

## Formalism of Chemical Kinetics

### 1. Main concepts of chemical kinetics

#### 1.1 LINEAR LAWS OF CONSERVATION

Let the substances participating in a chemical reaction be  $A_1, \dots, A_n$ . Their chemical composition is specified. Let their constituent elements be  $B_1, \dots, B_m$ . The number of atoms of the  $j$ th element in the molecule of  $A_j$  is  $a_{ij}$ . The matrix  $(a_{ij}) = \vec{A}$  is called a molecular matrix.

Let  $N_i$  be the content (mole) of substance  $A_i$  in the system,  $\vec{N}$  the vector column with components  $N_i$ . Similarly, let  $b_j$  be the content (mole) of  $B_j$  in the system and  $\vec{b}$  the vector column with components  $b_j$ . They are related by matrix  $\vec{A}^T$  ( $A$  transposed)

$$b_j = \sum_{i=1}^n a_{ij} N_i \quad \vec{b} = \vec{A}^T \vec{N} \quad (1)$$

Matrix  $\vec{A}^T$  will be used more often than  $\vec{A}$ . Therefore it would be more correct to introduce this matrix immediately and to designate it as "atomic" rather than "molecular", but we will adopt the conventional approach. Historically, the introduction of the designations and terminology used is substantiated by the relationship between vector columns of molecular  $\vec{M}$  and atomic  $\vec{M}_a$  weights

$$m_i = \sum_{j=1}^m a_{ij} m_{aj} \quad \vec{M} = \vec{A} \vec{M}_a \quad (2)$$

In closed systems the content of any element remains unchanged with time, i.e. for any  $j$

$$\frac{db_j}{dt} = \frac{d}{dt} \sum_{i=1}^n a_{ij} N_i = 0 \quad b_j = \text{const.} \quad (3)$$

or in matrix form

$$\frac{d\vec{b}}{dt} = \vec{A}^T \frac{d\vec{N}}{dt} = \vec{0} \quad \vec{b} = \vec{A}^T \vec{N} = \text{const.} \quad (4)$$

These laws of conservation are independent of what reactions take place between the substances  $A_1, A_2, A_3, \dots, A_n$ . These substances consist of  $m$

elements. Consequently there exist  $m$  linear laws of conservation of the type of eqn. (3). But they are not always independent. Sometimes part of these laws can be represented through the rest of them. The simplest example is the reaction of butene isomerization. Let  $A_1$  be butene-1,  $A_2$  be *cis*-butene-2, and  $A_3$  be *trans*-butene-2. They consist of two elements, i.e. carbon and hydrogen. Since the whole of  $A_i$  have the same composition  $C_4H_8$ , the molecular matrix is of the form

$$\vec{A} = \begin{bmatrix} 4 & 8 \\ 4 & 8 \\ 4 & 8 \end{bmatrix}$$

and the laws of conservation  $b_C = 4(N_1 + N_2 + N_3) = \text{const.}$ ,  $b_H = 8(N_1 + N_2 + N_3) = \text{const.}$  are linearly dependent:  $2b_C = b_H$ .

## 1.2 STOICHIOMETRY OF COMPLEX REACTIONS

A complex chemical reaction is represented as a sum of some elementary reactions. The step consists of two elementary reactions, direct and reverse. We will treat the reaction as elementary if its rate is dependent on concentrations specified in some simple way, e.g. this dependence fits the law of mass action (as will be discussed below).

A step can be written as



Here  $\alpha_{si}$  and  $\beta_{si}$  are stoichiometric coefficients, i.e. non-negative numerals indicating the number of molecules of the substance taking part in the elementary reaction, and  $s$  is the step number.

It is the list of elementary steps (5) that is called a complex reaction mechanism. This list implies that the same substance can participate in the step as both the initial substance and the reaction product. An example is the step [1]



where  $M$  is any other substance. Steps of such type are called autocatalytic. As a rule, they are applied by the Prigogine school and their associated groups of research workers to construct hypothetical models demonstrating a complex dynamic behaviour.

Recently, a whole "zoo of models" has been investigated. Its most known inhabitants, the "brussellator" and "oregonator" Ref. [2], contain the steps



i.e. autocatalytic steps. But in real mechanisms of complex reactions that are not speculative these steps are observed very rarely. This was suggested,

for example by Kondratiev and Nikitin, from their analysis of the mechanisms for complex gas-phase reactions [3]. Our viewpoint is the same. Therefore in what follows special attention will be given to reactions involving no autocatalytic steps. Formally it means that at any value of  $s$  and  $i$  at least one of the two values  $\alpha_{si}$  or  $\beta_{si}$  is zero.

Stoichiometric coefficients of elementary steps are often imposed by natural limitations, i.e. for any coefficient

$$\sum_{i=1}^n \alpha_{si} \leq 3$$

$$\sum_{i=1}^n \beta_{si} \leq 3$$
(6)

It means that we consider only mono-, bi- and (rarely) termolecular reactions. The coefficients  $\alpha_{si}$  and  $\beta_{si}$  themselves can take the values 0, 1, 2 and (rarely) 3. One should not confuse the stoichiometric coefficients and stoichiometric numbers observed in the Horiuti-Temkin theory of steady-state reactions. The latter indicate the number by which the elementary step must be multiplied so that the addition of steps involved in one mechanism will provide a stoichiometric (brutto) equation containing no intermediates (they have been discussed in Chap. 2).

Each (sth) step corresponds to its stoichiometric vector  $\gamma_s$ , whose components are

$$(\gamma_s)_i = \beta_{si} - \alpha_{si} \quad i = 1, \dots, n$$
(7)

The vector  $\gamma_s$  indicates the direction of the composition variations due to the sth step. If  $\vec{N}$  is a vector, whose  $i$ th component is the number of molecules  $A_i$  in the system, then  $\vec{\gamma}_s$  is a variation of  $\vec{N}$  due to the action of one reaction:  $\vec{N}' = \vec{N} + \vec{\gamma}_s$  (for direct reactions) and  $\vec{N}' = \vec{N} - \vec{\gamma}_s$  (for reverse reactions).

$\vec{\gamma}$  also indicates variations in the vector of molar quantities  $\vec{N}$  per "mole" of elementary acts (1 "mole" is  $6.02 \times 10^{23}$  elementary acts just as one mole is  $6.02 \times 10^{23}$  molecules).

As a whole, a reaction corresponds to the stoichiometric matrix  $\vec{\Gamma}$

$$\vec{\Gamma} = (\gamma_{si}) = (\beta_{si} - \alpha_{si})$$
(8)

Its rows are the stoichiometric vectors  $\vec{\gamma}_s$ .

Each step is accounted for by its rate, i.e. some function  $w_s$ , for the mixture composition and temperature

$$w_s = w_s^+ - w_s^-$$
(9)

Here  $w_s^\pm$  are the direct and reverse reaction rates, respectively, indicating the number of elementary acts (or their "moles") per unit time in unit volume or per unit area for surface reactions. Their commonly used dimensions are molecules (mole)  $\text{cm}^{-3} \text{s}^{-1}$  or molecules (mole)  $\text{cm}^{-2} \text{s}^{-1}$ .

## 1.3 GRAPHICAL REPRESENTATIONS OF REACTION MECHANISMS

Mechanisms for complex chemical reactions can be represented by graphs having nodes of two types [4]. One corresponds to elementary reactions and the other accounts for substances.

It must be noted that the former correspond to elementary reactions and not to steps. It means that one reversible step corresponds to two nodes. Edges connect nodes—substances and nodes—reactions provided that the substances take part in the reaction. Edges will be oriented from substance  $A_i$  to reaction  $\Sigma\alpha_i A_i \rightarrow \Sigma\beta_i A_i$  if  $A_i$  is the initial reactant ( $\alpha_i \neq 0$ ) and vice

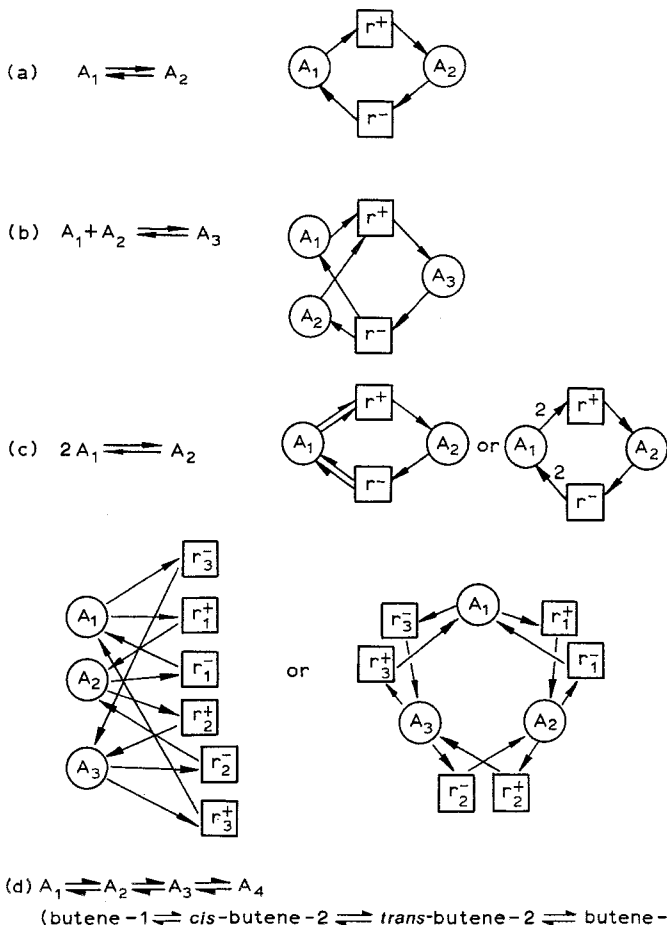


Fig. 1. Simple examples for bipartite graphs of reaction mechanisms.  $\square$ ; Reaction nodes;  $\circ$ , substance nodes.

versa from reaction to substance if  $A_i$  is the product ( $\beta_i \neq 0$ ). The numbers of edges from substance  $A_i$  to reaction and from reaction to  $A_i$  are  $\alpha_i$  and  $\beta_i$ , respectively. (Note that, in the case of autocatalysis, there are edges of both types.) Let us designate the constructed graph as a bipartite graph for the reaction mechanism. The simplest examples are given in Figs. 1 and 2 ( $r_s^\pm$  are the  $s$ th direct and reverse reactions, respectively). As more illustrative examples we shall consider the two detailed mechanisms for the oxidation of CO on Pt. They are impact (Eley-Rideal) and adsorption (Langmuir-Hinshelwood) mechanisms. The former does not involve any interactions of intermediates, i.e. in every elementary step both the right-hand and left-hand sides contain only one intermediate. Sometimes this intermediate, however, has a coefficient that is higher than unity



Let us consider transformation only of intermediates assuming that the gas-phase composition has been specified. In what follows we will often use this method to study catalytic reactions (surface dynamics is investigated with constant gas composition). Transformations of surface substances can be written as



The corresponding graph is illustrated in Fig 3(a). The Langmuir-Hinshelwood mechanism contains a step which is an interaction between intermediates (step 3)

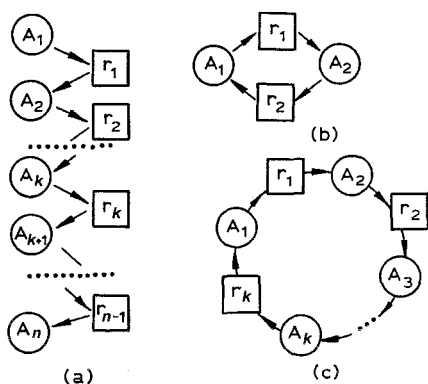


Fig. 2. Examples of simple bipartite graphs. (a) Acyclic graph for the reaction  $A_1 \rightarrow A_2 \rightarrow \dots \rightarrow A_n$ ; (b) cyclic graph for the reaction  $A_1 \rightleftharpoons A_2$ ; (c) graph for the irreversible cycle  $A_1 \rightarrow A_2 \rightarrow \dots \rightarrow A_k \rightarrow A_1$ .

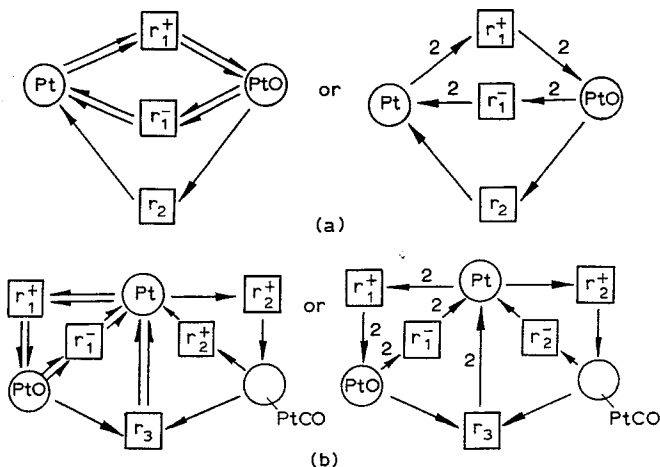
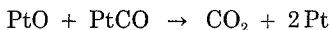
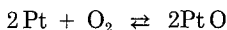
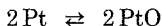


Fig. 3. Bipartite graphs for the mechanism of CO oxidation on Pt. (a) Eley-Rideal (impact) mechanism; (b) Langmuir-Hinshelwood (adsorption) mechanism.



or in the form of transformations of intermediates



The corresponding graph is illustrated in Fig. 3(b).

In the analysis of reaction graphs, the concept of a "cycle" is important. A cycle is the set of graph nodes  $\{p_1, p_2, \dots, p_k\}$  and the set of edges  $\{l_1, l_2, \dots, l_k\}$ . In this case  $l_1, l_2, l_i$  and  $l_k$  connect  $p_1$  with  $p_2, p_2$  with  $p_3, p_i$  with  $p_{i+1}$  and  $p_k$  with  $p_1$ , respectively. To analyze cycles, it is convenient to omit drawing two, three, etc., arrows at  $\alpha_i$  or  $\beta_i > 1$ . Let us simply write  $\alpha_i$  or  $\beta_i$  above the arrows if they are greater than unity (see Fig. 3). In the analysis of the stability of a complex chemical reaction, we meet with a problem of enumerating and investigating cycles in the bipartite graph for the reaction mechanism [5]. Let us enumerate cycles for Eley-Rideal and Langmuir-Hinshelwood mechanisms (Fig. 4).

