trochem. Soc. 1971, *118*, 1412–1415.
Smith, T.; Mansfeld, F. An Ellipsometric–Electrochemical Cell: Initial Films on Titanium in Water and Methanol Solutions. *J. Electrochem. Soc.* 1972, *119*, 663–668.
Syper, L. Partial Oxidation of Aliphatic Side Chains with Cerium IV. *Tetrahedron Lett.* 1966, *37*, 4493–4498.
Torii, S. Electrooxidation of Alkylbenzene Side-Chains. In *Electro-organic Syntheses*, Part I; Kodansha and VCH: Tokyo, Weinheim, 1985; pp 75–95.
Torii, S.; Tanaka, H.; Inokuchi, T.; Nakane, S.; Akada, M.; Saito, N.; Sirakawa, T. Indirect Electrooxidation (an Ex-Cell Method) of Alkylbenzenes by Recycle Use of (NH₄)₂Ce(NO₃)₆ in Various Solvent Systems. *J. Org. Chem.* 1982, *47*, 1647–1652.

Tzedakis, T. Etude de Procédés d'Electro-Oxydation Indirecte de Composés Aromatiques par l'Emploi d'Ions Métalliques. Doctorat de l'Université Paul Sabatier, Toulouse, France, 1989.
Tzedakis, T.; Savall, A. Performance Predictions in the Scale-up a Liquid-Liquid CSTR for Indirect Electro-Oxidation of Aromatic Hydrocarbons. *Chem. Eng. Sci.* 1991, *46*, 2269–2279.
Wendt, H.; Schneider, H. Reaction Kinetics and Reaction Techniques for Mediated Oxidation of Methylarenes to Aromatic Ketones. *J. Appl. Electrochem.* 1986, *16*, 134–146.

Structure-Oriented Lumping: Describing the Chemistry of Complex Hydrocarbon Mixtures

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A new method, called structure-oriented lumping (SOL), for describing the composition, reactions, and properties of complex hydrocarbon mixtures has been developed. Structure-oriented lumping represents individual hydrocarbon molecules as a vector of incremental structural features. A mixture of hydrocarbons is represented as a set of these vectors, each with an associated weight percent. The vector representation of molecules provides a convenient framework for constructing reaction networks of arbitrary size and complexity, for developing molecular-based property correlations, and for incorporating existing group contribution methods for the estimation of molecular thermodynamic properties. The SOL approach provides a foundation for molecular-based modeling of all refinery processes. This paper introduces the concepts and principles of structure-oriented lumping.

I. Introduction

Petroleum is a complex mixture of hydrocarbons containing thousands of distinct molecular species. Describing the behavior of petroleum mixtures is important to the design and operation of commercial refining processes but challenging from the standpoint of identifying the thousands of molecular components and establishing their complex catalytic reaction networks. Until very recently, analysis of feedstocks has been limited to bulk property measurements such as carbon and hydrocarbon content, NMR carbon and hydrogen types, limited mass spectroscopy analysis of predominant compound types (Robinson and Cook, 1969), and the boiling point distribution. Hence, feedstocks in the gas oil range were characterized at best only in terms of average compositions of wide boiling fractions. Consistent with analytical limitations, early models resorted to the techniques of lumping (Weekman, 1969; Jacob et al., 1976) where a relatively small number of lumps were used to describe the mixture.

In these coarsely lumped kinetic models the thousands of individual constituents in a complex feedstock are grouped into the broad but measurable categories of compound classes or boiling range, with simplified reaction networks between the lumps. Although satisfying the needs of reactor designers in the past, this form of lumping has several inherent limitations: (1) the approach often fails to extrapolate to different feedstocks because of composition differences within the same defined lumps; (2) the actual composition of lumps in terms of molecular components may change with overall conversion of the system and mask the true kinetics; (3) coarsely lumped models cannot be utilized to interpret the effects of catalyst properties on the phenomenological aspects of catalytic chemistry because fundamental catalytic reaction mech-

anisms are not incorporated into the kinetic scheme; and (4) insufficient detail exists in the lumped models to predict subtle changes in product properties—the main limitation.

The notion of a continuous mixture has received considerable attention as a method for modeling the reactions of complex mixtures (Aris, 1989; Astarita and Ocone, 1988). In the continuous mixture chemical identity is replaced by some continuous property index, such as boiling point, to describe the concentration distribution and conversion with respect to the index. *This approach lacks a convenient method for incorporating reaction chemistry at the molecular level and multiple product property information.*

Other concepts for modeling the kinetic behavior of complex mixtures include the "bond kinetics" approach first proposed by Jaffe (1974) and, more recently, the analogous group kinetics developed by Gray (1990). In bond kinetics the reactions of specific chemical bonds are followed as a lump, irrespective of the parent molecule, for the purpose of predicting heat release. Group kinetics lumps carbon types based on NMR analysis in an analogous manner. These approaches, however, are not formulated to predict the details of product composition or properties. McDermott et al. (1990) have developed a technique to construct and react the numerous molecules of a complex mixture using Monte Carlo methods and statistical analysis of mixture properties. Liguras and Allen (1989) have proposed describing a mixture with several hundred pseudocomponents whose selection is based on a set of typical routine analytical data and whose reactions are based on group contribution methods.

A new approach to model the chemistry of complex mixtures, called structure-oriented lumping (SOL), has been developed over the past several years at Mobil. The

Chart I

a = [A6 A4 A2 N6 N5 N4 N3 N2 N1 R br me IH AA NS RS AN NN RN NO RO KO]

S:	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
carbon	6	4	2	6	5	4	3	2	1	1	0	0	0	0	-1	0	-1	-1	0	-1	0	0
hydrogen	6	2	0	12	10	6	4	2	1	1	0	0	2	-2	-2	0	-1	-1	1	-2	0	0
sulfur	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0	0
nitrogen	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	0	0	0
oxygen	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1

basic concept of structure-oriented lumping is that hydrocarbon molecules can be described as a vector, with the elements of the vector representing structural features sufficient to construct any molecule. Each molecule in a mixture is then represented by a structure vector. The approach is still lumping, but at the level of molecular structure. Different molecules with the same set of structural groups, i.e., certain isomers, are lumped and represented by the same vector. The structure vector provides a framework to enable rule-based generation of reaction networks and rate equations involving thousands of components and many thousands of reactions. This modeling work is closely coupled with ongoing efforts to provide more detail on the molecular composition of petroleum materials. Recent developments by Mobil researchers in this laboratory and elsewhere (Sullivan et al., 1989) have shown that liquid chromatography coupled with field ionization mass spectroscopy and gas chromatography/mass spectroscopy (GC/MS) can determine the carbon number distribution of many homologous series yielding an analysis and characterization of the oil in terms of thousands of molecular types. The focus of this paper is on the structure vector concept and its application to constructing molecules, complex mixtures, and their reaction networks. Subsequent publications will discuss the incorporation of analytical techniques and pilot plant results for model development.

II. Hydrocarbon Structure Vector

Although a hydrocarbon stream may contain a very large number of distinct molecular components, only a small set of structural groups or building blocks are required to construct or represent the molecules. For example, a set of atomic elements (C, H, N, S, O) that constitute a molecule can be thought of as a set of structural groups with the empirical formula for the molecule providing the representation of the molecule. The empirical formula is limited because it can only provide information on the molecular weight of the molecule and cannot distinguish molecules among a large set of stoichiometric isomers. From the standpoint of modeling refinery processes, a set of structural groups that provides a convenient representation of fundamental process chemistry is needed. In the following, a set of structural groups is defined and ordered as a vector to provide this mathematical representation of hydrocarbon molecules. The approach and conventions employed are then demonstrated through examples.

II.a. Structure Groups. The hydrocarbon structure vector **a** and the stoichiometric matrix **S** are defined in Chart I. The columns of the stoichiometric matrix contain the C, H, S, N, and O atomic stoichiometry contribution of each element or structural group of the vector. The structural groups have the stoichiometry to construct a molecule *incrementally* and are referred to hereafter as *structural increments*. The definitions of each of the

structural increments, with examples, are as follows:

A6: A six carbon aromatic ring present in all aromatic molecules. The A6 element of the vector is a group that can exist by itself as benzene when all other incremental structures are absent (as indicated by zero):

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

The **A6** group has six carbons and six hydrogens, the proper carbon and hydrogen stoichiometry for the benzene molecule. All multiring aromatic compounds must contain at least one A6 ring and are built with the addition of other incremental ring structures to the A6 ring.

