

# The topology of energy hypersurfaces IV. Generator sets for the fundamental group of reaction mechanisms and the complete set of reaction paths

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A countable set of distinguished fundamental reaction mechanisms on a potential surface serves as the set of *generators* for the *fundamental group* of reaction mechanisms. The effects of a change in the upper limit for energy on such groups are described with the aid of a lower semilattice, introduced into the family of all fundamental groups of reaction mechanisms, supported by the given potential energy surface. The algebraic structure of all reaction paths is described with the aid of groupoids and various subgroupoids and semigroups derived from them.

**Key words:** Reaction mechanisms—synthesis planning—molecular design—potential surfaces—reaction path

## 1. Introduction

The general topological properties of potential energy hypersurfaces have obvious importance in the quantum chemical description of chemical reactions. These topological properties can be exploited in the development of techniques aimed at the *global analysis of all interconversion processes* among *all* chemical species composed from a fixed set of  $N$  nuclei and  $k$  electrons. Whereas topological methods have immediate applications in studying individual reactions, one of the ultimate aims of such global techniques is the development of computer-based quantum chemical synthesis design.

A *global approach* to the description of chemical properties and the interrelations between different molecules, in terms of a *single functional*, has been advocated in a series of studies on energy hypersurfaces (see e.g. Refs. [1, 2, 3] and references therein). Intriguing new developments, e.g. in the theory of density functionals

[4] and in a new interpretation of the role of Smoluchowski's equation in chemical kinetic phenomena [5], appear to support such a global approach.

In a previous study [6] (Part III in the series) some general relations have been established among all those reaction mechanisms which are confined to the chemically most important low energy regions of a potential surface. It has been shown that in any *level set*  $F^{-}(A)$  of the  $3N-6$  dimensional reduced nuclear configuration space  $M$  (which space is a *metric* space with metric  $d$ ), the complete set of all closed reaction mechanisms has an algebraic structure, the *fundamental group of reaction mechanisms*. Level set  $F^{-}(A)$  is obtained by truncating the potential energy hypersurface at energy value  $A$ , which energy value can be chosen arbitrarily. The fundamental reaction mechanisms, below energy  $A$ , are defined as *homotopy equivalence classes* of closed reaction paths. Within each such homotopy class any two reaction paths are equivalent in the following sense: they can be continuously deformed into each other within level set  $F^{-}(A)$ , i.e. without reaching or exceeding energy value  $A$ . The fundamental group of reaction mechanisms is a *topological invariant*, hence it is isomorphic to any group of any level set  $F^{-}(B)$  having the same topology. It has been shown that variations in energy value  $A$  on the same hypersurface, or comparisons between different excited state energy hypersurfaces over the same nuclear configuration space  $M$ , lead to isomorphism and homomorphism relations between the respective fundamental groups of reaction mechanisms [6].

In the present study we shall consider explicit constructions for these groups and describe some further features of the above model. On the one hand, we shall study certain special relations by focussing on the *generator sets* of these groups, and on the other hand, we shall also generalize the model by analysing the algebraic structure of a set much larger than that of the fundamental group of reaction mechanisms: the *complete set of all reaction paths*. This algebraic structure is a *groupoid*, which contains, as a *subgroup*, the fundamental group of reaction mechanisms.

Throughout the paper the notations of Part III will be used. An introduction into the topological concepts used in the analysis of potential energy hypersurfaces can be found in the bibliography cited in earlier papers in the sequence, a detailed introduction into the relevant properties of free groups and free generators can be found in Refs. [7, 8], whereas for an easy reference, the definition and some general properties of groupoids are listed in the Appendix.

## 2. Generators for the fundamental group of reaction mechanisms

In order to analyse the general properties of groups of reaction mechanisms, we shall describe them in terms of a suitable set of group generators. Knowing these generators (generator mechanisms), we shall have a convenient tool for the description of the internal structure of the fundamental groups of reaction mechanisms and their various subgroups. One may expect that these generators have special chemical significance of their own, since any fundamental reaction mechanism can be expressed as a product of some generator mechanisms.

First we shall consider the following problem: under what conditions is the fundamental group of reaction mechanisms a commutative (abelian) group? We shall organize the exploration of these groups around the problem of commutativity, since this is a concept simple to visualize for reaction mechanisms. One may expect on the basis of the definition of fundamental reaction mechanisms as homotopy equivalence classes of closed reaction paths, and on the basis of the definition of the product  $P_1P_2$  of two reaction paths  $P_1$  and  $P_2$  as the "continuation" of  $P_1$  by  $P_2$  (Part III), that these groups are not in general commutative. Evidently, it is not in general indifferent which reaction mechanism follows the other. In spite of this, we shall find in every group of fundamental reaction mechanisms various commutative subgroups. In the following we shall consider a rather general condition for commutativity, and later on after exploring some properties of generator mechanisms, the condition will be given in simpler terms.

We recall that it has been proven in Part III that for any arcwise connected level set  $F^-(A)$  of the potential surface the fundamental group of reaction mechanisms, as an abstract group, does not depend on the choice of reference point  $K_0 \in F^-(A)$ , i.e. on the endpoint of equivalent reaction paths. In particular, it has been shown that if  $R_1$  is a reaction path in  $F^-(A)$  with origin  $K_0$  and extremity  $K_1$ , then a  $V_{R_1}$  mapping of  $K_0$ -based fundamental reaction mechanisms  $[P_i]$  to  $K_1$ -based reaction mechanisms  $[Q_i] = [R_1^{-1}P_iR_1]$ , which mapping is defined as

$$V_{R_1}([P_i]) = [R_1^{-1}P_iR_1] = [Q_i] \quad (1)$$

is an *isomorphism* from fundamental group  $\Pi_1(F^-(A), T_{d/A}, K_0)$  to  $\Pi_1(F^-(A), T_{d/A}, K_1)$ . This is the very reason why one can refer to *the* fundamental group  $\Pi_1$  of reaction mechanisms within  $F^-(A)$ , and why the reference to a base point can be omitted. (Note, however, that the actual topology is always assumed).

In terms of mapping  $V_{R_1}$ , the general condition for commutativity can be stated as follows:

If in an arcwise connected level set  $F^-(A)$  of potential energy hypersurface  $E(K)$

$$V_{R_1} = V_{R_2} \quad (2)$$

for mappings  $V$  defined by any two reaction paths  $R_1$  and  $R_2$ , which paths have the same endpoints  $K_0$  and  $K_1$ , then and only then the fundamental group  $\Pi_1$  of reaction mechanisms is a commutative group.

This can be seen easily by choosing any two reaction paths  $P_i$  and  $P_j$  from arbitrary two homotopy classes (reaction mechanisms)  $[P_i]$  and  $[P_j]$ , defined relative to  $K_0 \in F^-(A)$ , and taking, in addition to reaction path  $R_1 \subset F^-(A)$ , the following two paths:

$$R_2 = P_j^{-1}P_iR_1 \subset F^-(A) \quad (3)$$

and

$$R_3 = P_iR_1 \subset F^-(A). \quad (4)$$

Evidently, for the endpoints of these reaction paths

$$R_1(0) = R_2(0) = R_3(0) = K_0 \quad (5)$$

$$R_1(1) = R_2(1) = R_3(1) = K_1. \quad (6)$$

Condition (2) as applied to  $R_1$ ,  $R_2$  and  $R_3$ , gives

$$[Q_i][Q_j] = [R_k^{-1} P_i R_k][R_k^{-1} P_j R_k] = [R_k^{-1} P_i P_j R_k], k = 1, 2, 3 \quad (7)$$

where properties (iv) and (v) of the product of reaction paths have been utilized (see Part III). Taking the actual  $R_2$  and  $R_3$  paths in a sequence of substitutions, one obtains

$$\begin{aligned} [Q_i][Q_j] &= [R_1^{-1} P_i P_j R_1] = [R_2^{-1} P_i P_j R_2] = [R_1^{-1} P_i^{-1} P_j P_i P_j^{-1} P_i R_1] \\ &= [R_1^{-1} P_i^{-1} P_j P_i P_i R_1] = [R_3^{-1} P_j P_i R_3] = [R_1^{-1} P_j P_i R_1] = [Q_j][Q_i]. \end{aligned} \quad (8)$$

Since  $V_{R_1}$  is an isomorphism between the two groups, one based on  $K_0$  the other on  $K_1$ , relation (8) is equivalent to

$$[P_i][P_j] = [P_j][P_i] \quad (9)$$

i.e. the fundamental group  $\Pi_1$  of fundamental reaction mechanisms is commutative. On the other hand, since  $[P_i]$  and  $[P_j]$  can be chosen as *any* two equivalence classes, and reaction paths  $P_i$  and  $P_j$  as any two representatives, it follows that  $R_2$  and  $R_3$  can be any two paths from  $F^-(A)$ , fulfilling the endpoint conditions. Consequently, condition (2) is both a *necessary* and a *sufficient* condition for commutativity. (Note that in the topological literature a space with property analogous to (2) is often referred to as a *1-simple space* [9].)