We will leave it to the reader (as a simple but useful exercise) to enumerate all the cycles in all the graphs depicted in Figs. 1 and 2 and also for the Prigogine autocatalytic trigger [6]:

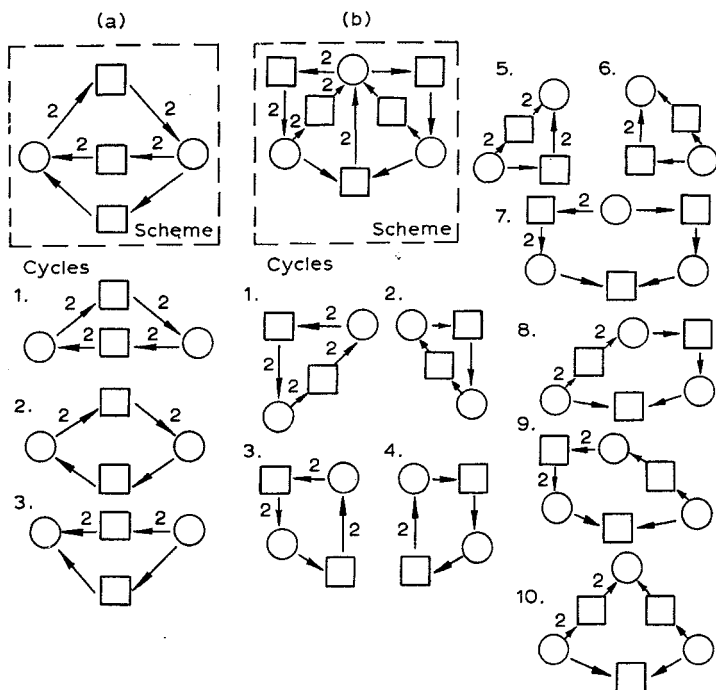
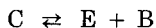


Fig. 4. Cycles in bipartite graphs for CO oxidation on Pt. (a) Impact mechanism; (b) adsorption mechanism.



(14)

(remember that in the autocatalytic case the graph has two arrows, from substance to reaction and from reaction to substance, therefore one autocatalytic reaction already provides a cycle even without taking a reverse reaction into account).

In a certain sense, the simplest class of reaction mechanism is that whose bipartite graphs do not contain cycles, i.e. are acyclic. The dynamic behaviour of the corresponding reactions is always extremely simple [7]. An example for such a mechanism can be  $A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow \dots \rightarrow A_n$  [see Fig. 2(a)]. The contribution of acyclic mechanisms to the kinetics of catalytic reactions is not of importance. The mechanisms of catalytic reactions always contain cycles and these cycles are oriented, the directions of all the arrows being matched [the end of the  $i$ th arrow is the beginning of the

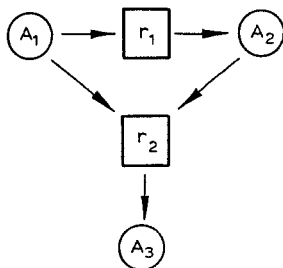
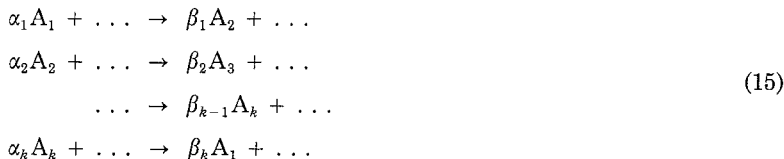


Fig. 5. Bipartite graph for the reaction mechanism  $A_1 \rightarrow A_2$ ,  $A_1 + A_2 \rightarrow A_3$ .

( $i + 1$ )th arrow]. Catalyst is not consumed but enters into the reaction, first combining with the other reactants and then being liberated again. The corresponding sequence of elementary reactions is



where the dots denote various substances taking part in the reactions.

A graph for the mechanism having the sequence of steps shown by eqn. (15) contains a cycle [see Fig. 2(c)] all lines in which are oriented so that the end of the  $i$ th edge is the beginning of the ( $i + 1$ )th ("oriented over a circle"). But this is not the case for all possible cycles. For example, the two-step mechanism  $A_1 \rightarrow A_2$ ,  $A_1 + A_2 \rightarrow A_3$  has a cycle (Fig. 5), but the branches from  $A_1$  are directed "oppositely" and those to  $r_2$  are directed "towards each other". The absence of oriented cycles also ensures simple dynamic behaviour [7]. Bipartite graphs for the Eley-Rideal and Langmuir-Hinshelwood mechanisms have cycles of both types, i.e. those that are "oriented over a circle" and those that are not [Fig. 4(a), (b)]. In what follows we will come back to the analysis of cycles in bipartite graphs of reaction mechanisms. It will be done in answering the question whether it is possible at a given reaction mechanism to observe a multiplicity of surface steady states, self-oscillations, etc.

If all the elementary reactions are monomolecular, i.e. can be written as  $A_i \rightarrow A_j$ , it is more convenient to represent reaction mechanisms in a different way, namely nodes correspond to substances, edges are elementary reactions, and edge directions are the directions of reaction processes. As usual, this graph is simpler than the bipartite graph. For example, for the system of three isomers  $A_1$ ,  $A_2$  and  $A_3$  we obtain





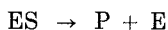
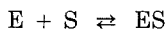
(16)

This graph can be compared with that represented in Fig. 2(c).

Strictly speaking, mechanisms for heterogeneous catalytic reactions can never be monomolecular. Thus they always include adsorption steps in which the initial substances are a minimum of two in number, i.e. gas and catalyst. But if one considers conversions of only surface compounds (at a constant gas-phase composition), a catalytic reaction mechanism can also be treated as monomolecular. It is these mechanisms that Temkin designates as linear (see Chap. 2).

Let us consider some examples.

The simplest mechanism for an enzyme-catalysed reaction (Michaelis-Menten scheme) is

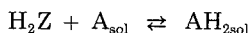
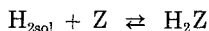


where S and P are the substrate and product, respectively, and E and ES are various enzyme forms.

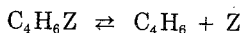
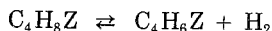
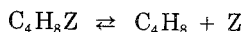
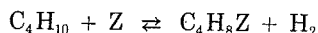
A graph for the conversions of intermediates for this mechanism is



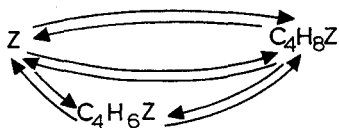
The graph for simple reaction mechanism of the liquid-phase hydrogenation  $A + H_2 = AH_2$  is similar.



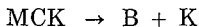
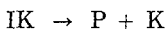
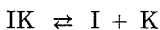
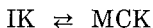
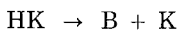
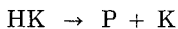
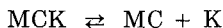
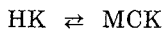
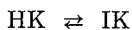
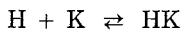
The reaction mechanism for the dehydrogenation of butane can be simplified by the combination of steps



A graph for the surface conversions is

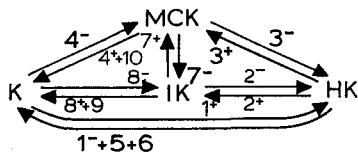


A fragment of *n*-hexane conversions on supported Pt catalysts is represented as



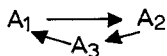
where H, I, B, MC, and P are *n*-hexane, hexane isomers, benzene, methylcyclopentane and cracking products, respectively, and K, HK, MCK and IK are intermediates.

A graph for surface conversions is

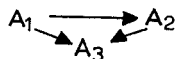


The numerals over the oriented arc of the graph indicate the numbers of the steps (or a step) with the help of which one intermediate is formed from the other.

Cycles in the graph for a linear mechanism are usually called the "regularly oriented" cycles, i.e. sets of substances and reactions of the type  $A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow \dots \rightarrow A_n \rightarrow A_1$  (the reactions can also be reversible). Thus the combination of reactions



is a cycle, but the mechanism



is acyclic.

#### 1.4 CHEMICAL KINETICS EQUATIONS

Chemical kinetics equations for the closed heterogeneous "gas-solid" systems are of the type

$$\frac{d\vec{N}}{dt} = S \sum_s \vec{\gamma}_s \vec{w}_s + V \sum_\sigma \vec{\gamma}_\sigma \vec{w}_\sigma \quad (17)$$

$$\begin{aligned}
 \frac{d\vec{N}^{\text{gas}}}{dt} &= S \sum_s \vec{\gamma}_s^{\text{gas}} \vec{w}_s + V \sum_\sigma \vec{\gamma}_\sigma \vec{w}_\sigma \\
 \frac{d\vec{N}^{\text{sur}}}{dt} &= S \sum_s \vec{\gamma}_s^{\text{sur}} \vec{w}_s
 \end{aligned} \quad (18)$$

where  $\vec{N}^{\text{gas}}$  is the vector of substance concentration in the gas phase,  $\vec{N}^{\text{sur}}$  the vector of substance concentrations on the surface,  $\vec{\gamma}_s^{\text{gas}}$  the part (projection) of the stoichiometric vector for surface reactions composed of stoichiometric coefficients for the gas-phase substances,  $\vec{\gamma}_s^{\text{sur}}$  the part (projection) of the stoichiometric vector for surface reactions composed of stoichiometric coefficients for the surface compounds,  $\vec{\gamma}_\sigma$  the stoichiometric vector for gas-phase reactions,  $V$  the gas volume and  $S$  the catalyst surface.

To discriminate between reactions on solid surfaces and in the gas phase, we have introduced different indices, i.e.  $s$  for the former reactions and  $\sigma$  for the latter.

Equations (17) and (18) describe the process of complex homogeneous-heterogeneous reactions.

*Example 1.* Let us consider a catalytic isomerization reaction (the simplest model case). Let the gas phase contain two isomers,  $A_1$  and  $A_2$ , and the catalyst surface have three intermediates,  $A_3 = Z$  (active sites),  $A_4 = A_1Z$  and  $A_5 = A_2Z$ . Steps will be listed as follows: (0)  $A_1 \rightleftharpoons A_2$  (gas) and (1)  $A_1 + Z \rightleftharpoons A_1Z$ ; (2)  $A_1Z \rightleftharpoons A_2Z$ ; (3)  $A_2 + Z \rightleftharpoons A_2Z$  (solid surface). The stoichiometric vector  $\vec{\gamma}_\sigma$  for the gas-phase reaction  $A_1 \rightleftharpoons A_2$  is of the form  $[-1]$  and for the surface reactions  $\vec{\gamma}_s$  is

$$\vec{\gamma}_1 = \begin{bmatrix} -1 \\ 0 \\ -1 \\ 1 \\ 0 \end{bmatrix} \quad \vec{\gamma}_2 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix} \quad \vec{\gamma}_3 = \begin{bmatrix} 0 \\ -1 \\ -1 \\ 0 \\ 1 \end{bmatrix}$$

In this case

$$\begin{aligned} \vec{\gamma}_1^{\text{gas}} &= \begin{bmatrix} -1 \\ 0 \end{bmatrix}, & \vec{\gamma}_2^{\text{gas}} &= \begin{bmatrix} 0 \\ 0 \end{bmatrix}, & \vec{\gamma}_3^{\text{gas}} &= \begin{bmatrix} 0 \\ -1 \end{bmatrix} \\ \vec{\gamma}_1^{\text{sur}} &= \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix}, & \vec{\gamma}_2^{\text{sur}} &= \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}, & \vec{\gamma}_3^{\text{sur}} &= \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \end{aligned}$$

If the isomerization rate in the gas phase is  $w_0$  and that on the surface is  $w_1, w_2, w_3$ , then the kinetic equations can be written as

$$\begin{aligned} \dot{N}_1 &= S(-w_1) - Vw_0 \\ \dot{N}_2 &= S(-w_3) + Vw_0 \\ \dot{N}_3 &= S(-w_1 - w_3) \\ \dot{N}_4 &= S(w_1 - w_2) \\ \dot{N}_5 &= S(w_2 + w_3) \end{aligned} \quad (19)$$

or

$$\begin{aligned} \frac{d}{dt} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} &= S(\vec{\gamma}_1^{\text{gas}} w_1 + \vec{\gamma}_2^{\text{gas}} w_2 + \vec{\gamma}_3^{\text{gas}} w_3) + V\gamma_0 w_0 \\ \frac{d}{dt} \begin{bmatrix} N_3 \\ N_4 \\ N_5 \end{bmatrix} &= S(\vec{\gamma}_1^{\text{sur}} w_1 + \vec{\gamma}_2^{\text{sur}} w_2 + \vec{\gamma}_3^{\text{sur}} w_3) \end{aligned} \quad (20)$$

Kinetic equations can be reduced to a more compact form using a stoichiometric matrix and writing the rates for the various steps as a vector column. Then

$$\frac{d\vec{N}}{dt} = S\vec{\Gamma}_s^T \vec{w}_s + V\vec{\Gamma}_g^T \vec{w}_g \quad (21)$$

where  $\vec{\Gamma}_s$  is the stoichiometric matrix for surface reactions,  $\vec{\Gamma}_g$  that for gas-phase reactions,  $\vec{w}_s$  is the vector column for surface reaction rates and  $\vec{w}_g$  that for gas-phase reactions. For the above example of catalytic isomerization reaction

$$\vec{\Gamma}_s = \begin{bmatrix} -1 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & -1 & 1 \\ 0 & -1 & -1 & 0 & 1 \end{bmatrix}$$

$$\vec{\Gamma}_g = (-1, 1, 0, 0, 0)$$

$$\vec{w}_s = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix}$$

$$\vec{w}_g = w_0$$

Let us establish the limitations imposed on the coefficients (17) and (18) by the linear laws of conservation, eqn. (4)

$$\frac{d\vec{A}}{dt} \vec{N} = \vec{S}\vec{A}^T \vec{\Gamma}_s^T \vec{w}_s + \vec{V}\vec{A}^T \vec{\Gamma}_g^T \vec{w}_g = \vec{0} \quad (22)$$

Since linear laws of conservation must be fulfilled at any rate of individual steps, we obtain

$$\vec{A}^T \vec{\Gamma}_s^T = \vec{A}^T \vec{\Gamma}_g^T = \vec{0} \quad (23)$$

or, by using the equality  $\vec{A}^T \vec{\Gamma}^T = (\vec{\Gamma}\vec{A})^T$

$$\vec{\Gamma}\vec{A} = \vec{0} \quad (24)$$

where  $\vec{\Gamma}$  is the arbitrary stoichiometric matrix.

For individual steps condition (24) in the vector form is

$$\begin{aligned} \vec{A}^T \vec{\gamma}_s &= \vec{0} \\ \sum_i a_{ij} \gamma_{si} &= 0 \end{aligned} \quad (25)$$

According to eqn. (25) the vectors  $\vec{\gamma}_s$  lie in the subspace composed of the solutions for the equation  $\vec{A}^T \vec{x} = \vec{0}$ , i.e. the core of the matrix  $\vec{A}^T$ .

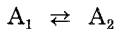
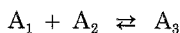
If the family of the vectors  $\{\vec{\gamma}_s\}$  does not provide this subspace, i.e. the family rank is lower than the matrix defect

$$\text{rg} \{\vec{\gamma}_s\} < n - \text{rg} \vec{A}^T \quad (26)$$

the number of linearly independent reactions is lower than their maximum possible number, i.e. the defect of the matrix  $\vec{A}^T$ .

In this case, new linear laws of conservation appear that are not associated with the conservation of any atoms and are simply of the kinetic type [8].