A4: A four carbon aromatic ring increment attached to an A6 (or another A4 ring) to construct condensed multiring structures such as naphthalene and phenanthrene:

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

The **A4** ring is an *incremental* structure that must be attached to either an A6 or another A4 and cannot exist by itself. Although the A4 ring has four carbons, it contains only the two additional hydrogens required to maintain the proper stoichiometry for addition to the A6 ring (hydrogens shown for clarity):

A2: A two carbon aromatic increment that results in a peri-condensed multiring structure as in pyrene, formed by the addition of an A2 to the "bay region" of a multiring aromatic system such as phenanthrene:

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

N6 and N5: Six and five carbon naphthenic ring increments. The N6 and N5 rings are also, in addition to the A6, groups of the structure vector that can exist independently as cyclohexane and cyclopentane:
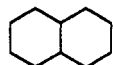
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

All multiring naphthenic molecules contain at least one N6 or N5 and are built through the addition of incremental naphthenic ring structures.

N4, N3, N2, and N1: Additional four, three, two, and one carbon naphthenic ring increments that must be attached to other naphthenic *or* aromatic ring structures.

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
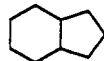
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
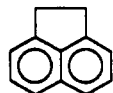
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
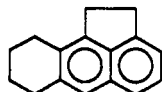
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
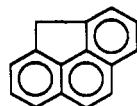
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	2	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	1	1	1

R: Carbon number of the total alkyl-group structure on ring compounds or the carbon number of aliphatic molecules if no rings are present. R has the stoichiometry of a $-CH_2-$ group for incremental alkyl group addition to a ring structure.
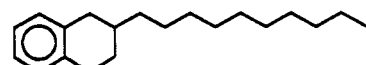
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	1	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0

IH: Incremental hydrogen to specify the degree of unsaturation of molecules (in addition to that from aromatic rings). IH adds two hydrogen atoms to the stoichiometry of a vector (molecule). If no rings are present, IH = 1 for paraffins, IH = 0 for monoolefins, and IH = −1 for diolefins. If there are naphthenic rings present, IH = −1 indicates a cycloolefin.

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	0	0	0	0	0	0	10	0	0	1	0	0	0	0	0	0	0	0	0

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	0	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0

A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	1	0	0	0	0	0	0	0	0	−1	0	0	0	0	0	0	0	0	0

br: Indicates the number of branch points on the alkyl side chain R or on a paraffin or olefin. It does not distinguish between, methyl, ethyl, or propyl branching (by convention it is assumed that only methyl branching exits). The location of the branch on the side chain or paraffin is also not specified. The **br** group contributes no hydrogen or carbon to the stoichiometry of the molecule.
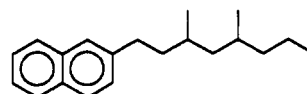
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	0	0	10	2	0	0	0	0	0	0	0	0	0	0	0

me: Specifies the number of carbons of the total alkyl structure R which are attached as methyl groups to the carbon atoms on aromatic or naphthenic rings of a molecule. The group **me** also does not contribute carbon or hydrogen to the stoichiometry of the molecule. By the convention it is not used to denote the obvious methyl group when R = 1 or when **me** = R − 1.
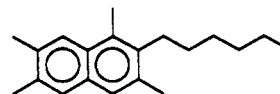
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	0	0	10	0	4	0	0	0	0	0	0	0	0	0	0

me can be used to distinguish xylene and ethylbenzene, for example:
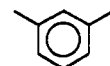
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	0	0	0	0	2	0	1	0	0	0	0	0	0	0	0	0	0
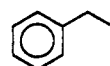
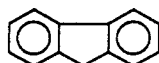| A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0

AA: The biphenyl bridge between any two nonincremental rings (A6, N6, or N5). AA contributes no carbon to the structure but eliminates two hydrogen atoms to form the bridge between the rings:
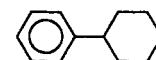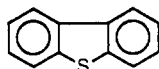
A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0

The remaining elements of the structure vector involve sulfur, nitrogen, and oxygen for heteroatom-bearing compounds. Heteroatom structures are built by analogy to hydrocarbons.

NS, NN, and NO: A sulfur, nitrogen, or oxygen located in a naphthenic ring or paraffin and bound to two carbon atoms. NS, NN, or NO replaces a CH_2 methylene unit (one carbon and two hydrogens) with an S atom, an >N–H group, or an oxygen atom in the structure, respectively.

A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
2	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0

A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
2	0	0	0	0	0	0	0	1	0	0	0	0	1	1	0	0	0	0	0	0	0
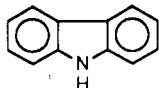
A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
2	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	1	0	0	0	0

As shown above for dibenzothiophene, the N1 ring is still present but with a sulfur atom replacing the CH_2 in the N1 ring. The NS groups therefore has –1 carbon and –2 hydrogen stoichiometry.

RS, RN, and RO: A sulfur atom, nitrogen –NH– group, or oxygen atom inserted between a carbon and hydrogen atom to form a mercaptan, amine, or alcohol group, respectively. RS and RO do not contribute to the carbon or hydrogen stoichiometry of the molecule; i.e., a C–H becomes a C–S–H or C–O–H. RN contributes one additional hydrogen in addition to the nitrogen.

A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	0	0	0	0	0	0	0	0	10	1	0	0	1	0	0	0	0	0	0
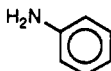
A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0

AN: A nitrogen group substitution for carbon in an aromatic ring as in pyridine or quinoline. The AN group replaces =CH– with =N–. The AN group stoichiometry is therefore +1 for the nitrogen addition, –1 for the carbon replacement, and –1 for the hydrogen because no hydrogen is bound to the the nitrogen atom in the aromatic ring.

A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
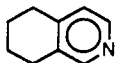
A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0

KO: A ketone or aldehyde group where a $-CH_2-$ is replaced by >C=O, resulting in a stoichiometric change +1 oxygen and –2 hydrogen.
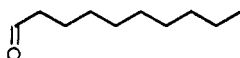
A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
0	0	0	0	0	0	0	0	0	0	0	10	1	0	0	0	0	0	0	0	0	1

The overall C, H, S, N, and O stoichiometric content of any molecule is simply the product of the **S** matrix and its structure vector:

$$\text{C, H, S, N, O stoichiometry} = \mathbf{S} \times \mathbf{a}$$

Common observed ring structures in petroleum and their structure vectors are shown in Figure 1.

II.b. Structural Isomers. Although most hydrocarbon molecules can be represented by this set of structural groups, the method only indicates which structural groups are present in a molecule, not their specific arrangement within the molecule. A specific structure vector may actually represent many molecules having the same set of structural groups, but with different spatial positioning of the groups. These are called structural isomers in this context and may involve different placements of aromatic and naphthenic rings, numerous configurations of the alkyl groups, positioning of branching, and the location of heteroatoms and olefinic bonds. The rationale behind neglecting the arrangement of structural groups in the vector is the assumption that the chemical and physical properties of the structural isomers are similar. Lumping structural isomers reduces the modeling complexity of the system from perhaps millions of molecules to thousands of components. Furthermore, analytical techniques to speciate isomers are not yet available. Resolution of isomers by GC methods is possible only in the lower molecular weight naphtha range (C_4–C_9). Analytical techniques for distillate and larger hydrocarbons are, except in certain special cases (e.g., normal paraffins, bare ring aromatics, biomarkers), incapable of distinguishing structural isomers. Only molecular mass and number of aromatic rings, from which structural increments can be assigned, are measurable.

The strategy for dealing with isomer complexity is to use a set of *conventions* to select one isomer to represent the lump of structural isomers corresponding to a particular structure vector. These conventions are based on our knowledge of the molecular structure of crude oil hydrocarbons and on thermodynamic arguments. Petroleum-derived organic compounds tend to have regularities in structural patterns (Tissot and Welte, 1984) because of their biological origin. Examples of structural isomers and conventions for selecting the one representative isomer are discussed below.