With the aid of the following two dimensional example one can easily demonstrate some of the commutativity properties of the fundamental group of reaction mechanisms and its subgroups. (Two dimensional examples are useful since they are easily visualized and can be discussed in terms of simple geographical analogies. One should be cautious, however, since not all two dimensional results can be generalized for higher dimensions.)

Take a two dimensional level set  $F^-(A)$  of a two dimensional model potential surface  $E(K)$ , which level set is analogous to a lake with  $m$  islands in it. If energy value  $A$  is taken as the height of the water level, then  $F^-(A)$  can be visualized as a bounded subset of the two dimensional plane with  $m$  "holes" in it. This level set is topologically equivalent to a two dimensional sphere  ${}^2S(m+1)$  with  $m+1$  holes in it. For example, if  $m=0$ , i.e.  $F^-(A)$  is a simply connected domain with *no* holes in it, then it is topologically equivalent to a sphere with *one* hole in it, the perimeter of which hole corresponding to the boundary of  $F^-(A)$ . (In Fig. 1 the  $m=2$  case is shown.) This topological equivalence means that there exists a homeomorphism  $f$

$$f: F^-(A) \rightarrow {}^2S(m+1) \quad (10)$$

that maps the level set onto the sphere with holes.

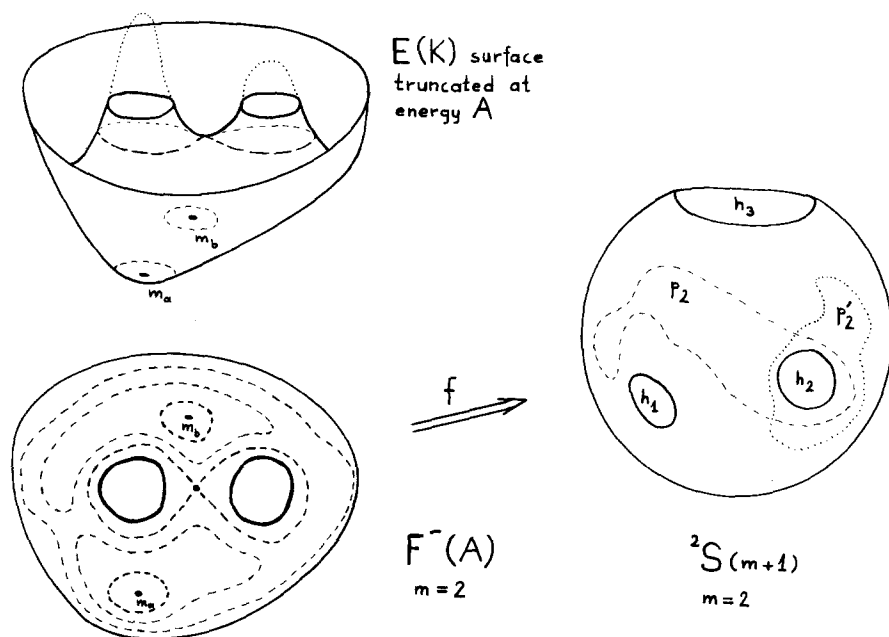


Fig. 1. Energy surface  $E(K)$  truncated at energy value  $A$ , the corresponding level set  $F^-(A)$  with  $m=2$  holes in it and a topologically equivalent sphere  ${}^2S(m+1)$  with  $m+1=3$  holes on it. Minima  $m_a$  and  $m_b$  of  $E(K)$  and some equipotential contours are shown, as well as two homotopically equivalent loops,  $p_2$  and  $p'_2$  from homotopy equivalence class  $[p_2]$  on sphere  ${}^2S(m+1)$

Although most of the following analysis can be carried out directly on level sets  $F^-(A)$ , we shall use various spheres to obtain our conclusions, since topological results are readily applicable and the easiest to visualize on spheres. The topological equivalence of  $F^-(A)$  and  ${}^2S(m+1)$  guarantees that their fundamental groups, as abstract groups, are the same, since group  $\Pi_1(F^-(A), T_{d/A})$  is a topological invariant.

Let us denote the holes on  ${}^2S(m+1)$  by

$$h_1, h_2, \dots, h_m, h_{m+1}. \tag{11}$$

For convenience, we shall take  $h_{m+1}$  as the hole with perimeter corresponding to the “outside boundary” of  $F^-(A)$ , more precisely, to the boundary of the unbounded maximum connected component of the complement  $M \setminus F^-(A)$  of  $F^-(A)$ . Consider a sequence of loops

$$p_1, p_2, \dots, p_m, p_{m+1} \tag{12}$$

where each loop  $p_i$  separates hole  $h_i$  from all other holes  $h_j, j \neq i$ , and winds around hole  $h_i$  precisely once, with either (but fixed) orientation. Then, according to a general topological result on  ${}^2S(m+1)$  for the homotopy classes  $[p_i]$  represented by these loops, the following relation [9] holds:

$$[p_1]^{\alpha_1} [p_2]^{\alpha_2} \dots [p_m]^{\alpha_m} [p_{m+1}]^{\alpha_{m+1}} = [1] \tag{13}$$

where

$$\alpha_i = \pm 1 \quad (14)$$

and where  $[1]'$  denotes the homotopy class of all loops *not* separating any hole from any other hole on the sphere. The product of these homotopy classes is defined analogously to the definition [Eq. (63), Part III] of the product of fundamental reaction mechanisms.

Evidently, any equivalence class of loops on  ${}^2S(m+1)$ , however complicated, can be expressed as some product of classes  $[p_1]^{\alpha_1}, [p_2]^{\alpha_2}, \dots, [p_{m+1}]^{\alpha_{m+1}}$ , with repetitions and both  $+1$  and  $-1$  powers allowed. Hence, the set

$$\{[p_i]_{i=1}^{m+1}\} \quad (15)$$

is a generator set for the fundamental group of  ${}^2S(m+1)$ .

By topological equivalence, the homeomorphism  $f: F^-(A) \rightarrow {}^2S(m+1)$  generates an isomorphism  $f^*: \Pi_1(F^-(A), T_{d/A}) \rightarrow \Pi_1({}^2S(m+1), T)$  between the fundamental groups of  $F^-(A)$  and the punctured sphere  ${}^2S(m+1)$ . Hence the inverse images  $[P_i]$  of generators  $[p_i]$  are themselves generators for the fundamental group of reaction mechanisms on level set  $F^-(A)$ :

$$[P_i] = f^{*-1}([p_i]). \quad (16)$$

Evidently, relation (13) is also "inherited", and

$$[P_1]^{\alpha_1} [P_2]^{\alpha_2} \cdots [P_m]^{\alpha_m} [P_{m+1}]^{\alpha_{m+1}} = [1] \quad (17)$$

where the  $\alpha_i$  numbers are precisely the same as before in (13), and fulfill the conditions

$$\alpha_i = \pm 1, \quad (18)$$

and  $[1]$  is the zero reaction mechanism in  $F^-(A)$ .