*Example 2.* Let the reactions



take place, where  $A_1$  and  $A_2$  are isomers and  $A_3$  dimer. For this system the

linear law of conservation  $N_1 + N_2 + 2N_3 = b_1$  holds. Let us assume that the reaction  $A_1 \rightleftharpoons A_2$  does not take place. Then a kinetic law of conservation will again appear in the system:  $b_2 = N_1 - N_2$ .

This situation is observed rather rarely, but it is still possible. To establish these laws, one can examine, for example, a set of linear equations with respect to the  $n$ -dimensional vector row  $x$

$$\vec{x} \vec{\gamma}_s = \vec{0} \text{ for each } s, \vec{A}^T \vec{x}^T = \vec{0} \text{ or } \vec{x} \vec{A} = \vec{0} \quad (27)$$

This equation is the condition of  $\vec{x}$  rows orthogonality to  $\vec{A}^T$  ( $A$  columns). It is necessary in order to eliminate the need to obtain once again the laws of conservation for the number of atoms or their linear combinations when determining  $x$ . To establish some additional kinetic laws of conservation, one must solve Eqns. (27) and obtain a complete linearly independent set of  $\vec{x} - \{x_1, \dots, x_k\}$  which satisfy it. The laws of conservation are specified by the relationships  $x_j \vec{N} = \text{const.}$  ( $j = 1, \dots, k$ ).

In what follows when discussing the general properties of the chemical kinetic equations, we will assume that the additional laws of conservation (if there are any) have been discovered and the respective values of  $x$  are included in the matrix  $\vec{A}^T$  as additional rows.

### 1.5 REACTION POLYHEDRON

In the system (18) there exist laws of conservation (22) and it is imposed by the natural condition of having positive amounts (mole) of reactants. Hence it is possible to describe the region of composition spaces in which the solution for eqn. (18)  $\vec{N}(t)$  ( $0 \leq t < \infty$ ) with non-negative initial conditions lies. It is a convex polyhedron specified by the set of linear equations and non-equalities [9, 10].

$$\sum_{i=1}^n a_{ij} N_i = b_j \quad (j = 1, \dots, m) \quad (28)$$

$$N_i \geq 0 \quad i = 1, \dots, n$$

where

$$b_j = \sum_{i=1}^n a_{ij} N_i(0)$$

Let us designate this polyhedron as  $\vec{D}(\vec{b})$  and call it a reaction polyhedron. Examples of the construction of  $\vec{D}(\vec{b})$  for catalytic reactions are given below.

*Example 3.* Let us consider a system of three isomers  $A_1, A_2$  and  $A_3$  taking part in catalytic isomerization reactions.



Such a scheme for the catalytic isomerization of *n*-butenes over  $\text{Al}_2\text{O}_3$  has been studied in detail previously [11]. Each reaction has a rate that is a function of both the gas composition and the surface state. In this case the assumption that the concentration of surface intermediates on the catalyst is a function of the gas composition is often used. It is a hypothesis about a quasi-steady state that is considered in detail in what follows. According to this hypothesis, for the reaction under study there exist three functions of the gas composition,  $w_1 w_2$ , and  $w_3$ , so that the kinetic equations can be written as

$$\begin{aligned} \dot{N}_1 &= -w_1 + w_3 \\ \dot{N}_2 &= w_1 - w_2 \\ \dot{N}_3 &= w_2 - w_3 \end{aligned} \quad (30)$$

It has been shown [11] that, even when we assume  $w_i$  to be such linear functions of the gas concentrations as if the three reaction steps of eqn. (29) were elementary, experimental results can be described well. Let us assume, in accordance with ref. 11, that the three reaction steps of eqn. (29) are elementary. Their stoichiometric vectors are

$$\vec{\gamma}_1 = \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \quad \vec{\gamma}_2 = \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} \quad \vec{\gamma}_3 = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \quad (31)$$

and the stoichiometric matrix is

$$\vec{\Gamma} = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 1 & 0 & -1 \end{bmatrix} \quad (32)$$

Molecules  $A_1$ ,  $A_2$ , and  $A_3$  are isomers and have the same composition. Therefore the amount of any element in the system is proportional to  $N_1 + N_2 + N_3$

$$b_j = a_j(N_1 + N_2 + N_3) \quad (33)$$

where  $a_j$  is the amount of the *j*th element in the isomer molecule.

For our system it is sufficient to consider only one law of conservation

$$b = N_1 + N_2 + N_3 \quad (34)$$

The respective "molecular matrix" is the vector column

$$\vec{A} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (35)$$

$$\vec{b} = \vec{A}^T \vec{N} = (1, 1, 1) \times \begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix}$$

Relationship (24) ( $\vec{\Gamma}\vec{A} = \vec{0}$ ) can readily be tested. The reaction polyhedron  $\vec{D}$  is the intersection of the plane specified by eqn. (34) with a positive octant [Fig. 6(a)]; as is seen in Fig. 6(a),  $\vec{D}$  is a triangle.

Due to the law of conservation (34), the amount of one substance can be expressed in terms of those of two others, e.g.

$$N_3 = b - N_1 - N_2 \quad (36)$$

Hence, eqn. (30) can be represented as a set of two equations containing  $N_1(t)$  and  $N_2(t)$ . The reaction polyhedron  $\vec{D}$  in the coordinates  $N_1$  and  $N_2$  is specified by the conditions  $N_1 \geq 0$ ,  $N_2 \geq 0$ ,  $N_3 = b - N_1 - N_2 \geq 0$ . This is illustrated in Fig. 6(b). It is the same  $\vec{D}$  [Fig. 6(a)], but in the other coordinates; we consider only the limits for  $N_1$  and  $N_2$  variations since  $N_3$  is a function of  $N_1$  and  $N_2$  [eqn. (36)].

*Example 4.* Let us return to the catalytic isomerization reaction described in example 1 and give it a complete consideration without using the suggestion about the low amount of the catalyst and the quasi-steady state hypothesis (in contrast to example 3). Substances for this reaction are: isomers  $A_1$  and  $A_2$ ; surface compounds  $A_3 = Z$  (active size);  $A_4 = A_1Z$ ;  $A_5 = A_2Z$ . There exist two laws of conservation: under conservation are the overall number of isomers (both in the gas and on the surface) and the overall number of active sites

$$\begin{aligned} b_1 &= N_1 + N_2 + N_4 + N_5 \\ b_2 &= N_3 + N_4 + N_5 \end{aligned} \quad (37)$$

The respective "molecular matrix" is

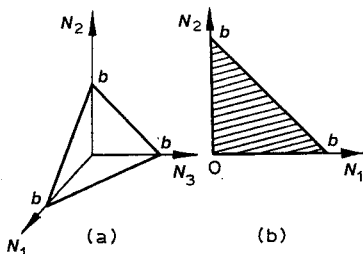


Fig. 6. Reaction polyhedron for butene isomerization (a) in the coordinates of  $N_1$ ,  $N_2$  and  $N_3$  and (b) in the coordinates of  $N_1$  and  $N_2$ .



$$\vec{A} = \begin{bmatrix} 1 & 0 \\ 1 & 0 \\ 0 & 1 \\ 1 & 1 \\ 1 & 1 \end{bmatrix}$$

$$\vec{b} = \vec{A}^T \vec{N}$$

$$\begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} 1 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \\ N_3 \\ N_4 \\ N_5 \end{bmatrix} \quad (38)$$

The number of substances is five, therefore for every values of  $b_1$  and  $b_2$  the two equations (37) specify a three-dimensional plane (linear manifold in the space of compositions). Its intersection with the set of non-negative vectors ( $N_i \geq 0, i = 1, \dots, 5$ ) gives a three-dimensional reaction polyhedron. Let us describe its structure with various ratios of the balance values for  $b_1$  and  $b_2$ . First we will recall one fact from linear algebra: let  $L_1$  and  $L_2$  be linear manifolds (planes) in the  $n$ -dimensional space and their sizes be equal to  $n_1$  and  $n_2$ , respectively. Then, "as a rule", the size of their intersection is  $n_1 + n_2 - n$  if this number is non-negative, otherwise, "as a rule", there is no intersection (the intersection is empty). Let us remind ourselves that the size of a point is zero. "As a rule" here means: (a) if the intersection size is  $n_1 + n_2 - n$ , no sufficiently low variations of  $L_1$  and  $L_2$  (a shift or a turn) can change this size; (b) if the intersection size is different, there exist arbitrarily low variations of  $L_1$  and  $L_2$  (shifts or turns) after which this size becomes equal to  $n_1 + n_2 - n$ . For example, two straight lines on the plane intersect, as a rule, at a point  $n_1 + n_2 - n = 1 + 1 - 2 = 0$ . The exception is either parallel (the intersection is empty) or coincident (the size of intersection equals unity) straight lines. In both cases it suffices to turn one of the straight lines at an arbitrarily small angle and they will intersect at a point.

As a rule, in three-dimensional space the intersection of two straight lines is empty. In case it is not empty, then a small shift of one of the straight lines can make it empty. The intersection of a plane and a straight line is, as a rule, a point, and that of two planes is a straight line. To describe a reaction polyhedron, the first thing to do is to specify its nodes (vertices). They are the intersections of a plane specified by eqn. (37) with some faces of the set (a cone) of non-negative vectors. Faces of this cone are specified by the sets of equations and inequalities

$N_i = 0$  (for  $i$  from a certain set of the indices I).

$N_j \geq 0$  (for  $j$  not entering into I).

Thus, for example 3 the nodes  $\bar{D}$  are the intersection of the plane  $N_1 + N_2 + N_3 = b$  with the edges of the cone for non-negative vectors (Fig. 6), rays

$$\begin{aligned} N_1 = N_2 = 0 \quad N_3 &\geq 0 \\ N_2 = N_3 = 0 \quad N_1 &\geq 0 \\ N_3 = N_1 = 0 \quad N_2 &\geq 0 \end{aligned} \quad (39)$$

It is natural to assume that, as a rule, in the case under consideration (catalytic isomerization) the nodes of  $\bar{D}$  will form at intersections with two-dimensional faces (the space is five-dimensional whilst the face is three-dimensional,  $2 + 3 - 5 = 0$ ). These faces are specified by the conditions  $N_{i_1} = N_{i_2} = N_{i_3} = 0$  at  $j = i_1, i_2, i_3$ . It is also possible that there are special cases of such  $b_1$  to  $b_2$  ratios that a vertex is formed at a point of intersection with a one dimensional face-ray:  $N_{i_1} = N_{i_2} = N_{i_3} = N_{i_4}$ ;  $N_j > 0$  at  $j = i_1, i_2, i_3, i_4$ .

Let  $b_1 > b_2$ . This corresponds to an ordinary case, when the catalyst weight is lower than that of gaseous substances. It is also evident that  $b_1, b_2 > 0$ . We will find vertices of a polyhedron  $\bar{D}$  in the following way. Let some  $N_i$  be equal to zero and under this condition we will examine a set of balance equations (37). If it has only a non-negative solution, then it is this solution that is the vertex of  $\bar{D}$ . If this solution is not the only one, it must be suggested that some other  $N_i = 0$  and it is necessary to examine eqns. (37) once again. After examining all possible combinations of indices  $i$  and assuming that  $N_i = 0$ , we will find all the vertices for the polyhedron  $\bar{D}$ . Since the set of balance equations (37) consists of two equations regarding five unknown quantities, to obtain its only solution it must be supplemented by at least three equations. At  $b_1 > b_2$  we will obtain the following results. System (37) supplemented by one of the conditions  $N_1 = N_2 = N_3 = 0$ ,  $N_1 = N_2 = N_4 = 0$ , or  $N_1 = N_2 = N_5 = 0$  has no non-negative solutions, i.e. the system mass cannot be concentrated in the pairs of substances (a)  $A_1Z, A_2Z$ , (b)  $Z, A_1Z$ , (c)  $Z, A_2Z$ . This is due to the inequality  $b_1 > b_2$ . If eqns. (37) are supplemented by the condition  $N_3 = N_4 = N_5 = 0$ , it appears that the set obtained does not have solutions at all. This is natural, since  $b_2 \neq 0$  and we assume the absence of surface compounds, which leads to this contradiction. For all the rest of the conditions, type  $N_{i_1} = N_{i_2} = N_{i_3} = 0$ , the set of balance equations supplemented by them has the only non-negative solution. These conditions and their solutions are

$$N_1 = N_3 = N_4 = 0 \quad N_2 = b_1 - b_2, \quad N_5 = b_2 \quad (40a)$$

$$N_1 = N_3 = N_5 = 0 \quad N_2 = b_1 - b_2, \quad N_4 = b_2 \quad (40b)$$

$$N_1 = N_4 = N_5 = 0 \quad N_2 = b_1, \quad N_3 = b_2 \quad (40c)$$

$$N_2 = N_3 = N_4 = 0 \quad N_1 = b_1 - b_2, \quad N_5 = b_2 \quad (40d)$$

$$N_2 = N_3 = N_5 = 0 \quad N_1 = b_1 - b_2, \quad N_4 = b_2 \quad (40e)$$

$$N_2 = N_4 = N_5 = 0 \quad N_1 = b_1, \quad N_3 = b_2 \quad (40f)$$

In the cases (40a) and (40d), the whole of the catalyst (its active centres) is concentrated in substance  $A_2Z$ , whereas in cases (40b) and (40e) and (40c) and (40f) it is in  $A_1Z$  and  $Z$ , respectively.

To construct the reaction polyhedron  $\bar{D}$ , it is insufficient to know only its vertices. We must also find its edges, i.e. one-parametric families of the positive solution for set (37) supplemented by the conditions  $N_i = 0$  for a pair of indices  $i_{1,2}$ . Two-dimensional (flat) faces are found as two-parametric families of solutions for eqn. (37) supplemented by the condition  $N_i = 0$  with the only value of  $i$ .

It is convenient to represent the polyhedron  $\bar{D}$  schematically in three-dimensional space. For this purpose, by using the laws of conservation (37), we can eliminate two coordinates by expressing them through the remaining three. It is possible to eliminate any pair of coordinates except for  $N_1, N_2$  and  $N_4, N_5$ . Let us eliminate  $N_3$  and  $N_1$  by using the relationships

$$\begin{aligned} N_3 &= b_2 - N_4 - N_5 \\ N_1 &= b_1 - N_2 - N_4 - N_5 \end{aligned} \quad (41)$$

In the coordinates of  $N_2, N_4$  and  $N_5$  and taking into account eqns. (41), the polyhedron  $\bar{D}$  will be specified only by the inequalities

$$\begin{aligned} N_1 &= b_1 - N_2 - N_4 - N_5 \geq 0 \\ N_3 &= b_2 - N_4 - N_5 \geq 0 \end{aligned}$$

The form of  $\bar{D}$  is illustrated in Fig. 7(a)–(c). The figure also shows what substances concentrate the whole of the mass of the system for vertices of  $\bar{D}$ .