Ring Isomers and Conventions. The four-ring aromatic chrysene has a cata-condensed structure:
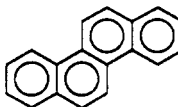
A8	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

The following four-ring aromatics also have the same structure vector:
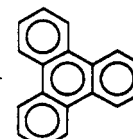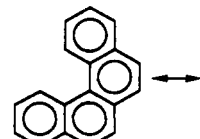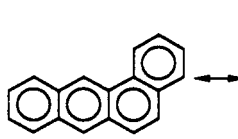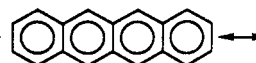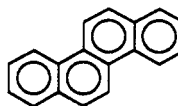
In another example, the placement of N4 and N3 rings is unspecified:
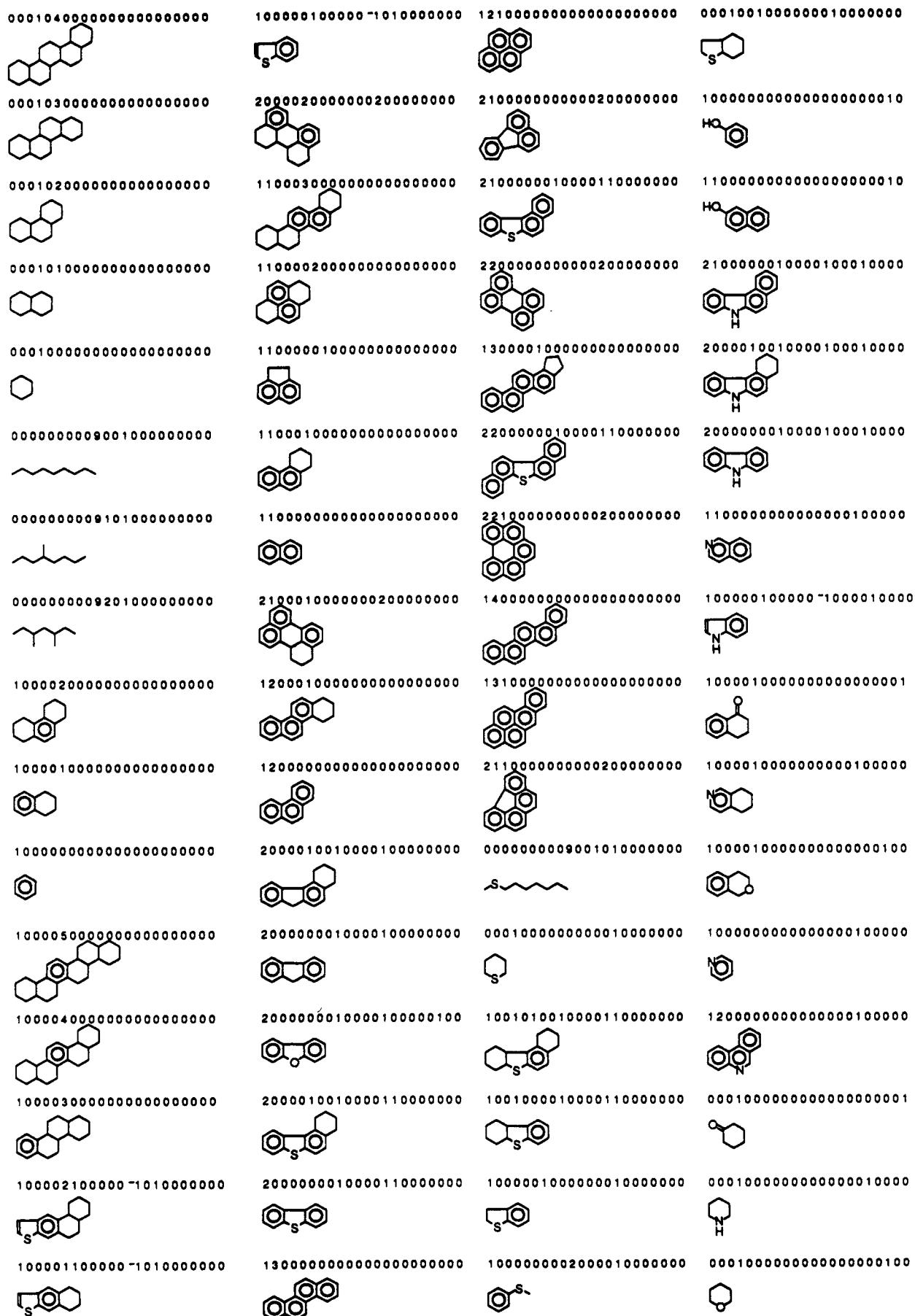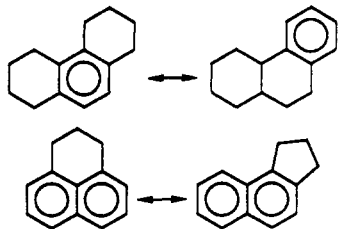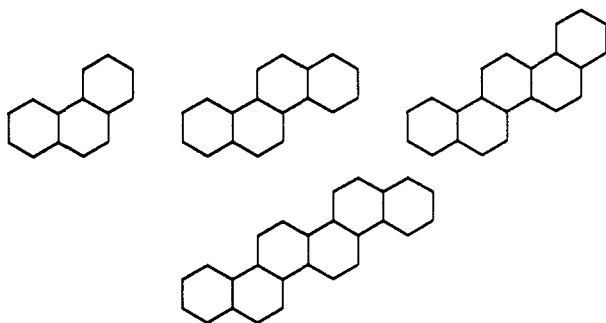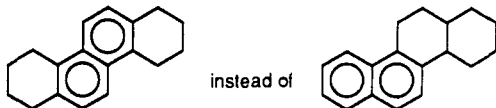
Figure 1. Common structures in crude oil.

The following set of conventions are used to determine typical ring structures.
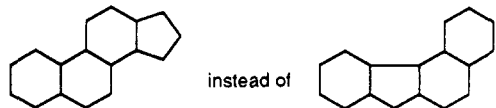
(a) All benzenoid multiring aromatics or their partially hydrogenated and naphthenic analogues assume a cata-condensed arrangement of rings:

(b) The external rings on partially saturated aromatic compounds are saturated first:

instead of

(c) The N3 ring is always an external ring:

instead of

Actually, the two rings on the left of the latter structure are constructed with the N1, AA, and N6 groups instead of an N3 and an N4.

Heteroatom Isomers and Conventions. Heteroatoms can occur almost anywhere in molecules but tend to have specific placements in ring structures. The following conventions are employed to locate heteroatoms and associated double bonds on ring structures to generate the most common molecular types in crude oil:

(a) Heteroatoms are placed in the smallest naphthenic ring if a structure has more than one naphthenic ring, i.e., N1 before N3, N3 before N4, etc.:

instead of
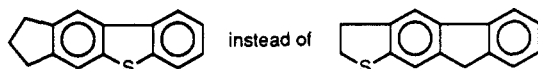
(b) Double bonds are first associated with the hetero-atom-bearing ring:

instead of

Alkyl Group Isomeric Structure and Conventions. The most difficult aspect to address of structural isomers is that of alkyl groups on aromatics and naphthenes. The number of possible configurations of side chains in a molecule of a given alkyl group carbon number R can be large. For example, the following naphthalenes all have the same carbon number.
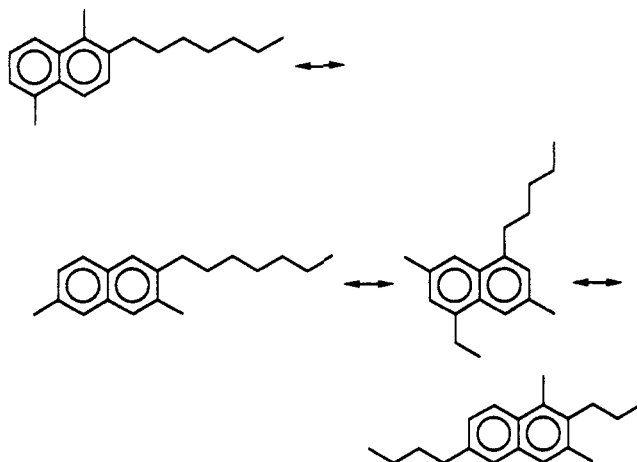
The common alkyl group configuration on ring compounds is thought to be a long alkyl chain and a rough average of one methyl group per ring (Hood et al., 1959), as shown in the first two examples. Although analytical techniques cannot yet determine the heterogeneity of alkyl groups on larger multiring molecules, it is assumed by convention that alkyl groups are structured in this manner.

The **br** group is included in the vector to denote the degree of branching (primarily for paraffins, which can be analytically determined), but not the location of branching. The **me** group specifies the number of methyl groups on the rings, but not their location. Examples of the use of **me** and **br** are shown in Figure 2. The convention for multiring molecules is that the total number of methyls on rings, **me**, is equal to the number rings for multiring molecules if R is large enough as shown in the homologous series of phenanthrenes in Figure 3. The **br** and **me** groups may take on noninteger values to represent an average value for a lump of structural isomers.

Use of conventions to select the most representative molecular structures out of a set of isomers has an impact on how reaction pathways and networks are defined and in the development of thermodynamic and physical property correlations.

