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CONTRACT REPORT NO. 107

ESTIMATION OF GAS-PHASE THERMOKINETIC PARAMETERS

VOLUME I

A FORTRAN PROGRAM FOR COMPUTING THE THERMOCHEMICAL PROPERTIES OF COMPLEX GAS MOLECULES BY THE METHOD OF GROUP ADDITIVITY

BOOK 1

VOLUME II

DEFINITION OF REQUIREMENTS FOR ESTIMATION OF KINETIC PARAMETERS

Prepared by

McDonnell Douglas Astronautics Company
Huntington Beach, California

April 1973

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USA BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MARYLAND

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CONTRACT REPORT NO. 107

REPORT NO. MDC G4388

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VOLUME I

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BOOK 1

APRIL 1973

BY

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FOR

BALLISTIC RESEARCH LABORATORIES

PREPARED BY

MCDONNELL DOUGLAS ASTRONAUTICS COMPANY
HUNTINGTON BEACH, CALIFORNIA

Approved for public release; distribution unlimited.

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PREFACE

This document comprises the final report for the program "Automated Estimation of Gas Phase Thermokinetic Parameters for High Ignition Temperature Solid Gun Propellants." The work was performed for the Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland, by McDonnell Douglas Astronautics Company, under Contract DAAD05-72-C-0098. This final report covers the period from 15 November 1971 to 15 January 1973.

The report is submitted in two volumes:

Volume I – A FORTRAN Program for Computing the Thermochemical Properties of Complex Gas Molecules by the Method of Group Additivity
(Books 1 and 2)

Volume II – Definition of Requirements for Estimation of Kinetic Parameters

ABSTRACT

A FORTRAN program for calculating the thermodynamic properties of complex gas molecules by the method of group additivity is documented herein. Included are descriptions of the computational method, characteristics, functions, input/output formats, and logic structure of the program. Seventeen case calculations for diversely structured molecules are presented. Also depicted are a listing of the program, a complete glossary of the program variables and the tables of data comprising the data library input.

ACKNOWLEDGEMENTS

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Special acknowledgement is due Dr. S. W. Benson who developed the group additivity method and Dr. J. J. Grossman without whose deep interest and zealous efforts this project would not have been initiated.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Book 1

Section 1 INTRODUCTION 1

Section 2 PRINCIPAL PROPERTIES AND CHARACTERISTICS 2

2.1 Computational Method 2
2.2 Program Functions 5
2.3 Computational Accuracy 6
2.4 Dimension Limits of Principal Variables 7
2.5 Computer Core Requirements 7
2.6 Run Time Requirements 7

Section 3 INPUT/OUTPUT PROCEDURES 9

3.1 Input Formats 9
3.2 Output Format 14

Section 4 EXAMPLES OF COMPUTATIONAL OUTPUT 19

Section 5 LOGIC FRAMEWORK OF PROGRAM 70

5.1 Procedure for Group Identification 70
5.2 Procedures for Chain and Ring Identification 73
5.3 Procedures for Determination of Nongroup Interactions and Symmetry 76

Section 6 REFERENCES 97

Book 2

Appendix A TGAP GROUP ADDITIVITY DATA LIBRARY

A.1 Thermochemical Group Contributions
A.2 Corrections for Ring Structures
A.3 Next-Nearest Neighbor Corrections

Appendix B FLOW LIST OF TGAP PROGRAM

Appendix C GLOSSARY OF PROGRAM VARIABLES

FIGURES

3-1	Maximum Number of Directions Available for Chemical Bonding	12
5-1	Flow Chart for Main Control Routine TGAP	71
5-2	Subroutine Cross Reference Map for Section 1	72
5-3	Subroutine Cross Reference Map for Section 2	74
5-4	Subroutine Cross Reference Map for Section 3	77
5-5	Aromatic Carbon and Nitrogen-Containing Ring Groups Requiring Special Processing	84
5-6	Main Logic Flow Chart for Symmetry Calculations: Part I	87
5-7	Main Logic Flow Chart for Symmetry Calculations: Part II	89

TABLES

3-1	Punched Card Data Format for Program TGAP	10
3-2	Symbols for Specification of Graphic Formula	12
3-3	Permissible Atomic Postions for Radicals	13
4-1	List of Sample Molecules	20
4-2	Comparison of Calculated and Published Thermochemical Properties	21
4-3	List of Input Data for Sample Calculations	64
5-1	Rules for Determination of Gauche Interactions	79
5-2	Number of Gauche Interactions for C-C, C-N and C-O Central Atoms	80
5-3	Rules for Determination of Cis Interactions	82
5-4	Non-Standard Cis Corrections for Specific Configurations	83
A-1	Tables of Thermochemical Group Contributions	
A-2	Corrections for Ring Structures	
A-3	Next-Nearest Neighbor Corrections	

Section 1
INTRODUCTION

The increased emphasis in recent years on high level material performance and controlled chemical reactions has intensified the need for versatile analytical programs capable of estimating the thermodynamic and kinetic properties of compounds. Moreover, there are more specific reasons why these capabilities are important. First, the size, cost, and purity of the sample and the expense and time required for measurement of the data are frequently excessive. Secondly, an accurate thermokinetic computational method can serve as a material screening device and predictive tool for estimating the properties of promising new compounds and postulated chemical structures.

The objectives of this investigation are related to the above requirements. They comprised the (1) development of an automated program and (2) preliminary tasks prerequisite to future development of an automated program for estimating the respective thermodynamic and kinetic properties of gas molecules. The results achieved in the present study are twofold: (1) development of a large computer program for calculating the thermodynamic properties of complex gas molecules and (2) definition and extension of methods and requirements for estimating the kinetic parameters of several classes of gas-phase chemical reactions. The latter work is described in Volume II of this report. The future goals of the program, which were instrumental to the initiation of the present study, can be summarized as follows: (1) characterization of the thermodynamic profiles of high-temperature solid gun propellants and (2) estimation of the burning rates of gaseous-solid propellant mixtures.

The computation of the thermodynamic properties in our computer program is based on the principle of additivity of group properties developed by Benson and coworkers (1 through 3). This method was selected for its applicability to

both chemical thermodynamics and kinetics and its accuracy and versatility in handling gas molecules with complex functional groups using only very simple molecular structural data as input.

A complete documentation and description of the program are presented herein. Sections 2 and 3 contain descriptions of the computational method and other basic properties of the program as well as the input/output procedures. Section 4 contains examples of case calculations representing a broad spectrum of organic compounds. The logic structure and computational criteria of the program are discussed in Section 5 for those interested in probing further the logic operations of the program. The appendices contain a complete listing of the program, a glossary of the program variables and a listing of the program data library.

Section 2
PRINCIPAL PROPERTIES AND CHARACTERISTICS

The Thermochemical Group Additivity Computer Program (TGAP) is a highly automatic, self-consistent FORTRAN IV computer program for calculating the thermochemical properties of complex gas molecules as a function of temperature and one atmosphere of pressure. The program is capable of handling neutral, non-fragmented molecules composed by hydrogen, carbon, oxygen and/or nitrogen atoms.

The input to the program has been minimized as much as possible for facile and rapid utilization not only by physical scientists and engineers but also by persons with a more limited knowledge of chemistry.

2.1 COMPUTATIONAL METHOD

In TGAP, the thermochemical properties of the molecule are calculated by the Group Additivity Method of Benson (1 through 3). Unlike the more simple atomic additivity techniques for the evaluation of various types of molecular properties, the group additivity method is primarily an empirical second-order approximation technique that generally yields results well within the limits of experimental data.

The group additivity method treats a molecular thermodynamic property as a composite of the thermochemical contributions resulting from the various atomic groups in the molecule and from the higher order structural interactions and symmetry of the molecule. The latter include those contributions arising from nonbonded next-nearest-neighbors (cis, ortho, gauche) interactions, ring (strain) corrections, rotational symmetry and optical isomerism. In the assignment of the group property values themselves, account is also taken whenever possible of differences in the bond environments of next-nearest-neighbors and next-next-nearest-neighbors. For example, the

thermodynamic properties of the group $C-(H)_2(C)(C^*)$, are different depending whether the ligand C* is bonded to another carbon atom by means of a single, double or triple bond.

In the terminology of group additivity, a group is defined as any polyvalent atom (ligancy ≥ 2) in a molecule together with all its ligands. Any molecule composed of two or more groups, such as CH_3CH_3 and $CH_3CHOHCH_3$, is amenable to treatment by the group additivity method. In this report, the central atom in the group is referred to as the "core" atom and the remaining components of the group that are bonded to the core atom are frequently described as "ligands."

The equation for the calculation of the thermochemical property F by the method of group additivity is

$$F = \sum_{i=1}^{N_G} (f_i)_{group} + \sum_{i=1}^{N_C} (f_i)_{cis} + \sum_{i=1}^{N_{GA}} (f_i)_{gauche}$$

$$\sum_{i=1}^{N_R} (f_i)_{ring} + \sum_{i=1}^{N_O} (f_i)_{ortho} + R \sum_{i=1}^{N_\sigma} \ln (\sigma_i)_{internal}$$

$$- R \ln(\sigma)_{external} + R \ln (n)_{optical\ isomers}$$

where the number and type of each contribution are specified explicitly.

In the Thermochemical Group Additivity Program, the data for calculating the first five terms of the above equation are derived from the tables of group properties, ring corrections, and second-order interactions of Benson (1 and 2) for hydrocarbons and oxygen and nitrogen-containing compounds. These data are listed in Appendix A.

2.2 PROGRAM FUNCTIONS

TGAP is a structurally integrated program designed for minimum data input by the user. An important feature of the program is its capability of performing a detailed structural delineation of a molecule.

For the purposes of the calculation, the molecule can be regarded as a topological network of interconnected atoms which can form linear arrays, branch junctions, closed loops or rings, as well as complex combinations of these. The computational objectives are achieved by a series of scanning, pattern recognition, comparison tests, and other subtle logical, topology-oriented operations which enable the computer to identify the molecule and recognize such structural complexities as ring closure, branch splitting, and symmetry. The principal logical determinations and calculations performed by the program are listed below.

A. Identification of core ligand and constituents.
B. Determination of bond order and direction.
C. Identification of single and fused ring structures.
D. Determination of longest chain in the molecule.
E. Detection of gauche interactions in non-cyclic groups and between cyclic and non-cyclic structures.
F. Detection of cis interactions in non-cyclic groups and non-aromatic ring structures.
G. Identification of ortho interactions in aromatic-type structures
H. Detection of ditertiary-ether structures.
I. Identification of pyridine-type structures and of ortho and para substitutions therein.
J. Determination of internal rotational symmetry.
K. Determination of external rotational symmetry and optical isomer properties (i.e., identification of enantiomers, meso structures, pseudoasymmetric atom.
L. Calculation of the individual thermochemical contributions and the gross thermochemical properties of the molecule.

Operation K is somewhat limited in its applicability. At present, the external symmetry number is computable for molecules whose central atom is not part of a ring structure or else is part of a monocyclic benzene-type ring. If the molecule contains one or more ring structures but the central atom is not a ring atom, the symmetry number can be calculated also. The reason other centralized ring structures cannot be handled is that virtually every ring constitutes a unique symmetrical situation that must he treated independently in the absence of molecular coordinate data. In the case of optically active molecules, the logic and mathematical constraints (1) require the presence of asymmetric carbon atoms and (2) take into account only those asymmetric atoms which form part of the principal chain. Fortunately, these conditions are satisfied by the majority of such molecules.

The program executes the calculations by performing a (1) topological structural analysis of the molecule for the identification of structural groups, second-order interactions, and ring structures; (2) a symmetry analysis of each atom in the molecule and of the molecule as a whole; (3) a specification of the secondary, ring, and symmetry contributions to the thermodynamic properties; and (4) a cross match of each group with the corresponding group values contained in the Data Library and summation of these results.

If all the thermochemical data for a particular group value are missing from the Data Library, the program identifies the group or groups involved, and prints a warning message.

2.3 COMPUTATIONAL ACCURACY

The thermochemical properties calculated by the program are usually in good agreement with corresponding experimental values up to the upper temperature limits of availability of the empirical data (about 1000° to 1500°K). The original heat capacity data of Benson are recorded at regular temperature intervals up to 1500°K for those compounds of interest here. These data have been curve fitted to a regular third order polynomial for utilization by the program. The temperature range of the

thermochemical properties calculated by the program extends from 298°K to 5000°K. Obviously, the validity of the data at the upper temperature range is uncertain particularly since complex organic gas molecules are unstable at these elevated temperatures. However, it does serve to provide extrapolated data limits for the unstable superheated gas state.

A number of calculations executed by the program are presented in Section 4 that illustrate the versatility of the program and its accuracy at 398°K and 1000°K. The molecules selected for this purpose represent a broad spectrum of structural and topological properties.

2.4 DIMENSION LIMITS OF PRINCIPAL VARIABLES

The program is capable of handling essentially any size molecule the user is likely to input. The following is a list of the prevailing dimensional limits on the size of the molecule and its structural properties. If any of these dimensions are exceeded, the program will print an explanatory diagnostic and terminate the case calculation.

Core atoms in molecule	100
Number of unique rings	40
Core atoms in ring structure	30
Number of chain segments	60
Core atoms per chain segment	50

2.5 COMPUTER CORE REQUIREMENTS

The program was developed and tested on a Control Data 6500 computer with the RUN compiler and CP loader under the scope 3.3 operating system. In this system, the program requires 34595 or 103443_8 core locations exclusive of the auxiliary system routines. The only auxiliary mathematical system routine required is the standard natural logarithm subprogram which occupies 55 or 67_8 core locations.

2.6 RUN TIME REQUIREMENTS

The computation time requirements are a function of the size and complexity of the molecule. On the CDC 6500, the thermochemical properties of a

large molecule composed of 27 carbon atoms and 46 hydrogen atoms with one ring structure and 13 second-order corrections can be calculated in approximately 3 seconds. Molecules of more conventional size, i.e., 15 or less core atoms require on the average 1.5 seconds or less. Compilation of the program takes 8 seconds and loading 3 seconds.

