A Computer Program Package for the Analysis, Creation, and Estimation of Generalized Reactions—GRACE. I. Generation of Elementary Reaction Network in Radical Reactions—A/GRACE(I)†

Yukio Yoneda
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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The system GRACE generates elementary reaction networks for simple reactions including free radicals, ions and even active sites in heterogeneous catalysis, and also predicts the overall reaction rates and the product distributions in radical reactions in the gas phase where the Arrhenius parameters of elementary reactions are available. In this paper, A/GRACE (part A of GRACE) is explained, which prepares elementary reaction networks for radical reactions. The reactant and the product are represented by square symmetric matrices. The off-diagonal elements represent bond multiplicity, or the number of localized electrons, between corresponding atoms, whereas the diagonal elements imply the number of unshared electrons on radical atoms. A reacting system, an ensemble of the participating molecules, is composed of atom groups, each of which consists of a center atom (usually non-hydrogen) and attached hydrogen atom(s), if any. Firstly, all the possible changes in the atom groups are selected, and the permitted combinations are preapred bearing in mind the equivalent groups in the system and the restrictions optioned. The major restriction is the complexity, *i.e.*, the number of ruptured or formed bonds. A direct sum of matrices are prepared from one of the combinations, and the elementary reaction is completed by setting the appropriate numerals, 1 or −1, to the outside elements. Secondly, the procedures are repeated until all the feasible networks are prepared. As an illustration the hydrogenation of ethylene over a heterogeneous catalyst has been cited.

In chemical research and development, both pure and applied, computers can be used for creation and estimation of chemical facts with the aid of chemical logic, as well as mere numerical calculations. Chemical facts may be divided into two groups: the static physical properties of substances and the reaction characteristics among them. The present author has already published¹⁾ the outline of a computer program package, EROICA, for the esitimation and the retrieval of physical properties of organic molecules.

Recently several systems of chemical logic with programs for the creation, or generation, of chemical reactions have been published by Corey,²⁾ Ugi,³⁾ Wipke,⁴⁾ and Bersohn.⁵⁾ Earlier works include DENDRAL by Feigenbaum *et al.*⁵ᵃ⁾ The features and the aims of these systems are rather different, reflecting the main interests of the authors. The present author has intended to develop a system that is capable of creating all of the possible reaction routes, or an elementary reaction network, in simpler organic reactions, and estimating quantitatively the reaction rates and product distribution. The system, GRACE (*G*eneralized *R*eaction *A*nalysis for *C*reation and *E*stimation) is fundamentally similar to that of Ugi *et al.*,³⁾ although the systems have been developed independently, and employs square matrices for manipulation of reacting systems. The outline of our system in the earlier stage was first published in 1970 as a part of a review.⁶⁾

This program package has the ability to create radical and ionic reactions and to accurately estimate the quantitative values of overall reaction rates and product distributions of hydrocarbon pyrolyses in gaseous phase. However, the stereochemistry is ignored. This system may be extended to find out parasitic reactions when a target reaction is given, as well as to survey all the possible reaction schemes from given raw materials to valuable products.

Outline of GRACE

The system of GRACE consists of three sub-systems, A/GRACE, B/GRACE, and C/GRACE, as shown in Fig. 1, and may be operated following the arrows in the flow chart. The functions of the sub-systems are as follows:

(1) A/GRACE: A given overall reaction (radical or ionic reaction) is analyzed into a network of elementary reactions, which generates the product system from the reactant system through various intermediate systems.

(2) B/GRACE: Arrhenius parameters of all the elementary reactions prepared by A/GRACE will be searched by information retrieval from a file of observed data, estimated by searching the data of resembling reactions from the file, or also estimated with the aid of empirical linear free energy relationships. However, processing is at present limited to radical reactions in gaseous phase due to the lack of observed Arrhenius parameters.

(3) C/GRACE: Simultaneous differential equations corresponding to the material balance among

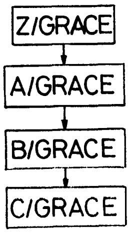

Fig. 1. Flow chart of GRACE.

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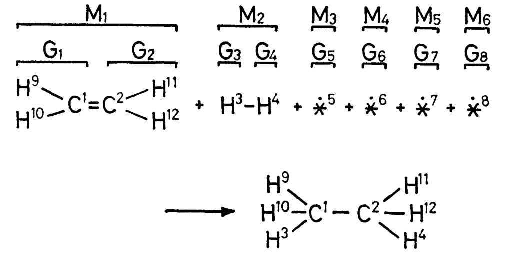
† CHEMOGRAM, a Computer Program Package for Chemical Logic, Part 2.

species in the network are prepared automatically. Overall rate and product distribution are calculated with the given initial conditions by direct integration of the equations or assuming the stationary state. Both flow and batch reactions may be dealt with.