In the high-vacuum experiment, when the quantities of gaseous substances  $N_1$  and  $N_2$  are extremely low, a situation is possible when all the balance values of  $b_1$  and  $b_2$  are commensurable, even  $b_1 < b_2$ . In the latter case the total amount of catalyst active centres is higher than the quantity of gaseous substances. If  $b_1$  approaches  $b_2$  but remains higher than  $b_2$ , some pairs of  $\bar{D}$  vertices also come closer. As seen from eqns. (40), the following vertices will converge: ( $N_2 = b_1 - b_2, N_5 = b_2$ ) [eqn. (40a)] with ( $N_1 = b_1 - b_2, N_5 = b_2$ ) [eqn. (40d)], and ( $N_2 = b_1 - b_2, N_4 = b_2$ ) [eqn. (40b)] with ( $N_1 = b_1 - b_2, N_4 = b_2$ ) [eqn. (40e)].

We have presented here only the non-zero values of the coordinates. In both cases the Euclidean distance between the variants inside these pairs,  $[\sum_{i=1}^5 (N_i - N_i')^2]^{1/2}$ , is equal to  $2^{1/2}|b_1 - b_2|$  and tends to zero at  $b_1 \rightarrow b_2$ . For the other pairs of vertices the situation is different.

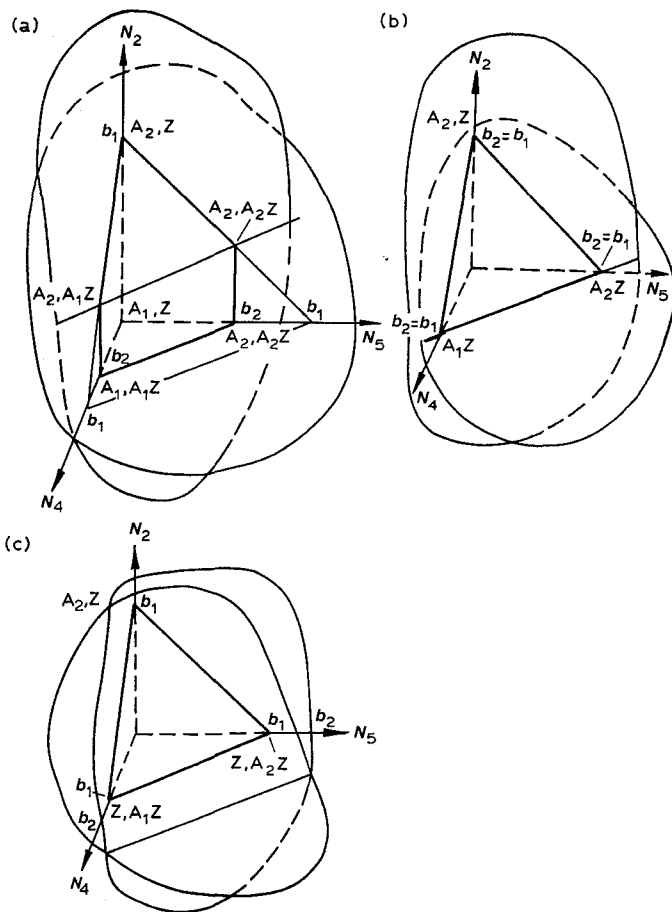


Fig. 7. Reaction polyhedron for catalytic isomerization. (a)  $b_1 > b_2$ ; (b)  $b_1 = b_2$ ; (c)  $b_1 < b_2$ .

At  $b_1 = b_2$ , the value of  $N_1$  in vertices (40d) and (40e) and of  $N_2$  in (40a) and (40b) reduce to zero, and instead of four vertices there remain two, i.e. ( $N_5 = b_1 = b_2$ ) and ( $N_4 = b_1 = b_2$ ). The rest of the coordinates for these points are zero [see Fig. 7(b)]. With further increases in  $b_2$ , we obtain  $b_1 < b_2$ . The vertices ( $N_3 = b_2 - b_1$ ,  $N_4 = b_1$ ) and ( $N_3 = b_2 - b_1$ ,  $N_5 = b_2$ ) appear [Fig. 7(c)]. For these vertices the whole of the gas is adsorbed: for the former in the form of  $A_1Z$  and for the latter as  $A_2Z$ . There are two more vertices, (40c) and (40f), in which gas and catalyst are separated (clean surface) and the whole of the gas is concentrated either in isomer  $A_1$  (40f) or in  $A_2$  (40c). These vertices are common to all the three cases of  $b_1 \geq b_2$  [Fig. 7(a)–(c)].

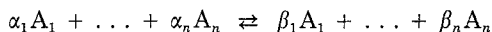
## 1.6 REACTION RATE

When introducing the concept of the elementary reaction rate, we treated it as a number of elementary acts per unit volume or per unit surface for a unit time. But as a rule, the elementary character of a reaction and the number of elementary acts cannot be tested experimentally. Therefore it is important to determine a rate of reaction step using the kinetic equation

$$\vec{N} = S \sum_s \vec{\gamma}_s \vec{w}_s + V \sum_\sigma \vec{\gamma}_\sigma \vec{w}_\sigma$$

Here the step rate  $\vec{w}_{s,\sigma}$  acts as a coefficient for the stoichiometric vector  $\vec{\gamma}_{s,\sigma}$ , and it is this coefficient that is found when processing data of kinetic experiments.

A difference between "elementary" (e.g.,  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ ) and non-elementary (e.g.  $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$ ) reactions is in the form of the  $\vec{w}$  dependence on the reactant concentrations. For elementary reactions the law of mass action (the law of acting surfaces) is assumed to hold. According to these laws, the rates for direct and inverse elementary reactions



are specified as

$$w^{+,-}(c) = k^{+,-}(T) \prod_{i=1}^n c_i^{\alpha_i, \beta_i} \quad (42)$$

The reaction rate for a step,  $w_s$ , is the difference between the rates for the direct and inverse reactions ( $w_s^+$  and  $w_s^-$ , respectively), i.e.  $w = w_s^+ - w_s^-$ . Here  $c_i$  is the concentration of the  $i$ th substance, i.e.  $c_i = N_i/V$  for the gas-phase substance and  $c_i = N_i/S$  for the surface compound and  $\vec{c}$  is the concentration vector. We will use  $\vec{c}^g$  and  $\vec{c}^s$  for the concentration vectors of gas and surface compounds, respectively.

The temperature dependence of the rate constant is usually taken as a generalized Arrhenius law

$$k^\pm(T) = A_0^\pm T^{n^\pm} \exp(-E^\pm/RT) \quad (43)$$

where  $A_0^\pm$  is a constant,  $E^\pm$  the activation energies for the direct and inverse reactions and  $n^\pm$  the exponents of a power that are seldom given a direct physical sense. Sometimes they are associated with the number of degrees of freedom (heat capacity) for the initial reactants and reaction products [3]. At present, we believe it is most reasonable to treat the constants for the generalized Arrhenius law ( $A_0^\pm$ ,  $n^\pm$  and  $E^\pm$ ) as matching parameters found by the interpolation of experimental data. In different elementary act models these parameters can, however, be given a concrete physical sense. In particular,  $E^\pm$  can be interpreted as real activation energies, i.e. values of potential barriers that must be overcome so that a reaction can take place. But one must remember that this is not obligatory.

According to various model considerations, one can often obtain more complicated temperature dependences of rate constants than eqn. (43) (see, for example, ref. 3).

### 1.7 CONCENTRATION EQUATIONS

If a reaction proceeds at a constant reaction volume, eqns. (17) and (18) can be readily rewritten relative to concentrations

$$\frac{1}{V} \frac{d\bar{N}^{\text{gas}}}{dt} = \frac{S}{V} \sum_s \bar{\gamma}_s^{\text{gas}} \bar{w}_s(\bar{c}) + \sum_{\sigma} \bar{\gamma}_{\sigma} \bar{w}_{\sigma}(\bar{c}^{\text{g}}) \quad (44)$$

$$\frac{1}{S} \frac{d\bar{N}^{\text{sur}}}{dt} = \sum_s \bar{\gamma}_s^{\text{sur}} \bar{w}_s(\bar{c})$$

or

$$\frac{d\bar{c}^{\text{g}}}{dt} = \frac{S}{V} \sum_s \bar{\gamma}_s^{\text{gas}} \bar{w}_s(\bar{c}) + \sum_{\sigma} \bar{\gamma}_{\sigma} \bar{w}_{\sigma}(\bar{c}^{\text{g}}) \quad (45)$$

$$\frac{d\bar{c}^{\text{s}}}{dt} = \sum_s \bar{\gamma}_s^{\text{sur}} \bar{w}_s(\bar{c})$$

A somewhat complicated case occurs when the reaction volume is variable. An equation for varying gas concentrations can be obtained from eqns. (17) and (18) using the relationship

$$\frac{d\bar{c}^{\text{g}}}{dt} = \frac{1}{V} \frac{d\bar{N}^{\text{gas}}}{dt} - \frac{\bar{N}^{\text{gas}}}{V^2} \frac{dV}{dt} = \frac{1}{V} \frac{d\bar{N}^{\text{gas}}}{dt} - \bar{c}^{\text{g}} \frac{1}{V} \frac{dV}{dt} \quad (46)$$

$$\frac{d\bar{c}^{\text{s}}}{dt} = \sum_s \bar{\gamma}_s^{\text{s}} \bar{w}_s(\bar{c})$$

and the state equation.

Let us consider it in more detail. Let  $V$  be expressed through concentrations using the balance relationships

$$b_j = \sum_i a_{ij} N_i = \sum_i a_{ij} N_i^{\text{gas}} + \sum_i a_{ij} N_i^{\text{sur}} \quad (47)$$

$$= V \sum_i a_{ij} c_i^{\text{g}} + S \sum_i a_{ij} c_i^{\text{s}}$$

Hence

$$V = \frac{b_j - S \sum a_{ij} c_i^g}{\sum a_{ij} c_i^g} \quad (48)$$

where  $a_{ij}$  are the elements of a molecular matrix and summation in the numerator and denominator is made over the indices corresponding to the surface compounds and gas, respectively. It is convenient to use the gas mass balance since  $\sum m_i c_i^g$  reduce to zero only in the case  $c_i^g = 0$

$$V = \frac{m - S \sum m_i c_i^g}{\sum m_i c_i^g} \quad (49)$$

where  $m_i$  in the numerator is the gas mass entering into a mole of the  $i$ th surface compound\* and in the denominator the mass of a mole of the  $i$ th substance of the gas phase, and  $m$  is the total mass of the system gas (both adsorbed and in the gas phase). Equation (49) has a simple physical sense. Its numerator is the mass of substances that are present in the gas phase (the total mass minus the mass of adsorbed gas) and the denominator is the gas phase density. Accordingly, in eqn. (48) the numerator is the amount of the  $j$ th element in the gas phase and the denominator is its amount per unit volume of gas.

Equation (49) must be substituted for  $V$  in eqn. (46) and  $dV/dt$  is to be expressed through reaction rates using equations of states under given conditions. For isobaric isothermal conditions and in the case of the applicability of the ideal gas model

$$V = N_{\text{tot}}^g \frac{RT}{P} \quad (50)$$

where  $P$  is a constant pressure,  $T$  is a constant temperature,  $N_{\text{tot}}^g$  is the number of gas moles,  $N_{\text{tot}}^g = N_i^g$ , and  $R$  is the universal gas constant.

From eqn. (50) we obtain

$$\frac{dV}{dt} = \frac{RT}{P} \left[ S \sum_s \left( \bar{w}_s(\bar{c}) \sum_i \gamma_{si}^{gas} \right) + V \sum_\sigma \left( \bar{w}_\sigma(\bar{c}^g) \sum_i \gamma_{\sigma i} \right) \right] \quad (51)$$

Using eqns. (49) and (51), eqns. (46) can be represented as

$$\begin{aligned} \frac{d\bar{c}^g}{dt} &= \frac{S \sum m_i c_i^g}{m - S \sum m_i c_i^g} \sum_s w_s(\bar{c}) (\bar{\gamma}_s - \bar{c}^g \frac{RT}{P} \sum_i \gamma_{si}^g) \\ &+ \sum_\sigma w_\sigma(\bar{c}^g) \left( \bar{\gamma}_\sigma - \bar{c}^g \frac{RT}{P} \sum_i \gamma_{\sigma i} \right) \end{aligned} \quad (52)$$

\* The authors have not found a better designation to define a surface substance component transferred from the gas phase.

$$\frac{d\vec{c}^s}{dt} = \sum_s \vec{\gamma}_s^s \vec{w}_s(\vec{c})$$

This equation accounts for variations in the reaction volume for the  $s$ th and  $\sigma$ th steps (per one "mole" of elementary acts in the direct reactions)

$$\Delta V_s = \frac{RT}{P} \sum_i \gamma_{si}^{\text{gas}} \quad \Delta V_\sigma = \frac{RT}{P} \sum_i \gamma_{\sigma i} \quad (53)$$

Thus a method has been demonstrated, taking into account the equation of state, for proceeding from the kinetic equations of the amounts of substance to the equations for concentrations (isobaric process).

It might seem that, for the derivation of kinetic equations describing variations in the amounts of substance eqns. (17) and (18), the equation of state is unnecessary. But this is not so. In the case of a variable reaction volume, it may be necessary to express gas-phase substance concentrations through their amounts, since step rates  $w$  are specified as functions of concentrations. For isobaric isothermal processes and ideal gases  $c^g = N^g/V = PN^g/N_{\text{tot}}^g RT$ .

Note that volume  $V$  can be determined through balance equations and substance concentrations using eqns. (48) and (49) without an equation of state. But to express volume  $V$  through balance equations and substance amounts appears to be impossible and the equation of state must be used. If a process is either non-isothermal or non-isobaric, it is also necessary to give a law of either temperature or pressure variations.

A question arises in what cases have equations for substance concentrations the same form as for substance amounts

$$\begin{aligned} \frac{d\vec{c}^g}{dt} &= \frac{S}{V} \sum_s \vec{\gamma}_s^{\text{gas}} \vec{w}_s(\vec{c}) + \sum_\sigma \vec{\gamma}_\sigma \vec{w}_\sigma(\vec{c}^g) \\ \frac{d\vec{c}^s}{dt} &= \sum_s \vec{\gamma}_s^{\text{sur}} \vec{w}_s(\vec{c}) \end{aligned} \quad (54)$$

It only occurs in the cases when the reaction volume remains unchanged or where its variations during the course of the reaction can be neglected.

We discuss the equation for concentrations in detail since, in many cases, their wrong derivation results in errors.

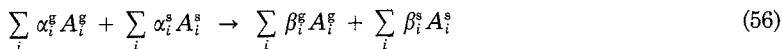
In many cases partial pressures are used as variables. For ideal gases

$$P_i = c_i^g RT \quad (55)$$

and to write  $P_i$  is not difficult (in the isothermal case) if equations for concentrations have been derived. If  $P_i$  are treated as the main variables to



describe the gas phase state, it is natural that reaction rates are also expressed through  $P_i$ . The rate of reaction



is specified as

$$w = k \prod_i (P_i)^{\alpha_i^g} \prod_i (c_i^s)^{\alpha_i^s} \quad (57)$$

In this case if the reaction takes place on the surface,  $w$  has, as usual, a dimension of mole  $\text{cm}^{-2} \text{s}^{-1}$  and accordingly  $k$  is expressed in  $(\text{mole cm}^{-2} \text{s}^{-1} \text{ torr}^{-1})^{\sum \alpha_i^g} \times (\text{mole cm}^{-2})^{\sum \alpha_i^s}$ .