Many data processing systems are capable of accepting a compiled deck or a compiled program file directly. This type of input requires approximately 3 seconds for loading.

Section 3

INPUT/OUTPUT PROCEDURES

This section describes in detail the input/output data formats of the program. Basic operational instructions are also presented.

3.1 INPUT FORMATS

The input to the program consists of (1) punched cards comprising data which are characteristic of each molecule, and (2) the TGAP GROUP ADDITIVITY DATA LIBRARY which is a fixed data package permanently stored in the program.

3.1.1 Punched Card Input

The definitions and formats for the punched card data input are given in Table 3-1. As shown therein, each case deck is followed by a *** card whereas the data deck itself is followed by an END card.

The Tables of Thermochemical Group values are printed at the very beginning of the first case calculation, providing, of course, the output flag is appropriately set. Accordingly, it is necessary to set this flag only once in the data deck of case one. This printout operation is never repeated when subsequent cases of a run are executed regardless of the value of the output flag in these cases. The user also has the option to print an identification label and to eliminate the printout of the program title and case number. The program title printout flag can be individually set for each case calculation. The printout of the case number in all case calculations of a given run is controlled by the case number printout flag of case number one.

The program always computes the external rotational symmetry number and optical isomer contributions unless the molecular structure is of the type described in Section 2.2, in which case a warning message is printed. In any event, the user has the option to input the symmetry

Table 3-1

PUNCHED CARD DATA FORMAT FOR PROGRAM TGAP

Number	Column Number	Type/Symbol	Format	Description
1	4-6	Numeric	I3*	Printout options (0JK): K=0 no printout of Data Library K≠0 data are printed. J=0 title and case number printed. J=1 title and case number not printed. J=2 title - yes; case number - no. J=3 title - no; case number - yes.
1	7-9	Numeric	I3	External rotation symmetry number (optional).
1	10-12	Numeric	I3	Number of enantiomers (optional).
1	13-15	Numeric	I3	Number of meso structures (optional).
1	31-80		50A1	Molecule identification label (optional).
2 to N (N ≤ 51)	1-80	H, C, O, N, -, =, $	80A1	Graphic formula of the molecule.
N+1	1-3	***	A3	Denotes end of case.
. . . . .	. . . . .	. . . . .	. . . . .	. . . . .
. . . . .	. . . . .	. . . . .	. . . . .	. . . . .
Last Card	1-3	END	A3	Denotes end of data deck.

*I3 data are right adjusted in the data field

number and/or the asymmetric properties (number of enantiomers and meso structures) directly. These are utilized by the program to compute the corresponding contributions to the entropy. The program then prints both the input and computed preliminary parameters and entropy contributions. When the symmetry number and/or optical parameters are input, the entropy contributions derived from these data are used to compute the total entropy and free energy of the molecule. In the more general case when these parameters are not input, the parameters calculated by the program are used instead of the input parameters to calculated the corresponding molecular properties.

Table 3-2 depicts the FORTRAN symbols available for inputting the graphic formula of the molecule. The codes for the chemical atoms and radicals are identical to their conventional chemical symbols. The graphic formula is constructed essentially the same as the handwritten version. The following rules describe the procedures for punching the graphic formula onto the input cards.

A. Always use the designated bond symbols to represent the bonds between atoms, but do not insert bonds between the atoms of a radical. For example, input -CN but not -C-N for the radical CN.

B. Chemical symbols must be placed at the end of the bond symbol, but not on the side. For example C----H not C----H.

C. The number and types of bonds assigned to an atom or radical must be sufficient to satisfy its valence.

D. There are a maximum of eight bond positions available about a particular atom, as shown in Figure 3-1. If the atom is located near a card boundary, the number of locations that are available for bonding, is, of course, reduced.

E. The bond between two chemical entities can be any length but its direction must be linear. Absolutely no deviation from linearity is allowed when constructing a bond.

F. There is considerable freedom in the way the bonds connecting a radical can be positioned. Table 3-3 shows various permissible positions for the different radical types listed in Table 3-2. The actual order of the atoms in the radical does not matter, for instance -NO2, -N20, -2NO, etc., are all acceptable.

Table 3-2

SYMBOLS FOR SPECIFICATION OF GRAPHIC FORMULA

Atoms
H
C
O
N
Radicals
CO
CN
NO
NO2
Bonds
Single -
Double =
Triple $

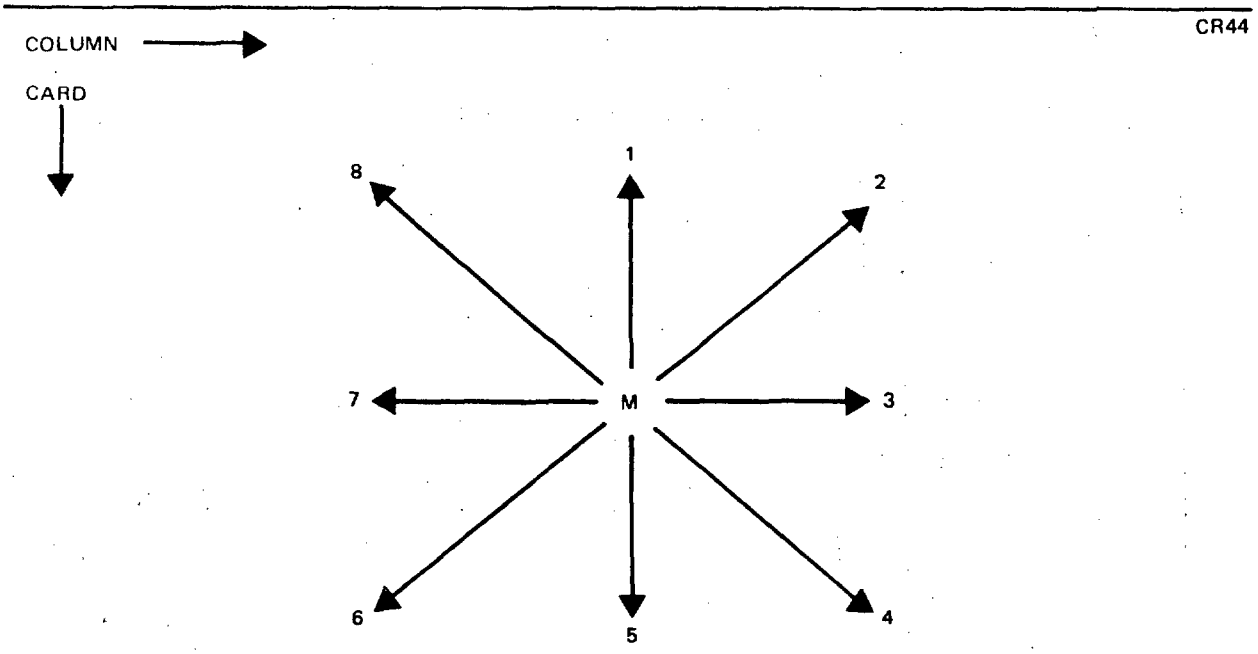

Figure 3-1. Maximum Number of Directions Available for Chemical Bonding

Table 3-3

PERMISSIBLE ATOMIC POSITIONS FOR RADICALS

Type 1. Components = 2, Connectivity = 1

N α C-	N C-	NC-	C- N	C- N	$45° \leq \alpha \leq 315°$
(a)	(b)	(c)	(d)	(e)*	

Type 2. Components = 2, Connectivity = 2

-CO	O -C-	-C- O	O -C-	C- O
(a)	(b)	(c)	(d)	(e)*

Type 3. Components = 3, Connectivity = 1

2 O -N	2 O -N	-NO2	-N O 2	$45° \leq \alpha \leq 315°$
(a)	(b)	(c)	(d)	

Also

N -O 2
(e)

*Do not use if radical is in the top leftmost location of the molecule.

G. Atoms and radicals cannot be adjacent to bonds to which they are not connected. Thus the linkage

$$\begin{array}{l} =C-H_1 \\ \quad {}^{-}H_2 \end{array}$$

is not allowed because H_1 is also adjacent to the bond between C and H_2. This is easily corrected by adding an additional bond symbol between C and H_1, namely,

$$\begin{array}{l} =C--H_1 \\ \quad {}^{-}H_2 \end{array}$$

This rule is perhaps the easiest to overlook and, consequently, should be given special attention when formulating the structural input. In the event any of these rules are violated, a diagnostic message is printed, the current case calculation is aborted, and the next case calculation (if any) is begun.

3.1.2 Data Library Input

The TGAP GROUP ADDITIVITY DATA LIBRARY is composed of Benson's thermochemical group additivity values and interaction corrections for hydrocarbons and compounds containing oxygen and nitrogen. These data are listed in Appendix A. Except for the contributions of rotational symmetry and entropy of mixing due to optical isomerism which are handled separately, the DATA LIBRARY constitutes the basic data bank for the calculation of the thermochemical properties of the molecule. Once the specific molecular groups and interactions are identified by the various logic routines of the program, the group contributions and corrections specified by the program are abstracted from the DATA LIBRARY and summed to determine the gross thermochemical properties of the molecule.

The principal components of the DATA LIBRARY are the Tables of Thermochemical Group Values which the program will output when so directed by the user. A listing of this output is given in Table A-1. The remaining data consist principally of the thermochemical corrections for ring structures (Table A-2) and the thermochemical contributions for various types of gauche, cis, and ortho interactions (Table A-3).

The data in the LIBRARY are permanently stored in the program by means of data statements. These are positioned in the block data subprogram DATA1 and Subroutine CORCIG.

3.2 OUTPUT FORMAT

All output occurs via the printed mode and comprises both input and calculated data. In addition to the thermodynamic properties, the output of the program provides information on the structure and symmetry properties of

the molecule. These data are, in essence, by-products of the thermochemical computations. The individual output arrays are described below in the order in which they are printed by the program.

3.2.1 Molecular Structure

This is a printout of the graphic formula of the molecule in exactly the same form it is input into the program. The structure is automatically centered on the printout sheet regardless of where it appears on the input card.

3.2.2 Atomic Composition

The types of atoms in the molecule and the number of each are printed next. This includes, of course, the atomic constituents of each radical.

3.2.3 Group Structure and Composition

This is a printout of a multi-group property array; it comprises the following items.

A. Group number — the ordinal number assigned to each group. This number identifies the group as well as the core atom thereof.

B. Group weight — an integer which is unique to each chemical group and which correlates the group with its thermochemical group values.

C. Chemical symbol of the individual components of the group.

D. Row and column coordinates of group components. For single atoms, the row and column coordinates represent the particular card and column in the structural input deck containing the species. For radicals, the coordinates may be shifted one or two locations away from the input coordinates since the program ultimately packs all the symbols of a radical into one word.

E. Bond vector — the bond direction between a ligand and the core atom in a group. The numbers represent the bond directions depicted in Figure 3-1.

F. Bond type — the multiplicity of each chemical bond in the group.

G. Group number of core atom — this number identifies those ligands in a group which are also core atoms.

3.2.4 Ring Specifications

If ring structures are present, the program prints the total number of members in each unique ring in the molecule together with the group number of each member.

3.2.5 Ligand Identification

This printout identifies each unique pair of complex ligands in the molecule which have identical structures. The corresponding core atom is also specified. Here the term ligand refers to all the atoms in a particular chain or branch which is bonded to a specific core atom. The ligand is considered complex if it has one or more core atoms, and not merely atoms with connectivities of one like hydrogen, CN, etc.

3.2.6 Atomic Composition of Group Components

In this printout, the atomic composition of each ligand and core atom in a group is specified. Here the term ligand has the same significance as in 3.2.5. If the core atom happens to be part of a ring, the atomic distribution of the ligands which form part of the ring structure is quite arbitrary. In either case, the total number of atoms of a particular type which are contained in a group should correspond to the total number of such atoms in the molecule.

3.2.7 Properties of the Longest Chain

This printout gives the number of core atoms present in the longest chain in the molecule and the group number of each atom.

3.2.8 Nongroup Interaction and Symmetry Contributions

The nongroup interaction correction for the heat of formation of ring structures includes a correction for the strain energy. The majority of the ring corrections are for monocyclic rings whose ring number is printed in column two. A few are for dicyclic and tricyclic fused ring structures.

Other nongroup interaction corrections include ortho, para, cis, gauche alkene, and ditertiary ether corrections. In this case, the group numbers of the core atoms involved in the interaction are printed in column two and the number of interactions of each type is displayed in column three.

The symmetry corrections refer to internal rotations of twofold and threefold symmetry.

3.2.9 External Rotational Symmetry Contribution

The calculated symmetry number and the corresponding entropy contributions are printed next. If the symmetry number is not calculable, it is indicated in the printout. In this case the calculated symmetry number is set to one and the entropy to zero. If the symmetry number is input, it is also output together with the entropy contribution computed therefrom.

3.2.10 Optical Isomer Contribution

This contribution accounts for the entropy of mixing associated with the presence of optical isomers and asymmetric carbon atoms. The program computes and prints the number of asymmetric and pseudoasymmetric atoms, enantiomers, meso structures and the corresponding entropy (Section 5.3.7.5). If these properties are not calculable, it is indicated in the printout and all pertinent values are set to zero. If the number of enantiomers and meso compounds are input, they are also output together with their entropy value.

The program also outputs the group numbers of the asymmetric atoms and of the pseudoasymmetric atom (if any).