In addition to these three sub-systems, a minor sub-system Z/GRACE, the part Zero of GRACE, may be employed to prepare the input data for A/GRACE concerning the reactant and product from a CHEMO input, a linear input of a rational formula also proposed by the present author.[7]

Representation of Reacting System by Matrices

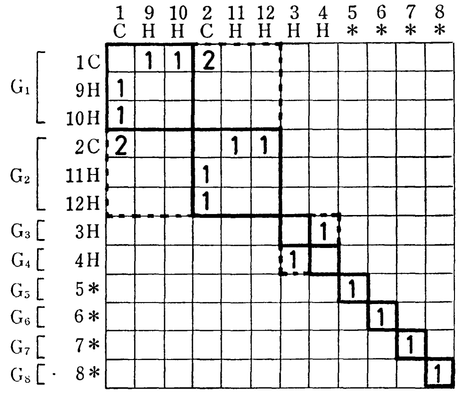
In this paper, a *system* is defined as an *ensemble*[3] of molecules which are employed as components of a given reaction; a *reacting system* implies all of the systems of the reactant, intermediates and the product. The representation method of reacting systems will be explained for heterogeneous hydrogenation of ethylene, as a simple example.



(1)

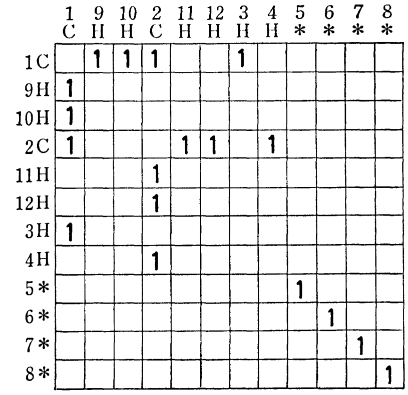
Equation 1 shows the overall reaction of hydrogenation, where the asterisks, *, represent the active sites over the solid catalyst, *e.g.*, metallic nickel, the dots over the symbols indicate radicals, and the superscripts over atomic symbols give the *atom ordinals* in this system. Symbols G and M given above in the reactant system represent *atom groups* and molecules, respectively. Here, an atom group implies the smallest ensemble of atoms, consisting of a *center atom* (usually non-hydrogen atom) and up to six *attached hydrogen* atoms, if any, although both of the hydrogen atoms in a hydrogen molecule are the center atoms; the reactant in Eq. 1 is thus composed of six molecules and eight atom groups.

Reactant and Product Matrices. A reactant matrix, symmetric and very sparse, may be prepared from Eq. 1 by appropriately assigning a row and a column to each atom. In this way the molecules and atom groups may be arranged to follow faithfully the order of chemical bonds in the system as shown in Fig. 2(a). The matrix elements represent the multiplicity of chemical bonds: 1 for a single bond, 2 for a double bond, and 3 for a triple bond. At the present stage of development, a bond with a bond order of 1.5, that is, a conjugated double bond, may not be entertained. The matrix thus prepared is termed a reactant bonding matrix, $\boldsymbol{X}_\mathrm{b}$, where $\boldsymbol{X}$ represents the reactant system and b the bonding matrix. It can be seen that each element of the matrix represents also the number of valence electrons belonging to an atom which are localized on a bond designated by the matrix. Hence, a radical atom that has at least one unshared valence electron should have valence electron(s) localized on it; *i.e.*, there is a numeral in the diagonal element.



		1 C	9 H	10 H	2 C	11 H	12 H	3 H	4 H	5 *	6 *	7 *	8 *
G1	1C		1	1	2								
	9H	1											
	10H	1											
G2	2C	2				1	1						
	11H				1								
	12H				1								
G3	3H								1				
G4	4H							1					
G5	5*									1			
G6	6*										1		
G7	7*											1	
G8	8*												1

Fig. 2a. Reactant bonding matrix, $\boldsymbol{X}_\mathrm{b}$.



	1 C	9 H	10 H	2 C	11 H	12 H	3 H	4 H	5 *	6 *	7 *	8 *
1C		1	1	1			1					
9H	1											
10H	1											
2C	1				1	1		1				
11H				1								
12H				1								
3H	1											
4H				1								
5*									1			
6*										1		
7*											1	
8*												1

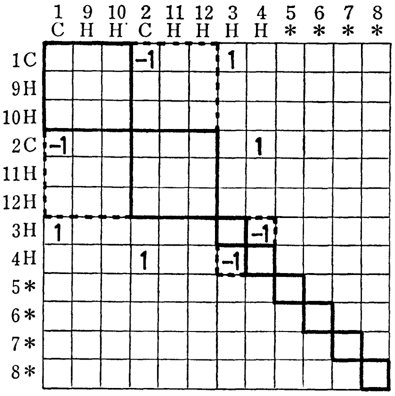
Fig. 2b. Product bonding matrix, $\boldsymbol{Y}(\boldsymbol{X}_\mathrm{b})$.