It is also possible to use other pressure units. A detailed analysis for the derivation of kinetic equations for reactions taking place under various conditions is given in ref. 12.

To describe the surface state of catalysts during the course of reactions, one can also use new variables that are surface coverages. They have a simple distinct sense when active centres are of the same type. If the number of active centres and their concentration are designated as  $b_z$  and  $c_z = b_z/S$ , respectively, any compound on the surface  $A_i^s$  can be written as

$$\theta_i = \frac{N_i^s}{b_z} = \frac{c_i^s}{c_z} \quad (58)$$

We do not give a superscript  $s$  for  $\theta_i$  or  $g$  for  $P_i$  since  $\theta$  is a specific characteristic for surface compounds and cannot refer to gases. It is not difficult to rewrite the basic equations in new variables (surface coverages), since  $b_z$  is constant.

Then the balance equation for surface coverages is

$$\sum_i a_{iz} \theta_i = 1 \quad (59)$$

Here  $a_{iz}$  is the number of active centres in the  $i$ th surface substance  $A_i^s$ . If all these substances contain one active centre, eqn. (59) takes the form that is typical for heterogeneous catalysis

$$\sum_i \theta_i = 1 \quad (60)$$

One must remember, however, that in the general case eqn. (59) should be used.

If active centres are of different types, it is possible to introduce surface coverages corresponding to every type of these centres.

## 1.8 NON-IDEAL SYSTEMS

A law of mass action/acting surfaces is the simplest of all the possible kinetic laws. But it seems to be far from being valid in every case. Progress

in the application of this law can be attributed, in particular, to the fact that, for a given series of substances, it is possible, by increasing the number of steps and using the appropriate rate constants and solving kinetic eqns. (17) and (18) for any finite time period, to approximate fairly well any differentiable function  $\bar{N}(t)$  that fits the condition of non-negativity and balance equations (4) and has no points of self-intersection:  $\bar{N}(t_1) \neq \bar{N}(t_2)$  at  $t \neq t_2$ . Roughly speaking, it means that this law can describe any dynamic behaviour in cases where there are no additional limitations (e.g. a principle of detailed equilibrium we will speak about in what follows). If, besides some additional steps, we also introduce new "intermediate substances", then even when the principle of detailed equilibrium holds we can obtain an accurate description for any dynamic behaviour for a finite time period by kinetic equations derived in accordance with the law of mass action/acting surfaces (for details see ref. 13).

Note that the worse this law fits the real conditions the larger is the number of steps (and "intermediate substances") that must be introduced to describe a reaction. It is possible to describe the rate of an elementary reaction in terms of the other kinetic law. An important generalization for the law of mass action (acting surfaces) is the Marcelin-de Donder kinetics [14]. According to this law, every substance  $A_i$  is described by a certain function of concentration, the activity  $a_i(\bar{c})$ . Then the rate of reaction



is described as in eqn. (42), but instead of concentrations reaction activities are given

$$w = k(T) \prod_i a_i^{\alpha_i} \quad (62)$$

Function  $a_i(\bar{c})$  must satisfy the apparent limitation

$$a_i(\bar{c}) = 0 \quad \text{if } c_i = 0 \quad (63)$$

This limitation is adequate to the fact that the rate of substance consumption is zero when this substance is absent.

The law of mass action is a traditional base for modelling chemical reaction kinetics, but its direct application is restricted to ideal systems and isothermal conditions. More general is the Marcelin-de Donder kinetics examined by Feinberg [15], but this also is not always sufficient. Let us give the most general of the reasonable forms of kinetic law matched to thermodynamics. The rate of the reversible reaction eqn. (5) is

$$w(\bar{c}, T) = w^0(\bar{c}, T) (\exp \sum \alpha_i \mu_i - \exp \sum \beta_i \mu_i) \quad (64)$$

where  $w^0(\bar{c}, T)$  is a positive function and  $\mu_i(\bar{c}, T)$  is the pseudo-chemical potential of substance  $A_i$ . As usual,  $\mu_i$  is a chemical potential divided by  $RT$ . A kinetic equation for a closed system is eqn. (17). For a homogeneous system

$$\vec{N} = V \Sigma \vec{\gamma}_s w_s \quad (65)$$

where  $\vec{N}$  is the vector of amounts  $N_i$  of substance  $A_i$ ,  $V$  is the system volume,  $w_s$  is the rate of the  $s$ th step of the type of eqn. (64), and  $\vec{\gamma}_s$  is the stoichiometric vector with components  $\gamma_{si} = \beta_{si} - \alpha_{si}$ . Values of  $N_i$  are the principal variables characterizing the state of the reaction mixture. Under the conditions given, the rest of the values can be expressed through  $\vec{N}$  and the values that are constant under the conditions specified. Then let us assume that it is done every time.

The potentials  $\mu_i$  must satisfy the following conditions.

(1) Condition of symmetry.

$$\frac{\partial \mu_i}{\partial N_j} = \frac{\partial \mu_j}{\partial N_i} \quad (66)$$

(2) Condition of positive values.

(a) A quadratic form

$$\sum_{i,j} x_i \frac{\partial \mu_i}{\partial N_j} x_j \quad (67)$$

is non-negatively determined in  $R^n$ .

(b) A quadratic form (67) is positively determined in any hyperplane with a positive normal  $\nu$  (every  $\nu_i > 0$ ).

Conditions (66) and (67) ensure the existence of Lyapunov's convex function for eqns. (17):  $\partial G / \partial N_i = \mu_i$ . With a known type of the potentials  $\mu_i$  for which condition (1) is fulfilled, one can obtain Lyapunov's thermodynamic functions for various (including non-isothermal) conditions. Thus, for an ideal gas and the law of mass action [16]

$$\mu_i(\bar{c}, T) = \ln c_i + \frac{u_i}{RT} + \frac{C_{Vi}}{R} \ln T + \delta_i$$

where  $u_i$  is the energy for the basic state of  $A_i$ ,  $C_{Vi}$  is the specific partial heat capacity, and  $\delta_i$  is a constant accounting for the position of an equilibrium point. The obtained expression for  $\mu(\bar{c}, T)$  makes it possible to obtain an explicit form for the Lyapunov's function of  $G$ . For example, for a thermostated system under the conditions  $V, U = \text{const.}$  (where  $U$  is the internal energy for the system)

$$G = \Sigma N_i \left( \ln \frac{N_i}{V} + \delta_i - 1 \right) + \frac{C_V}{R} (\ln T + 1)$$

where

$$C_V = \Sigma C_{Vi} N_i$$

and

$$T = \frac{(U - \Sigma u_i N_i)}{C_V}$$

The approach suggested provides the possibility of generalizing similar formulae for  $\mu_i$  and  $G$  for the case of variable specific partial heat capacities, more complex equations of state, non-ideal kinetics at  $V, T = \text{const.}$ , etc. [16, 17]. Note that, at constant heat capacity,  $T$  can be treated as a "substance" [18]. However, to extend this analogy to the general case is incorrect.

## 2. Principle of detailed equilibrium and its corollaries

### 2.1 PRINCIPLE OF DETAILED EQUILIBRIUM

So far (Sect. 1) we have discussed only approaches to derive chemical kinetic equations for closed systems, i.e. those having no exchange with the environment. Now let us study their dynamic properties. For this purpose let us formulate the basic property of closed chemical systems expressed by the principle of detailed equilibrium: a rest point for the closed system is a point of detailed equilibrium (PDE), i.e. at this point the rate of every step equals zero

$$w_s^+ = w_s^-, w_s = w_s^+ - w_s^- = 0 \quad (68)$$

Hence if in the closed system  $\dot{c} = \dot{N} = 0$ , then for every step  $w_s = 0$ .

Fundamental results in substantiating and extending the principle of detailed equilibrium to a wide range of chemical processes were obtained in 1931 by Onsager, though chemists had also applied this principle (see Chap. 2). A derivation of this principle from that of microscopic reversibility was reported by Tolman [19] and Boyd [20]. In the presence of an external magnetic field it is possible that equilibrium is not detailed. Respective modifications of this principle were reported by de Groot and Mazur [21].

Note that, when speaking about closed systems, one should remember not only the extent of the closed nature, i.e. the absence of in-flux and off-flux of the substance, but also about the equilibrium of the environment with which the system interacts. The ideal interaction with an equilibrium environment can be of several types, e.g. (a) according to the heat, they are isothermal (interacting with a thermostat) or heat insulating and (b) according to volume and pressure these interactions are isobaric or isochoric.

The principle of detailed equilibrium accounts for the specific features of closed systems. For kinetic equations derived in terms of the law of mass/surface action, it can be proved that (1) in such systems a positive equilibrium point is unique and stable [22–25] and (2) a non-steady-state behaviour of the closed system near this positive point of equilibrium is very simple. In this case even damped oscillations cannot take place, i.e. the positive point is a stable node [11, 26–28].

Let us recall that a point is called positive if all its coordinates are above zero ( $N_i > 0$  or, which is the same,  $c_i > 0$ ). Postulates (1) and (2) will be

proved below. The existence of the PDE imposes limitations on the equilibrium constants, i.e. the ratios of the direct to reverse reaction rate constants. Let us establish a form of these limitations

$$w_s^+ = w_s^- \quad (69)$$

$$k_s^+ \prod_i c_i^{*\alpha_{si}} = k_s^- \prod_i c_i^{*\beta_{si}}$$

where  $c_i^*$  is the equilibrium concentration of  $A_i$ .

After simple transformations and taking the logarithms of both sides of eqn. (69), we obtain

$$\sum_i (\beta_{si} - \alpha_{si}) \ln c_i^* = \ln(k_s^+/k_s^-) = \ln K_s \quad (70)$$

where  $K_s$  is the equilibrium constant for the  $s$ th step.

If for convenience the vector with the components  $\ln c_i^*$  and  $\ln K_s$  are expressed through  $\ln \vec{c}^*$  and  $\ln \vec{K}$ , respectively, eqn. (70) will take the form

$$\vec{\Gamma} \ln \vec{c}^* = \ln \vec{K} \quad (71)$$

Since, for the time when  $\vec{c}^*$  runs through a multitude of positive vectors,  $\ln \vec{c}^*$  moves across the whole of the linear  $n$ -dimensional space (ln projects a positive real semi-axis to the total axis), the only limitation on  $\vec{K}$  resulting from the existence of a PDE is

$$\ln \vec{K} \in \text{Im } \vec{\Gamma} \quad (72)$$

This means that the vector with the components  $\ln K_s$  lies in the  $\text{Im } \vec{\Gamma}$ , which is the image pattern for a matrix  $\vec{\Gamma}$ , i.e. there exists such an  $n$ -dimensional vector  $\vec{x}$  as

$$\vec{\Gamma} \vec{x} = \ln \vec{K} \quad (73)$$

$$\sum_i \gamma_{si} x_i = \ln K_s$$

The question arises of how an explicit form for the limitations on  $K_s$  associated with the conditions (72) and (73) can be found. For this purpose it is necessary to find all the solutions for the set of equations

$$\sum_s y_s \gamma_{si} = 0 \quad i = 1, \dots, n; \quad \vec{y} \vec{\Gamma} = \vec{0} \quad (74)$$

where  $\vec{y}$  is the row vector.

After obtaining a complete set of linear-independent solutions for eqn. (74),  $\vec{y}^1, \dots, \vec{y}^l$ , it is possible to derive limitations on  $K_s$  that are equivalent to eqns. (72) and (73)

$$\vec{y}^j \ln \vec{K} = \vec{0} \quad (75)$$

$$\sum_s y_s^j \ln k_s = 0 \quad j = 1, \dots, l$$

Some examples are given below. The simplest example is given by the system

of three isomers (the isomerization of butenes): (1)  $A_1 \rightleftharpoons A_2$ ; (2)  $A_2 \rightleftharpoons A_3$ , and (3)  $A_3 \rightleftharpoons A_1$ .

$$\bar{\Gamma} = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 1 & 0 & -1 \end{bmatrix}$$

$$\bar{y}\bar{\Gamma} = \bar{0}: \begin{cases} -y_1 + y_3 = 0 \\ y_1 - y_2 = 0 \\ y_2 - y_3 = 0 \end{cases} \quad (76)$$

It is evident from eqn. (76) that  $y_1 = y_2 = y_3$ . This set of equations has the only solution accurate to a constant coefficient, say  $\bar{y} = (1, 1, 1)$ . The respective limitation on the equilibrium constants is

$$\bar{y} \ln \bar{K} = \bar{0} \quad (77)$$

$$\ln K_1 + \ln K_2 + \ln K_3 = 0$$

or  $K_1 K_2 K_3 = 1$ .

Similarly, for an arbitrary linear (monomolecular) cycle (edges = steps, not to be confused with a bipartite graph of the mechanism) we have

$$\begin{aligned} (1) & A_1 \rightleftharpoons A_2 \\ (2) & A_2 \rightleftharpoons A_3 \\ & \dots \dots \dots \\ (n-1) & A_{n-1} \rightleftharpoons A_n \\ (n) & A_n \rightleftharpoons A_1 \end{aligned} \quad (78)$$

$$\bar{\Gamma} = \begin{bmatrix} -1 & 1 & 0 & \dots & 0 \\ 0 & -1 & 1 & \dots & 0 \\ 0 & 0 & -1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots -1 & 1 \\ 1 & 0 & 0 & \dots 0 & -1 \end{bmatrix}$$

$$\bar{y}\bar{\Gamma} = \bar{0}: \begin{cases} -y_1 + \dots + y_n = 0 \\ y_1 - y_2 = 0 \\ y_2 - y_3 = 0 \\ \dots \dots \dots \\ y_{n-1} - y_n = 0 \end{cases} \quad (79)$$

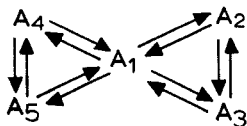
It is evident that  $y_1 = y_2 \dots = y_n$ , and we have the only solution accurate to a constant factor, hence it is possible to choose  $\bar{y} = (1, 1, \dots, 1)$ . Whence the limitations on the equilibrium constants will be

$$\ln K_1 + \ln K_2 + \dots + \ln K_n = 0$$

or

$$K_1 K_2 \dots K_n = 1 \quad (80)$$

It can be shown that, for any monomolecular mechanism, all limitations on the equilibrium constants resulting from the principle of detailed equilibrium will be exhausted if, for every simple cycle in the graph of this mechanism (edges - reactions), correlations (80) are written. Thus, for the mechanism: (1)  $A_1 \rightleftharpoons A_2$ ; (2)  $A_2 \rightleftharpoons A_3$ ; (3)  $A_3 \rightleftharpoons A_1$ ; (4)  $A_1 \rightleftharpoons A_4$ ; (5)  $A_4 \rightleftharpoons A_5$ ; (6)  $A_5 \rightleftharpoons A_1$

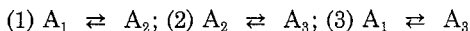


Limitations on the equilibrium constants will be:  $K_1 K_2 K_3 = 1$  and  $K_4 K_5 K_6 = 1$ .