In fact the very relations (13) and (17) imply that in both sequences  $\{[p_i]_{i=1}^{m+1}\}$  and  $\{[P_i]_{i=1}^{m+1}\}$  of generators, *one* equivalence class is redundant. From Eq. (17) *any* one of the  $[P_i]$  reaction mechanisms can be expressed in terms of the others, e.g.

$$[P_{m+1}] = [P_1]^{\beta_1} [P_2]^{\beta_2} \cdots [P_m]^{\beta_m} \quad (19)$$

where

$$\beta_i = -\alpha_i \alpha_{m+1} = \pm 1. \quad (20)$$

Hence, the reduced set

$$\{[P_i]_{i=1}^m\} \quad (21)$$

is also a generator set for the fundamental group  $\Pi_1$  of reaction mechanisms. Since relation (13) is the *only* relation on the sphere  ${}^2S(m+1)$  among generators  $[p_i]$ ,  $i = 1, \dots, m+1$ , it follows by topological equivalence that the *m* generator reaction mechanisms in set  $\{[P_i]_{i=1}^m\}$  are already independent. Hence, the funda-

mental group  $\Pi_1(F^-(A), T_{d/A})$  of reaction mechanisms on level set  $F^-(A)$  is a *finitely generated free group* with *generator reaction mechanisms*  $[P_1], [P_2], \dots, [P_m]$  as free generators.

This finite set of generator mechanisms represents the chemically most important fundamental mechanisms on level set  $F^-(A)$ , since *any* fundamental reaction mechanism  $[P] \in \Pi_1$  can be expressed in terms of them as some product:

$$[P] = [P_{i_1}]^{\alpha_{i_1}} [P_{i_2}]^{\alpha_{i_2}} \cdots [P_{i_k}]^{\alpha_{i_k}} \quad (22)$$

where  $\alpha_{i_k} = \pm 1$  and repetitions are allowed. If we do not insist on any further restriction, then the same fundamental mechanism  $[P]$  can be expressed in many (infinitely many) different ways. However, since  $\Pi_1$  is a finitely generated free group, every reaction mechanism  $[P]$  can be expressed in one and only one way as a *reduced product*. A reduced product [7] is a product of form (22), where

$$[P_{i_j}] = [P_{i_{j+1}}] \quad (23)$$

implies

$$\alpha_{i_j} \neq -\alpha_{i_{j+1}} \quad (24)$$

that is, where no neighbors in sequence (22) are inverses of each other. Evidently, whenever in a product expression for a fundamental reaction mechanism such inverse pairs occur, they can always be replaced with mechanism [1], and also omitted from the product, unless  $[P] = [1]$ . Hence, it is convenient to express all fundamental reaction mechanisms within the  $F^-(A)$  subset of the nuclear configuration space  $M$  as a reduced product, expressed in a *unique* form in terms of the generator reaction mechanisms.

The *length of a fundamental reaction mechanism*  $[P]$ , with respect to generator set  $\{[P_i]\}_{i=1}^m$  of  $\Pi_1(F^-(A), T_{d/A})$ , is the number  $k$  in expression (22), if  $[P]$  is given as a reduced product. As an example, in a level set  $F^-(A)$  with  $m \geq 4$  the length of fundamental reaction mechanism

$$[P] = [P_4]^{-1} [P_1]^{-1} [P_3] [P_3]^{-1} [P_1] [P_1] [P_1] \quad (25)$$

is 3 (and not 7), since the above mechanism, rewritten as *the* reduced product, is

$$[P] = [P_4]^{-1} [P_1] [P_1]. \quad (26)$$

Now, in the possession of a set of free generator mechanisms, we may return to the problem of commutativity. That group  $\Pi_1$  on level set  $F^-(A)$  is non-abelian whenever  $m > 1$ , is evident, since  $[P_1][P_2]$  and  $[P_2][P_1]$  are two different reduced products in a free group, hence they are different, representing two different reaction mechanisms:

$$[P_1][P_2] \neq [P_2][P_1] \quad (27)$$

and  $\Pi_1$  is non-abelian.

On the other hand, with the exception of  $m = 0$ , when  $\Pi_1 = \{[1]\}$ , the trivial group,  $\Pi_1$  always contains a special abelian group, the infinite cyclic group as a subgroup.

Indeed, one can easily show that the group  $G \subset \Pi_1$ , given as

$$G = \{[P_i]^\gamma : \gamma = \text{any integer}\} \quad (28)$$

for any fixed  $i$ ,  $1 \leq i \leq m$ , is the infinite cyclic group. Here we identify  $[P_i]^0$  with  $[1]$ .

Evidently, each reaction mechanism  $[P_i]^\gamma \in \Pi_1$ . Furthermore, each such reaction mechanism is a reduced product of length  $|\gamma|$ , and

$$[P_i]^\gamma = [P_i]^{\gamma'} \quad (29)$$

if and only if

$$\gamma = \gamma'. \quad (30)$$

Hence group  $G \subset \Pi_1$ , generated by *one* generator reaction mechanism is the infinite cyclic group. In the special case of  $m = 1$ , there is only one choice,  $i = 1$ , and then  $\Pi_1 = G$ .

### 3. Energy dependence within the family of groups of reaction mechanisms

The set of free generator mechanisms is also a useful tool for studying *energy dependent variations* in the structure of the fundamental group of reaction mechanisms on  $F^-(A)$ . The following property of level sets has been already pointed out in Part III, using elementary properties of critical levels [10]: if the connectivity of level set  $F^-(A)$  changes monotonically during an energy change  $A \rightarrow B$ , then the group at the level set of *lower* connectivity is a *subgroup* of the group at the level set of *higher* connectivity.

We shall show now that by considering all possible energy values  $A$  and the induced changes in a connected level set  $F^-(A)$  of the potential energy surface, the *family* of the fundamental groups of reaction mechanisms obtained has an algebraic structure of its own. If each critical level  $C$  is non-degenerate within each connected level set component  $F(C)$ , then these groups form a *lower semilattice*.

We shall first consider the example shown in Fig. 2. On this model surface  $m$ ,  $s$  and  $M$  stand for minimum, saddle point, and maximum, respectively, with the energy value of the critical point given in parentheses. Equipotential contours of whole numbers for energy are shown, with the energy value indicated for each contour. We shall consider connected level set components  $F^-(A)$  for various  $A$  values, such as the level set  $F_1^-(1.0)$ , containing minimum  $m_1$  and no other critical point. Note that there is another connected level set component  $F_3^-(1.0)$  of the *same* energy bound  $A = 1.0$  on this potential surface, with minimum  $m_3 \in F_3^-(1.0)$  and these two sets are disjoint:

$$F_1^-(1.0) \cap F_3^-(1.0) = \emptyset. \quad (31)$$

Due to the strict inequality ( $<$ ) in the definition of the  $F^-(A)$  level sets (Part III), there is *no* level set  $F^-(1.0)$  that contains  $m_2(1.0)$ .