A *product bonding matrix*, $\boldsymbol{Y}(\boldsymbol{X}_\mathrm{b})$ (Fig. 2(b)), may be prepared from Eq. 1 following the arrangement of the atom ordinals in $\boldsymbol{X}_\mathrm{b}$, where $\boldsymbol{Y}$ represents a reactant and $(\boldsymbol{X}_\mathrm{b})$ defines the arrangement of atoms in the matrix as following the matrix $\boldsymbol{X}_\mathrm{b}$. In the matrix $\boldsymbol{Y}$, two matrix elements having had a value of 2 in $\boldsymbol{X}_\mathrm{b}$ are changed to 1 due to hydrogenation of the double bond.

Reaction Matrix. A reaction matrix, $\boldsymbol{R}_\mathrm{b}$, may be defined as the difference between product $\boldsymbol{Y}$ and reactant $\boldsymbol{X}$:

$$\boldsymbol{R}_\mathrm{b} = \boldsymbol{Y}(\boldsymbol{X}_\mathrm{b}) - \boldsymbol{X}_\mathrm{b}. \tag{2}$$

A reaction matrix, Fig. 2(c), is symmetric. The elements in the matrix represent the appearance or the disappearance of the localized valence electrons, and indicate bond formation and rupture, including changes in the bond multiplicity. Usually in elementary reactions, changes in the value of the matrix elements may not exceed two, since the change by two implies, for example, the sudden formation or rupture of a double bond in a single elementary step. The transformation of the double bond in ethylene to a single bond, the rupture of a single bond in a hydrogen molecule and the addition of two hydrogen atoms to ethylene may be found in Fig. 2(c). The active



	1 C	9 H	10 H·	2 C	11 H	12 H	3 H	4 H	5 *	6 *	7 *	8 *
1C				−1			1					
9H												
10H												
2C	−1							1				
11H												
12H												
3H	1							−1				
4H				1			−1					
5*												
6*												
7*												
8*												

Fig. 2c. Reaction matrix, $\boldsymbol{R}_b = \boldsymbol{Y}(\boldsymbol{X}_b) - \boldsymbol{X}_b$.

sites ($*$) show no change in overall reaction because they are catalysts.

The sum of the matrix elements in each row as well as in each column of a reaction matrix should be zero, since the number of total valence electrons belonging to each atom does not change during reaction as far as radical reactions are concerned.

Preparation of One Step Reaction in the Elementary Reaction Network

Elementary Reaction Matrix. An elementary reaction may be defined as a simple reaction that cannot be decomposed further into simpler reactions in the sense of the transformation of the bonding. In general, only two-centered and there-centered reactions have been adopted as elementary reactions, although in some cases, such as concerted reactions, four-centered reactions may also be allowable. In a reaction matrix, the number of non-zero off-diagonal elements in the upper-right half implies the number of bonds, formed and ruptured. This number is defined as the *complexity* of a reaction (κ); complexity 1 corresponds to two-centered, complexity 2 to two- and three-centered, complexity 3 to three- and four-centered, and complexity 4 to four-centered reactions, respectively. Hereafter, an elementary reaction will be defined as a reaction with complexity not exceeding the maximum complexity (κ_{max}), for which the value of 3 or 4 is usually chosen.

An overall reaction through the r-th route will be decomposed into elementary reactions $\boldsymbol{R}^{el}{}_{rs}$ as

$$\boldsymbol{R}^{over}(r) = \sum_s \boldsymbol{R}^{el}{}_{rs}, \tag{3}$$

where $\boldsymbol{R}^{over}(r)$ represents the matrix of the above-mentioned overall reaction and s indicates the step number in the network. If the intermediate systems $\boldsymbol{I}_{r,s-1}$ and $\boldsymbol{I}_{r,s}$ are the reactant and the product of step s in route r, respectively, then

$$\boldsymbol{I}_{r,s} = \boldsymbol{R}^{el}{}_{rs} + \boldsymbol{I}_{r,s-1}. \tag{4}$$

By adding Eq. 4 recursively, Eq. 2 will be derived with Eq. 3; $\boldsymbol{R}_b$ in Eq. 2 is exactly the same as $\boldsymbol{R}^{over}(r)$ given in Eq. 3, although the latter clearly indicates the component of the network. The strategy therefore to develop a network that connects the overall reactant and the overall product is to create logically the above mentioned elementary reactions.