Note that eqn. (80) will apply in the case when in all steps the direct reactions are oriented as shown in eqns. (78). Otherwise some  $k^+$  change places with  $k^-$ ,  $K_s$  becomes  $1/K_s$  and eqn. (80) can be replaced by

$$\prod_s (K_s)^{\sigma_s} = 1 \quad (81)$$

where  $\sigma_s = 1$  when in sth step the direct reaction is oriented as shown in eqns. (78), and in reverse case  $\sigma_s = -1$ . For example, for the scheme



we obtain  $K_1 K_2 / K_3 = 1$  or  $K_3 = K_1 K_2 (\sigma_3 = -1)$ .

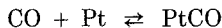
In studies of catalytic reactions, linear (monomolecular) mechanisms are observed in the following two cases.

(1) The stoichiometric (brutto) equations for the conversion of gas-phase substances are considered. According to them, linear kinetic equations can be obtained, apparently, if only the time scale is changed. These reactions are pseudo-monomolecular and comprehensively treated by Wei and Prater [11]. An example is the familiar reaction of butene isomerization.

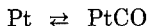
(2) Conversions of only surface compounds are considered. It is suggested that the gas-phase composition remains unchanged. If, in this case, the mechanism is linear with respect to intermediates, the conversion mechanism for these intermediates is monomolecular.

In the first case (pseudo-monomolecular reactions) the application of a

relationship for the equilibrium constants is necessary and grounded. In the second case (a monomolecular scheme for the conversion of surface substances) "equilibrium constants" are not real equilibrium constants, but include concentrations of gas-phase reactants. For example, for the step



the real equilibrium constant is  $k^+/k^-$ , whereas for the proper step of a linear mechanism for the intermediate conversions



we will obtain  $k^+[\text{CO}]/k^-$  instead of an equilibrium constant since

$$w^+ = (k^+[\text{CO}])[\text{Pt}]$$

and

$$w^- = k^-[\text{PtCO}]$$

Therefore in the second case, the limitations on "equilibrium constants" given by eqns. (80) and (81) are not applicable. They must be used to study constants of the real mechanism, including gas-phase substances. The limitations thus obtained will also affect "rate constants" for the conversion scheme of intermediates.

It is of importance to understand that the limitation on rate constants (to be more precise, on their ratios, i.e. equilibrium constants) resulting from the detailed equilibrium principle, are fulfilled irrespective of the system under which the reaction takes place (either closed or open) since the rate constants are the same. The difference is that the right-hand sides in the equations for open systems contain additional factors accounting for the substance exchange with the environment. When choosing kinetic parameters, one must remember that not all of them are independent. It will reduce laborious difficulties and preclude probable mistakes.

Let us consider one more example and examine once again the simplest reaction of catalytic isomerization [example (1)] with substances  $A_1, A_2, A_3 = Z, A_4 = A_1Z$  and  $A_5 = A_2Z$  and the mechanism (0)  $A_1 \rightleftharpoons A_2$ ; (1)  $A_1 + A_3 \rightleftharpoons A_4$ ; (2)  $A_4 \rightleftharpoons A_5$ ; (3)  $A_2 + A_3 \rightleftharpoons A_5$ . The corresponding stoichiometric matrix is

$$\bar{\Gamma} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ -1 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & -1 & 1 \\ 0 & -1 & -1 & 0 & 1 \end{bmatrix}$$



$$\vec{y}\vec{\Gamma} = \vec{0}: \begin{cases} -y_0 - y_1 & = 0 \\ y_0 & - y_3 = 0 \\ -y_1 & - y_3 = 0 \\ y_1 - y_2 & = 0 \\ y_2 + y_3 & = 0 \end{cases}$$

whence  $y_0 = -y_1 = y_3 = -y_2$ . We have the only solution accurate to a constant factor and can suggest that  $\vec{y} = (1, -1, -1, 1)$ . Hence, from eqn. (75), we obtain

$$K_0 K_3 = K_1 K_2$$

or

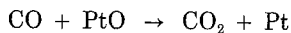
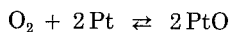
$$K_0 = \frac{K_1 K_2}{K_3}$$

A physical sense of this limitation is simple. It implies that catalysis "does not shift the equilibrium", i.e. in the presence of a catalyst the equilibrium gas composition is in equilibrium itself. Generally speaking, it does not only hold for catalytic reactions. Limitations on the equilibrium constants of eqns. (72), (73), and (75) suggest that reactions do not "shift the equilibrium of the others" since the equilibrium is detailed.

Limitations (75) do not apply if all the  $\vec{y}_s$  are linearly independent. Then the conditions  $\vec{y}\vec{\Gamma} = \vec{0}$  are not fulfilled for any of the non-zero  $\vec{y}$  values since it is equivalent of the relationship

$$\sum_s y_s \vec{y}_s = \vec{0}$$

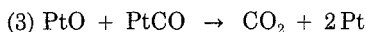
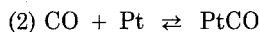
Thus, for the Eley-Rideal mechanism



the stoichiometric vectors ( $A_1 = \text{O}_2$ ,  $A_2 = \text{CO}$ ,  $A_3 = \text{Pt}$ ,  $A_4 = \text{PtO}$ , and  $A_5 = \text{CO}_2$ )

$$\vec{y}_1 = \begin{bmatrix} -1 \\ 0 \\ -2 \\ 2 \\ 0 \end{bmatrix} \quad \vec{y}_2 = \begin{bmatrix} 0 \\ -1 \\ 1 \\ -1 \\ 1 \end{bmatrix}$$

are linearly independent (if they were linearly dependent, we would have the proportionality  $\vec{\gamma}_1 = \sigma\vec{\gamma}_2$ ). The same is true for the Langmuir–Hinshelwood mechanism

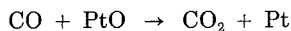


Here,  $A_1 = \text{O}_2$ ,  $A_2 = \text{CO}$ ,  $A_3 = \text{Pt}$ ,  $A_4 = \text{PtO}$ ,  $A_5 = \text{PtCO}$ , and  $A_6 = \text{CO}_2$ .

$$\vec{\gamma}_1 = \begin{bmatrix} -1 \\ 0 \\ -2 \\ 2 \\ 0 \\ 0 \end{bmatrix} \quad \vec{\gamma}_2 = \begin{bmatrix} 0 \\ -1 \\ -1 \\ 0 \\ 1 \\ 0 \end{bmatrix} \quad \vec{\gamma}_3 = \begin{bmatrix} 0 \\ 0 \\ 2 \\ -1 \\ -1 \\ 1 \end{bmatrix}$$

Vectors  $\vec{\gamma}_1$ ,  $\vec{\gamma}_2$ , and  $\vec{\gamma}_3$  are linearly independent. This is evident since each of them has a component with non-zero value at a place where the other two have zero values. Therefore, in this case, a standard procedure to test a linear independence is unnecessary.

Let us consider now the limitations on the constants of a joint four-step mechanism. As a fourth step, the Langmuir–Hinshelwood mechanism will be supplemented by



To enable the possibility of speaking about equilibrium constants, steps (3) and (4) will be assumed to be reversible (in principle, this must be so but the rate constants for reverse reactions are so small that they are usually neglected).

$$\vec{\Gamma} = \begin{bmatrix} -1 & 0 & -2 & 2 & 0 & 0 \\ 0 & -1 & -1 & 0 & 1 & 0 \\ 0 & 0 & 2 & -1 & -1 & 1 \\ 0 & -1 & 1 & -1 & 0 & -1 \end{bmatrix}$$

$$\bar{y}\bar{\Gamma} = \bar{0}: \begin{cases} y_1 & & & = 0 \\ & -y_2 & & -y_4 = 0 \\ 2y_1 - y_2 + 2y_3 + y_4 & = 0 \\ 2y_1 & & -y_3 - y_4 & = 0 \\ & y_2 - y_3 & & = 0 \\ & & y_3 + y_4 & = 0 \end{cases}$$

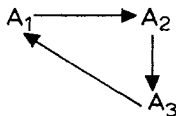
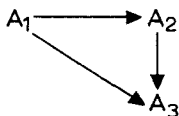
whence  $y_1 = 0$ ,  $y_2 = y_3 = -y_4$ . Taking  $\bar{y} = (0, 1, 1, -1)$ , the respective limitations will be

$$\ln K_2 + \ln K_3 - \ln K_4 = 0 \quad \text{or} \quad K_2 K_3 = K_4 \quad (82)$$

According to eqn. (82), the third and the fourth steps can be almost irreversible only simultaneously ( $K_{3,4} = k_{3,4}^+/k_{3,4}^- \rightarrow \infty$  when  $K_2$  is not reducing to zero).

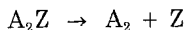
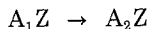
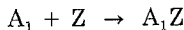
Thus, assuming that one of the mechanisms (either the Langmuir-Hinshelwood or the Eley-Rideal) is irreversible, the second mechanism must also be assumed to be irreversible provided that  $K_2 \neq 0$ . If the process is carried out at high temperatures and  $K_2$  is a minute value, the equality  $K_4 = K_2 K_3$  can also be fulfilled in the case when the fourth step is reversible and the third is practically irreversible. It does not contradict the principle of detailed equilibrium.

This principle also imposes limitations on which combinations of steps can be reversible and which can not. For example, mechanism (a) can be and mechanism (b) can not.

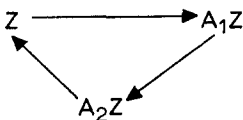


Indeed, according to eqn. (80) for the reaction mechanism  $A \rightleftharpoons A_2$ ;  $A_2 \rightleftharpoons A_3$ ;  $A_3 \rightleftharpoons A_1$ , we obtain  $K_1 K_2 K_3 = 1$ . In case (a) (for "almost complete irreversibility"),  $K_1 \rightarrow \infty$ ,  $K_2 \rightarrow \infty$ ,  $K_3 \rightarrow 0$  and their product can tend to 1. In case (b), all the three constants  $K_1$ ,  $K_2$  and  $K_3$  tend to infinity and their product cannot tend to 1.

Let us remember once again that all these limitations refer to the constants of the real mechanism also involving gas-phase substances. For the conversion mechanisms for intermediates (under the assumption of constant concentrations for gas-phase reactants), the conditions (75) cannot be used directly. Thus mechanism (b) (an irreversible linear cycle) for intermediates is possible. The simplest example is the irreversible catalytic isomerization



Conversions of intermediates are



Limitations on the conversion mechanism for intermediates can result from the analysis of the mechanism involving the participation of gases. Thus for the four-step mechanism of CO oxidation on Pt the third and the fourth steps must be simultaneously either reversible or irreversible.

Rate constants and reaction mechanisms for non-ideal systems (the Marcelin-de Donder kinetic law) are subject to the same limitations. For them eqns. (69)–(71) include  $a_i(\bar{c}^*)$  instead of  $c_i^*$ ; the remaining equations and all the reasoning are the same [28].

## 2.2 THE UNIQUENESS AND STABILITY OF EQUILIBRIUM IN CLOSED SYSTEMS

Let the equilibrium constants satisfy the conditions (72) (73) and (75). This suggests that there exists at least one positive PDE,  $\bar{c}^*$ . Let us show that in this case any steady-state point is that of detailed equilibrium when the law of mass action (active surfaces) is valid.

(a) *Reaction at a constant volume.* Let us introduce the function

$$G = \sum_{i=1}^n N_i \left[ \ln \left( \frac{c_i}{c_i^*} \right) - 1 \right]$$

and calculate its derivative from a set of the kinetic equations (17) and (18)

$$\frac{dG}{dt} = \sum_i \frac{\partial G}{\partial N_i} \frac{dN_i}{dt}$$

$$\frac{\partial G}{\partial N} = \ln \left( \frac{c_i}{c_i^*} \right)$$

Taking into account that  $\bar{c}^g = \bar{N}^g/V$  and  $\bar{c}^s = \bar{N}^s/S$

$$\frac{dG}{dt} = S \sum_{i,s} w_s \gamma_{si} \ln \left( \frac{c_i}{c_i^*} \right) + V \sum_{i,\sigma} w_\sigma \gamma_{\sigma i} \ln \left( \frac{c_i}{c_i^*} \right)$$

But for every  $s$  (and similarly for every  $\sigma$ )

$$\sum_i \gamma_{si} \ln \left( \frac{c_i}{c_i^*} \right) = \ln \left( \frac{\prod_i c_i^{\gamma_{si}}}{\prod_i c_i^{*\gamma_{si}}} \right)$$

Note that

$$\begin{aligned}\frac{w_s^-(\bar{c})}{w_s^+(\bar{c})} &= \frac{k_s^-}{k_s^+} \prod_i c_i^{\beta_{si} - \alpha_{si}} \\ &= \frac{k_s^-}{k_s^+} \prod_i c_i^{\gamma_{si}}\end{aligned}$$

At a PDE we have  $w^+(\bar{c}^*) = w^-(\bar{c}^*)$  and

$$\begin{aligned}\frac{k_s^-}{k_s^+} \prod_i c_i^{*\gamma_{si}} &= 1 \\ \frac{k_s^+}{k_s^-} &= \prod_i c_i^{*\gamma_{si}}\end{aligned}$$

whence

$$\begin{aligned}\sum_i \ln \left( \frac{c_i}{c_i^*} \right) \gamma_{si} &= \ln \left( \frac{w_s^-}{w_s^+} \right) = - \ln \left( \frac{w_s^+}{w_s^-} \right) \\ \frac{dG}{dt} &= -S \sum_s w_s \ln \left( \frac{w_s^+}{w_s^-} \right) - V \sum_\sigma w_\sigma \ln \left( \frac{w_\sigma^+}{w_\sigma^-} \right)\end{aligned}\tag{83}$$

A logarithm is a monotonic function. If  $w^+ > w^-$ , then  $\ln w^+ > \ln w^-$  and vice versa: if  $w^+ < w^-$ , then  $\ln w^+ < \ln w^-$ ; therefore for every  $s$  we obtain

$$w_s \ln \left( \frac{w_s^+}{w_s^-} \right) = (w_s^+ - w_s^-)(\ln w_s^+ - \ln w_s^-) \geq 0$$

and the equality to zero is obtained only in the case when, at a point of equilibrium,  $w_s^+ = w_s^-$ .