3.2.11 Thermochemical Properties of the Molecule

The coefficients for the heat capacity of the molecule are those for the regular third-order polynomial

$$C_p^\circ = c_o + c_1 T + c_2 T^2 + c_3 T^3$$

The data in the DATA LIBRARY are expressed in terms of $\Delta H_{f,\,298}^\circ$, S_{298}°, and the four heat capacity coefficients. The remaining thermochemical

properties of the molecule are computed by means of the standard relationships below:

$$H^\circ_T - H^\circ_0 = \frac{1}{1000}\left(c_o T + 1/2\, c_1 T^2 + 1/3\, c_2 T^3 + 1/4\, c_3 T^4\right)$$

$$s_{cons} = S^\circ_{298} - \left[c_o T + 1/2\, c_1 (298) + 1/2\, c_2 (298)^2 + 1/3\, c_3 (298)^3\right]$$

$$S^\circ_T = c_o \ln T + 1/2\, c_2 T^2 + 1/3\, C_3 T^3 + s_{cons}$$

$$-(G^\circ_T - H^\circ_{298})/T) = -\left[1000\,(H^\circ_T - H^\circ_{298}) - TS^\circ_T\right]\Big/T$$

$$H^\circ_T\ (\text{Total}) = \Delta H_{f,\,298} + H^\circ_T - H^\circ_{298}$$

Section 4
EXAMPLES OF COMPUTATIONAL OUTPUT

This section contains complete listings of 17 thermochemical calculations performed by the program for a variety of different molecular structures. As shown in Table 4-1, the examples include hydrocarbons, saturated and unsaturated, symmetric and asymmetric molecules, as well as fused and monocyclic, aromatic and nonaromatic ring structures. Nearly all types of nongroup interactions and symmetry contributions are represented. Table 4-2 presents a comparison of the calculated and published thermodynamic properties of 12 of these molecules. The agreement in the majority of cases is very good.

Case 17 requires some special comments. The molecule in question is a highly complex hypothetical structure formulated with the objective of demonstrating the program's symmetry detection capabilities. It has the basic structure CX_2YZ, where carbon atom C is defined by group number 12. An analyses of the printout reveals, that the two X ligands (group numbers 9 and 16) have been identified correctly as well as the six subordinate pairs of complex ligands. These data were used to compute the listed symmetry and optical isomer properties of the molecule. The computation time for case 17 was approximately 3 seconds on the CDC-6500 computer.

Table 4-3 lists the input data for all 17 cases in the same order as the computational output.

Table 4-1

LIST OF SAMPLE MOLECULES

Case Number	Name
1	Ethane
2	Octyl alcohol
3	Valeraldehyde
4	tert-Butyl ether
5	Butyronitrile
6	1 - Cyclohexylheptane
7	Phenol
8	2, 2, 3 - Trimethylhexane
9	Styrene
10	Aniline
11	Naphthalene
12	cis -1 -Methyl—2-ethyl cyclopentane
13	Trimethylmethane
14	Benzenehexacarbonitrile
15	bis (2-nitro -5— hydroxycyclohexyl)-malononitrile
16	Fused nitrogen tricyclic ring
17	Hypothetical molecule

Table 4-2

COMPARISON OF CALCULATED AND PUBLISHED THERMOCHEMICAL PROPERTIES

Case Number	Temperature °K	ΔH_f°(calc)	ΔH_f°	S°(calc)	S°	C_p°(calc)	C_p°	Ref
		Kcal/mole		cal/°K-mole				
1	298	-20.16	-20.24	55.08	54.85	12.27	12.58	4
1	1000			79.75	79.39	29.55	29.33	4
2	298	-86.16	-85.34	123.85	124.14	48.18	48.17	4
2	1000			217.11	217.08	107.72	107.58	4
3	298	-54.58	-54.45	91.60	91.53	30.28	29.96	4
3	1000			147.70	147.69	63.86	64.00	4
4	298	-87.78	-87.20	105.18	102.12	48.92	48.76	4
4	1000			201.02	195.26	109.77	107.86	4
5	298	7.47	8.14	77.85	77.78	22.63	23.19	4
5	1000			120.56	120.40	48.40	48.22	4
6	298	-65.63	-65.73	138.58	137.51	64.27	65.89	4
6	1000			274.63	274.79	162.61	162.70	4
7	298	-23.20	-23.03	74.17	75.43	24.26	24.75	4
7	1000			124.11	124.65	55.50	55.49	4
8	298	-57.70	-57.65	112.00	111.34	50.49	50.43	4
8	1000			213.00	212.42	117.29	117.38	4
9	298	35.22	35.22	82.46	82.48	29.20	29.18	4
9	1000			141.52	141.50	67.83	67.92	4
10	298	20.80	20.76	76.29	76.28	25.70	25.91	4
10	1000			128.17	128.38	59.05	59.18	4
11	298	36.08	36.08	80.22	80.22	31.67	31.68	4
11	1000			147.41	147.36	78.30	78.38	4
12	298	-35.66	-35.9					1

GROUP ADDITIVITY THERMOCHEMICAL PROPERTY PROGRAM

CASE NUMBER 1

MOLECULAR STRUCTURE

```
   H  H
   |  |
H-C--C-H
   |  |
   H  H
```

ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	6
C	2

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	3	3			1
		C	3	6	3	1	2
		H	3	1	7	1	0
		H	1	3	1	1	0
		H	5	3	5	1	0
2	296	C	3	6			2
		C	3	3	7	1	1
		H	1	6	1	1	0
		H	3	8	3	1	0
		H	5	6	5	1	0

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 2

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	2	1		-2.183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	6	-3.56069

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0.00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-3.35847668E-01	4.88658852E-02	-2.33428712E-05	4.38070270E-09

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298.0	12.268586	55.076078	1.872337	55.076078	0.000000	-20.160000
300.0	12.340738	55.158384	1.896946	55.076352	.024609	-20.135391
400.0	15.754652	59.185116	3.304843	55.603851	1.432506	-18.727494
500.0	18.806365	63.034981	5.035803	56.708048	3.163466	-16.996534
600.0	21.522042	66.708734	7.054915	58.071104	5.182578	-14.977422
700.0	23.927846	70.210848	9.329382	59.557211	7.457046	-12.702454
800.0	26.049943	73.547508	11.831027	61.099145	9.958690	-10.201310
900.0	27.914496	76.725799	14.531286	62.660300	12.658949	-7.501051
1000.0	29.547669	79.753327	17.406214	64.219450	15.533877	-4.626123
1200.0	32.224534	85.387997	23.595371	67.285469	21.723034	1.563034
1400.0	34.249852	90.517041	30.255257	70.243526	28.382921	8.222921
1600.0	35.952937	95.207694	37.284496	73.075094	35.412159	15.252159
1800.0	37.423101	99.520091	44.623571	75.777405	42.751234	22.591234
2000.0	38.909660	103.546886	52.254829	78.355640	50.382493	30.222493

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 2

MOLECULAR STRUCTURE

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H H H H H H H H
| | | | | | | |
H-C-C-C-C-C-C-C-C-O-H
| | | | | | | |
H H H H H H H H
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ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	18
C	8
O	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	3	11			1
		C	3	13	3	1	2
		H	3	9	7	1	0
		H	1	11	1	1	0
		H	5	11	5	1	0
2	399	C	3	13			2
		C	3	11	7	1	1
		C	3	15	3	1	3
		H	1	13	1	1	0
		H	5	13	5	1	0
3	399	C	3	15			3
		C	3	13	7	1	2
		C	3	17	3	1	4
		H	1	15	1	1	0
		H	5	15	5	1	0
4	399	C	3	17			4
		C	3	15	7	1	3
		C	3	19	3	1	5
		H	1	17	1	1	0
		H	5	17	5	1	0
5	399	C	3	19			5
		C	3	17	7	1	4
		C	3	21	3	1	6
		H	1	19	1	1	0
		H	5	19	5	1	0
6	399	C	3	21			6
		C	3	19	7	1	5
		C	3	23	3	1	7
		H	1	21	1	1	0
		H	5	21	5	1	0
7	399	C	3	23			7
		C	3	21	7	1	6
		C	3	25	3	1	8
		H	1	23	1	1	0
		H	5	23	5	1	0
8	434	C	3	25			8
		C	3	23	7	1	7
		C	3	27	3	1	9
		H	1	25	1	1	0
		H	5	25	5	1	0
9	309	C	3	27			9
		C	3	25	7	1	8
		H	3	29	3	1	0

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	13	6	1	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	11	5	1	0
	LIGAND	5	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	9	4	1	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	7	3	1	0
	LIGAND	9	4	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	5	2	1	0
	LIGAND	11	5	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	3	1	1	0
	LIGAND	13	6	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	1	0	1	0
	LIGAND	15	7	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
9	CORE	0	0	1	0
	LIGAND	17	6	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 9

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3, 4, 5, 6, 7, 8, 9,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	1	1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-1,03205952E-01	1,51907042E-1	-1,07097052E-04	2,30119994E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	48,103426	123,846770	7,593946	123,846770	0,000000	-86,160000
300,0	48,441496	124,169964	7,607561	123,847846	,096635	-86,063365
400,0	60,906850	139,866396	13,173821	125,909209	5,582575	-80,577125
500,0	71,952552	154,682614	19,833963	130,196580	12,243017	-73,916983
600,0	81,456672	168,662194	27,515945	135,453862	19,924999	-66,235001
700,0	89,647284	181,849855	36,081513	141,149044	28,490568	-57,669432
800,0	96,662456	194,298842	45,406220	147,021748	37,815275	-48,344725
900,0	102,640267	206,038675	55,379426	152,932364	47,788480	-38,371520
1000,0	107,718783	217,115036	65,904297	158,801685	58,313352	-27,846648
1200,0	115,730224	237,508522	88,290742	170,250692	80,699796	-5,460204
1400,0	121,801357	255,814184	112,067033	181,188408	104,476087	18,316087
1600,0	127,036757	272,423437	136,955569	191,570548	129,364623	43,204623
1800,0	132,541001	287,695969	162,899659	201,413350	155,308713	69,148713
2000,0	139,418665	301,999628	190,063531	210,763336	182,472585	96,312585