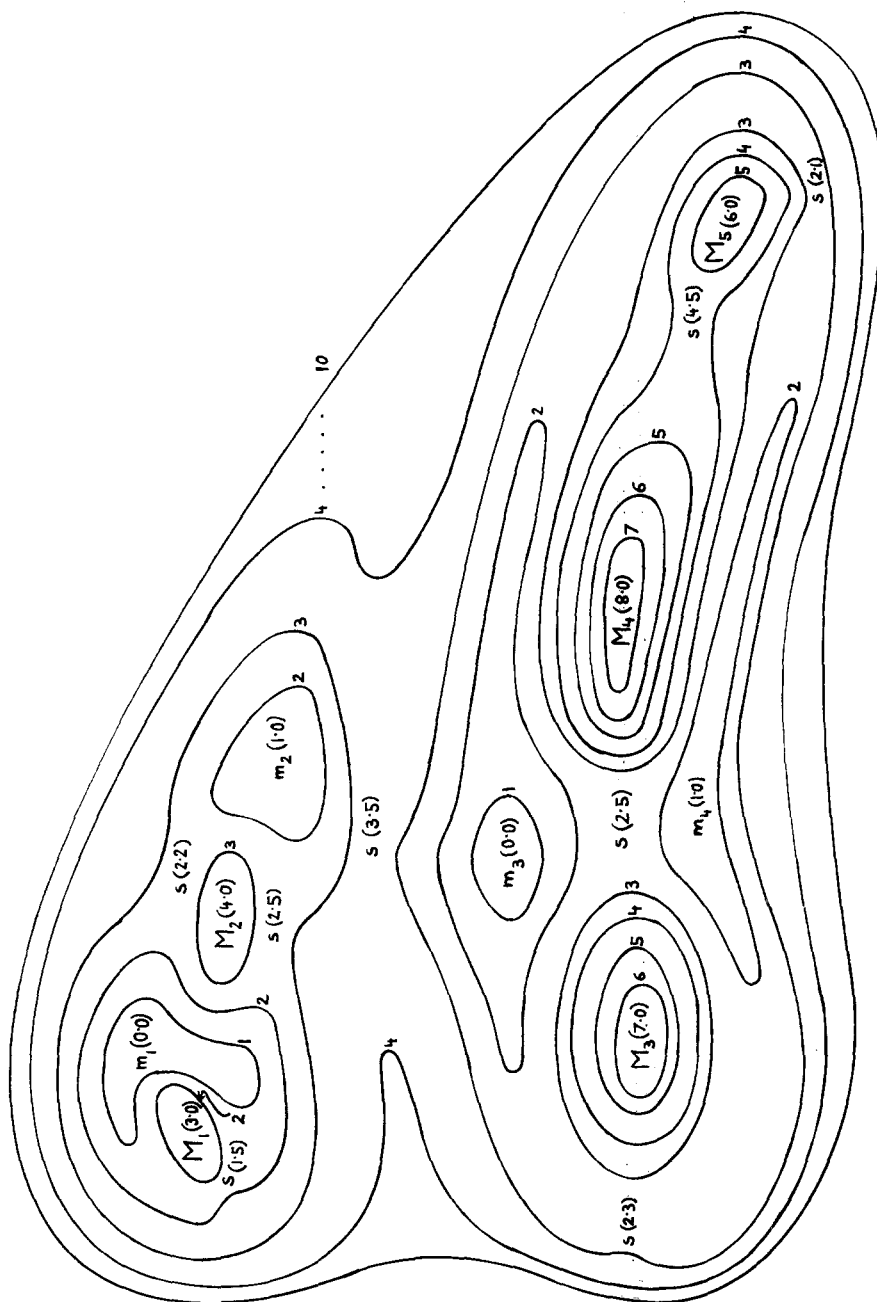


Fig. 2. Model potential energy surface with minima  $m_i$ , saddle points  $s_j$  and maxima  $M_i$  shown. The energy values of these critical points as well as some equipotential contour lines are also indicated

For any energy value  $A$  one may associate each generator reaction mechanism  $[P_i]$  of the actual  $F_j^-(A)$  level set with the *highest maximum*  $M_i$  of the original energy surface  $E(K)$ , which maximum  $M_i$  is encircled by all closed paths of equivalence class  $[P_i]$ . Hence, one may match the indices in sequences  $\{M_i\}$  and  $\{[P_i]\}$ . For example, equivalence class  $[P_4]$  encircles both the higher maximum  $M_4$  and the lower maximum  $M_5$  within any level set  $F^-(A)$  of energy bound  $2.1 < A \leq 4.5$ , but  $[P_4]$  encircles only  $M_4$  if  $A > 4.5$ .

In Table 1 two sequences of *energy dependent* fundamental groups of reaction mechanisms of the example are given.  $\Pi_1(A, B)$  stands for the group obtained in a level set  $F^-(A')$  of energy bound  $A'$  falling within the open-closed energy interval  $(A, B]$ ,  $A' \in (A, B]$ . Each group is specified in terms of generator mechanisms  $[P_i]$ . In the first (second) sequence the connected level set component  $F_1^-(A)$  ( $F_3^-(A)$ ) that contains minimum  $m_1(0.0)$  (minimum  $m_3(0.0)$ , respectively) is considered, as the energy  $A$  of the level set is increased from  $A = 0.0$  to  $A > 8.0$ .

Evidently, a critical level  $A$  of a saddle point is required for any new generator mechanism to enter the group  $\Pi_1$ , and reaching the level of a maximum eliminates one generator. An evident, nevertheless important, special property of such groups is the fact that if during an energy increase any given generator mechanism is eliminated from the group, it never returns at higher energies.

Note that the level set  $F^-(A) = \emptyset$ , the empty set for any  $A \leq 0.0$ , in particular, at  $A = 0.0$  no fundamental group of reaction mechanisms exists on this surface. In the  $(0.0, 1.5]$  open-closed energy interval

$$\Pi_1(F_1^-(A), T_{d/A}) = \{[1]\} \quad (32)$$

the trivial group, and as the energy is further increased, in the interval  $(1.5, 2.5]$  one obtains the infinite cyclic group generated by  $[P_1]$ . When the energy is further increased, more complicated but still fairly simple groups are obtained.

**Table 1.** Energy-dependent<sup>a</sup> fundamental groups of reaction mechanisms,  $\Pi_1(A, B)$ , and their generator mechanisms  $[P_i]$  in the two sequences of level sets of the example of Fig. 2

Sequence $F_1^-(A)$		Sequence $F_3^-(A)$	
Group	Generator reaction mechanisms <sup>b</sup>	Group	Generator reaction mechanisms <sup>b</sup>
—	no group for $A \leq 0$	—	no group for $A \leq 0$
$\Pi_1(0.0, 1.5]$	no generators, trivial group $\{[1]\}$	$\Pi_1(0.0, 2.3]$	no generators, trivial group $\{[1]\}$
$\Pi_1(1.5, 2.5]$	$[P_1]$	$\Pi_1(2.3, 2.5]$	$[P_4]$
$\Pi_1(2.5, 3]$	$[P_1], [P_2]$	$\Pi_1(2.5, 3.5]$	$[P_4], [P_3]$
$\Pi_1(3, 3.5]$	$[P_2]$	$\Pi_1(3.5, 4]$	$[P_4], [P_3], [P_2]$
$\Pi_1(3.5, 4]$	$[P_2], [P_3], [P_4]$	$\Pi_1(4, 4.5]$	$[P_4], [P_3]$
$\Pi_1(4, 4.5]$	$[P_3], [P_4]$	$\Pi_1(4.5, 6]$	$[P_4], [P_3], [P_5]$
$\Pi_1(4.5, 6]$	$[P_3], [P_4], [P_5]$	$\Pi_1(6, 7]$	$[P_4], [P_3]$
$\Pi_1(6, 7]$	$[P_3], [P_4]$	$\Pi_1(7, 8]$	$[P_4]$
$\Pi_1(7, 8]$	$[P_4]$	$\Pi_1(8, \infty)$	no generators, trivial group $\{[1]\}$
$\Pi_1(8, \infty)$	no generators, trivial group $\{[1]\}$		

<sup>a</sup> Group  $\Pi_1(A, B)$  is invariant within open-closed energy interval  $(A, B]$

<sup>b</sup> Free generators, for further details see text

The two sequences of connected level sets, one starting from  $m_1(0.0)$  the other from  $m_3(0.0)$ , become identical above energy bound  $A = 3.5$ ,

$$F_1^-(A) = F_3^-(A) \quad \text{if } A > 3.5. \quad (33)$$

Consequently, the two sequences of fundamental groups of reaction mechanisms also become identical above this energy bound.

In each sequence of groups one may consider the subgroup relation as an ordering principle, and turn the sequence into a partially ordered set (poset). In doing this, we consider the actual, concrete groups and their actual, concrete subgroups, as specified by their generator mechanisms, and a group will *not* be regarded necessarily a subgroup of another, if it is merely *isomorphic* to a subgroup of the other.