(b) *Reaction at constant pressure.* For this case let us introduce the function

$$G = \sum_i N_i^g \ln \left( \frac{c_i^g}{c_i^{*g}} \right) + \sum_i N_i^s \left[ \ln \left( \frac{c_i^s}{c_i^{*s}} \right) - 1 \right]\tag{84}$$

Assuming that we have an ideal gas, let us calculate a  $G$  derivative from eqn. (18).

$$\begin{aligned}\frac{dG}{dt} &= \sum_i \frac{\partial G}{\partial N_i} \frac{dN_i}{dt} \\ \frac{\partial G}{\partial N_i^g} &= \ln \left( \frac{N_i^g}{N_i^{*g}} \right) - \ln \left( \frac{\sum_i N_i^g}{\sum_i N_i^{*g}} \right) \\ &= \ln \left( \frac{c_i^g}{c_i^{*g}} \right)\end{aligned}$$

Here we have taken into account that  $\vec{c}^g = \vec{N}^g/V$ , therefore

$$\ln \left( \frac{c_i^g}{c_i^{*g}} \right) = \ln \left( \frac{N_i^g}{N_i^{*g}} \right) - \ln \left( \frac{\sum_i N_i^g}{\sum_i N_i^{*g}} \right)$$

and

$$G = \sum_i N_i^g \ln \left( \frac{N_i^g}{N_i^{*g}} \right) - N_{\text{tot}}^g \ln \left( \frac{N_{\text{tot}}^g}{N_{\text{tot}}^{*g}} \right) + \sum_i N_i^g \left[ \ln \left( \frac{c_i^s}{c_i^{*s}} \right) - 1 \right]$$

where  $N_{\text{tot}}^g = \sum_i N_i^g$  is the total amount of the gas-phase substance (in moles). As in the case of a constant volume

$$\frac{\partial G}{\partial N_i^g} = \ln \left( \frac{c_i^s}{c_i^{*s}} \right)$$

therefore

$$\frac{dG}{dt} = -S \sum_s w_s \ln \left( \frac{w_s^+}{w_s^-} \right) - V \sum_\sigma w_\sigma \ln \left( \frac{w_\sigma^+}{w_\sigma^-} \right) \quad (85)$$

$dG/dt \leq 0$ , hence the equality with zero is obtained only at PDEs.

Consequently, if the law of mass/surface action is suggested from the existence of at least one PDE, then it follows that there exists a dissipation function of the composition  $G$  whose derivative equals zero only at PDEs. The product RTG has the dimensions of energy.

The existence of this dissipation function results in the fact that any positive steady-state point for eqns. (17) and (18) is that of detailed equilibrium and any positive  $\omega$ -limit point is also an equilibrium point. Determining  $G$  on the boundary of the reaction polyhedron (some  $N_i = 0$ ) according to the limit transition, we can readily see that any non-negative (including a boundary)  $\omega$ -limit point (including the steady-state point) is also a PDE [7]. The value  $G$  is redetermined on the boundary in the following way. If  $N_i \neq 0$ ,  $N_i \rightarrow 0$ , we obtain  $N_i \ln N_i \rightarrow 0$ , therefore if  $N_i = 0$ , the item in  $G$  corresponding to the  $i$ th substance is omitted (is assumed to equal zero).  $G$  is a strictly convex function in the reaction polyhedron  $\bar{D}$ . This means that, for any two points of  $\bar{D}$ ,  $\bar{N}$  and  $\bar{N}'$ , a value for  $G$  at a segment between them at a point  $N + \lambda(\bar{N}' - \bar{N})$  ( $0 < \lambda < 1$ ) satisfies the inequality

$$G[\bar{N} + \lambda(\bar{N}' - \bar{N})] < G(\bar{N}) + \lambda[G(\bar{N}') - G(\bar{N})] \quad (86)$$

i.e. at any segment the plotted dependence of  $G$  lies under its chord. For the case of constant volume, the function  $f(x) = x \ln ax$  (at  $a > 0$ ) is strictly convex and the sum of a convex function is convex.  $G$  is the sum of such a

function from all  $N_i$  values. In the case of constant pressure, one must prove the convexity for the function

$$\sum_i N_i^g \ln N_i^g - \left( \sum_i N_i^g \right) \ln \left( \sum_i N_i^g \right) = G_0$$

(Here, for convenience, we omit in eqn. (84) all items that are linear with respect to  $\bar{N}$  containing  $\ln N_i^{*g}$  and also convex function of  $\bar{N}^{surf}$ .) Let us make use of one more characteristic property of smooth, strictly convex functions: in any direction a second derivative of  $G_0$  in  $\bar{D}$  must be rigorously positive. To check it, let us write

$$N_i = N_{0i} + x\delta_i$$

where  $\delta_i$  are components of a guiding vector along which a second derivative will be taken. If substance  $A_i$  is a surface compound, then  $\delta_i = 0$ . On the other hand, there exists such a gas-phase substance  $A_j$  that  $\delta_j = 0$

$$\frac{d^2 G_0}{dx^2} = \sum_{i=1}^n \left( \frac{\delta_i^2}{N_{0i}^g} \right) = \frac{\left( \sum_{i=1}^n \delta_i \right)^2}{\sum_{i=1}^n N_{0i}^g}$$

After an elementary transformation, we obtain (it is recommended that the reader do it for himself)

$$\frac{d^2 G_0}{dx^2} = \sum_{i>j} \left( \frac{\delta_i \sqrt{N_{0j}^g}}{\sqrt{N_{0i}^g}} - \frac{\delta_j \sqrt{N_{0i}^g}}{\sqrt{N_{0j}^g}} \right)^2 \bigg/ \sum_{k=1}^n N_{0k}^g \geq 0$$

The equality to zero is obtained only in the case where, for any  $i, j = 1, \dots, n$  we have  $\delta_i/N_{0i}^g = \delta_j/N_{0j}^g$ , i.e. when the vector  $\vec{\delta}$  (with components  $\delta_i$ ) is proportional to that with components  $N_{0i}^g$ , in other words there exists a value of  $\lambda$  such that  $\delta_i = \lambda N_{0i}^g$ . But this is possible only in the case in which all the components  $\delta_i$  are simultaneously either positive or negative. Since, at some non-zero value of  $x$ , the vectors with components  $N_{0i}$  and  $N_{0i} + \delta_i$  must lie in the same reaction polyhedron, the simultaneous positivity or negativity for all the  $\delta_i$  values is forbidden by, for example, the law of conservation of the overall (taking into account its adsorption) gas mass:  $\sum m_i N_{0i} = \sum m_i (N_{0i} + x\delta_i)$ ;  $\sum m_i \delta_i = 0$ , for any  $A_i^g$  we have  $m_i > 0$ , hence  $\delta_i$  cannot have the same signs. Consequently, in the reaction polyhedron,  $G$  is a strictly convex function since the sum of a strictly convex  $G_0$  with a linear function of  $\bar{N}^g$  and a strictly convex function of  $\bar{N}$  is strictly convex in this polyhedron.

The strict convexity of the function  $G$  in the reaction polyhedron  $\bar{D}$  results in the following important property. In this polyhedron  $G$  has the unique local minimum. At the same time this local minimum is a global one.

It is this property that was used by Zel'dovich [22] to prove the uniqueness of the equilibrium specified as a point of the free energy minimum.

Note that the positive point for the  $G$  minimum in the reaction polyhedron is that of detailed equilibrium:  $dG/dt \leq 0$ , hence at the point of minimum we have  $dG/dt = 0$  (a decrease is possible "no-where") and according to eqns. (83)–(85),  $dG/dt = 0$  only at the PDEs.

It was Zel'dovich who showed [22] that  $G$  cannot have a local minimum in  $\bar{D}$  on the  $\bar{D}$  boundary, where it is characterized by one specific property:  $\partial G/\partial N_i \rightarrow \infty$  at  $N_i \rightarrow 0$ . Therefore when  $G$  tends to go along a straight line out of the  $\bar{D}$  interior to any boundary point, starting from a certain instant the  $G$  value will increase.

These notes suggest that each reaction polyhedron has a positive PDE coinciding with a point at which  $G$  is a minimum (we assumed the existence of a positive point at least in one reaction polyhedron and as a consequence the existence of such a point for every polyhedron).

Not a single steady-state point in kinetic equations cannot be asymptotically stable in  $\bar{D}$  if it does not coincide with a point of  $G$  minimum. Indeed, let us denote this steady-state point as  $\bar{N}_0$  and assume that it is not the point of  $G$  minimum. Then in any vicinity of  $\bar{N}_0$  there exist points  $\bar{N}$  for which  $G(\bar{N}) < G(\bar{N}_0)$  (otherwise  $\bar{N}_0$  would be a point of local minimum). But a solution of the kinetic equations whose initial values are such values of  $\bar{N}$ , since  $G(\bar{N}) < G(\bar{N}_0)$ , at  $t \rightarrow \infty$  cannot tend to  $\bar{N}_0$ :  $G(\bar{N})$  can only diminish with time. Consequently,  $\bar{N}_0$  is not an asymptotically stable rest point in  $\bar{D}$ . In its vicinity in  $\bar{D}$  there exists such  $\bar{N}$  points that, coming from these points, solutions for kinetic equations do not tend to  $\bar{N}_0$  at  $t \rightarrow \infty$ .

Let us consider the behaviour of a chemical system in the vicinity of a positive PDE  $\bar{N}^*$  ( $\bar{N}_i^* > 0$  for all values of  $i$ ). An equation for linear approximation is

$$\begin{aligned} \frac{dN_i}{dt} = & S \sum_{s,j} \gamma_{si} \left. \frac{\partial w_s}{\partial N_j} \right|_{\bar{N}^*} (N_j - N_j^*) \\ & + V(\bar{N}^*) \sum_{\sigma,j} \gamma_{\sigma i} \left. \frac{\partial w_\sigma}{\partial N_j} \right|_{\bar{N}^*} (N_j - N_j^*) \end{aligned} \quad (87)$$

Let us calculate  $(\partial w_{s,\sigma}/\partial N_j)|_{\bar{N}^*}$

$$\begin{aligned} w_s &= k_s^+ \prod_j \left( \frac{N_j^g}{V} \right)^{\alpha_{sj}} \prod_j \left( \frac{N_j^s}{S} \right)^{\alpha_{sj}} - k_s^- \prod_j \left( \frac{N_j^g}{V} \right)^{\beta_{sj}} \prod_j \left( \frac{N_j^s}{S} \right)^{\beta_{sj}} \\ w_\sigma &= k_\sigma^+ \prod_j \left( \frac{N_j^g}{V} \right)^{\alpha_{sj}} - k_\sigma^- \prod_j \left( \frac{N_j^g}{V} \right)^{\beta_{sj}} \end{aligned}$$

For the case of a constant volume  $V$ , we obtain



$$\begin{aligned} \left. \frac{\partial w_s}{\partial N_j} \right|_{\bar{N}^*} &= \frac{1}{N_j^*} \left[ k_s^+ \alpha_{sj} \prod_k \left( \frac{N_k^{*g}}{V} \right)^{\alpha_{sk}} \prod_k \left( \frac{N_k^{*s}}{S} \right)^{\alpha_{sk}} \right. \\ &\quad \left. - k_s^- \beta_{sj} \prod_k \left( \frac{N_k^{*g}}{V} \right)^{\beta_{sk}} \prod_k \left( \frac{N_k^{*s}}{S} \right)^{\beta_{sk}} \right] \end{aligned} \quad (88)$$

Note that

$$k_s^+ \prod_k \left( \frac{N_k^{*g}}{V} \right)^{\alpha_{sk}} \prod_k \left( \frac{N_k^{*s}}{S} \right)^{\alpha_{sk}} = k_s^- \prod_k \left( \frac{N_k^{*g}}{V} \right)^{\beta_{sk}} \prod_k \left( \frac{N_k^{*s}}{S} \right)^{\beta_{sk}}$$

The left- and the right-hand sides of the equality are  $w_s^+$  and  $w_s^-$ , respectively, taken at a PDE:  $w_s^+(\bar{c}^*) = w_s^-(\bar{c}^*)$ . Let us express  $w_s^* = w_s^+(\bar{c}^*) = w_s^-(\bar{c}^*)$  and rewrite eqn. (88) as

$$\left. \frac{\partial w_s}{\partial N_j} \right|_{\bar{N}^*} = - \gamma_{sj} \frac{w_s^*}{N_j^{*g}} \quad (89)$$

Similarly, for gas-phase reactions we obtain

$$\left. \frac{\partial w_s}{\partial N_j} \right|_{\bar{N}^*} = - \gamma_{aj} \frac{w_s^*}{N_j^{*g}} \quad (90)$$

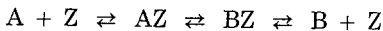
Hence the linear approximation equations will take the form

$$\begin{aligned} \frac{dN_i}{dt} &= - S \sum_s w_s^* \gamma_{si} \left[ \sum_j \gamma_{sj} \frac{(N_j - N_j^*)}{N_j^*} \right] \\ &\quad - V \sum_\sigma w_\sigma^* \gamma_{\sigma i} \left[ \sum_j \gamma_{\sigma j} \frac{(N_j - N_j^*)}{N_j^*} \right] \end{aligned} \quad (91)$$

This expression can be simplified further. For this purpose let us introduce into the space of compositions (vectors of  $\bar{N}$ ) a scalar product designated as  $\langle | \rangle$

$$\langle \bar{N} | \bar{N}' \rangle = \sum \frac{N_i N'_i}{N_i^*} \quad (92)$$

For example, for the catalytic isomerization



this scalar product will take the form

$$\langle \bar{N} | \bar{N}' \rangle = \frac{N_A N'_A}{N_A^*} + \frac{N_B N'_B}{N_B^*} + \frac{N_Z N'_Z}{N_Z^*} + \frac{N_{AZ} N'_{AZ}}{N_{AZ}^*} + \frac{N_{BZ} N'_{BZ}}{N_{BZ}^*}$$

It can be represented in the matrix form

$$\langle \vec{N} | \vec{N}' \rangle = (N_A, N_B, N_Z, N_{AZ}, N_{BZ})$$

$$\times \begin{bmatrix} 1/N_A^* & 0 & 0 & 0 & 0 \\ 0 & 1/N_B^* & 0 & 0 & 0 \\ 0 & 0 & 1/N_Z^* & 0 & 0 \\ 0 & 0 & 0 & 1/N_{AZ}^* & 0 \\ 0 & 0 & 0 & 0 & 1/N_{BZ}^* \end{bmatrix} \times \begin{bmatrix} N'_A \\ N'_B \\ N'_Z \\ N'_{AZ} \\ N'_{BZ} \end{bmatrix}$$

We can also introduce the expression  $x_i = N_i/N_i^{*1/2}$ . Then the scalar product (92) will be

$$\langle \vec{N} | \vec{N}' \rangle = \sum_i x_i x'_i \quad (93)$$

A formula for the linear approximation in the case of a constant volume can be rewritten as

$$\frac{d\vec{N}}{dt} = -S \sum_s w_s^* \vec{\gamma}_s \langle \vec{\gamma}_s | \vec{N} - \vec{N}^* \rangle -$$

$$-V \sum_\sigma w_\sigma^* \vec{\gamma}_\sigma \langle \vec{\gamma}_\sigma | \vec{N} - \vec{N}^* \rangle \quad (94)$$

The introduced scalar product  $\langle | \rangle$  possesses all the properties of an ordinary scalar product, i.e.