II.c. Equivalent Structure Relationships. The above discussion reveals how one structure vector can represent many possible isomer configurations. In certain cases, however, one molecule can be represented by several structure vectors. The following examples illustrates these *equivalence relationships*:

A benzene ring is an A6 group, which could also be constructed as a cyclohexane (N6) ring with three double bonds (IH = −3):

A6 = 1   NA6 = 1   IH = −3
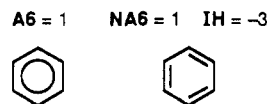
Six, four, and two carbon aromatic and naphthenic rings could be interchanged with the use of the IH term to set the proper hydrogen deficiency, but the equivalence is not universally applicable to all molecules. The A6, A4, and A2 groups are intended to indicate aromaticity, not just hydrogen deficiency. For example, the following structures have equivalent stoichiometry but are obviously not the same molecule:

A6 = 1   N6 = 1   N4 = 1   IH = −3
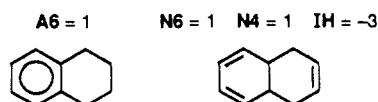
The equivalence between an A6 = 1 and the combination of N6 = 1 and IH = −3 fails here because the latter

A6=1 R=0 br=0 me=0   A6=1 R=4 br=1 me=0   A6=1 R=5 br=2 me=1   A6=1 R=6 br=2 me=1

A6=1 R=1 br=0 me=0   A6=1 R=4 br=1 me=1   A6=1 R=6 br=0 me=0   A6=1 R=6 br=2 me=2

A6=1 R=2 br=0 me=0   A6=1 R=4 br=2 me=0   A6=1 R=6 br=0 me=1   A6=1 R=6 br=3 me=0

A6=1 R=2 br=0 me=1   A6=1 R=5 br=0 me=0   A6=1 R=6 br=0 me=2

A6=1 R=3 br=0 me=0   A6=1 R=5 br=0 me=1   A6=1 R=6 br=0 me=3

A6=1 R=3 br=0 me=1   A6=1 R=5 br=0 me=2   A6=1 R=6 br=0 me=4

A6=1 R=3 br=0 me=2   A6=1 R=5 br=0 me=3   A6=1 R=6 br=0 me=5

A6=1 R=3 br=1 me=0   A6=1 R=5 br=0 me=4   A6=1 R=6 br=1 me=0

A6=1 R=4 br=0 me=0   A6=1 R=5 br=1 me=0   A6=1 R=6 br=1 me=1

A6=1 R=4 br=0 me=1   A6=1 R=5 br=1 me=1   A6=1 R=6 br=1 me=2

A6=1 R=4 br=0 me=2   A6=1 R=5 br=1 me=2   A6=1 R=6 br=1 me=3

A6=1 R=4 br=0 me=3   A6=1 R=5 br=2 me=0   A6=1 R=6 br=2 me=0

Figure 2. Examples of branching indices: br and me.

Chart II

	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
reactant	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
product rule	-1		+1																			
product	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

structure is ambiguous with respect to double bond location; the double bonds are not necessarily in one ring. A convention could be included to place three double bonds in one ring, but this seems unnecessary.

In another example, the phenanthrene molecule is constructed with an A6 and two A4 rings or, alternatively, as two A6 rings, an A2 ring, and the AA biphenyl bridge:

A4   AA   A6

A4   A6   A2
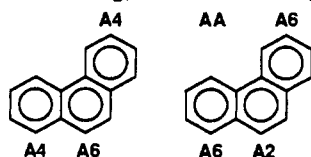
Either representation is satisfactory; the A2 representation derives from the partially hydrogenated 9,10-dihydrophenanthrene with an N2 ring and the A4 from the tetrahydrophenanthrene:

A6 = 2   AA = 1   N2 = 1   A6 = 1   A4 = 1   N4 = 1

This does not indicate inconsistency or redundancy in the choice of structural increments, but rather consistency in

A6=1 A4=1 R=0 br=0 me=0

A6=1 A4=1 R=12 br=0 me=2

A6=1 A4=1 R=24 br=0 me=2

A6=1 A4=1 R=1 br=0 me=0

A6=1 A4=1 R=13 br=0 me=2

A6=1 A4=1 R=25 br=0 me=2

A6=1 A4=1 R=2 br=0 me=1

A6=1 A4=1 R=14 br=0 me=2

A6=1 A4=1 R=26 br=0 me=2

A6=1 A4=1 R=3 br=0 me=2

A6=1 A4=1 R=15 br=0 me=2

A6=1 A4=1 R=27 br=0 me=2

A6=1 A4=1 R=4 br=0 me=2

A6=1 A4=1 R=16 br=0 me=2

A6=1 A4=1 R=28 br=0 me=2

A6=1 A4=1 R=5 br=0 me=2

A6=1 A4=1 R=17 br=0 me=2

A6=1 A4=1 R=29 br=0 me=2

A6=1 A4=1 R=6 br=0 me=2

A6=1 A4=1 R=18 br=0 me=2

A6=1 A4=1 R=30 br=0 me=2

A6=1 A4=1 R=7 br=0 me=2

A6=1 A4=1 R=19 br=0 me=2

A6=1 A4=1 R=31 br=0 me=2

A6=1 A4=1 R=8 br=0 me=2

A6=1 A4=1 R=20 br=0 me=2

A6=1 A4=1 R=32 br=0 me=2

A6=1 A4=1 R=9 br=0 me=2

A6=1 A4=1 R=21 br=0 me=2

A6=1 A4=1 R=33 br=0 me=2

A6=1 A4=1 R=10 br=0 me=2

A6=1 A4=1 R=22 br=0 me=2

A6=1 A4=1 R=34 br=0 me=2

A6=1 A4=1 R=11 br=0 me=2

A6=1 A4=1 R=23 br=0 me=2

A6=1 A4=1 R=35 br=0 me=2

Figure 3. Homologous series of naphthalenes.

the stoichiometric balance of the increments. In an equivalence relation, the preferred representation of a molecule is based on convenience with respect to the correlating molecular properties or reaction chemistry with structural increments.

III. Rule-Based Reaction Networks

The advantage of using a molecular-based representation of a complex mixture is that the fundamental mechanisms of catalytic reaction chemistry can be incorporated in the process model. A complex mixture can be modeled in terms of the kinetics of actual molecular transformations rather than in terms of the interconversion between lumps of poorly defined materials as in other approaches. However difficulty arises in determining the chemical reaction pathways and relevant kinetic parameters in large sets of molecules. This is especially true in hydrocarbon catalysis where a single molecule can react via parallel pathways. Structure-oriented lumping provides a convenient framework for treating chemical reactions as transformations of the reactant structural increments to the product struc-

tural increments. Specific transformations of the structural increments that reflect fundamental reaction chemistry are termed *reaction classes* in structure-oriented lumping and determined by a set of *reaction rules*. Just as a limited number of structural groups are used to represent thousands of molecular types, a limited number of reaction rules can be used to establish the large reaction networks of the mixture. A single reaction rule is applied to all molecules which can undergo a particular transformation. The concepts underlying reaction rules of structure vectors and the generation of multireaction networks are developed in this section.

III.a. Chemical Reactions. A reaction rule is a specification of a class of reactions that many different molecules may undergo. A reaction rule has two components: (1) a *reactant selection rule* to determine if a molecule has the proper structural increments for that reaction and (2) a *product generation rule* to generate the product molecule from the reactant's structure vector. A reactant selection rule for a particular reaction is a logical construct involving the elements of the structure vector.

Chart III

	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
reactant	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
product rule		-1				+1																
product	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

When the reactant selection rule is applied, a 1 or 0 results to indicate whether a molecule can participate in that reaction. Some product rules are easily constructed, requiring a simple vector transformation as shown below. For other reactions that result in the formation of two or more products, such as paraffin cracking or dealkylation, the product rule requires an algorithm designed to generate multiple products with the proper carbon and hydrogen stoichiometry. The reaction rules presented in this paper are intended for illustration only; they are different in specific process applications. The reaction rule concept is developed and demonstrated through the following examples:

Rule: *A6 Saturation.* The hydrogenation of a benzene ring proceeds through the addition of three H_2 molecules to yield a cyclohexane ring:
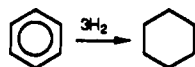
In terms of the structural increments, the reaction can be expressed as a rule for generating the product [For convenience, reaction rules are specified using the ISO-APL standard notation (Polivka and Pakin, 1975). Functions shown in this text have the following meaning: $\wedge$, logical **and**; $\vee$, logical **or**; =, equal; $\neq$, not equal; $\leftarrow$, becomes.]:

$$A6 \leftarrow A6 - 1$$
$$N6 \leftarrow N6 + 1$$

The mathematical representation of the reaction as a vector transformation of reactant to product is given in Chart II. The stoichiometry of the reaction is balanced; i.e., the N6 ring has six more hydrogen atoms than the A6 ring. The A6 saturation reaction shown above can be applied to *any* molecule or structure vector provided an A6 ring is present *and* that there are no A4 rings. The reactant generation rule for this reaction is then

$$(A6 \neq 0) \wedge (A4 = 0)$$

Additional examples of the reaction rule for A6 saturation are shown in Figure 4.

