mathbf{J} = (J_1, J_2, \dots, J_n)$  because of the relations  $r < n$  and (25).

It should be noted that the inequality (13) imposes a restriction as to the sign of the rate constants.

In practice, the special case of fluids is most often studied that permit the choice of the standard state in such a way that

$$\mathbf{a} = \mathbf{c} \quad (26)$$

(*e.g.*, a mixture of ideal gases). In this case<sup>5</sup> the starting assumption (9) takes the form of (6), the assumption (14) represents equilibrium constants in terms of concentrations, and the assumption (16) a polynomial in concentrations. Hence, the result will be Eq. (22) containing concentrations instead of activities and we arrive at the common mass action law in concentrations.

### ILLUSTRATIVE EXAMPLES

We shall first consider a mixture of three components with a single independent chemical reaction



The system (1) is formed by all whole-numbered multiples of the reaction (27). If we restrict ourselves to  $M \leq 5$ , then this reaction will be the only one from the system (1) obeying the condition (17) (for  $M \leq 2$  no such reaction exists), so that, *e.g.*, for  $M = 3$  Eq. (22) takes the form

$$J = (a_1 a_2^2 - K a_3) k_1 \quad (28)$$

where  $J$  is the rate of the reaction (27) and  $K$  its equilibrium constant. The rate  $J$  can be expressed with the aid of Eqs (1), (3), (5), and (27) as follows:



$$J = \frac{1}{8}(J_1 + 2J_2 - J_3) = \frac{1}{8}[J_1(2M_1 + 2M_2)/M_3 + J_2(2M_1 + 5M_2)/M_3]. \quad (29)$$

If the affinity is negative, the expression  $R_1 = a_1 a_2^2 - K a_3$  is also negative (according to Eqs (8), (9), and (12)) and according to the entropic inequality (13) the  $J$  value is positive, hence the rate constant  $k_1$  in Eq. (28) is negative. This is in agreement with the expected form of the mass action law, since in this case the reaction (27) proceeds from the left to the right,  $-Kk_1$  and  $-k_1$  are the classical rate constants of the forward and back reactions, respectively,  $J_1, J_2$ , and hence by Eq. (29) also  $J$  are positive quantities. In the special case of a closed homogeneous system we have  $J_2 = 2J_1$  and hence  $J = J_1$  after Eq. (29).

For  $M = 6$  we find that Eq. (20) contains two terms:  $R_1$  corresponding to the reaction (27) with a general polynomial  $P_1$  of the third degree, and  $R_2$  corresponding to the doublet reaction (27) with  $P_2$  equal to constant. By rearranging into the form (21) it turns out that a linear relation exists among three  $R'_h$  terms, hence from the original 21 constants 20 independent ones remain. If we write the result (22) with  $m = l = 2$ , we obtain a similar form as before except that, e.g., in  $P_1$  the term containing  $a_3$  is missing. Another equivalent form of (22) with  $m = 1$  and a polynomial of the third degree can be obtained more easily in view of the fact that only one independent reaction proceeds in the mixture (as already mentioned in the derivation of Eq. (22)).

We now shall treat this case by the elimination method for  $M = 4$  restricting ourselves for the sake of simplicity to the special case (26). The first and third starting assumptions (9) and (16) take the form:

$$J = J(T, c_1, c_2, c_3) = \sum_{v_1, v_2, v_3} k_{v_1 v_2 v_3}(T) c_1^{v_1} c_2^{v_2} c_3^{v_3}, \quad v_1 + v_2 + v_3 \leq 4 \quad (30)$$

and the starting assumption of an equilibrium (14), (15) is

$$K = c_1 c_2^2 / c_3, \quad J = 0. \quad (31)$$

By eliminating  $c_1$  from (30) and (31) and rearranging we obtain a polynomial in  $c_2$  and  $c_3$  equal to zero, whence follow the general conditions

$$\begin{aligned} Kk_{120} + k_{001} &= 0, & Kk_{220} + k_{101} &= 0, \\ Kk_{130} + k_{011} &= 0, & Kk_{121} + k_{002} &= 0, \end{aligned} \quad (32)$$

whereas the remaining coefficients  $k_{v_1 v_2 v_3}$  are identically equal to zero. By introducing (32) into (30) and rearranging into the form corresponding (27) we obtain finally the result of the type (22)

$$J = (c_1 c_2^2 - K c_3) (k_{120} + k_{220} c_1 + k_{130} c_2 + k_{121} c_3). \quad (33)$$

For  $M = 3$ , this result is reduced to Eq. (28) (by the additional condition (26) we have  $k_1 = k_{120}$ ); the additional terms in (33) can be interpreted as the influence of autocatalysis.