As shown in Fig. 3, in each sequence the groups of fundamental reaction mechanisms form a *lower semilattice*. In these diagrams on the base level (level 0) one finds one group, the trivial group of reaction mechanism,  $\{[1]\}$ , that is a subgroup of any other group. On subsequent levels  $l$  of the diagrams the corresponding groups have precisely  $l$  generator reaction mechanisms. Whereas the actual groups at the same level  $l$  of the diagram are different, if they differ in at least *one* generator mechanism, nevertheless, they are isomorphic within any fixed level  $l$ , and as *abstract* free groups, are identical. Since the ordering relation within the diagram is the subgroup relation,

$$\Pi_1(A, A'] \subset \Pi_1(B, B'] \quad (34)$$

starting from any group  $\Pi_1(B, B']$  along a *descending* line one finds a *subgroup*  $\Pi_1(A, A']$  of  $\Pi_1(B, B']$ .

The binary lattice operations “meet” and “join” [8] can be defined for these diagrams as having a largest common subgroup or a smallest common supergroup, respectively, where the latter term means a group containing both groups as subgroups. Evidently “meet” of any two elements of the diagram can be formed since the trivial group  $\{[1]\}$  is a subgroup of any two groups. However, as our example shows, the “join” does not always exist for every pair of groups. For example, there is no “join” for groups  $\Pi_1(3.5, 4]$  and  $\Pi_1(4.5, 6]$ , that is, there is no fundamental group of reaction mechanisms that contains both of these groups as subgroups. Hence, the relevant algebraic structure of these diagrams is not in general a lattice, only a *lower semilattice*. Note, however, that in special cases both the “meet” and “join” may exist for all pairs of groups, and then a lattice is obtained. Furthermore, by artificially adding a formal group  $G$ , generated by  $k$  free generators, where  $k$  is the total number of maxima which exist or can be encircled within level set  $F^-(A_{\max})$ , and  $A_{\max}$  is the maximum energy value considered, this group  $G$  may serve as a maximum element, turning a lower semilattice into a lattice. In our case,  $G$  is formally generated by the set of all generator mechanisms  $\{[P_i]\}_{i=1}^k$  occurring in the groups below and at energy value  $A_{\max}$ .

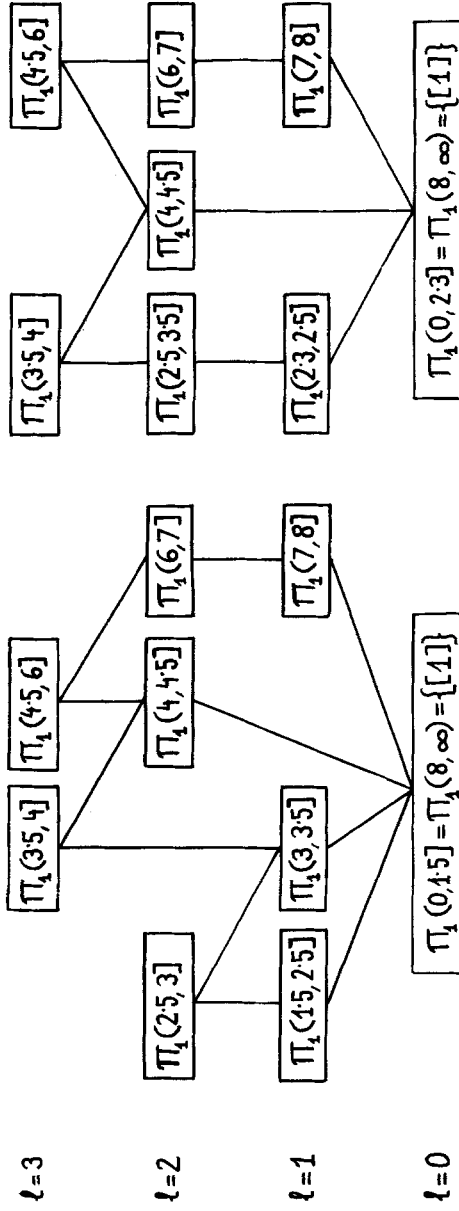


Fig. 3. The lower semilattice structures of two group sequences listed in Table 1. Along a descending line from a group  $G_i$  a subgroup  $G_2$  of  $G_1$  is found. See text for more details

A necessary but not in general sufficient condition for moving “up” (moving “down”) in the semilattice within any energy interval is the existence of a saddle point (maximum, respectively) within this energy interval. However, if the actual critical level at the saddle point (or maximum) is a non-degenerate critical level, i.e. one with a *single* critical point, then the same condition becomes a necessary and sufficient condition.

It is instructive to trace the effects of energy changes in such a semilattice, and in particular, to relate energy changes to changes in the semilattice level  $l$ . The higher the level the “larger” the group of reaction mechanisms, with more free generators, implying a “reacher” family of reaction mechanisms. At low energies, below and at  $A_{\min}$  (in general at any lower bound of the potential surface) one does not have any group (no chemical structures, no reactions). Immediately above  $A_{\min}$ , that value is necessarily that of an energy minimum, one obtains the trivial group  $\{[1]\}$ , representing one energy basin, one chemical structure. Initially, as the energy is further increased, usually one obtains more free generators, that corresponds to moving to higher levels  $l$  in the semilattice. Number  $l$  then is a *simple measure of the complexity* of the family of reaction mechanisms.

The increase in the degree of complexity,  $l$ , with increasing energy, is not necessarily monotonic, even at low energies, although the general trend is an initial increase. Eventually, however, beyond an energy value that is  $A = 4.5$  in our example, the dominant trend is a *decrease* in level  $l$ , i.e. in the level of complexity of the family of reaction mechanisms, as the energy is further increased. Finally, above an energy value that is  $A = 8.0$  in our example, the fundamental group of reaction mechanisms becomes again the trivial group  $\{[1]\}$ . Physically, at such high energy values all reaction mechanisms are topologically equivalent within the given subset of the potential energy surface. In such a case, unless some energy is subsequently lost by the chemical system, this subset of the surface behaves as a single, simple basin, with no detailed features being topologically significant.

Comparison of the two lower semilattices in Fig. 3 suggests that such semilattices do have common sub-semilattices. In our example the groups above energy value  $A = 3.5$  are identical in the two sequences of groups, implying that the corresponding parts of the two semilattices are identical.

We may generalize this observation. Let us denote by  $\{F^-(A)\}_{A_1}^{A_2}$  the *family* of all level sets of upper bounds  $A$  within the  $(A_1, A_2]$  open-closed energy interval. Take two continua of connected level sets  $\{F_1^-(A)\}_{A(m_1)}^{A_{\max}}$  and  $\{F_2^-(A)\}_{A(m_2)}^{A_{\max}}$ , on the same potential surface, one starting at minimum  $m_1$ , the other at minimum  $m_2$ . Consider the corresponding two semilattices,  $S_1(m_1)$  and  $S_2(m_2)$ , respectively. Denote by  $A(s)$  the highest energy bound, for which  $F_1^-(A(s))$  and  $F_2^-(A(s))$  are still disjoint:

$$A(s) = \max \{A: F_1^-(A) \cap F_2^-(A) = \emptyset\}. \quad (35)$$

This energy value, if exists below  $A_{\max}$ , is necessarily that of a saddle point  $s$ ,

$$s \in F_1^-(A_{\max}). \quad (36)$$

Then, the semilattice  $S_3(s)$ , obtained for the continuum of level sets  $\{F_3^-(A)\}_{A(s)}^{A_{\max}}$  is a *sub-semilattice* of both  $S_1(m_1)$  and  $S_2(m_2)$ , in fact it is the *largest* common sub-semilattice, and