Rule: *A4 Saturation.* Note in the above example that A6 saturation was restricted to molecules without an A4 ring. An A4 ring, if present, will saturate before the A6 ring, according to our understanding of hydrogenation chemistry. This is an example of another reaction rule— A4 saturation to N4. Naphthalene hydrogenation, the simplest example of the A4 saturation rule, is as follows:
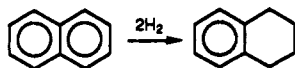
reactant selection rule: $(A4 \neq 0) \wedge (A2 = 0)$

product generation rule: $A4 \leftarrow A4 - 1$
$N4 \leftarrow N4 + 1$

or in vector notation for naphthalene, see Chart III. Any molecule satisfying the reactant rule criterion for A4 saturation can undergo this particular reaction. The application of the A4 saturation reaction rule to many types of molecules is shown in Figure 4. Note that A4 saturation

will not occur in the presence of an A2 ring, as in a pyrene type structure that first hydrogenates via A2 saturation to N2. Thus there is also an A2 saturation reaction rule.

Rule: *N4 Ring Opening on Aromatics.* If a molecule contains an N4 increment, the naphthenic ring with four carbon atoms, the ring may open and add to the total alkyl group structure of the molecule:
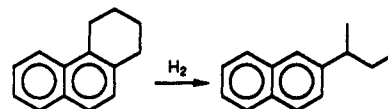
The reactant and product generation rules for this reaction are

reactant selection rule:
$(A6 \neq 0) \wedge (N4 \neq 0) \wedge (0 = N3 + N2 + N1) \wedge (R > 0)$
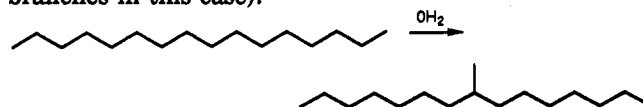
product generation rule: $R \leftarrow R + 3$

$$N4 \leftarrow N4 - 1$$
$$br \leftarrow br + 1$$

The reactant must have an A6 ring to be an aromatic and must, obviously, have an N4 ring to open. In addition it is assumed that an N3, N2, or N1 ring would open before an N4 ring. There must also be at least a methyl group in the product to allow for the formation of a secondary carbenium ion as a surface intermediate. The product rule transforms the reactant by subtracting one N4 ring and adding the carbon to the alkyl group R.

Rule: *Paraffin Isomerization.* Any paraffin can isomerize by increasing the number of branches (methyl branches in this case):

The reactant and product rules for this reaction are

$(hetero = NS + RS + AN + NN + RN + NO + RO + KO)$:

reactant selection rule:
$(0 = A6 + N6 + N5 + hetero) \wedge (IH = 1) \wedge ((R > 3)$
$\wedge\ br = 0) \vee ((R > 5) \wedge br = 1) \vee ((R > 6) \wedge br = 2)$

product generation rule: $br \leftarrow br + 1$

The reactant must be a paraffin, i.e., having no rings or heteroatoms, with a minimum carbon number depending upon the number of branches in the reactant. The product vector is simply constructed by adding 1 to the br term.

Rule: *Aromatic Dealkylation.* The dealkylation of an aromatic is known to occur by complete removal of an alkyl group through acid-catalyzed cleavage of the α-carbon at the ring, forming an isoparaffin and the stripped parent ring compound. Using the convention that one methyl group is typically associated with each ring, the rule retains one methyl group per ring if R is sufficiently large. If R is not sufficiently large, then the Paring reaction (Sullivan et al., 1961) is invoked by assuming that the methyl groups migrate around the ring structure until an isobutane
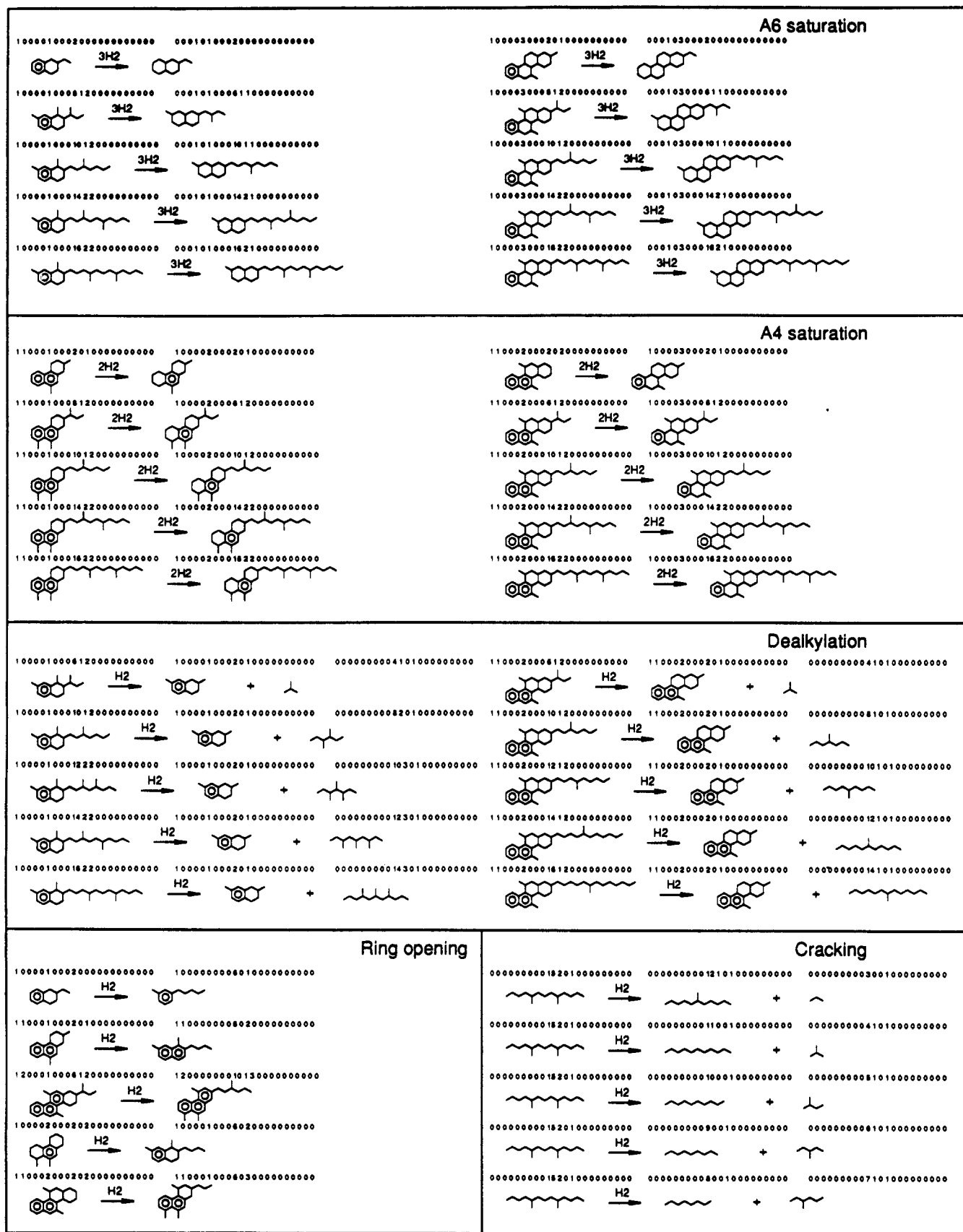
Figure 4. Example reactions.

fragment can be formed. Propane may also be formed from dealkylation but not ethane. Since two products are formed and the mode of dealkylation is dependent on the reactant, this reaction rule is an example of a more complex use of rule-based chemistry to incorporate fundamental
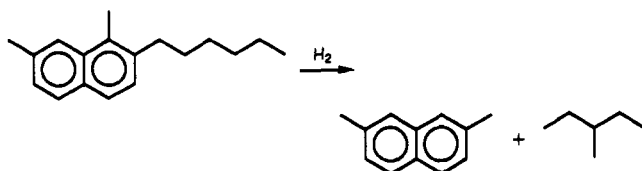
reaction mechanisms. The reaction rule for aromatic dealkylation has three cases depending upon the reactant (product 1 is the parent ring compound, product 2 is the paraffin and the variable **rings** is **A6 + A4 + A2 + N6 + N5 + N4 + N3**):

1. reactant selection rule: (A6 ≠ 0) ∧ (R >3 + rings)

product generation rule:

product 1	**R ← rings**
	me ← rings – 1
product 2	**R ← R – rings**
	IH ← 1
	br ← 1

Example:

2. reactant selection rule:
    (A6 ≠ 0) ∧ (R <3 + rings) ∧ (R > 3)

product generation rule:

product 1	**R ← R – 4**
	me ← R – (4 – 1)
product 2 (isobutane)	**R ← 4**
	IH ← 1
	br ← 1

Example:
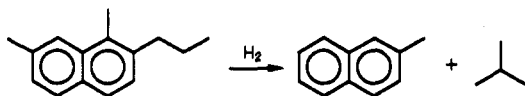
3. reactant selection rule: ((A6 ≠ 0) ∧ R = 3)

product generation rule:

product 1	**R ← 0**
	me ← 0
product 2 (propane)	**R ← 3**
	IH ← 1

Example:
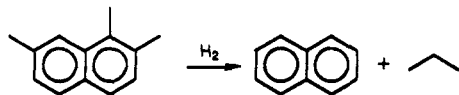
Rule: Paraffin Hydrocracking. Paraffin cracking is an example of a reaction rule that requires a more complicated product generation rule: an algorithm to generate all the statistically possible product molecules. Paraffins are known to crack via multibranched carbenium ion intermediates. Long-chain paraffins can crack at any carbon–carbon bond in the chain and produce two products. Application of the product generation rule to a single reactant produces many product pairs. Cracking that yields a methane or an ethane is very slow due to unfavorable carbenium ion intermediates and is neglected in the present treatment.

reactant selection rule:
  (rings = 0) ∧ (hetero = 0) ∧ (R > 7) ∧ (br > 2) ∧
                             (IH = 1)

product generation rule: **Crackparaffins**

Crackparaffins is an algorithm that splits a paraffin at each carbon–carbon bond to yield a pair of paraffin products (vectors) from each split. For example, if **R** = 12, **Crackparaffins** will generate five product pairs:

product 1	product 2
R = 2	R = 10
R = 3	R = 9
R = 4	R = 8
R = 5	R = 7
R = 6	R = 6

The algorithm also assigns IH = 1 to all products and **br** = 1 to all products with **R** > 3.