Preparation of an Elementary Reaction. During an elementary reaction, a change in valence electrons takes place within atom groups and between them. The change within an atom group may depend on the structure of that group, whereas the change between groups may depend on the change within groups. Thus, the following procedures will be employed as a tactics to create elementary reaction matrices.

(a) Restrictions for an elementary reaction should be given at first. The major restrictions are the maximum complexity of the elementary reaction and the maximum number of radicals involved. There may also be various minor restrictions such as the prohibition of hydrogen radicals in the gaseous phase and the prohibition of homogeneous reactions in which no active sites participate.

(b) Allowable group reaction matrices are selected for each atom group. *A group reaction matrix*, $\boldsymbol{\rho}$, is a small matrix whose order is the same as that of the atom group matrix, and represents the change within the atom group. Each group reaction matrix should satisfy the restrictions mentioned in (a).

(c) Appropriate combinations of $\boldsymbol{\rho}$'s (one $\boldsymbol{\rho}$ for each group) are selected so that these combinations again satisfy the restrictions; for example, odd number of radicals cannot be allowed in Eq. 1. In addition, the systems commonly have equivalent molecules or atom groups; (G_1 and G_2), (G_3 and G_4), and (G_5, G_6, G_7, and G_8) in Eq. 1 are equivalent atom groups, and M_3—M_6 are equivalent molecules. Such redundancy as imposing the same $\boldsymbol{\rho}$ repeatedly on equivalent atom groups should be avoided.

(d) The direct sum of a combination of $\boldsymbol{\rho}$'s are prepared along the diagonal of a blank reaction matrix. The remaining procedure is to supply the appropriate numerals, 1 or -1, in the *intergroup domain*, *i.e.*, the domain outside the atom groups, so that the filled matrix satisfies the requirement of a reaction matrix that the sum of the elements in each row should be zero. When the completed elementary reaction matrix satisfies all the restrictions, it is used to create an intermediate system, otherwise it should be discarded.

(e) Procedure (d) is repeated until all the combinations prepared in procedure (c) are exhausted. Thus all the intermediate systems which are logically allowable are created from the preceding intermediate.

Group Reaction Matrix. In general, there are several group reaction matrices which are applicable for a specified group; an example of a set of the group reaction matrices is shown in Fig. 3. This set is applicable for AH_2 groups where A designates an atomic species that has a valency not less than 2 like carbon and nitrogen; methylene groups in ethylene, dichloroethane or carbene, and an amino group in methyl amine or amino radical is represented by an AH_2 group.

In Fig. 3, $\boldsymbol{x}$ designates a group matrix representing the atom group AH_2, where n (n=0, 1, or 2) implies the number of unshared electrons localized on the

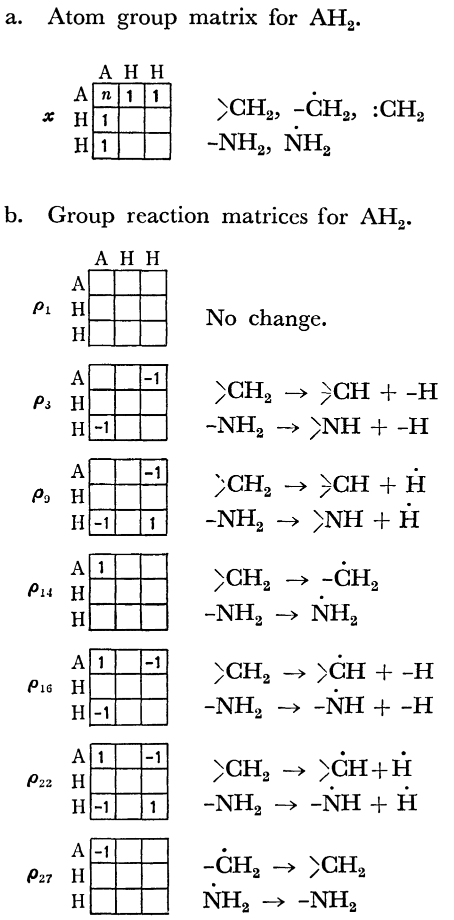


Fig. 3. Group reaction matrices for AH_2 group.

atom A. For example, carbon with $n=2$ represents a carbene molecule, and nitrogen with $n=1$ represents an amino radical.

A blank matrix $\boldsymbol{\rho}_1$ implies that no change takes place within this atom group. Matrices $\boldsymbol{\rho}_3$ to $\boldsymbol{\rho}_{27}$ represent changes illustrated in the right-hand margin, where a short bar indicates one localized electron on a bond connected to other atoms. Thus two bars implies two single bonds or a double bond and a dot indicates an unshared electron. The matrix $\boldsymbol{\rho}_{27}$ represents the disappearance of a radical atom, or an unshared electron, on the atom A, because a diagonal element, -1, on A indicates the decrease of the number of unshared electrons in the reactant. Naturally, this $\boldsymbol{\rho}_{27}$ should be applied only for $\boldsymbol{x}$ with $n \geqq 1$. All the possible changes in the atom group AH_2 are represented with these seven group reaction matrices, as far as it is assumed that only one valence electron on an atom moves from the formerly localized position to the new one.