$$S_3(s) = S_1(m_1) \cap S_2(m_2). \quad (37)$$

The algebraic structure of the family of fundamental groups of reaction mechanisms becomes the same *above energy value*  $A(s)$ , that is, it becomes independent of the initial choice, which chemical structure (which basin) of the  $F^-(A_{\max})$  domain of the potential surface is provided gradually with more and more energy, or equivalently, of the choice, along which continuum of level sets does one initially follow the variations in the fundamental groups. The higher energy sub-semilattices “forget” the history of group-subgroup relations of the fundamental groups of reaction mechanisms at lower energies. One should notice that for any two families  $\{F_1^-(A)\}_{A(m_1)}^{A_{\max}}$  and  $\{F_2^-(A)\}_{A(m_2)}^{A_{\max}}$  where level set  $F^-(A_{\max})$  is simply connected, such common sub-semilattices *must exist*, since then

$$\Pi_1(A_{\max}) = \{[1]\} \quad (38)$$

and

$$S(c) \subset S_3(s) = S_1(m_1) \cap S_2(m_2) \quad (39)$$

where sub-semilattice  $S(c)$  is one defined for any critical point  $c \in F^-(A_{\max})$  such that

$$E(c) \geq E(s). \quad (40)$$

#### 4. The algebraic structure of the complete set of all reaction paths

Consider the set  $\mathbf{P}$  of all reaction paths within level set  $F^-(A)$  of the potential energy hypersurface  $E(K)$ . This set has much too many elements, and we shall seek to replace it with a smaller set, that still reflects the most important relations among reaction paths of  $\mathbf{P}$ . For a general element  $p \in \mathbf{P}$  the origin  $p(0)$  and extremity  $p(1)$  may well be different, as opposed to the closed paths  $P \in \mathbf{P}$  for which  $P(0) = P(1)$ . In the remainder of this study we shall use lower case notation  $p$  for reaction paths whenever we wish to emphasize the possibility of  $p(0) \neq p(1)$ .

A general reaction path  $p \in \mathbf{P}$ , as defined in Part III, is a continuous mapping  $p: I \rightarrow F^-(A)$  of the unit interval  $I$  to level set  $F^-(A)$ . In particular, any constant path  $P$  for which  $P(I) = K \in F^-(A)$ , i.e. a path with image a single point  $K$  in level set  $F^-(A)$ , is also an element of  $\mathbf{P}$ .

For each path  $p \in \mathbf{P}$  we define two mappings,  $L^*$  and  $R^*$ , as

$$L^*: \mathbf{P} \rightarrow \mathbf{P} \quad (41)$$

$$R^*: \mathbf{P} \rightarrow \mathbf{P} \quad (42)$$

$$L^*(p) = q \in \mathbf{P} \quad (43)$$

where

$$q(I) = p(0) \in F^-(A) \quad (44)$$

and

$$R^*(p) = q' \in \mathbf{P} \quad (45)$$

where

$$q'(I) = p(1) \in F^-(A). \quad (46)$$

That is, mapping  $L^*$  (mapping  $R^*$ ) assigns to each path  $p \in \mathbf{P}$  the constant path  $q$  at the origin  $p(0)$  (the constant path  $q'$  at the extremity  $p(1)$ , respectively). One may refer to  $L^*(p)$  and  $R^*(p)$  as the left and right zero paths of reaction path  $p$ , respectively.

Evidently, for a closed path  $P$ ,  $P(0) = P(1)$  implies

$$L^*(P) = R^*(P). \quad (47)$$

Furthermore, in terms of mappings  $L^*$  and  $R^*$  the condition  $p_1(1) = p_2(0)$  for the existence of product reaction path  $p_1 p_2$  of  $p_1, p_2 \in \mathbf{P}$  (Eq. 34, Part III) can be given in equivalent form as

$$R^*(p_1) = L^*(p_2). \quad (48)$$

We also recall that the homotopy equivalence classes  $[p]$  of elements of  $\mathbf{P}$  are

$$[p] = \{p' : p' \sim p, p' \in \mathbf{P}\} \quad (49)$$

where  $\sim$  denotes homotopical equivalence relative to fixed endpoints. This definition implies that

$$L^*(p) = L^*(p') \quad (50)$$

$$R^*(p) = R^*(p') \quad (51)$$

for any two  $p, p' \in [p]$ .

Let us denote the family of all such equivalence classes by  $\Pi(F^-(A), T_{d/A})$  or in short, by  $\Pi$ :

$$\Pi(F^-(A), T_{d/A}) = \{[p_\alpha] : p_\alpha \in \mathbf{P}\}. \quad (52)$$

This set  $\Pi$  is simpler than set  $\mathbf{P}$  of all reaction paths. We may define two mappings  $L$  and  $R$  on  $\Pi$  as

$$L : \Pi \rightarrow \Pi \quad (53)$$

$$R : \Pi \rightarrow \Pi \quad (54)$$

$$L([p_\alpha]) = [L^*(p_\alpha)] \in \Pi \quad (55)$$

$$R([p_\alpha]) = [R^*(p_\alpha)] \in \Pi. \quad (56)$$

Due to relations (50) and (51) these mappings are well defined. Analogously to condition (48), the condition

$$R([p_1]) = L([p_2]) \quad (57)$$

implies the existence of the *product*  $[p_1][p_2]$  of equivalence classes  $[p_1]$  and  $[p_2]$  of reaction paths, defined as

$$[p_1][p_2] = [p_1 p_2] \in \Pi. \quad (58)$$

This product, if exists (i.e. if (57) is fulfilled), is unique and does not depend on the choice of reaction paths  $p_1, p_2 \in P$ , representing equivalence classes  $[p_1], [p_2] \in \Pi$ .

The family  $\Pi$  of all homotopy equivalence classes of the complete set  $P$  of all reaction paths within level set  $F^{-}(A)$ , together with mappings  $L$  and  $R$ , fulfill the following conditions.

(i)

$$L \cdot L = L = R \cdot L \quad (59)$$

$$L \cdot R = R = R \cdot R \quad (60)$$

where  $\cdot$  denotes the composition of mappings.

(ii) For any class  $[p] \in \Pi$  the products  $L([p])[p]$  and  $[p]R([p])$  exist and

$$L([p])[p] = [p] = [p]R([p]) \in \Pi. \quad (61)$$

(iii) The products  $L([p])L([p])$  and  $R([p])R([p])$  exist for each  $[p] \in \Pi$  and

$$L([p])L([p]) = L([p]) \in \Pi \quad (62)$$

$$R([p])R([p]) = R([p]) \in \Pi \quad (63)$$

i.e. both  $L([p])$  and  $R([p])$  are idempotent.

(iv) For any two  $[p_1], [p_2] \in \Pi$ , fulfilling condition (57)

$$L([p_1][p_2]) = L([p_1 p_2]) = L([p_1]) \quad (64)$$

$$R([p_1][p_2]) = R([p_1 p_2]) = R([p_2]) \quad (65)$$

hence, if in addition to (57), the condition

$$L([p_3]) = R([p_2]) \quad (66)$$

is also valid for some  $[p_3] \in \Pi$ , then the following product also exists:

$$([p_1][p_2])[p_3] \in \Pi \quad (67)$$

$$[p_1]([p_2][p_3]) \in \Pi. \quad (68)$$

(v) The homotopic associativity of product  $p_1 p_2 p_3$  of reaction paths, if the product exists (Part III, Eq. 56) implies that for the products (67) and (68) of homotopy classes of reaction paths associativity is also assured:

$$([p_1][p_2])[p_3] = [p_1]([p_2][p_3]) \quad (69)$$

and one may simply write  $[p_1][p_2][p_3]$ .



(vi) One may also recall from Part III the existence of a unique inverse path  $p^{-1}$  for every  $p \in \mathbf{P}$ , that implies the existence of a unique inverse

$$[p]^{-1} = [p^{-1}] \in \Pi \quad (70)$$

for every  $[p] \in \Pi$ , for which  $[p], [p]^{-1}$  pair

$$L([p]) = R([p]^{-1}) \quad (71)$$

$$R([p]) = L([p]^{-1}). \quad (72)$$

Properties (i)-(vi) of set  $\Pi$  of homotopy classes of the complete set  $\mathbf{P}$  of all reaction paths on  $F^{-}(A)$ , equipped with mappings  $L$  and  $R$ , imply that  $\Pi$  has an algebraic structure: that of a *groupoid*, with product defined by (58).