Reaction rules for hydrocracking chemistry, including hydrogenation, ring opening, dealkylation, desulfurization, denitrogenation, isomerization, and cracking are derived from the broad published literature of the catalytic reaction pathways of hydrocracking. Examples of rules are shown in Figure 4. Each reaction rule is applicable to many molecules, each molecule may undergo more than one type of reaction, and each molecule may result from more than one reaction, resulting in a complete reaction network based on fundamental catalytic chemistry involving thousands of molecular components. An example of the application of the set of reaction rules to a single molecule is shown in Figure 5. The next section discusses how complex reaction networks and a set of rate equations that constitute a kinetic model are developed from the set of reaction rules.

III.b. Complex Reaction Networks and Kinetics. The rate equation for a chemically reacting multicomponent system is frequently expressed as a matrix differential equation of the form (Wei and Prater, 1962)

$$y' = Ky$$

where **y** is the composition vector, **y**' is the derivative of **y** with respect to time or distance through a reactor, and **K** is a square matrix whose elements are the rate constants for the reactions that take place. A complex reaction network would have many components and many nonzero elements in the matrix **K**, reflecting that a reaction of a single component may yield multiple products and that a single component may undergo many different reactions or pathways. If the number of components is small (10–20), the complete reaction network and the matrix **K** are easily conceived and readily constructed. If the number of components is large, construction of the entire network or rate constant matrix becomes complicated. Utilizing the rule-based approach to reaction chemistry, structure-oriented lumping enables the computer generation of large complex reaction networks and their rate equations.

A complex mixture in structure-oriented lumping is a set of structure vectors, each with its associated weight percent. Entire reaction networks employing fundamental reaction chemistry can be generated for the mixture by application of all reaction rules to the set of structure vectors. The reactant selection rules and the corresponding product generation rules identify reactant–product pairs in terms of the column–row positions of rate constants in the matrix **K** as well as the position in the composition vector **y**. Integration of the rate equation solves for the composition of the mixture in terms of the weight (or mole) fraction vector **y** for all components as a function of time or position in a reactor. Model results can be examined on a molecular basis, or on a lumped product basis as is often the form of experimental results.

IV. Structure–Property Relationships

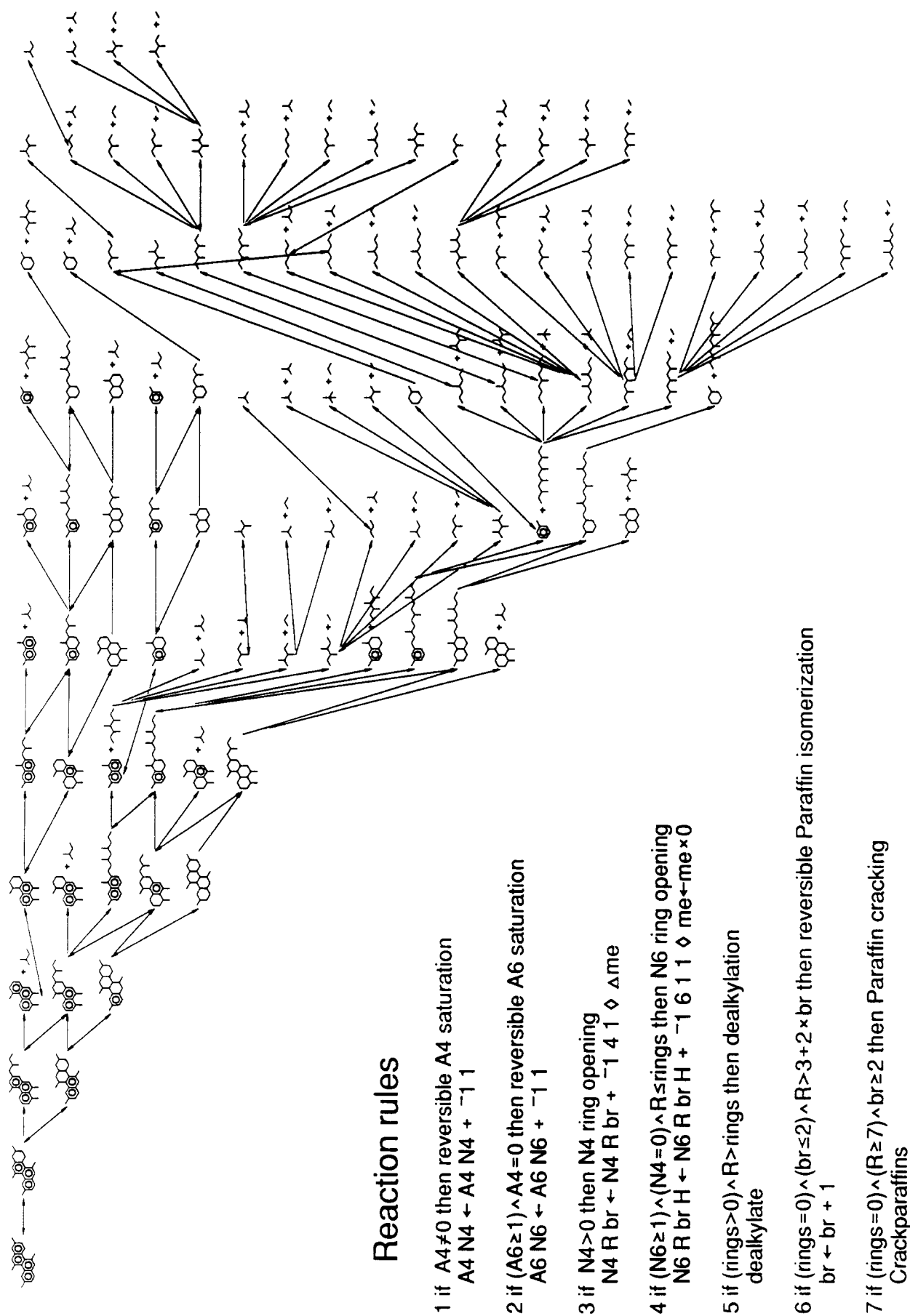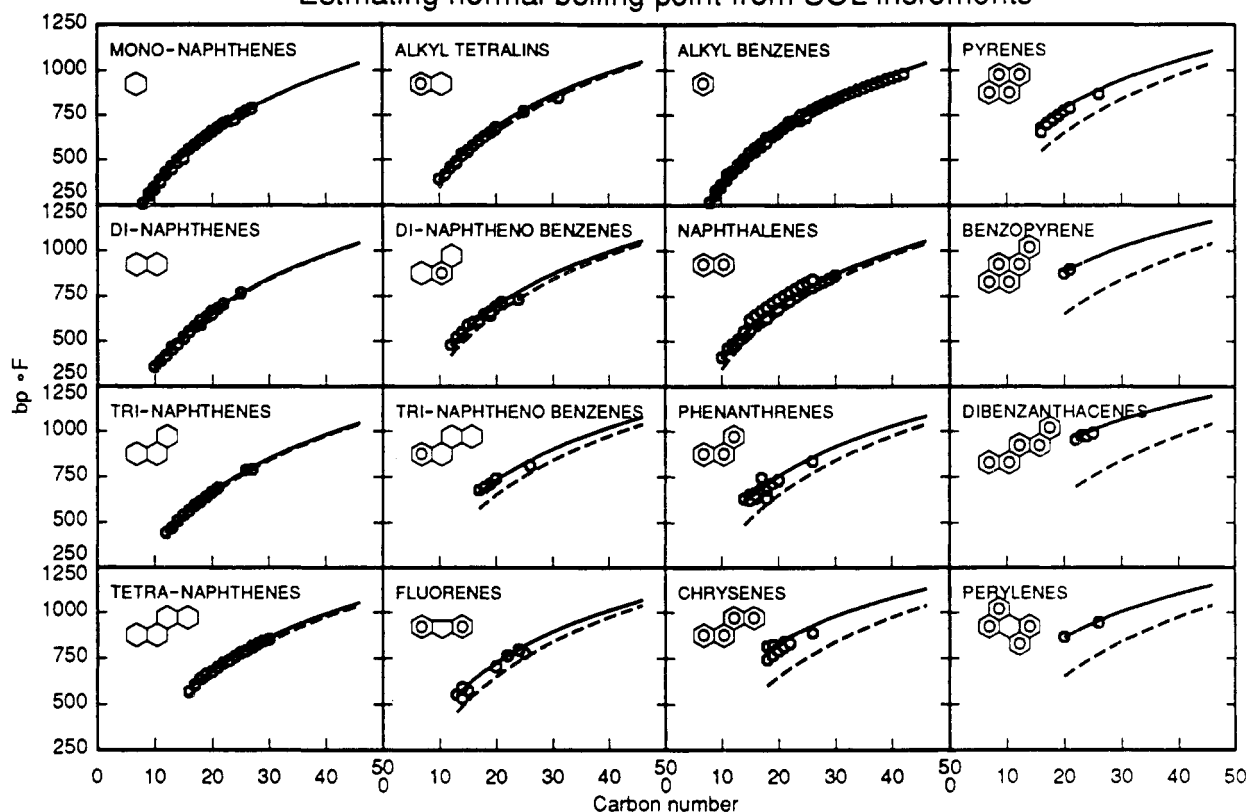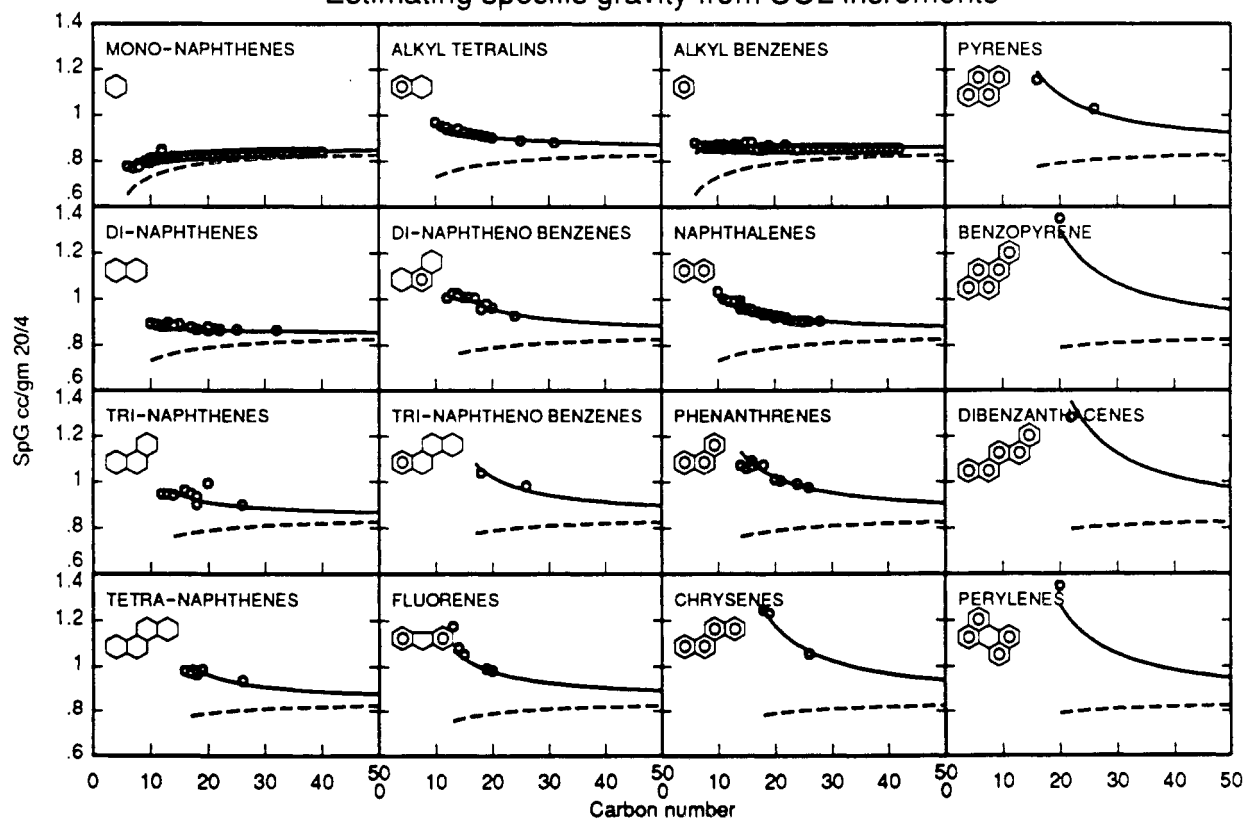An essential need of future process models is the capability of predicting physical and performance properties