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 3

MOLECULAR STRUCTURE

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H H H H
 * * * *
H-C-C-C-C-C-H
 * * * *
H H H H
```

ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	10
C	5
O	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	3	10			1
		C	3	12	3	1	2
		H	3	8	7	1	0
		H	1	10	1	1	0
		H	5	10	5	1	0
2	399	C	3	12			2
		C	3	10	7	1	1
		C	3	14	3	1	3
		H	1	12	1	1	0
		H	5	12	5	1	0
3	399	C	3	14			3
		C	3	12	7	1	2
		C	3	16	3	1	4
		H	1	14	1	1	0
		H	5	14	5	1	0
4	955	C	3	16			4
		C	3	14	7	1	3
		CO	3	18	3	1	5
		H	1	16	1	1	0
		H	5	16	5	1	0
5	843	CO	3	18			5
		C	3	16	7	1	4
		H	3	20	3	1	0

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	7	4	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	5	3	1	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	3	2	1	0
	LIGAND	5	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	1	1	1	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	1	0
	LIGAND	9	4	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 5

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3, 4, 5,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	1	1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
4,31392372E+00	1,01945774E-01	-5,28121152E-05	1,04074250E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	30,279255	91,596770	5,366798	91,596770	0,000000	-54,580000
300,0	30,425566	91,799797	5,427503	91,597447	,060705	-54,519295
400,0	37,308370	101,515347	8,821180	92,879391	3,454382	-51,125618
500,0	43,384710	110,507621	12,862295	95,516627	7,495497	-47,084503
600,0	48,717030	118,892745	17,473322	98,722205	12,106524	-42,473476
700,0	53,367776	126,767110	22,582982	102,172562	17,216184	-37,363816
800,0	57,399390	134,163108	28,126239	105,713807	22,759441	-31,820559
900,0	60,874319	141,129566	34,044304	109,265671	28,677506	-25,902494
1000,0	63,855007	147,701647	40,284628	112,783817	34,917830	-19,662170
1200,0	68,583437	159,784193	53,553096	119,628945	48,186298	-6,393702
1400,0	72,084235	170,631840	67,636161	126,153724	62,269363	7,689363
1600,0	74,856959	180,443684	82,338252	132,336525	76,971454	22,391454
1800,0	77,401166	189,407257	97,563710	138,186750	92,196912	37,616912
2000,0	80,216410	197,703424	113,316788	143,728429	107,949989	53,369989

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 4

MOLECULAR STRUCTURE

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 H  H  H H  H  H
  \ / \ / \ / \ /
H  C    C    C  H
 \ / \ / \ / \ /
H-C-C---O---C-O-H
 / \ / \ / \ / \
H  C    C    C  H
 \ / \ / \ / \ /
 H  H  H H  H  H
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ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	18
C	8
O	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	6	4			1
		C	6	6	3	1	2
		H	3	1	8	1	0
		H	9	1	6	1	0
		H	6	1	7	1	0
2	640	C	6	6			2
		C	6	4	7	1	1
		C	4	6	1	1	3
		C	6	10	3	1	4
		C	8	6	5	1	5
3	296	C	4	6			3
		C	6	6	5	1	2
		H	1	3	8	1	0
		H	1	6	1	1	0
		H	1	9	2	1	0
4	412	O	6	10			4
		C	6	6	7	1	2
		C	6	14	3	1	6
5	296	C	8	6			5
		C	6	6	1	1	2
		H	11	9	4	1	0
		H	11	6	5	1	0
		H	11	3	6	1	0
6	640	C	6	14			6
		C	6	10	7	1	4
		C	4	14	1	1	7
		C	6	16	3	1	8
		C	8	14	5	1	9
7	296	C	4	14			7
		C	6	14	5	1	6
		H	1	11	8	1	0
		H	1	14	1	1	0
		H	1	17	2	1	0
8	296	C	6	16			8
		C	6	14	7	1	6
		H	3	19	2	1	0
		H	6	19	3	1	0
		H	9	19	4	1	0
9	296	C	8	14			9
		C	6	14	1	1	6
		H	11	17	4	1	0
		H	11	14	5	1	0
		H	11	11	6	1	0

COMPLEX LIGANDS 7 AND 8 OF CORE ATOM 6 ARE EQUAL;

COMPLEX LIGANDS 7 AND 9 OF CORE ATOM 6 ARE EQUAL;

COMPLEX LIGANDS 2 AND 6 OF CORE ATOM 4 ARE EQUAL;

COMPLEX LIGANDS 1 AND 3 OF CORE ATOM 2 ARE EQUAL;

COMPLEX LIGANDS 1 AND 5 OF CORE ATOM 2 ARE EQUAL;

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	9	4	1	0
	LIGAND	3	1	0	0
3	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	0	1	0
	LIGAND	9	4	0	0
	LIGAND	9	4	0	0
5	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	9	4	1	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
7	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
9	CORE	0	1	0	0
	LIGAND	15	7	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 5

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 4, 6, 7,

NONORCUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER			AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
GAUCHE ETHER	2	4		2	,600					
GAUCHE ETHER	4	4		2	,600					
DITERTIARY ETHER	2	4	6	1	8,400					
INTERNAL ROTATION		1		1		-2,183				
INTERNAL ROTATION		2		1		-2,183				
INTERNAL ROTATION		3		1		-2,183				
INTERNAL ROTATION		5		1		-2,183				
INTERNAL ROTATION		6		1		-2,183				
INTERNAL ROTATION		7		1		-2,183				
INTERNAL ROTATION		8		1		-2,183				
INTERNAL ROTATION		9		1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	2	-1,37746

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-9,70221192E+00	2,47062417E-01	-1,86496026E-04	5,89057931E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	43,919654	105,176696	6,549823	105,176696	0,000000	-87,780000
300,0	49,222327	105,504931	6,647965	105,177791	,098142	-87,681858
400,0	63,053361	121,619164	12,282524	107,287412	5,732701	-82,047299
500,0	74,568214	136,965850	19,181431	111,702633	12,631608	-75,148392
600,0	84,120320	151,432697	27,130742	117,131166	20,580919	-67,199081
700,0	92,063114	165,034773	35,951852	123,011875	29,402029	-58,377971
800,0	98,750031	177,756622	45,5615.2	129,067024	38,951670	-48,828321
900,0	104,534505	189,728768	55,671777	135,148850	49,121953	-38,658047
1000,0	109,769972	201,016844	66,399133	141,176564	59,840280	-27,939720
1200,0	120,007621	221,925792	89,357338	152,919489	82,807515	-4,972485
1400,0	132,290457	241,303094	114,529497	164,174756	107,979674	20,199674
1600,0	149,445957	260,018097	142,598365	174,987759	136,048542	48,268542
1800,0	174,301599	278,965995	174,821223	185,481884	168,271400	80,491400
2000,0	209,684862	299,057011	213,020846	195,821500	206,471023	118,691023

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 5

MOLECULAR STRUCTURE

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   H H H
   - - -
H-C=C-C=CN
   - - -
   H H H
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ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	7
C	4
N	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	3	11			1
		C	3	13	3	1	2
		H	3	9	7	1	0
		H	1	11	1	1	0
		H	5	11	5	1	0
2	399	C	3	13			2
		C	3	11	7	1	1
		C	3	15	3	1	3
		H	1	13	1	1	0
		H	5	13	5	1	0
3	679	C	3	15			3
		C	3	13	7	1	2
		H	1	15	1	1	0
		CN	3	17	3	1	0
		H	5	15	5	1	0

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	4	3	0	1
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	2	2	0	1
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	5	2	0	0
	LIGAND	1	0	0	0
	LIGAND	0	1	0	1
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 3

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	1	1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

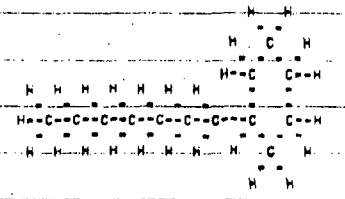
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
1,17035619E+00	8,53852661E-02	-4,77893232E-05	9,63714085E-09

T DEG K	G(T) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	22,606316	77,846770	3,737484	77,846770	0,000000	7,470000
300,0	22,745100	77,990514	3,782855	77,847276	,045371	7,515371
400,0	28,294946	85,319963	6,341136	78,810832	2,603652	10,073652
500,0	33,120301	92,165083	9,417695	80,804660	5,680211	13,150211
600,0	37,278962	98,580904	12,942974	83,238421	9,205490	16,675490
700,0	40,828813	104,601508	16,853196	85,864776	13,115713	20,585713
800,0	43,827618	110,255007	21,090369	88,563901	17,352885	24,822885
900,0	46,333220	115,546376	25,602280	91,272158	21,864796	29,334796
1000,0	48,403440	120,558781	30,342500	93,953765	26,605016	34,075016
1200,0	51,469029	129,674178	40,351063	99,162862	36,613579	44,083579
1400,0	53,486970	137,770196	50,860269	104,111064	47,122785	54,592785
1600,0	54,919843	145,009870	61,706846	108,779018	57,969362	65,439362
1800,0	56,230233	151,553094	72,820040	113,173895	69,082557	76,552557
2000,0	57,860722	157,557954	84,221613	117,315889	80,484129	87,954129

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 6

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	26
C	13

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	8	37			1
		C	8	40	3	1	2
		H	8	34	7	1	0
		H	6	35	8	1	0
		H	10	35	6	1	0
2	399	C	8	40			2
		C	8	37	7	1	1
		C	8	43	3	1	3
		H	6	38	8	1	0
		H	10	38	6	1	0
3	399	C	8	43			3
		C	8	40	7	1	2
		C	8	46	3	1	4
		H	6	41	8	1	0
		H	10	41	6	1	0
4	399	C	8	46			4
		C	8	43	7	1	3
		C	8	49	3	1	5
		H	6	44	8	1	0
		H	10	44	6	1	0
5	399	C	8	49			5
		C	8	46	7	1	4
		C	8	52	3	1	6
		H	6	47	8	1	0
		H	10	47	6	1	0
6	399	C	8	52			6
		C	8	49	7	1	5
		C	8	55	3	1	7
		H	6	50	8	1	0
		H	10	50	6	1	0
7	399	C	8	55			7
		C	8	52	7	1	6
		C	8	59	3	1	8
		H	6	53	8	1	0
		H	10	53	6	1	0
8	502	C	8	59			8
		C	10	61	4	1	10
		C	5	59	1	1	9
		C	8	55	7	1	7
		H	10	57	6	1	0
9	399	C	5	59			9
		C	8	59	5	1	8
		C	3	61	2	1	11
		H	5	56	7	1	0
		H	3	57	8	1	0
10	399	C	10	61			10
		C	8	63	2	1	12
		C	8	59	5	1	8
		H	12	63	4	1	0
		H	12	59	6	1	0
11	399	C	3	61			11
		C	5	59	6	1	9
		C	5	63	4	1	13
		H	1	59	8	1	0
		H	1	63	2	1	0
12	399	C	8	63			12
		C	5	63	1	1	13
		C	10	61	6	1	10
		H	8	66	3	1	0
		H	10	65	4	1	0
13	399	C	5	63			13
		C	3	61	8	1	11
		C	8	63	5	1	12
		H	3	65	2	1	0
		H	5	66	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 8, 9, 11, 13, 12, 10,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	23	12	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	21	11	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	19	10	0	0
	LIGAND	5	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	17	9	0	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	15	8	0	0
	LIGAND	9	4	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	13	7	0	0
	LIGAND	11	5	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	11	6	0	0
	LIGAND	13	6	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	15	7	0	0
	LIGAND	10	5	0	0
	LIGAND	1	0	0	0
9	CORE	0	1	0	0
	LIGAND	16	8	0	0
	LIGAND	8	4	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
10	CORE	0	1	0	0
	LIGAND	24	12	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
11	CORE	0	1	0	0
	LIGAND	18	9	0	0
	LIGAND	6	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
12	CORE	0	1	0	0
	LIGAND	22	11	0	0
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
13	CORE	0	1	0	0
	LIGAND	20	10	0	0
	LIGAND	4	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 13

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 13, 12, 10,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
RING CORRECTION	1	1	,000	18,800	-1,3120E+01	2,5547E-02	-1,1337E-05	1,0331E-03
GAUCHE ALKANE	8 7	1	,800					
INTERNAL ROTATION	1	1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-1,70210325E+01	3,28186431E-01	-1,8923574BE-04	4,14826526E-08

T DEG K	G(T) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	64,271413	138,576770	7,673965	138,576770	0,000000	-65,630000
300,0	64,723711	139,002192	7,802960	138,576208	,128995	-65,501005
400,0	85,830710	160,586412	15,354961	141,385922	7,680996	-57,949004
500,0	104,148576	181,758279	24,876131	147,353946	17,202166	-46,427834
600,0	119,926210	202,178175	36,1[illegible]002	154,801376	28,426037	-37,203963
700,0	133,412503	221,705399	48,784995	162,975395	41,111030	-24,518970
800,0	144,8[illegible]6352	240,285550	62,714421	171,487979	55,040456	-10,589544
900,0	154,5[illegible]6654	257,923717	77,696481	180,120922	70,022516	4,392516
1000,0	162,612304	274,634598	93,564264	188,744269	85,890299	20,260299
1200,0	175,185232	305,457318	127,413[illegible]8	205,674116	119,739843	54,109843
1400,0	184,566304	333,194977	163,425566	221,943834	155,751601	90,121601
1600,0	192,746686	358,376721	201,16[illegible]264	237,447771	193,486319	127,856319
1800,0	201,717551	381,579466	240,576940	252,188924	232,902975	167,272975
2000,0	213,470059	403,407665	282,[illegible]32747	266,228274	274,358782	208,728782

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 7

MOLECULAR STRUCTURE