(Although in some texts on algebra the existence of product for some ordered pairs of elements, within a set  $G$ , is all what is required for a groupoid, in this study we require, by definition, associativity and the existence of left and right units, as well. For an alternative definition and for some general properties of groupoids, see the Appendix).

### 5. Chemical significance, extensions, subgroupoids and subgroups of groupoid $\Pi$ of all reaction paths

The intuitive chemical interpretation of product  $[p_1][p_2]$  is the continuation of one set of equivalent reaction paths,  $[p_1]$ , by another,  $[p_2]$ , followed by a relaxation of the constraint that all these paths pass through the point where they have been joined. It is the homotopical equivalence of certain reaction paths that enables one to replace the set  $\mathbf{P}$  of *all reaction paths* with the much *simpler* set  $\Pi$ . Nevertheless, this set  $\Pi$  still contains the chemically most significant information about relations among all reaction paths on level set  $F^{-}(A)$  of the potential energy hypersurface  $E(K)$ .

In the following we shall consider:

- (a) an extension of groupoid  $\Pi$  to a *semigroup*  $\Pi'$  on level set  $F^{-}(A)$ ,
- (b) subgroups of groupoid  $\Pi$ , in particular, a subgroup obtained earlier by a different technique: the group  $\Pi_1$  of all fundamental reaction mechanisms on  $F^{-}(A)$ .

Groupoid  $\Pi$  is an associative algebraic structure, but the closure property is *not* necessarily valid for arbitrary two equivalence classes  $[p_1]$  and  $[p_2]$  of reaction paths, since a product  $[p_1][p_2]$  within  $\Pi$  exists *only* if condition (57) is satisfied. One may, however, formally assure closure, i.e. the existence of product for any two  $[p_1], [p_2] \in \Pi$ , by adding *one* element  $[t]$ , to set  $\Pi$ , which element  $[t]$  will be interpreted as the product of those equivalence classes  $[p_1]$  and  $[p_2]$  for which *no product exists within the original groupoid  $\Pi$* :

$$[p_1][p_2] = [t] \quad (73)$$

whenever

$$R([p_1]) \neq L([p_2]), [p_1], [p_2] \in \Pi. \quad (74)$$

Furthermore, we define

$$[p][t] = [t][p] = [t][t] = [t] \quad (75)$$

for every  $[p] \in \Pi$ .

Evidently, the new algebraic structure, defined as

$$\Pi'(F^-(A), T_{d/A}) = \Pi(F^-(A), T_{d/A}) \cup \{[t]\} \quad (76)$$

and denoted in short by  $\Pi'$ , is a *semigroup*, since the product in  $\Pi'$  already fulfills the closure property as well as the associative property for arbitrary elements of  $\Pi'$ .

One may attach an intriguing chemical interpretation to element  $[t] \in \Pi'$ . It represents, in some abstract sense, the product of all those equivalence classes of paths,  $[p_1]$  and  $[p_2]$ , which paths are *not* continuations of each other in the given order. For each such pair  $[p_1]$  and  $[p_2]$  *no reaction paths*  $p_1 \in [p_1]$  and  $p_2 \in [p_2]$  can be combined into a single reaction path that would lead from the *common origin*

$$K_1 = p_1(0), \quad K_1 \in F^-(A) \quad (77)$$

of all paths from class  $[p_1]$  to the *common extremity*

$$K_2 = p_2(1), \quad K_2 \in F^-(A) \quad (78)$$

of all paths from class  $[p_2]$ . In spite of this

$$[t] = [p_1][p_2] \quad (79)$$

holds, that is consistent with the assumption of the existence of a formal "element"

$$t_{1,2} \in [t] \quad (80)$$

of the new "equivalence class"  $[t]$ , which  $t_{1,2}$  element *does* formally interconnect points  $K_1$  and  $K_2$ . Evidently, for *any pair* of points  $K_1, K_2 \in F^-(A)$ ,  $K_1 \neq K_2$ , one can find some equivalence classes  $[p_1]$  and  $[p_2]$ , for which (79) holds. Consequently, this observation suggests an interpretation of  $[t]$  as the formal equivalence class of all those  $t_{1,2}$  interconversions of geometries within level set  $F^-(A)$ , which *do not follow a continuous geometry change along reaction paths*. Then, it is natural to associate  $[t]$  with an equivalence class of all formal *tunneling "paths"*  $t_{1,2}$  within level set  $F^-(A)$ .

We may conclude that the extension of the *groupoid*  $\Pi$  of all equivalence classes of all reaction paths in  $F^-(A)$  into a *semigroup*  $\Pi'$  is equivalent to the inclusion of an equivalence class  $[t]$  of *all formal tunneling paths* within level set  $F^-(A)$ . That is, a formal inclusion of tunneling *changes the algebraic structure* of the family of all chemical interconversion processes on the potential energy hypersurface, from a *groupoid* to a *semigroup*.

Let us consider now, instead of extensions, the internal structure: subgroupoids and subgroups of groupoid  $\Pi$ . In particular, it is simple to show that the

fundamental group of reaction mechanisms,  $\Pi_1$ , as an abstract group, is a subgroup of groupoid  $\Pi$  on  $F^-(A)$ .

For an arbitrary point  $K_0 \in F^-(A)$  consider the following subset  $\Pi'_1$  of groupoid  $\Pi$ :

$$\Pi'_1(K_0) = \{[P]: P(0) = P(1) = K_0, \forall P \in [P], [P] \in \Pi\}. \quad (81)$$

It follows, that

$$L([P]), R([P]) \in \Pi'_1(K_0) \quad (82)$$

$$[P_1][P_2] \in \Pi'_1(K_0) \quad (83)$$

and

$$[P_i]^{-1} = [P_i^{-1}] \in \Pi'_1(K_0), \forall [P], [P_1], [P_2] \in \Pi'_1(K_0). \quad (84)$$

These conditions (81)–(84), however, are equivalent to those listed in the Appendix as the criteria of *stability* for a subset of a groupoid, hence  $\Pi'_1(K_0)$  is *stable* within groupoid  $\Pi$ , for any choice  $K_0 \in F^-(A)$ . With mappings  $L$  and  $R$  restricted to subsets  $\Pi'_1(K_0)$ , these stable subsets are indeed subgroupoids of groupoid  $\Pi$ .

Furthermore, definition (81) of  $\Pi'_1(K_0)$  implies that

$$L([P]) = R([P]) = [P_0] \quad (85)$$

for every  $[P] \in \Pi'_1(K_0)$ , where equivalence class  $[P_0]$  contains the element constant path  $P_0$  at point  $K_0$

$$P_0 \in [P_0] \quad (86)$$

$$P_0(I) = K_0. \quad (87)$$

Hence both  $L$  and  $R$ , when restricted to  $\Pi'_1(K_0)$ , are *constant maps*. Consequently, condition (A33) of the Appendix is fulfilled for  $\Pi'_1(K_0)$ , and subgroupoid  $\Pi'_1$  is a *group*, a *subgroup* of groupoid  $\Pi$ . In fact, a comparison of elements of  $\Pi'_1(K_0)$  and of the fundamental group  $\Pi_1(F^-(A), T_{d/A}, K_0)$  at reference point  $K_0$  directly shows that  $\Pi'_1(K_0)$  is the fundamental group of reaction mechanisms, and the above derivation serves as an alternative proof that this set is indeed a group. As we have seen in Part III, for an arcwise connected level set  $F^-(A)$  the specification of reference point  $K_0$  can be omitted, hence, the fundamental group of reaction mechanisms  $\Pi_1$  is a *subgroup* of groupoid  $\Pi$ :

$$\Pi_1(F^-(A), T_{d/A}) \subset \Pi(F^-(A), T_{d/A}). \quad (88)$$

This latter relation (88) is no surprise, as it is always valid for the fundamental group and the fundamental groupoid of a topological space [9].