A practical example using Eq. 1 will now be given. The following processing will be conducted under the restrictions stated in Table 1. Figure 4 shows the allowable $\boldsymbol{\rho}$'s for the methylene group in the overall reactant $\boldsymbol{X}$ under the above restrictions, where $\boldsymbol{\rho}_9$ and $\boldsymbol{\rho}_{22}$ are excluded because the hydrogen radical in the gaseous phase is prohibited, and $\boldsymbol{\rho}_{27}$ is also excluded as the methylene groups in $\boldsymbol{X}$ have no radical atom ($n=0$).

TABLE 1. RESTRICTIONS OPTIONED FOR GENERATION OF ELEMENTARY REACTION NETWORK OF THE REACTION IN Eq. 1

1. Complexity of elementary reaction should not exceed 3.
2. Number of reaction centers should not exceed 4.
3. Molecularity of reaction including active sites should not exceed 3.
4. Number of radical atoms shold not exceed 4.
5. Number of uupaired electrons on an atom should not exceed 1.
6. No gaseous hydrogen radical is allowed, although hydrocarbon radicals may be allowed even in gaseous phase.
7. Number of valence electrons is 4 for carbon, and 1 for hydrogen and active sites.
8. At least one active site should participate in each elementary reaction.
9. Recombination of active sites is not allowed, as it may be impossible in actual reaction.

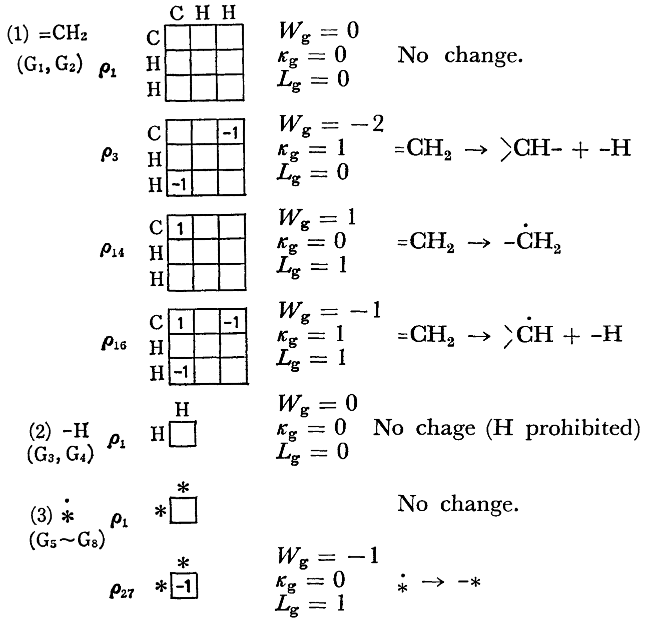
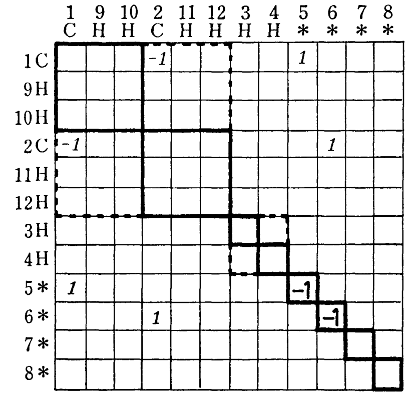


Fig. 4. Allowable group reaction matrices for methylene, hydrogen and active site groups.

For an atom group which consists of only the center atom without any attached atoms, three group reaction matrices of order 1, *i.e.*, $\boldsymbol{\rho}_1$, $\boldsymbol{\rho}_{14}$, and $\boldsymbol{\rho}_{27}$ are allowable. However, only one matrix ($\boldsymbol{\rho}_1$) will be allocated to the hydrogen atom groups in $\boldsymbol{X}$, and two ($\boldsymbol{\rho}_1$ and $\boldsymbol{\rho}_{27}$) to active sites, based on the similar reasoning as in the case of methylene.

Direct Sum of Group Reaction Matrices. The direct sum of group reaction matrices is a succession of an appropriate combination of corresponding group reaction matrices placed along the diagonal of a reaction matrix, which is shown surrounded by bold, solid lines in Fig. 5. The appropriate combination will be selected so that the elementary reaction matrix prepared satisfies both the chemical logic and given restrictions.