```
          H
          -
          O
          =
          C
         - =
     H-C     C-H
     =       -
     =       =
     H-C     C-H
         - =
          C
          =
          H
```

ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	6
C	6
O	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	1016	C	7	3			1
		C	5	5	2	1	2
		C	10	3	5	2	3
		H	7	1	7	1	0
2	1154	C	5	5			2
		C	7	7	4	2	5
		C	3	5	1	1	4
		C	7	3	6	1	1
3	1016	C	10	3			3
		C	7	3	1	2	1
		C	12	5	4	1	6
		H	10	1	7	1	0
4	1156	C	3	5			4
		C	5	5	5	1	2
		H	1	5	1	1	0
5	1016	C	7	7			5
		C	10	7	5	1	7
		C	5	5	8	2	2
		H	7	9	3	1	0
6	1016	C	12	5			6
		C	10	3	8	1	3
		C	10	7	2	2	7
		H	14	5	5	1	0
7	1016	C	10	7			7
		C	12	5	6	2	6
		C	7	7	1	1	5
		H	10	9	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 2, 5, 7, 6, 3, 1,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	O	C	N
1	CORE	0	1	0	0
	LIGAND	5	5	1	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	5	5	0	0
	LIGAND	1	0	1	0
3	CORE	0	1	0	0
	LIGAND	4	4	1	0
	LIGAND	1	1	0	0
	LIGAND	1	0	0	0
4	CORE	0	0	1	0
	LIGAND	5	6	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	[illegible]	1	1	[illegible]	0
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	LIGAND	1	0	[illegible]	0
6	CORE	0	1	0	0
	LIGAND	3	3	1	0
	LIGAND	2	2	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	2	2	1	0
	LIGAND	3	3	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 7

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 3, 6, 7, 5, 2, 4,

RING 1 IS SYMMETRICAL ABOUT ATOM 2.

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	2	1		-1.377				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0.00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0.00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

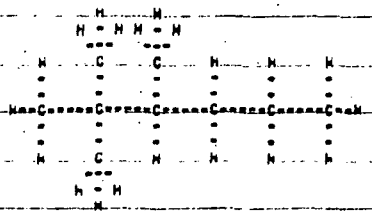
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-8.09401391E+00	1.36374651E-01	-1.02081739E-04	2.93033004E-08

T DEG K	CP(T) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298.0	24.255836	75.172540	2.801581	75.172540	0.000000	-23.200000
300.0	24.422214	75.335343	2.849759	75.173063	.048178	-23.151822
400.0	31.998180	83.432852	5.682164	76.228864	2.881583	-20.318417
500.0	38.235790	91.266346	9.264283	78.458941	6.403702	-16.796298
600.0	43.310664	98.702469	13.293571	81.219152	10.480990	-12.719010
700.0	47.399222	105.697430	17.833565	84.221738	15.032984	-8.167016
800.0	50.676684	112.248712	22.743385	87.320206	19.942805	-3.257195
900.0	53.319078	118.375497	27.947733	90.434217	25.147152	1.947152
1000.0	55.502199	124.109472	33.391691	93.518162	30.591310	7.391310
1200.0	59.193967	134.561641	44.868682	99.504890	42.068101	18.868101
1400.0	63.158546	143.971673	57.087665	105.195184	54.287084	31.087084
1600.0	68.802495	152.747297	70.244058	110.595124	67.443477	44.243477
1800.0	77.532372	161.317942	84.814391	115.754713	82.013811	58.813811
2000.0	90.754736	170.125540	101.556506	120.747577	98.755926	75.555926

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 8

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	20
C	9

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	7	4			1
		C	7	10	3	1	2
		H	7	1	7	1	0
		H	4	4	1	1	0
		H	10	4	5	1	0
2	605	C	7	10			2
		C	7	4	7	1	1
		C	4	10	1	1	3
		C	7	16	3	1	4
		C	10	10	5	1	5
3	296	C	4	10			3
		C	7	10	5	1	2
		H	2	8	8	1	0
		H	1	10	1	1	0
		H	2	12	2	1	0
4	502	C	7	16			4
		C	7	10	7	1	2
		C	4	16	1	1	6
		C	7	22	3	1	7
		H	10	16	5	1	0
5	296	C	10	10			5
		C	7	10	1	1	2
		H	12	12	4	1	0
		H	13	10	5	1	0
		H	12	8	6	1	0
6	296	C	4	16			6
		C	7	16	5	1	4
		H	2	14	6	1	0
		H	1	16	1	1	0
		H	2	18	2	1	0
7	399	C	7	22			7
		C	7	16	7	1	4
		C	7	28	3	1	8
		H	4	22	1	1	0
		H	10	22	5	1	0
8	399	C	7	28			8
		C	7	22	7	1	7
		C	7	34	3	1	9
		H	4	28	1	1	0
		H	10	28	5	1	0
9	296	C	7	34			9
		C	7	28	7	1	8
		H	4	34	1	1	0
		H	7	37	3	1	0
		H	10	34	5	1	0

COMPLEX LIGANDS 1 AND 3 OF CORE ATOM 2 ARE EQUAL,

COMPLEX LIGANDS 1 AND 5 OF CORE ATOM 2 ARE EQUAL,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	17	8	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	11	5	0	0
	LIGAND	3	1	0	0
3	CORE	0	1	0	0
	LIGAND	17	8	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	9	4	0	0
	LIGAND	3	1	0	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	17	8	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	17	8	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	13	6	0	0
	LIGAND	5	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	15	7	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
9	CORE	0	1	0	0
	LIGAND	17	8	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 6

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 4, 7, 8, 9,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER		AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
GAUCHE ALKANE	2	4	4	3,200					
GAUCHE ALKANE	4	7	1	,800					
INTERNAL ROTATION	1		1		-2,183				
INTERNAL ROTATION	2		1		-2,183				
INTERNAL ROTATION	3		1		-2,183				
INTERNAL ROTATION	5		1		-2,183				
INTERNAL ROTATION	6		1		-2,183				
INTERNAL ROTATION	9		1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	1	0	2	0	2	1,37746

GROUP NUMBER OF ASYMMETRIC CARBON ATOM(S) = 4,

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

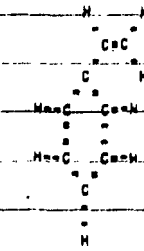
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-7,19215133E+00	2,32988113E-01	-1,41303630E-04	3,31543384E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	50,478162	111,996084	7,814934	111,996084	0,000000	-87,700000
300,0	50,832123	112,336848	7,116225	111,965213	,101290	-87,598710
400,0	65,396391	129,001393	12,943899	114,178978	5,928965	-81,771035
500,0	77,960296	144,979719	20,127824	118,753940	13,112890	-44,587110
600,0	88,692747	160,168521	28,474909	124,401897	21,459975	-36,240025
700,0	97,792687	174,543621	37,811956	130,547876	30,797022	-26,902978
800,0	105,459037	188,117318	47,985660	136,903911	40,970726	-16,729274
900,0	111,690723	200,921083	58,862608	143,312556	51,847674	-5,852326
1000,0	117,286678	212,997437	70,329280	149,683061	63,314346	5,614346
1200,0	125,767054	235,169722	94,677178	162,117852	87,662244	29,962244
1400,0	132,491597	255,074161	120,519045	173,999796	113,504111	55,804111
1600,0	139,051707	273,187213	147,662854	185,282263	140,647920	82,947920
1800,0	147,038793	290,004510	176,234860	195,993448	169,219926	111,519926
2000,0	158,044263	306,032734	206,679597	206,200403	199,664663	141,964663

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 8

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	8
C	8

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	1016	C	7	12			1
		C	5	14	2	1	2
		C	10	12	5	2	3
		H	7	9	7	1	0
2	1993	C	5	14			2
		C	7	16	4	2	5
		C	3	16	2	1	4
		C	7	12	6	1	1
3	1016	C	10	12			3
		C	7	12	1	2	1
		C	12	14	4	1	6
		H	10	9	7	1	0
4	2011	C	3	16			4
		C	5	14	6	1	2
		C	3	18	3	2	7
		H	1	14	8	1	0
5	1016	C	7	16			5
		C	10	16	5	1	8
		C	5	14	8	2	2
		H	7	19	3	1	0
6	1016	C	12	14			6
		C	10	12	6	1	3
		C	10	16	2	2	8
		H	15	14	5	1	0
7	1031	C	3	18			7
		C	3	16	7	2	4
		H	1	20	2	1	0
		H	5	20	4	1	0
8	1016	C	10	16			8
		C	12	14	6	2	6
		C	7	16	1	1	5
		H	10	19	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 2, 5, 8, 6, 3, 1,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS FOR EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	7	7	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	5	5	0	0
	LIGAND	3	2	0	0
3	CORE	0	1	0	0
	LIGAND	6	6	0	0
	LIGAND	1	1	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	5	6	0	0
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	3	3	0	0
	LIGAND	4	4	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	5	5	0	0
	LIGAND	2	2	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	6	7	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	4	4	0	0
	LIGAND	3	3	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 8

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 3, 6, 8, 5, 2, 4, 7,

RING 1 IS SYMMETRICAL ABOUT ATOM 2.

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	2	1		-1,377				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-7,28699714E+00	1,50034970E-01	-1,00151980E-04	2,52314903E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	29,175283	82,462540	3,656028	82,462540	0,000000	35,220000
300,0	29,379105	82,658475	3,714612	82,463193	,058584	35,278584
400,0	38,315528	92,370938	7,112121	83,730707	3,456093	38,676093
500,0	45,844467	101,794152	11,331135	86,403938	7,675107	42,895107
600,0	52,177311	110,685711	16,239477	89,713295	12,583450	47,803450
700,0	57,315449	119,123864	21,720107	93,318037	18,064079	53,284079
800,0	61,560269	127,064031	27,671123	97,045162	24,015095	59,235095
900,0	65,013162	134,521172	34,005763	100,799243	30,349736	65,569736
1000,0	67,825515	141,521506	40,652404	104,525130	36,996376	72,216376
1200,0	72,134159	154,280970	54,678889	111,776586	51,014861	86,234861
1400,0	75,597313	165,677915	69,456369	118,677671	65,800341	101,020341
1600,0	79,226090	176,036999	84,985856	125,206982	81,324828	116,544828
1800,0	85,431599	185,734424	101,458587	131,399669	97,802559	133,022559
2000,0	94,024953	195,147651	119,346018	137,304656	115,689991	150,909991

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 10

MOLECULAR STRUCTURE

```
          H   H
          - -
          N
          =
          =
          C
         - -
      H--C   C--H
         =   =
         =   =
      H--C   C--H
         - -
          C
          =
          =
          H
```

ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	7
C	6
N	1

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	1016	C	8	11			1
		C	6	13	2	1	2
		C	11	11	5	2	3
		H	8	8	7	1	0
2	1535	C	6	13			2
		C	8	15	4	2	5
		N	3	13	1	1	4
		C	8	11	6	1	1
3	1016	C	11	11			3
		C	8	11	1	2	1
		C	13	13	4	1	6
		H	11	8	7	1	0
4	1576	N	3	13			4
		C	6	13	5	1	2
		H	1	11	8	1	0
		H	1	15	2	1	0
5	1016	C	8	15			5
		C	11	15	5	1	7
		C	6	13	8	2	2
		H	8	18	3	1	0
6	1016	C	13	13			6
		C	11	11	8	1	3
		C	11	15	2	2	7
		H	16	13	5	1	0
7	1016	C	11	15			7
		C	13	13	6	2	6
		C	8	15	1	1	5
		H	11	18	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 2, 3, 7, 6, 3, 1,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	6	5	0	1
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	5	5	0	0
	LIGAND	2	0	0	1
3	CORE	0	1	0	0
	LIGAND	5	4	0	1
	LIGAND	1	1	0	0
	LIGAND	1	0	0	0
4	CORE	0	0	0	1
	LIGAND	5	6	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	[illegible]	2	[illegible]	[illegible]	[illegible]
	[illegible]	4	1	1	1
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	4	3	0	1
	LIGAND	2	2	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	3	2	0	1
	LIGAND	3	3	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 7

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 3, 6, 7, 5, 2, 4,

RING 1 IS SYMMETRICAL ABOUT ATOM 2.

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	2	1		-1,377				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

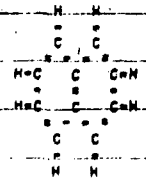
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-0,12150221E-00	1,47970592E-01	-1,14891510E-04	3,50932862E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	25,699603	76,292540	2,987690	76,292540	0,000000	20,600000
300,0	25,876958	76,445037	2,959266	76,293115	,051577	20,851577
400,0	33,933063	85,042618	5,962625	77,412261	3,054935	23,854935
500,0	40,527577	93,354718	9,696759	79,776579	6,789070	27,589070
600,0	45,830059	101,234194	14,026639	82,702612	11,118949	31,918949
700,0	50,108669	108,642835	18,838289	85,884837	15,930599	36,730599
800,0	53,692167	115,581946	24,038789	89,148072	21,131099	41,931099
900,0	56,572913	122,077283	29,556277	92,467742	26,648587	47,448587
1000,0	59,050866	128,168696	35,339945	95,736441	32,432256	53,232256
1200,0	63,640632	139,339607	47,607873	102,089454	44,700184	65,500184
1400,0	69,145944	149,540773	60,857234	108,148241	57,949545	78,749545
1600,0	77,251279	159,264806	75,439586	113,932371	72,531896	93,331896
1800,0	89,641115	169,028767	92,843379	119,508940	89,135690	109,935690
2000,0	107,999930	179,363814	111,693964	124,970677	108,786274	129,886274

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 11

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	8
C	10

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	1016	C	5	3			1
		C	7	3	5	1	3
		C	3	5	2	2	2
		H	5	1	7	1	0
2	1016	C	3	5			2
		C	5	3	6	2	1
		C	5	7	4	1	4
		H	1	5	1	1	0
3	1016	C	7	3			3
		C	9	5	4	2	5
		C	5	3	1	1	1
		H	7	1	7	1	0
4	999	C	5	7			4
		C	7	7	5	2	7
		C	3	9	2	1	6
		C	3	5	8	1	2
5	1016	C	9	5			5
		C	7	7	2	1	7
		C	7	3	8	2	3
		H	11	5	5	1	0
6	1016	C	3	9			6
		C	5	7	6	1	4
		C	5	11	4	2	8
		H	1	9	1	1	0
7	999	C	7	7			7
		C	9	9	4	1	9
		C	5	7	1	2	4
		C	9	5	6	1	5
8	1016	C	5	11			8
		C	3	9	8	2	6
		C	7	11	5	1	10
		H	5	13	3	1	0
9	1016	C	9	9			9
		C	7	11	2	2	10
		C	7	7	8	1	7
		H	11	9	5	1	0
10	1016	C	7	11			10
		C	5	11	1	1	8
		C	9	9	6	2	9
		H	7	13	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 7, 4, 6, 8, 10, 9,

RING NUMBER 2 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 1, 3, 5, 7, 4, 2,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS OF EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	6	8	0	0
	LIGAND	1	1	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	7	9	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	5	7	0	0
	LIGAND	2	2	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	4	5	0	0
	LIGAND	4	4	0	0
5	CORE	0	1	0	0
	LIGAND	4	6	0	0
	LIGAND	3	3	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	4	6	0	0
	LIGAND	3	3	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	4	4	0	0
	LIGAND	4	5	0	0
8	CORE	0	1	0	0
	LIGAND	5	7	0	0
	LIGAND	2	2	0	0
	LIGAND	1	0	0	0
9	CORE	0	1	0	0
	LIGAND	7	9	0	0
	LIGAND	1	0	0	0
10	CORE	0	1	0	0
	LIGAND	6	8	0	0
	LIGAND	1	1	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 11

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 2, 1, 3, 5, 7, 9, 10, 8, 6, 4, 2,

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
INPUT	4	-2.75463
NOT CALCULABLE	1	0.00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0.00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

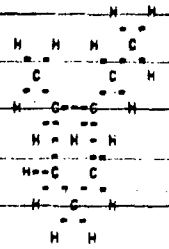
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-1.36025232E+01	1.87339939E-01	-1.28794942E-04	3.33550420E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298.0	31.649967	80.220073	3.194351	80.220073	0.000000	36.080000
300.0	31.908500	80.432716	3.257930	80.220781	.063579	36.143579
400.0	42.840964	91.157058	7.012033	81.612854	3.817682	39.897682
500.0	52.038091	101.738183	11.772947	84.594591	8.576596	44.656596
600.0	59.639956	111.924192	17.367143	88.258873	14.172791	50.252791
700.0	65.866692	121.597706	23.653130	92.370922	20.458749	56.538749
800.0	70.918447	130.734716	30.501315	96.601012	27.306964	63.386964
900.0	74.955344	139.331675	37.804294	100.876103	34.609943	70.689943
1000.0	78.297516	147.410053	45.474559	105.129844	42.280208	78.360208
1200.0	83.378199	162.157277	61.667095	113.429990	58.472744	94.552744
1400.0	87.761846	175.337982	78.739350	121.348698	75.544998	111.664998
1600.0	93.048579	187.383129	96.831958	128.859625	93.637607	129.717607
1800.0	100.840358	198.760141	116.165764	135.998245	112.971413	149.051413
2000.0	112.737921	209.957459	137.441820	142.833724	134.247469	170.327469

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 12

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	16
C	8

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP OF CORE	NUMBER ATOM
1	296	C	5	3				1
		C	7	5	4	1		2
		H	3	1	8	1		0
		H	3	5	2	1		0
		H	7	1	6	1		0
2	502	C	7	5				2
		C	5	3	8	1		1
		C	7	9	3	1		3
		C	11	5	5	1		4
		H	9	3	6	1		0
3	502	C	7	9				3
		C	11	9	5	1		6
		C	5	11	2	1		5
		C	7	5	7	1		2
		H	9	7	6	1		0
4	399	C	11	5				4
		C	7	5	1	1		2
		C	13	7	4	1		7
		H	13	3	6	1		0
		H	11	2	7	1		0
5	399	C	5	11				5
		C	7	9	6	1		3
		C	3	13	2	1		8
		H	3	9	8	1		0
		H	7	13	4	1		0
6	399	C	11	9				6
		C	13	7	6	1		7
		C	7	9	1	1		3
		H	9	11	2	1		0
		H	13	11	4	1		0
7	399	C	13	7				7
		C	11	5	8	1		4
		C	11	9	2	1		6
		H	15	9	4	1		0
		H	15	5	6	1		0
8	296	C	3	13				8
		C	5	11	6	1		5
		H	1	11	8	1		0
		H	1	15	2	1		0
		H	5	15	4	1		0

RING NUMBER 1 IS 5 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 2, 3, 6, 7, 4,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	13	7	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	12	6	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	4	2	0	0
	LIGAND	5	2	0	0
	LIGAND	6	3	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	14	7	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	11	6	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	10	5	0	0
	LIGAND	4	2	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	12	6	0	0
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	13	7	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 8

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 4, 7, 6, 3, 5, 8,

NONBOND INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER		AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
RING CORRECTION	1		1	6,300	27,300	-1,2010E+01	1,7322E-02	-8,8451E-06	1,6456E-09
CIS	2	3	1	1,000	0,000	-2,7196E+00	5,8531E-03	-4,7848E-06	1,3942E-09
GAUCHE ALKANE	3	5	1	,800					
INTERNAL ROTATION	1		1		-2,183				
INTERNAL ROTATION	8		1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
INPUT	1	0,00000
NOT CALCULABLE	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

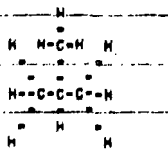
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-1,953408776E+01	2,166373995E-01	-1,308322176E-04	3,054162938E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	34,213673	97,293540	2,704093	97,293540	0,000000	-35,660000
300,0	34,586655	97,523375	2,772813	97,294306	,068721	-35,591279
400,0	46,142380	109,365060	6,921736	98,820952	4,217643	-31,442357
500,0	59,694259	121,403457	12,338561	102,134640	9,634408	-26,025592
600,0	69,945743	133,236369	18,843938	106,336677	16,139815	-19,520185
700,0	78,480082	144,677750	26,277078	111,002057	23,572986	-12,087014
800,0	85,680524	155,641172	34,495461	115,901961	31,791368	-3,868632
900,0	91,730321	166,092566	43,374828	120,902860	40,670736	5,010736
1000,0	96,812721	176,028051	52,809276	125,922865	50,105186	14,445186
1200,0	104,868331	194,422393	73,011443	135,632934	70,307351	34,647351
1400,0	111,133353	211,065734	94,621238	145,410630	91,917145	56,257145
1600,0	117,253785	226,299229	117,451145	154,582321	114,747052	79,087052
1800,0	124,635625	240,516393	141,606846	163,348197	138,902753	103,242753
2000,0	134,744872	254,140926	167,487222	171,749361	164,783130	129,123130

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 13

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	10
C	4

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	6	4			1
		C	6	6	3	1	2
		H	3	1	8	1	0
		H	9	1	6	1	0
		H	6	1	7	1	0
2	502	C	6	6			2
		C	6	4	7	1	1
		C	3	6	1	1	3
		C	6	8	3	1	4
		H	8	6	5	1	0
3	296	C	3	6			3
		C	6	6	5	1	2
		H	3	4	7	1	0
		H	1	6	1	1	0
		H	3	8	3	1	0
4	296	C	6	8			4
		C	6	6	7	1	2
		H	3	11	2	1	0
		H	6	11	3	1	0
		H	9	11	4	1	0

COMPLEX LIGANDS 1 AND 3 OF CORE ATOM 2 ARE EQUAL.

COMPLEX LIGANDS 1 AND 4 OF CORE ATOM 2 ARE EQUAL.

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	C	N
1	CORE	0	1	0	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 3

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
INTERNAL ROTATION	1	1		-2,183				
INTERNAL ROTATION	3	1		-2,183				
INTERNAL ROTATION	4	1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	3	-2,18323

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-2,22708940E+00	9,98394101E-02	-5,54334602E-05	1,21785257E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H( ) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	22,924630	70,427082	3,304418	70,427082	0,000000	-32,140000
300,0	23,064543	70,580892	3,350407	70,427594	,045989	-32,094011
400,0	29,618746	78,134170	5,991679	71,416017	2,687261	-29,452739
500,0	35,356567	85,374275	9,246944	73,489223	5,942526	-26,197474
600,0	40,351073	92,272745	13,038216	76,049749	9,733798	-22,406202
700,0	44,675337	98,825761	17,294817	78,839477	13,990399	-18,149601
800,0	48,432429	105,040863	21,953377	81,729664	18,648959	-13,491041
900,0	51,605421	110,931560	26,957833	84,649988	23,653415	-8,486585
1000,0	54,357384	116,514882	32,259427	87,559763	28,955009	-3,184991
1200,0	58,800508	126,834598	43,595542	93,260661	40,291124	8,151124
1400,0	62,316370	136,172933	55,717813	98,734793	52,413395	20,273395
1600,0	65,409539	144,701845	68,499244	103,955078	65,194826	33,054826
1800,0	68,904585	152,607342	81,929754	108,926600	78,625336	46,485336
2000,0	73,146076	160,076875	96,116175	113,670997	92,811757	60,671757

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 14

MOLECULAR STRUCTURE