## 6. Summary

Using a suitable generator set of reaction mechanisms, actual constructions have been given for the fundamental groups of reaction mechanisms over potential

energy surfaces. Within the family of *all* groups of fundamental reaction mechanisms, obtained by variations in the upper bound for energy, subgroup relations lead to a *lower semilattice* structure. The algebraic structure of *all reaction paths* is a groupoid  $\Pi$ , that can be extended into a *semigroup*, by formally including tunneling on the potential energy hypersurface. An alternative derivation of the group properties of the fundamental group of reaction mechanisms is given, which group is a subgroup of groupoid  $\Pi$ .

In a subsequent study we shall explore the relations between the algebraic structure of reaction mechanisms and the fuzzy catchment region topology induced by the  $G_i$  neighborhoods of catchment regions, used in the differentiable manifold model of potential energy hypersurfaces [11].

## Appendix

A non-empty set  $G$  is called a *groupoid* if for certain (but not necessarily all) ordered pairs of elements  $a, b \in G$  a unique product  $ab$  is defined, which  $ab$  product is also an element of  $G$

$$ab \in G \quad (\text{A1})$$

and if the following relations, (A.i), (A.ii) and (A.iii) are fulfilled:

A.i.

$$a(bc) = (ab)c \quad (\text{A2})$$

if either side of the above equation can be formed within  $G$  for certain elements  $a, b, c \in G$ ; i.e., the product, when exists, is associative.

A.ii. For any two elements  $a, b \in G$  there exists at least one element  $x \in G$  such that both

$$ax, xb \in G. \quad (\text{A3})$$

A.iii. If exists  $x \in G$  such that both products  $xa$  and  $xb$  exist in  $G$ , then the equation

$$ay = b \quad (\text{A4})$$

can be solved for  $y \in G$ .

Element  $x$  is a common left multiplier of  $a$  and  $b$ .

Similarly, if  $c, d \in G$  have a common right multiplier  $z \in G$ , i.e.  $cz, dz \in G$ , then the equation

$$uc = d \quad (\text{A5})$$

can be solved for  $u \in G$ .

We list few additional properties of groupoids, relevant to their applications to the complete set of reaction paths.

A.iv. For each element  $a \in G$  there exists a *left unit*  $\lambda(a)$  and *right unit*  $\rho(a)$  such that

$$\lambda(a), \rho(a) \in G \quad (\text{A6})$$

$$\lambda(a)a = a = a\rho(a). \quad (\text{A7})$$

A.v. If there exists a common left multiplier  $x$ , of  $a$  and  $b$ ,

$$xa, xb \in G (a, b, x \in G) \quad (\text{A8})$$

then

$$\lambda(a) = \lambda(b). \quad (\text{A9})$$

Similarly, from

$$cy, dy \in G(c, d, y \in G) \quad (\text{A10})$$

$$\rho(c) = \rho(d) \quad (\text{A11})$$

follows.

Hence, both  $\lambda(a)\lambda(a)$  and  $\rho(a)\rho(a)$  are defined in  $G$  for every  $a \in G$ , and they are idempotents:

$$\lambda(a)\lambda(a) = \lambda(a) \quad (\text{A12})$$

$$\rho(a)\rho(a) = \rho(a). \quad (\text{A13})$$

A.vi. For any left unit  $\lambda(a)$  of  $a \in G$  an inverse  $a^{-1} \in G$  of  $a$  can be defined by

$$aa^{-1} = \lambda(a). \quad (\text{A14})$$

Since for any left unit  $\lambda'(a)$  of  $a$

$$\lambda'(a) = \lambda(a)\lambda'(a) = (aa^{-1})\lambda'(a) = a(a^{-1}\lambda'(a)) \quad (\text{A15})$$

and

$$a^{-1}\lambda'(a) = a^{-1} \quad (\text{A16})$$

it follows that the left unit of  $a$  is *unique*:

$$\lambda(a) = \lambda'(a). \quad (\text{A17})$$

Similarly, the right unit  $\rho(a)$  is *unique*,

$$\rho(a) = \rho'(a) \quad (\text{A18})$$

for any right units  $\rho(a)$  and  $\rho'(a)$  of  $a \in G$ .

A.vii. From the above it follows that for  $a \in G$

$$a^{-1}a = \rho(a) \quad (\text{A19})$$

$$\lambda(a^{-1}) = \rho(a) \quad (\text{A20})$$

$$\rho(a^{-1}) = \lambda(a). \quad (\text{A21})$$

A.viii. The inverse  $a^{-1}$  of  $a \in G$  is *unique*, and

$$(a^{-1})^{-1} = a. \quad (\text{A22})$$

A.ix. If

$$ay = b \quad (\text{A23})$$

then

$$y = a^{-1}b \quad (\text{A24})$$

and similarly, if

$$uc = d \quad (\text{A25})$$

then

$$u = dc^{-1} \quad (\text{A26})$$

for  $a, b, c, d, y, u \in G$

A.x.

$$(ab)^{-1} = b^{-1}a^{-1}. \quad (\text{A27})$$

A.xi. A subset  $H \subset G$  is said to be *stable in G* if and only if the following three conditions, (A), (B), and (C) are satisfied:

$$(A) \quad \lambda(H), \rho(H) \subset H \quad (A28)$$

where

$$\lambda(H) = \{x : x = \lambda(y), y \in H\} \quad (A29)$$

$$\rho(H) = \{z : z = \rho(u), u \in H\} \quad (A30)$$

$$(B) \quad ab \in H \quad (A31)$$

for any two  $a, b \in H$  such that  $\rho(a) = \lambda(b)$ .

(C) If  $a \in H$  then

$$a^{-1} \in H. \quad (A32)$$

A *stable subset*  $H \subset G$ , equipped with mappings left and right units  $\lambda$  and  $\rho$  restricted to  $H$ , is called a *subgroupoid* of groupoid  $G$ .

A.xii. If  $\sigma \in G$  is a left or right unit for some element  $a \in G$ , then the set defined as

$$g = \{x : x \in G, \lambda(x) = \rho(x) = \sigma \in G\} \quad (A33)$$

is a *group*, a *subgroup* of groupoid  $G$ . Every subgroup of  $G$  is also a subgroupoid of  $G$ .

*Partially ordered sets, lattices and semilattices*

Set  $A$  is a *partially ordered set* if for some pairs of its elements  $a, b, c, \dots \in A$  a relation (*partial ordering*)  $\rho$  can be given with the following properties:

$$a\rho a \quad (\rho \text{ is reflexive}) \quad (A34)$$

$$a\rho b \text{ and } b\rho c \Rightarrow a\rho c \quad (\rho \text{ is transitive}) \quad (A35)$$

$$a\rho b \text{ and } b\rho a \Rightarrow a = b \quad (\rho \text{ is antisymmetric}). \quad (A36)$$

Assume that in a partially ordered set  $A$  for two elements  $a, b \in A$  there exists an element  $c \in A$  that fulfills relations

$$a\rho c \quad (A37)$$

and

$$b\rho c. \quad (A38)$$

If for any  $c' \in A$  that fulfills both (A37) and (A38) the relation

$$c\rho c' \quad (A39)$$

is also valid, then  $c$  is called the “*join*” (or supremum) of elements  $a$  and  $b$ , in notation

$$a \vee b = c. \quad (A40)$$

Similarly, if for  $a, b, d \in A$

$$d\rho a \quad (A41)$$

$$d\rho b \quad (A42)$$

and

$$d'\rho d \quad (A43)$$

for any  $d' \in A$  that fulfills both (A41) and (A42), then  $d$  is called the “*meet*” (or infimum) of elements  $a$  and  $b$ , in notation

$$a \wedge b = d. \quad (A44)$$

If join (meet) exists for each pair of elements of set  $A$ , then  $A$  is an *upper semilattice* (*lower semilattice*, respectively). If both meet and join exist for each pair of elements of  $A$  then  $A$  is a *lattice*.

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