Reaction rules

1 if A4≠0 then reversible A4 saturation
   A4 N4 ← A4 N4 + ⁻1 1

2 if (A6≥1)∧A4=0 then reversible A6 saturation
   A6 N6 ← A6 N6 + ⁻1 1

3 if N4>0 then N4 ring opening
   N4 R br ← N4 R br + ⁻1 4 1 ◊ Δme

4 if (N6≥1)∧(N4=0)∧R≤rings then N6 ring opening
   N6 R br H ← N6 R br H + ⁻1 6 1 1 ◊ me←me×0

5 if (rings>0)∧R>rings then dealkylation
   dealkylate

6 if (rings=0)∧(br≤2)∧R>3+2×br then reversible Paraffin isomerization
   br ← br + 1

7 if (rings=0)∧(R≥7)∧br≥2 then Paraffin cracking
   Crackparaffins

Figure 5. Hydrocracking tetramethylchrysene.

Figure 6. Property correlations.
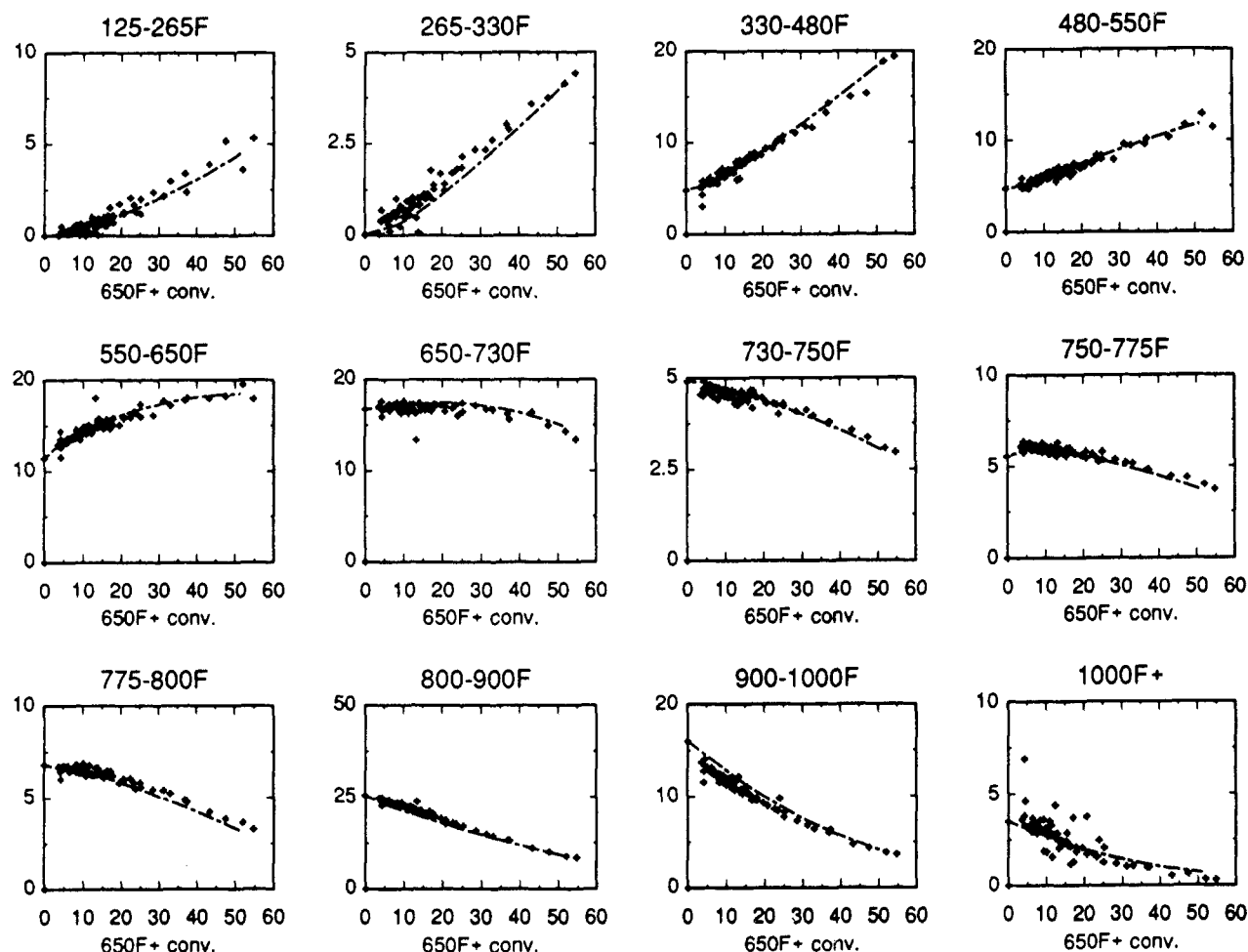
Figure 7. Narrow boiling cut yields (wt %) for model (lines) and pilot plant data.