```
          N
          C
          =
          C
          = =
     NC=C   C=CN
        =   =
     NC=C   C=CN
          = =
          C
          =
          C
          N
```

ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
C	12
N	6

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	1399	C	6	4			1
		C	8	4	5	2	3
		C	4	6	2	1	2
		CN	6	2	7	1	0
2	1399	C	4	6			2
		C	6	4	6	1	1
		C	6	8	4	2	4
		CN	2	6	1	1	0
3	1399	C	8	4			3
		C	10	6	4	1	5
		C	6	4	1	2	1
		CN	8	2	7	1	0
4	1399	C	6	8			4
		C	4	6	6	2	2
		C	8	8	5	1	6
		CN	6	10	3	1	0
5	1399	C	10	6			5
		C	8	8	2	2	6
		C	8	4	8	1	3
		CN	12	6	5	1	0
6	1399	C	8	8			6
		C	6	8	1	1	4
		C	10	6	6	2	5
		CN	8	10	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 1, 3, 5, 6, 4, 2,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	0	10	0	5
	LIGAND	0	1	0	1
2	CORE	0	1	0	0
	LIGAND	0	10	0	5
	LIGAND	0	1	0	1
3	CORE	0	1	0	0
	LIGAND	0	8	0	4
	LIGAND	0	2	0	1
	LIGAND	0	1	0	1
4	CORE	0	1	0	0
	LIGAND	0	2	0	1
	LIGAND	0	8	0	4
	LIGAND	0	1	0	1
5	CORE	0	1	0	0
	LIGAND	0	6	0	3
	LIGAND	0	4	0	2
	LIGAND	0	1	0	1
6	CORE	0	1	0	0
	LIGAND	0	4	0	2
	LIGAND	0	6	0	3
	LIGAND	0	1	0	1

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 6

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 3, 5, 6, 4, 2,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER		AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
ORTHO CORRECTION	1	2	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09
ORTHO CORRECTION	1	3	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09
ORTHO CORRECTION	2	4	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09
ORTHO CORRECTION	3	5	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09
ORTHO CORRECTION	4	6	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09
ORTHO CORRECTION	5	6	1	,570	-1,610	3,6765E-01	4,4047E-03	-6,2666E-06	2,0980E-09

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	12	-4,93816

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

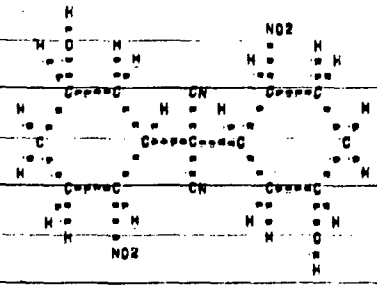
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
2,09928689E+01	2,03406124E-01	-1,99612199E-04	6,82401839E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	65,687413	108,401844	13,661233	108,401844	0,000000	218,220000
300,0	65,892093	108,841911	13,792813	108,403312	,131580	218,351580
400,0	74,784739	129,076998	20,847981	111,110128	7,186748	225,406748
500,0	81,322904	146,507035	28,671278	116,486945	15,010045	233,230045
600,0	85,916032	161,746361	37,047727	122,708891	23,386494	241,606494
700,0	88,973561	175,257100	45,803298	129,339865	32,142064	250,362064
800,0	90,904935	187,274202	54,804901	135,844617	41,143668	259,363668
900,0	92,119594	198,056421	63,960394	142,168464	50,299161	268,519161
1000,0	93,026978	207,810057	73,218577	148,252713	59,557344	277,777344
1200,0	95,557689	224,963669	92,042937	159,645582	78,381704	296,601704
1400,0	101,772597	240,092462	111,687266	170,073867	98,026033	316,246033
1600,0	114,947231	254,446811	133,215958	179,725108	119,554724	337,774724
1800,0	138,357120	269,220812	158,348509	188,838992	144,687276	362,907276
2000,0	175,277793	288,576127	189,459525	197,676981	175,798291	394,018291

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 15

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	20
C	15
O	6
N	4

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	399	C	9	23			1
		C	6	26	2	1	2
		C	12	26	4	1	3
		H	7	21	8	1	0
		H	11	21	6	1	0
2	537	C	6	26			2
		C	6	31	3	1	5
		O	3	26	1	1	4
		C	9	23	6	1	1
		H	3	23	8	1	0
3	399	C	12	26			3
		C	9	23	8	1	1
		C	12	31	3	1	6
		H	15	26	5	1	0
		H	14	24	6	1	0
4	309	O	3	26			4
		C	6	26	5	1	2
		H	1	26	1	1	0
5	399	C	6	31			5
		C	9	34	4	1	7
		C	6	26	7	1	2
		H	3	31	1	1	0
		H	4	33	2	1	0

6	615	C	12	31			6
		C	12	26	7	1	3
		C	9	34	2	1	7
		H	14	33	4	1	0
		NO2	16	31	5	1	0
7	502	C	9	34			7
		C	12	31	6	1	6
		C	6	31	8	1	5
		C	9	39	3	1	8
		H	7	36	2	1	0
8	1185	C	9	39			8
		C	9	34	7	1	7
		C	9	44	3	1	9
		CN	6	39	1	1	0
		CN	12	39	5	1	0
9	502	C	9	44			9
		C	9	39	7	1	8
		C	6	47	2	1	10
		C	12	47	4	1	11
		H	7	42	8	1	0
10	615	C	6	47			10
		C	9	44	6	1	9
		C	6	52	3	1	12
		H	4	45	8	1	0
		NO2	2	47	1	1	0
11	399	C	12	47			11
		C	9	44	8	1	9
		C	12	52	3	1	13
		H	15	47	5	1	0
		H	14	45	6	1	0
12	399	C	6	52			12
		C	6	47	7	1	10
		C	9	55	4	1	14
		H	3	52	1	1	0
		H	4	54	2	1	0
13	587	C	12	52			13
		C	12	47	7	1	11
		C	15	52	5	1	15
		C	9	55	2	1	14
		H	14	54	4	1	0
14	399	C	9	55			14
		C	6	52	8	1	12
		C	12	52	6	1	13
		H	7	57	2	1	0
		H	11	57	4	1	0
15	309	O	15	52			15
		C	12	52	1	1	13
		H	17	52	5	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 2, 5, 7, 6, 3, 1,

RING NUMBER 2 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 9, 10, 12, 14, 13, 11,

COMPLEX LIGANDS 7 AND 9 OF CORE ATOM 8 ARE EQUAL.

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	18	14	6	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	1	0	1	0
	LIGAND	18	14	5	4
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	16	13	6	4
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	0	1	0
	LIGAND	19	15	5	4
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	2	1	1	0
	LIGAND	16	13	5	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	15	12	4	3
	LIGAND	4	2	0	0
	LIGAND	1	0	0	0
	LIGAND	0	0	2	1
7	CORE	0	1	0	0
	LIGAND	4	2	1	0
	LIGAND	5	3	2	1
	LIGAND	10	9	3	3
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	10	6	3	1
	LIGAND	10	6	3	1
	LIGAND	0	1	0	1
	LIGAND	0	1	0	1
9	CORE	0	1	0	0
	LIGAND	10	9	3	3
	LIGAND	9	5	3	1
	LIGAND	1	0	0	0
10	CORE	0	1	0	0
	LIGAND	11	10	3	3
	LIGAND	8	4	1	0
	LIGAND	1	0	0	0
	LIGAND	0	0	2	1
11	CORE	0	1	0	0
	LIGAND	18	14	6	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
12	CORE	0	1	0	0
	LIGAND	12	11	5	4
	LIGAND	6	3	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
13	CORE	0	1	0	0
	LIGAND	16	13	5	4
	LIGAND	1	0	1	0
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
14	CORE	0	1	0	0
	LIGAND	14	12	5	4
	LIGAND	4	2	1	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
15	CORE	0	0	1	0
	LIGAND	19	15	5	4
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 13

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 4, 2, 1, 3, 6, 7, 8, 9, 10, 12, 14, 13, 15,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
RING CORRECTION	1	1	,000	18,800	-1,3120E-01	2,55475E-02	-1,13376E-05	1,03318E-09
RING CORRECTION	2	1	,000	18,800	-1,3120E-01	2,55475E-02	-1,13376E-05	1,03318E-09
GAUCHE ALKANE	7 8	4	3,200					
GAUCHE ALKANE	9 8	4	3,200					
INTERNAL ROTATION	6	1		-1,377				
INTERNAL ROTATION	10	1		-1,377				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	2	-1,37746

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0,00000

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

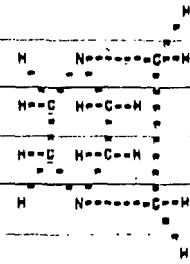
CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-3,188317556E-01	3,23817106E-01	-2,14954274E-04	5,53716684E-08

T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	46,990856	184,187616	3,089954	184,187616	0,000000	-148,460000
300,0	47,411107	184,503342	3,184356	184,188668	,094402	-148,365598
400,0	68,794770	200,872353	8,920786	186,295273	5,830832	-142,629168
500,0	83,208268	217,592487	16,444305	190,883785	13,354351	-135,105649
600,0	96,983830	234,016329	25,474508	196,710739	22,384554	-126,075446
700,0	108,493687	249,857266	35,764214	203,179752	32,674260	-115,785740
800,0	117,950068	264,979272	47,099463	209,987386	44,009509	-104,450491
900,0	125,805205	279,339790	59,299519	216,884717	56,209565	-92,250435
1000,0	132,351329	292,943924	72,216870	223,816608	69,126916	-79,333084
1200,0	142,845440	318,040873	99,779517	237,466237	96,689563	-51,770437
1400,0	152,090254	340,753908	129,271760	250,624047	126,181805	-22,278195
1600,0	162,743607	361,727807	160,709921	263,215578	157,619967	9,159967
1800,0	177,463338	381,693217	194,640294	275,276361	191,550340	43,090340
2000,0	198,907288	401,430045	232,143138	286,903453	229,053184	80,593184

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 16

MOLECULAR STRUCTURE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	12
C	6
N	2

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	815	C	7	4			1
		C	10	4	5	1	3
		N	4	7	2	1	2
		H	4	1	8	1	0
		H	7	1	7	1	0
2	905	N	4	7			2
		C	7	4	6	1	1
		C	4	15	3	1	4
		C	7	10	4	1	5
3	815	C	10	4			3
		N	13	7	4	1	6
		C	7	4	1	1	1
		H	13	1	6	1	0
		H	10	1	7	1	0
4	815	C	4	15			4
		N	4	7	7	1	2
		C	13	15	5	1	7
		H	1	18	2	1	0
		H	4	18	3	1	0
5	815	C	7	10			5
		N	4	7	8	1	2
		C	10	10	5	1	8
		H	7	13	3	1	0
		H	7	7	7	1	0
6	905	N	13	7			6
		C	10	10	2	1	8
		C	10	4	6	1	3
		C	13	15	3	1	7
7	815	C	13	15			7
		C	4	15	1	1	4
		N	13	7	7	1	6
		H	13	18	3	1	0
		H	16	18	4	1	0
8	815	C	10	10			8
		C	7	10	1	1	5
		N	13	7	6	1	6
		H	10	7	7	1	0
		H	10	13	3	1	0

RING NUMBER 1 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 6, 8, 5, 2, 4, 7,

RING NUMBER 2 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 1, 3, 6, 8, 5, 2,

RING NUMBER 3 IS 6 MEMBERED

GROUP NUMBERS OF RING CONSTITUENTS = 1, 3, 6, 7, 4, 2,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	10	5	0	2
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	0	0	1
	LIGAND	8	4	0	1
	LIGAND	4	2	0	0
3	CORE	0	1	0	0
	LIGAND	8	4	0	2
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
4	CORE	0	1	0	0
	LIGAND	8	4	0	2
	LIGAND	2	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	0	0	0	0
6	CORE	0	0	0	1
	LIGAND	4	2	0	0
	LIGAND	4	2	0	1
7	CORE	0	1	0	0
	LIGAND	10	5	0	2
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
8	CORE	0	1	0	0
	LIGAND	0	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 8

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 3, 6, 8, 5, 2, 4, 7,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER	AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
RING CORRECTION	1 2 3	1	3.400					

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
NOT CALCULABLE	1	0.00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	0	0	0	0	0	0.00000

WARNING --- ENTROPY AND FREE ENERGY DATA BELOW MAY BE OFF A FEW PERCENT DUE TO POSSIBLE CONTRIBUTION(S) FROM EXTERNAL ROTATIONAL SYMMETRY OR/AND OPTICAL ISOMERISM.

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-1.49738645E+01	2.27523176E-01	-1.81711793E-04	5.65212831E-08

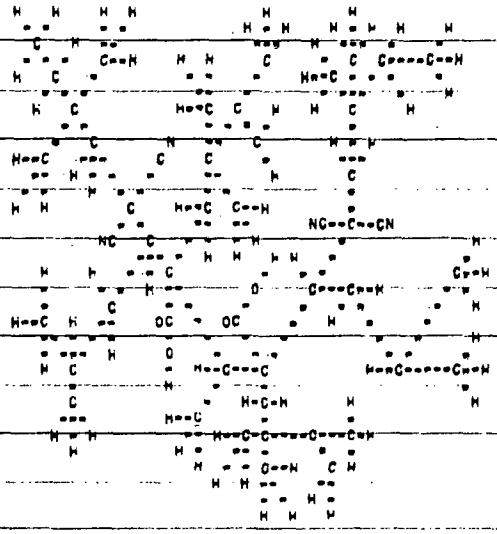
T DEG K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298.0	36.187064	31.880000	4.148791	31.680000	0.000000	12.600000
300.0	38.455102	32.136329	4.225433	31.880854	.076642	12.676642
400.0	50.576861	44.918117	8.697526	33.546278	4.548736	17.148736
500.0	60.424936	57.301349	14.265285	37.068360	10.116494	22.716494
600.0	66.332393	69.043939	20.717893	41.428787	16.569103	29.169103
700.0	74.645380	80.069493	27.878448	46.169982	23.729657	36.329657
800.0	79.688026	90.377977	35.603958	51.059018	31.455167	44.055167
900.0	83.814457	100.009498	43.785346	55.968881	39.636555	52.236555
1000.0	87.358602	109.027297	52.347447	60.828641	48.198656	60.798656
1200.0	94.057743	125.541111	70.482690	70.262861	66.333899	78.933899
1400.0	102.497869	140.634323	90.086623	79.250157	85.937832	98.537832
1600.0	115.392204	155.098198	111.778785	87.629451	107.629994	120.229994
1800.0	135.453767	169.764139	136.721320	96.112734	132.572529	145.172529
2000.0	169.393562	185.488686	166.618975	104.251594	162.470185	175.070185

GROUP ADDITIVITY THERMOCHEMICAL PROPERTIES PROGRAM

CASE NUMBER 17

MOLECULAR STRUCTURE

HYPOTHETICAL MOLECULE



ATOMIC COMPOSITION OF MOLECULE

ATOM	NUMBER
H	78
C	46
O	4
N	4

GROUP STRUCTURE AND COMPOSITION

GROUP NUMBER	GROUP WEIGHT	CHEMICAL SYMBOL OF COMPONENT	GRID ROW COORDINATE	GRID COLUMN COORDINATE	BOND VECTOR	BOND TYPE	GROUP NUMBER OF CORE ATOM
1	296	C	3	3			1
		C	5	5	4	1	2
		H	1	1	8	1	0
		H	1	5	2	1	0
		H	5	1	6	1	0
2	399	C	5	5			2
		C	3	3	8	1	1
		C	7	7	4	1	3
		H	3	7	2	1	0
		H	7	3	6	1	0