	1 C	9 H	10 H	2 C	11 H	12 H	3 H	4 H	5 *	6 *	7 *	8 *
1C				-1					1			
9H												
10H												
2C	-1									1		
11H												
12H												
3H												
4H												
5*	1								-1			
6*				1						-1		
7*												
8*												

Fig. 5. An example of elementary reaction matrix.

The attributes of a group reaction matrix are defined as follows:

W_g: sum of all the elements.
κ_g: complexity.
L_g: sum of absolute values of diagonal elements.

Figure 4 illustrates the various values.

An elementary reaction matrix $\boldsymbol{R}^{el}$ may be completed by placing the appropriate numerals in the intergroup domain. Since $\boldsymbol{R}^{el}$ is symmetric, the sum of the elements in the intergroup domain is zero or even. Therefore it is a necessary condition that the sum of the elements within the direct sum should be also zero or even, because the sum of the elements of $\boldsymbol{R}^{el}$ is zero by definition. Thus,

$$\sum W_g = \text{zero or even.} \tag{5}$$

A completed direct sum matrix is a direct sum, in which the sum of the elements in every row is zero, satisfying the criteria of a completed reaction matrix. Except for this case, some changes are also necessarily expected in the intergroup domain, and their contribution to κ is not less than unity. Thus, the sum of κ_g's of $\boldsymbol{\rho}$'s should be less than or equal to $\kappa_{max}-1$. Hence,

$$\sum \kappa_g \leqq \kappa_{max} - 1. \tag{6}$$

Finally, since only a pair or pairs of unshared electrons appear or disappear as far as radical reactions are concerned, the grand sum of the absolute values of the diagonal elements should also be zero or even,

$$\sum L_g = \text{zero or even.} \tag{7}$$

The three selection rules mentioned above are still necessary conditions. Table 2 is thus derived, where all the approved combinations of $\boldsymbol{\rho}$'s are shown for each group.

Completion of Elementary Reaction Matrix. The bold lines in Fig. 5 surround the direct sum of combination No. 1 in Table 2. Then, the appropriate numerals, 1 or -1, are given to the intergroup domain so that the resulting matrix satisfies the conditions of a reaction matrix. The datails of the tactics how to allocate them will be published later. It is worthy of mention, however, that more than one set of numerals may exist for one combination of $\boldsymbol{\rho}$'s. The completed matrix should be further checked as to whether it satisfies the given restrictions such as complexity, number of reaction centers, molecularity, and so on. In the GRACE system these critical examinations are made by complex and sophisticated algorithms in the programs.

Since the elementary reaction matrix shown in Fig. 5 satisfies all the restrictions, it will be adopted as a component of the reaction network. By adding this matrix to the overall reactant matrix given in Fig. 2(a), an intermediate matrix $\boldsymbol{I}_1$ will be given as shown in Fig. 6. The change from $\boldsymbol{X}_b$ to $\boldsymbol{I}_1$ represents the reaction in the chemical formula,

$$\mathrm{C_2H_4 + H_2} + 4\dot{*} \rightarrow \underset{\substack{| \\ *}}{\mathrm{CH_2}}\text{-}\underset{\substack{| \\ *}}{\mathrm{CH_2}} + \mathrm{H_2} + 2\dot{*} \tag{8}$$

These procedures will be repeated on all the combinations given in Table 2 under the restriction of $\kappa \leqq 6$, and the resulting intermediates from the overall reactant are tabulated in Table 3, where No. 1a is the intermediate shown in Eq. 6. Four intermediates have

	1 C	9 H	10 H	2 C	11 H	12 H	3 H	4 H	5 *	6 *	7 *	8 *
1C		1	1	1					1			
9H	1											
10H	1											
2C	1				1	1				1		
11H				1								
12H				1								
3H								1				
4H							1					
5*	1											
6*				1								
7*											1	
8*												1

Fig. 6. An example of intermediate matrix, $\boldsymbol{I}_1$, derived from the reaction matrix in Fig. 5.

TABLE 2. ALLOWABLE COMBINATIONS OF GROUP REACTION MATRICES

Combination No.	=CH$_2$		-H		$\dot{*}$				$\sum W_g$	$\sum \kappa_g$	$\sum L_g$
	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8			
1	1	1	1	1	27	27	1	1	-2	0	2
2	3	1	1	1	27	27	1	1	-4	1	2
3	14	1	1	1	27	1	1	1	0	0	2
4	16	1	1	1	27	1	1	1	-2	1	2
5	3	3	1	1	27	27	1	1	-6	2	2
6	3	14	1	1	27	1	1	1	-2	1	2
7	3	16	1	1	27	1	1	1	-4	2	2