- (1) symmetry:  $\langle \vec{N} | \vec{N}' \rangle = \langle \vec{N}' | \vec{N} \rangle$ ,
- (2) bilinearity:  $\langle \alpha \vec{N} + \beta \vec{N}' | \vec{N}'' \rangle = \alpha \langle \vec{N} | \vec{N}'' \rangle + \beta \langle \vec{N}' | \vec{N}'' \rangle$ , and
- (3) positive determinacy:  $\langle \vec{N} | \vec{N} \rangle \geq 0$ ,  $\langle \vec{N} | \vec{N} \rangle = 0$  when and only when  $\vec{N} = 0$ .

By applying these properties, we will prove that all the characteristic roots of the matrix for the linear approximation are real and non-positive whereas the characteristic roots of its limitation on the linear subspace generated by the vectors  $\vec{\gamma}_{s,\sigma}$  are negative. Let us express the linear approximation matrix as  $\vec{L}: \vec{N} = \vec{L}(\vec{N} - \vec{N}^*)$ . This matrix possesses an important property, i.e. self-conjugation relative the introduced scalar product  $\langle | \rangle$ . It suggests that, for any  $\vec{N}, \vec{N}'$ , we have

$$\langle \vec{L}\vec{N} | \vec{N}' \rangle = \langle \vec{N} | \vec{L}\vec{N}' \rangle$$

Indeed

$$\langle \vec{L}\vec{N} | \vec{N}' \rangle = -S \sum_s w_s^* \langle \vec{\gamma}_s | \vec{N}' \rangle \langle \vec{\gamma}_s | \vec{N} \rangle -$$

$$-V \sum_\sigma w_\sigma^* \langle \vec{\gamma}_\sigma | \vec{N}' \rangle \langle \vec{\gamma}_\sigma | \vec{N} \rangle$$

$$= \langle \vec{N} | \vec{L}\vec{N}' \rangle$$

Roots of a self-conjugated matrix are always real (this is a well-known fact; see, for example, ref. 29). To prove negative determinacy  $\bar{L}$  in the subspace generated by vectors  $\bar{\gamma}_{s,\sigma}$ , it is necessary and sufficient to show that  $\langle \bar{\gamma}_{s,\sigma} | \bar{L} \bar{\gamma}_{s,\sigma} \rangle < 0$  at any  $s$  or  $\sigma$ . We obtain

$$\begin{aligned} \langle \bar{\gamma}_s | \bar{L} \bar{\gamma}_s \rangle &= -S w_s^* \langle \bar{\gamma}_s | \bar{\gamma}_s \rangle^2 - S \sum_{s' \neq s} w_{s'}^* \langle \bar{\gamma}_s | \bar{\gamma}_{s'} \rangle^2 - \\ &- V \sum_{\sigma} w_{\sigma}^* \langle \bar{\gamma}_s | \bar{\gamma}_{\sigma} \rangle^2 < 0 \end{aligned}$$

since all  $w_s^* > 0$  and  $\langle \bar{\gamma}_s | \bar{\gamma}_s \rangle > 0$ . Similarly,  $\langle \bar{\gamma}_{\sigma} | \bar{L} \bar{\gamma}_{\sigma} \rangle < 0$ . Hence  $\bar{L}$  is negatively determined in the subspace generated by vectors  $\bar{\gamma}_{s,\sigma}$ . Whence it follows that  $\bar{N}^*$  is an asymptotically stable (in linear approximation) equilibrium point in the reaction polyhedron (recall that a reaction polyhedron is the intersection of a plane which is parallel to a linear envelope  $\bar{\gamma}_{s,\sigma}$  with a multitude of non-negative vectors). Since eigenvalues are real ( $\bar{L}$  is self-conjugated!) damped oscillations are impossible and  $\bar{N}^*$  is a stable node. For the entire space of compositions,  $\bar{L}$  is negatively half determined, i.e. it also has zero eigenvalues. Eigenvectors corresponding to zero values are those that are orthogonal to the whole of  $\bar{\gamma}_{s,\sigma}$ , since

$$\langle \bar{x} | \bar{L} \bar{x} \rangle = -S \sum_s w_s^* \langle \bar{\gamma}_s | \bar{x} \rangle^2 - V \sum_{\sigma} w_{\sigma}^* \langle \bar{\gamma}_{\sigma} | \bar{x} \rangle^2 \leq 0$$

and the equality to zero is obtained when and only when  $\langle \bar{\gamma}_s | \bar{x} \rangle = 0$  and  $\langle \bar{\gamma}_{\sigma} | \bar{x} \rangle = 0$  for all values of  $s$  and  $\sigma$ .

We have proved that any positive PDE  $\bar{N}^*$  is asymptotically stable in the polyhedron  $\bar{D}$  (it is even a "node"). In this point constructed above the  $G$  dissipation function, a minimum of free energy is achieved and the point of minimum is unique. Whence we obtain that  $\bar{N}^*$  is a point of minimum  $G$  and a unique positive PDE in  $\bar{D}$ .

Similar considerations are also possible for reactions at constant pressure. It is only necessary to introduce a new scalar product (assuming that we have an ideal gas and  $PV = N_{\text{tot}}^g RT$ )

$$\langle \bar{N} | \bar{N}' \rangle_P = \langle \bar{N} | \bar{N}' \rangle_V - \sum_i N_i^g \frac{\sum_i N_i^g}{\sum_i N_i^{*g}} \quad (95)$$

Equation (94) will remain unchanged. One must only introduce  $\langle | \rangle_P$  instead of  $\langle | \rangle_V$ . For catalytic isomerization

$$\begin{aligned} \langle \bar{N} | \bar{N}' \rangle_P &= \frac{N_A N'_A}{N_A^*} + \frac{N_B N'_B}{N_B^*} + \frac{N_Z N'_Z}{N_Z^*} + \frac{N_{AZ} N'_{AZ}}{N_{AZ}^*} \\ &+ \frac{N_{BZ} N'_{BZ}}{N_{BZ}^*} - \frac{(N_A + N_B)(N'_A + N'_B)}{N_A^* + N_B^*} \end{aligned}$$

the equation for the scalar product  $\langle | \rangle_P$  [eqn. (95)] can be rewritten as

$$\langle \vec{N} | \vec{N}' \rangle_P = \langle \vec{N} | \vec{N}' \rangle_V - \frac{N_{\text{tot}}^g N_{\text{tot}}^{g'}}{N_{\text{tot}}^{g*}} \quad (96)$$

Here  $N_{\text{tot}}^g$ ,  $N_{\text{tot}}^{g'}$  and  $N_{\text{tot}}^{g*}$  are the number of moles of substance in the gas phase for the first, second, and equilibrium states, respectively.

Unlike  $\langle | \rangle$ , the scalar product  $\langle | \rangle_P$  has been degenerated:  $\langle \vec{N}^* | \vec{N}^* \rangle_P = 0$ , but  $\vec{N}^*$  is the only direction with this property: within the plane of the polyhedron  $\vec{D}$ ,  $\langle | \rangle_P$  is positively determined. Therefore the assumptions concerning the uniqueness in  $\vec{D}$  and asymptotic stability of the PDE are also valid for the systems with constant pressures.

Hence, under the assumption of the law of mass action/acting surfaces, from the existence of at least one PDE  $\vec{N}^*$  we obtain

(1) each reaction polyhedron has a unique and asymptotically stable positive PDE,

(2) a positive PDE is a stable node and damped oscillations near it are impossible,

(3) there exists a convex function  $G$  that is strictly convex in each reaction polyhedron and possesses the following property: according to the differential chemical kinetic equation, the derivative of  $G$  is

$$\begin{aligned} \frac{dG}{dt} &= -S \sum_s w_s \ln \left( \frac{w_s^+}{w_s^-} \right) - V \sum_\sigma w_\sigma \ln \left( \frac{w_\sigma^+}{w_\sigma^-} \right) \\ &\leq 0 \end{aligned}$$

The equality to zero is obtained only at PDE,

(4) in each reaction polyhedron the positive PDE is the point of minimum  $G$ , and

(5) there exists a scalar product  $\langle | \rangle$ , that is not degenerated and is positively determined within the plane of the reaction polyhedron (the subspace generated by vectors  $\vec{\gamma}_s$ ). It can be applied to rewrite a linear approximation as

$$\begin{aligned} w_{s,\sigma} &= -w_{s,\sigma}^* \langle \vec{\gamma}_{s,\sigma} | \vec{N} - \vec{N}^* \rangle \\ \frac{d\vec{N}}{dt} &= -S \sum_s w_s^* \vec{\gamma}_s \langle \vec{\gamma}_s | \vec{N} - \vec{N}^* \rangle - V \sum_\sigma w_\sigma^* \gamma_{\sigma}^* \langle \vec{\gamma}_\sigma | \vec{N} - \vec{N}^* \rangle \end{aligned}$$

where  $w_{s,\sigma}^* = w_{s,\sigma}^+(\vec{c}^*) = w_{s,\sigma}^-(\vec{c}^*)$ . Functions of  $\langle \vec{N} - \vec{N}^* | \vec{N} - \vec{N}^* \rangle$  are quadratic terms in the expansion of  $G$  into the Taylor series near the equilibrium point.

For reactions at constant volume we have

$$G = G_V = \sum_{i=1}^n N_i \left( \ln \left( \frac{N_i}{N_i^*} \right) - 1 \right) \quad (98)$$

$$\langle \tilde{N} | \tilde{N}' \rangle = \langle \tilde{N} | \tilde{N}' \rangle_V = \sum \frac{N_i N_i'}{N_i^*} \quad (99)$$

For those at constant pressure we obtain

$$\begin{aligned} G &= G_p = \sum_i N_i^g \ln \left( \frac{C_i^g}{C_i^{g*}} \right) + \sum_i N_i^s \left[ \ln \left( \frac{N_i^s}{N_i^{s*}} \right) - 1 \right] \\ &= \sum_i N_i^g \left[ \ln \left( \frac{N_i^g}{N_i^{g*}} \right) - \ln \left( \frac{\sum N_i^g}{\sum N_i^{g*}} \right) \right] + \sum_i N_i^s \left[ \ln \left( \frac{N_i^s}{N_i^{s*}} \right) - 1 \right] \\ &= \sum_i N_i^g \left[ \ln \left( \frac{N_i^g}{N_i^{g*}} \right) - \ln \left( \frac{N_{tot}^g}{N_{tot}^{g*}} \right) \right] + \sum_i N_i^s \left[ \ln \left( \frac{N_i^s}{N_i^{s*}} \right) - 1 \right] \end{aligned} \quad (100)$$

where  $N_{tot}^g$  is the number of moles of substance in the gas phase

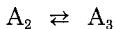
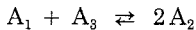
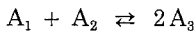
$$\begin{aligned} \langle \tilde{N} | \tilde{N}' \rangle &= \langle \tilde{N} | \tilde{N}' \rangle_P \\ &= \sum_{i=1}^n \frac{N_i N_i'}{N_i^*} - \sum_i N_i^g \frac{\sum_i N_i^g}{\sum_i N_i^{g*}} \\ &= \sum_{i=1}^n \frac{N_i N_i'}{N_i^*} - \frac{N_{tot}^g N_{tot}^{g'}}{N_{tot}^{g*}} \end{aligned} \quad (101)$$

In case the boundary PDEs, i.e. such  $\tilde{N}$  as a certain  $N_i = 0$  and  $w_{s,\sigma}^+(\tilde{c}^*) = w_{s,\sigma}^-(\tilde{c}^*)$ , are absent in any reaction polyhedron from any initial conditions, the solution of kinetic equation tends to the unique positive PDE  $\tilde{N}^*$  at  $t \rightarrow \infty$ .

Initially the possibility for the appearance of boundary PDEs was neglected. This possibility was emphasized by Vol'pert, in 1973, who posed the question as to whether the system from positive initial conditions can get to a boundary PDE (i.e. have this point as an  $\omega$ -limit).

Boundary PDE though rare are nevertheless encountered.

For example, let us consider a system of three substances  $A_1$ ,  $A_2$ , and  $A_3$  and the hypothetical reaction mechanism



In this system the point  $(N_1, 0, 0)$  is a PDE. It is evident that if  $N_2 = N_3 = 0$ , neither of the reactions takes place and  $w_1^+ = w_1^- = w_2^+ = w_2^- = w_3^+ = w_3^- = 0$ .

Recently, Gorban' has shown that, in the presence of boundary PDEs, from any positive initial condition the solution of kinetic equations tends at

$t \rightarrow \infty$  to a positive PDE whose existence is suggested according to the principle of detailed equilibrium. In general, if there is a positive PDE and the initial conditions are always positive (all  $N_i > 0$ ), for none of the substances does  $N_i$  reduce to zero during the reaction time or tend to zero at  $t \rightarrow \infty$ .

### 2.3 THERMODYNAMIC LIMITATIONS ON NON-STEADY-STATE KINETIC BEHAVIOUR

In the previous section we introduced the Lyapunov functions for chemical kinetic equations that are the dissipative functions  $G$ . The function  $RTG$  is treated as free energy. Since  $\dot{G} \leq 0$  and the equality is obtained only at PDE, and for the construction of  $G$  it suffices to know only the position of equilibrium  $\bar{N}^*$ , there exist limitations on the non-steady-state behaviour of a closed system that are independent of the reaction mechanism. If in the initial composition  $\bar{N} \neq \bar{N}^*$ , the other composition  $\bar{N}'$  can be realized during the reaction only in the case when

(a)  $\bar{N}'$  satisfies the same balance relationships as for  $\bar{N}$

$$\sum_i a_{ij} N_i' = \sum_i a_{ij} N_i$$

for any  $j$  or

$$\bar{A}^T \bar{N}' = \bar{A}^T \bar{N} \quad (102)$$

(b)

$$G(\bar{N}) > G(\bar{N}') \quad (103)$$

The latter means that  $G$  is a monotonically decreasing function among the solutions for kinetic equations.

With time the system can get from point  $\bar{N}$  to point  $\bar{N}'$  only in the case when  $G(\bar{N}') < G(\bar{N})$ . But it is not the only limitation. Let us return to a system of three isomers (isomerization of butenes) ( $A_1$ ,  $A_2$ , and  $A_3$ ) and specify its PDE. According to Wei [30], at 230°C  $N_1^* \cong 0.14$ ,  $N_2^* \cong 0.32$ , and  $N_3^* \cong 0.54$  (the normalization condition is  $N_1 + N_2 + N_3 = 1$ , i.e. the law of conservation). In this case

$$\begin{aligned} G &= N_1 \left( \frac{\ln N_1}{0.14} - 1 \right) + N_2 \left( \frac{\ln N_2}{0.32} - 1 \right) \\ &+ N_3 \left( \frac{\ln N_3}{0.54} - 1 \right) \\ &= N_1 \frac{\ln N_1}{0.14} + N_2 \frac{\ln N_2}{0.32} + \frac{N_3 \ln N_3}{0.54} - 1 \end{aligned}$$

Level lines for  $G$  [their equations are  $G(\bar{n}) = \text{const.}$ ] in the triangle  $N_1 + N_2 + N_3 = 1$  are shown in Fig. 8(a). At  $g > \min G(\bar{N})$  on the boundary