3	605	C	7	7			3
		C	5	5	8	1	2
		C	4	10	2	1	4
		C	9	9	4	1	5
		C	10	4	6	1	6
4	296	C	4	10			4
		C	7	7	8	1	3
		H	1	10	1	1	0
		H	1	13	2	1	0
		H	4	13	3	1	0
5	399	C	9	9			5
		C	7	7	8	1	3
		C	13	13	4	1	7
		H	12	9	5	1	0
		H	11	7	6	1	0
6	296	C	10	4			6
		C	7	7	2	1	3
		H	13	4	5	1	0
		H	13	1	6	1	0
		H	10	1	7	1	0
7	1165	C	13	13			7
		C	9	9	8	1	5
		C	15	15	4	1	8
		CN	10	16	2	1	0
		CN	15	11	6	1	0
8	502	C	15	15			8
		C	13	13	8	1	7
		C	17	17	4	1	9
		C	19	11	6	1	10
		H	18	15	5	1	0

9	1161	C	17	17			9
		C	15	15	8	1	8
		C	13	21	2	1	11
		C	23	23	4	1	12
		CO	20	17	5	1	13
10	399	C	19	11			10
		C	15	15	2	1	8
		C	23	7	6	1	14
		H	22	11	5	1	0
		H	17	9	8	1	0
11	399	C	13	21			11
		C	17	17	6	1	9
		C	10	21	1	1	15
		H	13	18	7	1	0
		H	16	21	5	1	0
12	502	C	23	23			12
		C	17	17	8	1	9
		C	23	27	3	1	16
		C	26	20	6	1	17
		H	23	20	7	1	0
13	981	CO	20	17			13
		C	17	17	1	1	9
		O	22	17	5	1	18
14	502	C	23	7			14
		C	19	11	2	1	10
		C	25	7	5	1	24
		C	20	4	8	1	25
		H	20	7	1	1	0
15	1479	C	10	21			15
		C	13	21	5	1	11
		C	7	21	1	1	19
		C	7	24	2	1	20
		C	13	24	4	1	21
16	1161	C	23	27			16
		C	23	23	7	1	12
		CO	20	24	8	1	26
		C	18	32	2	1	27
		C	25	27	5	1	28
17	296	C	26	20			17
		C	23	23	2	1	12
		H	29	20	5	1	0
		H	28	18	6	1	0
		H	26	17	7	1	0
18	665	O	22	17			18
		CO	20	17	1	1	13
		H	24	17	5	1	0
19	296	C	7	21			19
		C	10	21	5	1	15
		H	7	18	7	1	0
		H	4	18	8	1	0
		H	4	21	1	1	0
20	1237	C	7	24			20
		C	10	21	6	1	15
		C	4	27	2	1	22
		C	9	26	4	2	23
21	296	C	13	24			21
		C	10	21	8	1	15
		H	13	27	3	1	0
		H	15	26	4	1	0
		H	16	24	5	1	0
22	1170	C	4	27			22
		C	7	24	6	1	20
		H	2	25	8	1	0
		H	1	27	1	1	0
		H	2	29	2	1	0
23	1031	C	9	26			23
		C	7	24	8	2	20
		H	7	28	2	1	0
		H	11	28	4	1	0
24	296	C	25	7			24
		C	23	7	1	1	14
		H	27	9	4	1	0
		H	28	7	5	1	0
		H	27	5	6	1	0
25	296	C	20	4			25
		C	23	7	4	1	14
		H	23	4	5	1	0
		H	20	1	7	1	0
		H	17	4	1	1	0
26	981	CO	20	24			26
		C	23	27	4	1	16
		O	18	26	2	1	29
27	502	C	18	32			27
		C	23	27	6	1	16
		C	14	36	2	1	30
		C	18	36	3	1	31
		H	16	30	8	1	0

28	399	C	25	27			28
		C	23	27	1	1	16
		C	27	27	5	1	32
		H	29	29	3	1	0
		H	25	25	7	1	0
29	865	O	18	26			29
		CO	20	24	6	1	26
		H	16	28	2	1	0
30	1165	C	14	36			30
		C	18	32	6	1	27
		C	11	36	1	1	33
		CN	14	33	7	1	0
		CN	14	39	3	1	0
31	399	C	18	36			31
		C	18	32	7	1	27
		C	23	41	4	1	34
		H	18	39	3	1	0
		H	20	34	6	1	0
32	1479	C	27	27			32
		C	25	27	1	1	28
		C	27	32	3	1	40
		C	29	27	5	1	41
		C	27	25	7	1	42
33	399	C	11	36			33
		C	14	36	5	1	30
		C	7	36	1	1	35
		H	9	34	8	1	0
		H	9	38	2	1	0
34	502	C	23	41			34
		C	18	36	8	1	31
		C	17	47	2	1	45
		C	23	47	3	1	46
		H	23	38	7	1	0
35	605	C	7	36			35
		C	11	36	5	1	33
		C	5	34	8	1	36
		C	4	36	1	1	37
		C	4	39	2	1	38
36	296	C	5	34			36
		C	7	36	4	1	35
		H	7	32	6	1	0
		H	5	31	7	1	0
		H	3	32	8	1	0
37	296	C	4	36			37
		C	7	36	5	1	35
		H	2	34	8	1	0
		H	1	36	1	1	0
		H	2	38	2	1	0
38	399	C	4	39			38
		C	7	36	6	1	35
		C	4	44	3	1	39
		H	2	41	2	1	0
		H	7	42	4	1	0
39	296	C	4	44			39
		C	4	39	7	1	38
		H	2	46	2	1	0
		H	4	47	3	1	0
		H	6	46	4	1	0
40	1237	C	27	32			40
		C	27	27	7	1	32
		C	27	36	3	1	43
		C	29	34	4	2	44
41	296	C	29	27			41
		C	27	27	1	1	32
		H	29	30	3	1	0
		H	32	30	4	1	0
		H	32	27	5	1	0
42	296	C	27	25			42
		C	27	27	3	1	32
		H	30	25	5	1	0
		H	30	22	6	1	0
		H	27	22	7	1	0
43	1170	C	27	36			43
		C	27	32	7	1	40
		H	25	36	1	1	0
		H	27	38	3	1	0
		H	29	36	5	1	0
44	1031	C	29	34			44
		C	27	32	8	2	40
		H	32	34	5	1	0
		H	31	32	6	1	0
45	296	C	17	47			45
		C	23	41	6	1	34
		H	15	49	2	1	0
		H	17	50	3	1	0
		H	19	49	4	1	0
46	296	C	23	47			46
		C	23	41	7	1	34
		H	21	49	2	1	0
		H	23	50	3	1	0
		H	25	49	4	1	0

COMPLEX LIGANDS 19 AND 21 OF CORE ATOM 13 ARE EQUAL,

COMPLEX LIGANDS 36 AND 37 OF CORE ATOM 35 ARE EQUAL,

COMPLEX LIGANDS 45 AND 46 OF CORE ATOM 34 ARE EQUAL,

COMPLEX LIGANDS 41 AND 42 OF CORE ATOM 32 ARE EQUAL,

COMPLEX LIGANDS 9 AND 16 OF CORE ATOM 12 ARE EQUAL,

COMPLEX LIGANDS 24 AND 25 OF CORE ATOM 14 ARE EQUAL,

COMPLEX LIGANDS 4 AND 6 OF CORE ATOM 3 ARE EQUAL,

ATOMIC COMPOSITION OF CORE ATOM AND LIGANDS IN EACH GROUP

GROUP NUMBER	SUBGROUP	H	C	O	N
1	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
2	CORE	0	1	0	0
	LIGAND	73	46	4	4
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
3	CORE	0	1	0	0
	LIGAND	5	2	0	0
	LIGAND	3	1	0	0
	LIGAND	67	43	4	4
	LIGAND	3	1	0	0
4	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
5	CORE	0	1	0	0
	LIGAND	11	5	0	0
	LIGAND	65	42	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
6	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
7	CORE	0	1	0	0
	LIGAND	13	6	0	0
	LIGAND	65	39	4	2
	LIGAND	0	1	0	1
	LIGAND	0	1	0	1
8	CORE	0	1	0	0
	LIGAND	13	9	0	2
	LIGAND	55	34	4	2
	LIGAND	9	4	0	0
	LIGAND	1	0	0	0
9	CORE	0	1	0	0
	LIGAND	23	14	0	2
	LIGAND	13	7	0	0
	LIGAND	41	25	2	2
	LIGAND	1	1	2	0
10	CORE	0	1	0	0
	LIGAND	69	44	4	4
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
11	CORE	0	1	0	0
	LIGAND	65	41	4	4
	LIGAND	11	6	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
12	CORE	0	1	0	0
	LIGAND	37	23	2	2
	LIGAND	37	23	2	2
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
13	CORE	0	1	1	0
	LIGAND	77	47	2	4
	LIGAND	1	0	1	0
14	CORE	0	1	0	0
	LIGAND	71	45	4	4
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
15	CORE	0	1	0	0
	LIGAND	67	42	4	4
	LIGAND	3	1	0	0
	LIGAND	5	3	0	0
	LIGAND	3	1	0	0

16	CORE	0	1	0	0
	LIGAND	41	25	2	2
	LIGAND	1	1	2	0
	LIGAND	23	14	0	2
	LIGAND	13	7	0	0
17	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
18	CORE	0	0	1	0
	LIGAND	77	48	3	4
	LIGAND	1	0	0	0
19	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
20	CORE	0	1	0	0
	LIGAND	73	45	4	4
	LIGAND	3	1	0	0
	LIGAND	2	1	0	0
21	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
22	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
23	CORE	0	1	0	0
	LIGAND	76	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
24	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
25	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
26	CORE	0	1	1	0
	LIGAND	77	47	2	4
	LIGAND	1	0	1	0
27	CORE	0	1	0	0
	LIGAND	55	34	4	2
	LIGAND	13	9	0	2
	LIGAND	9	4	0	0
	LIGAND	1	0	0	0
28	CORE	0	1	0	0
	LIGAND	65	41	4	4
	LIGAND	11	6	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
29	CORE	0	0	1	0
	LIGAND	77	48	3	4
	LIGAND	1	0	0	0
30	CORE	0	1	0	0
	LIGAND	65	39	4	2
	LIGAND	13	6	0	0
	LIGAND	0	1	0	1
	LIGAND	0	1	0	1
31	CORE	0	1	0	0
	LIGAND	69	44	4	4
	LIGAND	7	3	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
32	CORE	0	1	0	0
	LIGAND	67	42	4	4
	LIGAND	5	3	0	0
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0

33	CORE	0	1	0	0
	LIGAND	65	42	4	4
	LIGAND	11	5	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
34	CORE	0	1	0	0
	LIGAND	71	45	4	4
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
35	CORE	0	1	0	0
	LIGAND	67	43	4	4
	LIGAND	3	1	0	0
	LIGAND	3	1	0	0
	LIGAND	5	2	0	0
36	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
37	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
38	CORE	0	1	0	0
	LIGAND	73	46	4	4
	LIGAND	3	1	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
39	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
40	CORE	0	1	0	0
	LIGAND	73	45	4	4
	LIGAND	3	1	0	0
	LIGAND	2	1	0	0
41	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
42	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
43	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
44	CORE	0	1	0	0
	LIGAND	76	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
45	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
46	CORE	0	1	0	0
	LIGAND	75	47	4	4
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0
	LIGAND	1	0	0	0

NUMBER OF CORE ATOMS IN LONGEST CHAIN = 15

GROUP NUMBER OF CORE CONSTITUENTS OF LONGEST CHAIN = 1, 2, 3, 5, 7, 8, 9, 12, 16, 27, 30, 33, 35, 38, 39,

NONGROUP INTERACTION AND INTERNAL ROTATIONAL SYMMETRY CONTRIBUTIONS

TYPE	RING NUMBER OR GROUP NUMBER		AMOUNT	HEAT OF FORMATION KCAL	ENTROPY CAL/DEG K	HEAT CAPACITY COEFFICIENTS CAL/DEG K	CAL/DEG K**2	CAL/DEG K**3	CAL/DEG K**4
GAUCHE ALKANE	2	3	2	1,600					
GAUCHE ALKANE	3	5	2	1,600					
GAUCHE ALKANE	5	7	2	1,600					
GAUCHE ALKANE	7	8	4	3,200					
GAUCHE ALKANE	8	9	4	3,200					
GAUCHE ALKANE	8	10	1	,800					
GAUCHE ALKANE	9	11	2	1,600					
GAUCHE ALKANE	9	12	4	3,200					
GAUCHE ALKANE	10	14	1	,800					
GAUCHE ALKANE	11	15	2	1,600					
GAUCHE ALKANE	12	16	4	3,200					
GAUCHE ALKANE	16	27	4	3,200					
GAUCHE ALKANE	16	28	2	1,600					
GAUCHE ALKANE	27	30	4	3,200					
GAUCHE ALKANE	27	31	1	,800					
GAUCHE ALKANE	28	32	2	1,600					
GAUCHE ALKANE	30	33	2	1,600					
GAUCHE ALKANE	31	34	1	,800					
GAUCHE ALKANE	33	35	2	1,600					
GAUCHE ALKANE	35	38	2	1,600					
GAUCHE ALKENE	9	13	2	,500					
GAUCHE ALKENE	15	20	2	,500					
GAUCHE ALKENE	16	26	2	,500					
GAUCHE ALKENE	32	40	2	,500					
INTERNAL ROTATION	1		1		-2,183				
INTERNAL ROTATION	4		1		-2,183				
INTERNAL ROTATION	6		1		-2,183				
INTERNAL ROTATION	17		1		-2,183				
INTERNAL ROTATION	19		1		-2,183				
INTERNAL ROTATION	21		1		-2,183				
INTERNAL ROTATION	22		1		-2,183				
INTERNAL ROTATION	24		1		-2,183				
INTERNAL ROTATION	25		1		-2,183				
INTERNAL ROTATION	36		1		-2,183				
INTERNAL ROTATION	37		1		-2,183				
INTERNAL ROTATION	39		1		-2,183				
INTERNAL ROTATION	41		1		-2,183				
INTERNAL ROTATION	42		1		-2,183				
INTERNAL ROTATION	43		1		-2,183				
INTERNAL ROTATION	45		1		-2,183				
INTERNAL ROTATION	46		1		-2,183				

EXTERNAL ROTATIONAL SYMMETRY CONTRIBUTION

SOURCE	SYMMETRY NUMBER	ENTROPY
COMPUTED	1	0,00000

OPTICAL ISOMER CONTRIBUTION

SOURCE	ASYMMETRIC	PSEUDOASYMMETRIC	ENANTIOMERS	MESO	TOTAL OPTICAL ISOMERS	ENTROPY
COMPUTED	4	1	12	4	16	5,50985

GROUP NUMBER OF ASYMMETRIC CARBON ATOM(S) = 8, 9, 16, 27,

GROUP NUMBER OF PSEUDOASYMMETRIC CARBON ATOM = 12

THERMOCHEMICAL PROPERTIES OF MOLECULE

HEAT CAPACITY COEFFICIENTS

CAL/DEG-MOLE	CAL/DEG**2-MOLE	CAL/DEG**3-MOLE	CAL/DEG**4-MOLE
-2,56412355E+01	1,02206455E+00	-6,53203824E-04	1,60886340E-07

T DEG-K	C(P) CAL/DEG-MOLE	S CAL/DEG-MOLE	H(T)-H(0) KCAL/MOLE	-(G(T)-H(298))/T CAL/DEG-MOLE	H(T)-H(298) KCAL/MOLE	DELHF(298)+H(T)-H(298) KCAL/MOLE
298,0	225,104519	525,954945	32,295776	525,954945	0,000000	-326,700000
300,0	226,533717	527,465711	32,747495	525,959981	,451719	-326,248281
400,0	286,966699	601,417773	58,603328	535,648893	26,307552	-300,392448
500,0	342,200876	671,779735	90,234474	555,902338	57,938698	-268,761302
600,0	387,195568	738,245249	126,768920	580,610009	94,473144	-232,226856
700,0	424,918091	800,871697	167,431182	607,671116	135,135406	-191,564594
800,0	456,333764	859,727219	211,542310	635,669051	179,246534	-147,453466
900,0	482,467904	915,026692	258,519884	663,668572	226,224108	-100,475892
1000,0	504,105831	967,012609	307,878017	691,430368	275,582241	-51,117759
1200,0	538,234314	1062,087480	412,275070	745,438068	379,979294	53,279294
1400,0	566,441757	1147,201622	522,777006	796,857886	490,481231	163,781231
1600,0	596,450704	1224,735585	638,971873	845,563025	606,676097	279,976097
1800,0	635,983699	1297,138655	761,992224	891,751739	729,696449	402,996449
2000,0	692,763288	1366,899733	894,515125	935,790058	862,219350	535,519350

Table 4-3 (Page 1 of 3)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
        1  0  0  0
     H  H
     -  -
  H-C--C-H
     -  -
     H  H
  ***
```

```
        0  0  0  0
           H H H H H H H H
           - - - - - - - -
        H-C-C-C-C-C-C-C-C-O-H
           - - - - - - - -
           H H H H H H H H
  ***
```

```
        0  0  0  0
           H H H H
           - - - - O
        H-C-C-C-C-C-H
           - - - -
           H H H H
  ***
```

```
        0  0  0  0
     H  H  H H  H  H
      - - -   - - -
  H   ---     ---   H
   -   C       C   -
      -  -     -  -
  H--C-C---O---C-C--H
      -  -     -  -
   -   C       C   -
  H   ---     ---   H
      - - -   - - -
     H  H  H H  H  H
  ***
```