We now shall consider a mixture of four components,  $B_1$  through  $B_4$ , with a single reaction (27), where the nonreacting component  $B_4$  influences the reaction rate  $J = J(T, c_1, c_2, c_3, c_4)$  (we shall again restrict ourselves to the case (26)). With similar assumptions (Eq. (30) for  $n = M = 4$ , Eq. (31)) we arrive at the result (33) supplemented by a term proportional to  $c_4 \cdot (c_1 c_2^2 - K c_3)$ , which can be interpreted as a homogeneous catalysis by the component  $B_4$ .

As an example of a system with more reactions, we shall consider a mixture of atoms  $B_1$ , diatomic molecules  $B_2$ , and triatomic molecules  $B_3$ . Here there are possible two independent reactions, for example



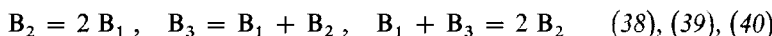
Assuming the case (26), we shall seek the conversion rates  $J_\alpha$  ( $\alpha = 1, 2, 3$ ). By the elimination method, when the starting assumption (14) is represented by the expressions for the equilibrium constants  $K_4$  and  $K_5$  in concentrations for the reactions (34) and (35), the result for  $M = 2$  will be

$$J_\alpha = (c_1^2 - K_1 c_2) k_{200}^{(\alpha)} + (c_1 c_2 - K_2 c_3) k_{110}^{(\alpha)} + (c_2^2 - K_3 c_1 c_3) k_{020}^{(\alpha)} \quad (36)$$

with

$$K_1 = K_4^{-1/2} K_5^{2/3}, \quad K_2 = K_4^{1/2} K_5^{1/3}, \quad K_3 = K_4^{2/3} K_5^{-1/3}. \quad (37)$$

This is in the form of (22), since the reactions



have their equilibrium constants  $K_1, K_2, K_3$ , respectively, which fulfil Eqs (37).

When using the direct method of constructing the expression for  $J$  in this case, we first find all reactions of the type (1) that fulfil the condition (17). This can be achieved, *e.g.*, as follows: It turns out from the stoichiometry (ref.<sup>4</sup>, Eq. (44)) that the stoichiometrical coefficients of the  $i$ -th reaction fulfil in this case the equation  $p_{i1} + 2p_{i2} + 3p_{i3} = 0$ ; by a choice of all whole-numbered  $p_{i2}$  and  $p_{i3}$  values not exceeding by their absolute value a fixed limit  $M$ , all such reactions can be found. For  $M \leq 1$  no such reaction exists, for  $M = 2$  we have the reactions (38)–(40) and for  $M = 3$  also (34) and (35). For  $M = 2$ , the constructed reaction rate (20) represents directly the results (36), since no other reduction is possible. For  $M = 3$  the value of  $l$  in Eq. (20) is equal to 5; by rearranging into the form of (21) we find out that a linear dependence exists among four triplets of the  $R_h^l$  terms. We shall mention two of the possible equivalent forms of Eq. (22) in this case, the first one for  $m = l = 5$ , the second one for  $m = 3$ :

$$\begin{aligned} J &= (c_1^2 - K_1 c_2) [k_1 + k_2 c_3] + (c_1 c_2 - K_2 c_3) [k_3 + k_4 c_1 + k_5 c_3] + \\ &+ (c_2^2 - K_3 c_1 c_3) [k_6 + k_7 c_1 + k_8 c_3] + (c_2^3 - K_4 c_3^2) k_9 + (c_1^3 - K_5 c_3) k_{10} = \\ &= (c_1^2 - K_1 c_2) [k_1 + k_{10} c_1 + k_2 c_3] + (c_1 c_2 - K_2 c_3) [(k_3 + k_{10} K_1) + \\ &+ k_4 c_1 + (k_5 + k_9 K_3) c_3] + (c_2^2 - K_3 c_1 c_3) [k_6 + k_7 c_1 + k_9 c_2 + k_8 c_3]. \quad (41) \end{aligned}$$

Here we have ten independent rate constants  $k_h$  (in the second expression these constants are expressed by those in the first one). For  $M = 2$ , Eq. (41) is reduced to the form of (36), the rate  $J$  being expressed by  $J_\alpha$ , *i.e.*,  $k_{200}^{(\alpha)} = k_1^{(\alpha)}$ ,  $k_{110}^{(\alpha)} = k_3^{(\alpha)}$ ,  $k_{020}^{(\alpha)} = k_6^{(\alpha)}$  (obviously  $k_{10}^{(\alpha)} = 0$ ). If we choose for expressing  $J$  two independent reactions (38) and (39), their rates  $J_1$  and  $J_2$  have a form similar to (36) with the rate constants  $-(k_\nu^{(2)} + k_\nu^{(3)})$  and  $-k_\nu^{(3)}$  as follows from Eqs (23) and (25);  $k_\nu^{(\alpha)}$  denotes the rate constants in Eq. (36) ( $\alpha = 2, 3; \nu = (200), (110), (020)$ ).