TABLE 3. ELEMENTARY REACTIONS IN THE FIRST STEP OF THE OVERALL REACTION

No.[a)]	Created intermediate	κ	Remark
1a	$\underset{\overset{\vert}{*}}{\mathrm{CH_2}}-\underset{\overset{\vert}{*}}{\mathrm{CH_2}}+\mathrm{H_2}+2\overset{\cdot}{\underset{*}{\vert}}$	3	Associative mechanism (first step; adsorption of ethylene)
1b	$\mathrm{CH_2}=\mathrm{CH_2}+2\underset{\overset{\vert}{*}}{\mathrm{H}}+2\overset{\cdot}{\underset{*}{\vert}}$	3	Associative mechanism (first step; adsorption of hydrogen)
1c	$\underset{\overset{\vert}{*}}{\mathrm{CH_2}}-\mathrm{CH_3}+\underset{\overset{\vert}{*}}{\mathrm{H}}+2\overset{\cdot}{\underset{*}{\vert}}$	5	Associative mechanism (second step)
2	$\underset{\overset{\vert}{*}}{\mathrm{CH}}=\mathrm{CH_2}+\underset{\overset{\vert}{*}}{\mathrm{H}}+\mathrm{H_2}+2\overset{\cdot}{\underset{*}{\vert}}$	3	Dissociative mechanism
3	$\underset{\overset{\vert}{*}}{\mathrm{CH_2}}-\dot{\mathrm{C}}\mathrm{H_2}+\mathrm{H_2}+3\overset{\cdot}{\underset{*}{\vert}}$	2	Precursor of 1a and 1c
4	$\mathrm{CH_2}=\dot{\mathrm{C}}\mathrm{H}+\underset{\overset{\vert}{*}}{\mathrm{H}}+\mathrm{H_2}+3\overset{\cdot}{\underset{*}{\vert}}$	2	Precursor of 2
5	$\mathrm{CH}\equiv\mathrm{CH}+2\underset{\overset{\vert}{*}}{\mathrm{H}}+\mathrm{H_2}+2\overset{\cdot}{\underset{*}{\vert}}$	5	Direct dehydrogenation
6	$\mathrm{H^9H^3H^4C}-\dot{\mathrm{C}}\mathrm{H_2}+\underset{\overset{\vert}{*}}{\mathrm{H^{10}}}+3\overset{\cdot}{\underset{*}{\vert}}$	6	Redundant exchange of hydrogen atoms
7	$\underset{\overset{\vert}{*}}{\mathrm{CH}}=\dot{\mathrm{C}}\mathrm{H}+2\mathrm{H_2}+3\overset{\cdot}{\underset{*}{\vert}}$	4	Adsorptive dehydrogenation

a) Numerals indicate the combination number in Table 2, and a to c implies that plural intermediates may be created from one combination.

a κ exceeding 3 and must be abandoned at this stage. The remaining five intermediates will thus be employed as the reactants of the second step. These intermediates can be transferred to the memory of the computer in two ways. One is in the form of connectivity tables which can reproduce the matrices, and the other is in the form of canonicalized formulas. The same intermediate may be produced at different steps through varied routes, and, by these algorithms, the same intermediates may be produced even from one and the same direct sum. Therefore, always when intermediates are created, they should be identified by comparing their cannonicalized (unique and unambiguous) chemical formulas. When they are found in the storage and are judged to be the intermediates already created in other step or route, two nodes, or intermediates, must be joined. In the GRACE system, the intermediate of Fig. 6 is stored in the form of Eq. 9, which is prepared with a sub-system CANON, whose details will be reported in a forthcoming paper.

1*Sl′-CH2-CH2-Sl′* + 1*Sl′*+1*Sl′* + 1*H-H** (9)

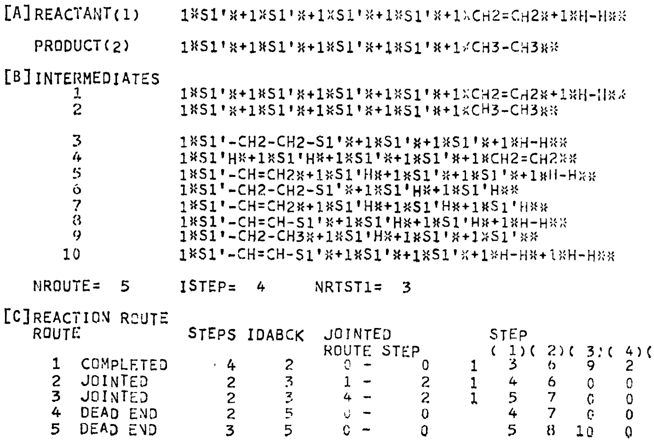
where Sl′ denotes an active site ($\overset{\cdot}{\underset{*}{\vert}}$), whereas * implies a delimiter for molecules and an equation.

Completion of Reaction Network

The procedures described above may be repeated step by step until no new intermediate is created from the products of the preceding elementary reactions. The overall product is also found as one of the created intermediate systems.