of hydrocarbon mixtures. Structure-oriented lumping provides a foundation for developing molecular-based property relationships and incorporating well-established correlations to estimate mixture properties. One approach is to develop a new group contribution method using the structural increments as the groups bearing partial molecular properties. A large database of molecular properties (e.g., boiling point or density) is accumulated and fit to a correlation based on the structural increments. Molecular-based correlations of this type for boiling point and specific gravity are shown in Figure 6.

A second approach is to map an existing correlation or group contribution method into structure-oriented lumping. An example of this approach is a map between Benson groups and the structural increments for estimation of thermodynamic properties for the molecular components. The map determines the number and type of Benson groups for each component from the structure vector of that component.

A third approach is to utilize existing property correlation based on bulk composition measurements. In this case the predicted bulk composition of a product from a model calculation is applied to the correlation. The advantage of this molecular approach to modeling is that numerous property correlations developed and published over the years, whether molecular, group contribution, or bulk composition based, can be used.

A comparison between model predictions and pilot plant results for a specific hydroprocessing operation is shown in Figure 7. The model tracks the evolution of thousands of molecular components, but results can be compiled and presented in the form of measured data from pilot plants

or commercial units. For the case shown in Figure 7, the predicted yields of narrow boiling point cuts were obtained by applying the boiling point correlation to the model's molecular results.

Acknowledgment

Literature Cited

Aris, R. On Reactions in Continuous Mixtures. *AIChE J.* **1989**, *35*, 539–548.

Astarita, G.; Ocone, R. Lumping Nonlinear Kinetics. *AIChE J.* **1988**, *34*, 1299.

Gray, M. R. Lumped Kinetics of Structural Groups: Hydrotreating of Heavy Distillates. *Ind. Eng. Chem. Res.* **1990**, *29*, 505–512.

Hood, A.; Clerc, R. J.; O'Neal, M. J. The Molecular Structure of Heavy Petroleum Compounds. *J. Inst. Pet.* **1959**, *45*, 168–173.

Jacob, S. M.; Gross, B.; Voltz, S. E.; Weekman, V. W. A Lumping and Reaction Scheme for Catalytic Cracking. *AIChE J.* **1976**, *22*, 701–713.

Jaffe, S. B. Kinetics of Heat Release in Petroleum Hydrogenation. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13*, 34–39.

Liguras, D. K.; Allen, D. T. Structural Models for Catalytic Cracking. 1. Model Compound Reactions. *Ind. Eng. Chem. Res.* **1989**, *28*, 665.

McDermott, J. B.; Libanati, C.; LaMarca, C.; Klein, M. T. Quantitative Use of Model Compound Information: Monte Carlo Simulation of the Reactions of Complex Macromolecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 22–29.

Polivka, R. P.; Pakin, S. *APL: The Language and Its Usage*; Prentice-Hall: Englewood Cliffs, NJ, 1975.

Robinson, C. J.; Cook, G. L. Low Resolution Mass Spectrometric Determination of Aromatic Fractions from Petroleum. *Anal. Chem.* 1969, *41*, 1548–1554.

Sullivan, R. F.; Boduszynski, M. M.; Fetzer, J. C. Molecular Transformations in Hydrotreating and Hydrocracking. *Energy Fuels* 1989, *3*, 603–612.

Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*; Springer Verlag: Berlin, 1984; pp 379–403.

Weekman, V. W. Lumps, Models, and Kinetics in Practice. *Chem. Eng. Prog. Monogr. Ser.* 1979, *75*,

Wei, J.; Prater, C. D. The Structure and Analysis of Complex Reaction Systems. *Adv. Catal.* 1962, *13*, 203.

Rate of Heterogeneous Catalytic Reactions Involving Ionic Intermediates

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A solution to the problem of the computation of the rate law of a catalytic reaction involving ionic intermediates and taking into account the ionic nature of the surface species is proposed in this work. It is shown that such a rate law is computable within the Langmuir–Hinshelwood–Hougen–Watson (LHHW) theory when an electric charge conservation equation is added to the usual set of equations. Using the approximation that the number of sites equal the number of negative charges of the surface species and neglecting the contribution of the bulk, a rate law can be computed exactly. This is illustrated by considering four examples of catalytic reactions involving ionic intermediates, namely the isomerization of unsaturated hydrocarbons by Bronsted acids, the hydrogenation of unsaturated hydrocarbons involving the heterolytic dissociation of hydrogen, the generation of methyl radicals in methane oxidative coupling, and the partial oxidation of hydrocarbons. With no approximations the rate law obtained is complex and includes, in an intricate manner, several initial concentrations of surface and bulk species characterizing the catalyst.

Introduction

Rate laws for catalytic reactions performed by nonmetallic catalysts are often established using the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism (Yang and Hougen, 1950). For redox reactions, redox models such as the well-known Mars–van Krevelen model (1954) are also often used. Rate laws obtained using these different models have been found very useful for the analysis of experimental results of kinetic studies (Smith, 1982) although in each case the formalism suffers from a number of simplifications and, in particular, the assumption that all of the sites are equivalent. Nevertheless, the rather simple equations obtained using these models are superior to empirical power rate laws as they are based on a description of the reaction mechanism and of the catalyst even though both are not, in general, known in great detail.

The various types of adsorption considered for the computation of LHHW rate laws are nondissociative or dissociative homolytic adsorption. Thus adsorbates are considered in the form of either a molecule, a fragment of a molecule, radicals, or atoms. However, a number of catalytic reactions on nonmetallic catalysts involve or are thought to involve ionic intermediates.

Catalytic reactions involving ionic intermediates can be eliminations, additions, or substitutions (Noller and Kladnig, 1976). A simple example is that of an olefin transformed into a carbocation by association with a proton of Bronsted acid catalysts such as zeolites. Thus a first way to generate an ionic intermediate on a catalytic surface is by an associative reaction of a reactant with a preexisting ionic surface species.

Heterolytic dissociation is another means of generating ionic intermediates, namely one negative and one positive species on the surface. The heterolytic dissociation of a number of molecules has been shown or is thought to occur on nonmetallic polar catalysts. Hydrogen has been shown

to dissociate heterolytically on ZnO forming a hydride ion H^- bonded to Zn^{2+} and a proton associated with an oxygen anion forming a hydroxyl ion OH^- also bonded to Zn^{2+} (Kokes and Dent, 1972). Olefins have been also found or proposed to dissociate heterolytically on a number of oxides giving π-allyl carbanion or π-allyl carbocation (Burwell et al., 1969; Stone, 1990). Other molecules may also dissociate heterolytically upon adsorption on an oxide catalyst such as H_2O (Burwell et al., 1969).

A third means of generating surface ionic intermediates is evidently by electron transfer from the adsorbed molecule to the catalyst or vice versa. This process is particularly important in oxidation reactions.

The ionic nature of the adsorbed species on the catalytic surface is usually not taken into account in the computation of rate laws according to LHHW or redox models. Then, from both a fundamental and an applied point of view, it appears of importance to be able to express, in a simple way, rate expressions for catalytic reactions involving ionic surface intermediates where the ionic nature of the species is explicitly taken into account.

The aim of this paper is to demonstrate that this can be done for a variety of catalytic reactions by adding an electric charge conservation equation to the classical method of computation of LHHW rate law. The method will be illustrated by selected examples of different reactions on nonmetallic catalyst involving heterolytic dissociation or electron transfer such as the isomerization of unsaturated hydrocarbons by Bronsted acids, the hydrogenation of unsaturated hydrocarbons via heterolytic dissociation, the generation of methyl radicals in methane oxidative coupling, and the partial oxidation of hydrocarbons.

Results and Discussion

Description of the Catalyst. A nonmetallic perfect oxide $M^{n+}_x O^{2-}_y$ with the cation symbolized by M and the