The chemical conversions in this case of three components with two independent chemical reactions can hence be entirely described by two equilibrium and six rate constants in an approximation of the second order (or twenty rate constants in a third-order approximation).

## DISCUSSION

For a reacting fluid mixture with linear transport properties and in an approximation of the constitutive equation for the reaction rate by a polynomial in terms of activities or concentrations, expressions were obtained that have the form of the mass action law of homogeneous chemical kinetics, Eq. (22). The described method leads to the mass action law in terms of only positive, whole-numbered powers of the variables corresponding to the stoichiometry. Fractional or negative powers occurring in the empirical expressions for the reaction rate can be obtained by introducing additional hypotheses analogous to those used in proposals of reaction mechanisms. As an example, we shall discuss the conversion of ozone,  $O_3$  ( $= B_3$ ), to molecular oxygen,  $O_2$  ( $= B_2$ ), a direct reaction of the type (34). By applying the mentioned method to this reaction we do not obtain the negative first order with respect to oxygen, as found experimentally in a certain range of conditions<sup>7</sup>. Let us assume, however, that atomic oxygen,  $O$  ( $= B_1$ ), coexists with  $O_2$  and  $O_3$ , hence two independent reactions are possible. Since the sought expression for the reaction rate is independent of the choice of these reactions, the reaction (34) of the conversion can be chosen as the first one, while the other can be an arbitrary reaction involving atomic oxygen,  $B_1$ , for example (35). The assumption (26) is acceptable and therefore the approximation of Eq. (6) by a polynomial of the second or third degree leads to the result (36) or (41). We shall consider the result (36) for  $\alpha = 3$  (ozone) and assume that the following two additional assumptions hold in a certain range of conditions:  $k_{200}^{(\alpha)}$  is negligible against  $k_{110}^{(\alpha)}$  and  $k_{020}^{(\alpha)}$ , *i.e.*, Eqs (39) and (40) represent the mechanism of the conversion (34), and the reaction (39) is in the equilibrium, *i.e.*,  $c_1 = K_2 c_2^{-1} c_3$ . In this way, Eq. (36) is reduced to its last term, from which we eliminate the concentration of atomic oxygen  $c_1$  by using the just mentioned relation and obtain

$$J_\alpha = -k_{020}^{(\alpha)} K_4 c_2^{-1} c_3^2 + k_{020}^{(\alpha)} c_2^2, \quad \alpha = 3, \quad (42)$$

where we used Eq. (37). The equilibrium constant,  $K_4$ , of the conversion (34) is large and Eq. (42) is therefore in accord with the experiments under restricted conditions<sup>7</sup>.

The results of the present work could be useful, *e.g.*, in proposing mechanisms in homogeneous kinetics. If we know *a priori* all components of the mixture (including unstable intermediate products), we can determine the most general expression for the reaction rate and the maximum number of equilibrium and rate constants characterizing such a system. From the phenomenological point of view there is an infinite number of equivalent systems of independent reactions describing chemical

changes in such a system, and if we know the mentioned constants of one of them it is possible to determine these quantities for any other independent system. As already shown on the derivation of Eq. (42), only additional hypotheses following from the experience or from molecular models (in substance about the relative magnitude of the rate and equilibrium constants and concentrations such as assumptions about equilibrium or the Bodenstein approximation) lead to an additional reduction of the general expressions. In this way we obtain, besides others, the concepts of direct, reversed, consecutive, and parallel reactions as special cases. If we restrict ourselves, e.g., to bi- or trimolecular reactions, we can use in the general expressions the approximations  $M = 2$  or  $3$ .

The fact that we obtained expressions of the type of the mass action law depends in a decisive manner on the choice of independent variables in the constitutive equation for the reaction rate. In choosing concentrations or activities (such a mass action law is sometimes mentioned<sup>8</sup>) we can expect a rapid convergence, which naturally follows from the experience or from molecular concepts (at least in the case of concentrations, i.e., with the validity of Eq. (26)). From a purely phenomenological point of view, all choices of the independent variables in the expressions for the reaction rate are equivalent. However, if we choose the affinities as the independent variables (compare the derivation of Eq. (13)), it is necessary to use more terms of the polynomial to obtain correct results. This is the choice made by nonequilibrium thermodynamics<sup>1</sup> which, however, by restricting itself to linear terms of the polynomial expansion gives results applicable only close to the equilibrium. It seems therefore that dividing the terms in the entropy production into "fluxes" and "forces" (compare the inequality (13)), which is characteristic for irreversible thermodynamics<sup>1</sup>, need not be always advantageous. In contrast, in rational thermodynamics the choice of independent variables leading to Eq. (6) is quite natural (the principle of determinism<sup>2</sup>) and in other linear irreversible processes gives similar results as irreversible thermodynamics<sup>4</sup>.

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