Figure 7 shows an example of the output format of A/GRACE for the reaction in Eq. 1 under severe restrictions. In this case, no radical has been allowed except for active sites, as usually postulated by catalytic chemists. This output has been interpreted into a more readable form in Fig. 8, where two prevailing reaction schemes can be found. The left-hand route, **1**, (**3** or **4**), **6**, **9**, and **2**, represents the associative adsorption mechanism for the hydrogenation by Horiuti and Polanyi,[8)] whereas the right-hand route, **1**, **5**, **8**, and **10**, represents the dissociative adsorption mechanism for isotope exchange between ethylene and hydrogen proposed by Farkas and Farkas.[9)]

The computation time to prepare the complete network amounted to 21 s on a HITAC 8800.



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[A]REACTANT(1)      1*S1'*+1*S1'*+1*S1'*+1*S1'*+1*CH2=CH2*+1*H-H**
   PRODUCT(2)       1*S1'*+1*S1'*+1*S1'*+1*S1'*+1*CH3-CH3**
[B]INTERMEDIATES
      1             1*S1'*+1*S1'*+1*S1'*+1*S1'*+1*CH2=CH2*+1*H-H**
      2             1*S1'*+1*S1'*+1*S1'*+1*S1'*+1*CH3-CH3**

      3             1*S1'-CH2-CH2-S1'*+1*S1'*+1*S1'*+1*H-H**
      4             1*S1'H*+1*S1'H*+1*S1'*+1*S1'*+1*CH2=CH2**
      5             1*S1'-CH=CH2*+1*S1'H*+1*S1'*+1*S1'*+1*H-H**
      6             1*S1'-CH2-CH2-S1'*+1*S1'H*+1*S1'H**
      7             1*S1'-CH=CH2*+1*S1'H*+1*S1'H*+1*S1'H**
      8             1*S1'-CH=CH-S1'*+1*S1'H*+1*S1'H*+1*H-H**
      9             1*S1'-CH2-CH3*+1*S1'H*+1*S1'*+1*S1'**
     10             1*S1'-CH=CH-S1'*+1*S1'*+1*S1'*+1*H-H*+1*H-H**

   NROUTE=  5       ISTEP=  4      NRTST1=  3

[C]REACTION ROUTE
   ROUTE               STEPS IDABCK  JOINTED          STEP
                                     ROUTE STEP       ( 1)( 2)( 3:( 4)(
    1  COMPLETED        4     2       0 -    0      1   3    6    9    2
    2  JOINTED          2     3       1 -    2      1   4    6    0    0
    3  JOINTED          2     3       4 -    2      1   5    7    0    0
    4  DEAD END         2     5       0 -    0          4    7    0    0
    5  DEAD END         3     5       0 -    0          5    8   10    0
```

Fig. 7. Computer output of reaction network of catalytic hydrogenation of ethylene.

[A] Intermediates **1** and **2** denote the canonicalized formulas of the overall reactant and product, respectively.

[B] Intermediates No. **3** to **10** which appear in the network.

[C] Description of the network. Captions at the right of ROUTE No. imply the sequence of elementaly reactions.

For example,

COMPLETED. Route No. 1 consists of sequence of reactant(**1**)—intermediate **3**—**6**—**9**—product(**2**) and leads the system to the overall product.

JOINED. Route No. 2(**1**—**4**—**6**) is joined to Route No. 1 at the intermediate **6** in th step 2.

DEAD END. Route No. 4(**1**—**4**—**7**) was terminated at the intermediate **7**, because **7** cannot change further under the given restrictions.

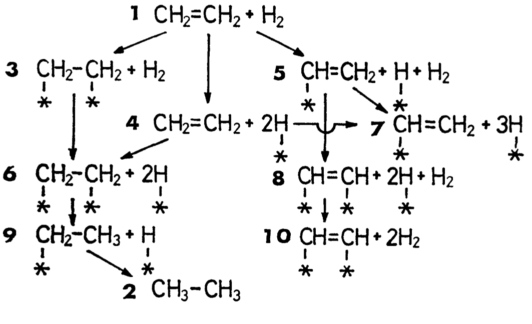

Fig. 8. Reaction routes in catalytic hydrogenation of ethylene.

Option of Restrictions in A/GRACE System. Numerous intermediates were produced even in the simplest system like that mentioned above, and hence the careful selection of restrictions is necessary to avoid the appearance of unrealistic, or thermodynamically unstable, molecules in intermediates. For example, no triple bond may be expected in the hydrogenation of ethylene, and no cyclopropene would be produced during the pyrolysis of propane. Only chemical knowledge and the experience of chemists will create a reasonable reaction network for a given reaction with the aid of the optimum selection of restrictions.

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