Table 4-3 (Page 2 of 6)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
        0   0   0   0
            H   H   H
            -   -   -
        H-C-C-C-CN
            -   -   -
            H   H   H
***
```

```
        0   0   0   0
                                                                    H   H
                                                                    -   -
                                                                H   C   H
                                                                -   -   -   -
                                                            H--C       C--H
                                                            -           -
                                                            -           -
                H   H   H   H   H   H   H
                -   -   -   -   -   -   -
            H--C--C--C--C--C--C--C---C       C--H
                -   -   -   -   -   -   -   -   -   -   -
                H   H   H   H   H   H   H   H   C   H
                                                    -   -
                                                    H   H
***
```

```
        0   0   0   0
      H
      -
      C
      -
      C
    - =
H-C     C-H
  =     -
  =     -
H-C     C-H
    - =
      C
      -
      H
***
```

Table 4-3 (Page 3 of 6)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
 0  0  0  0
          H     H
        H - H H - H
         ---   ---
H     C     C     H     H     H
-     -     -     -     -     -
-     -     -     -     -     -
H--C-----C-----C-----C-----C-----C--H
-     -     -     -     -     -
-     -     -     -     -     -
H     C     H     H     H     H
       ---
      H - H
        H
***
```

```
 0  0  0  0
          H     H
           -     -
          C=C
           -     -
          C     H
         - =
      H--C   C--H
         =     -
         =     -
      H--C   C--H
         - =
          C
          -
          -
          H
***
```

```
 0  0  0  0
          H     H
           -     -
          N
          -
          -
          C
         - =
      H--C   C--H
         =     -
         =     -
      H--C   C--H
         - =
          C
          -
          -
          H
***
```

Table 4-3 (Page 4 of 6)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
        0  4  0  0
      H    H
      -    -
      C    C
     = - - =
H-C    C    C-H
  -    =    -
H-C    C    C-H
     = - - =
      C    C
      -    -
      H    H
***
```

```
        0  1  0  0
                H    H
                - -
H    H    H    C
- -            - - -
  C            C    H
- -            - -
H    C---C    H
     --   --
  H - H - H
     -    --
H--C    C
  - - - -
  H    C    H
       - -
     H    H
***
```

```
        0  0  0  0
        H
        -
H   H-C-H   H
 -    -    -
  -   -   -
H--C-C-C--H
  -   -   -
 -    H    -
H           H
***
```

Table 4-3 (Page 5 of 6)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
        0   0   0   0
        N
        C
        -
        C
      - =
NC-C    C-CN
    =   -
NC-C    C-CN
      - =
        C
        -
        C
        N
***
```

```
        0   0   0   0
                          H
                          -                    NO2
                       H  O     H                -     H
                        - -     - H           H -     - H
                        --      --            --      --
                          C----C        CN      C----C
                     H    -       -    H  -  H    -       -    H
                        - -       - -    -    - -         - -
                       C          C----C----C          C
                        - -       -      -      -       - -
                     H    -       -      -      -       -    H
                          C----C        CN      C----C
                          --      --            --      --
                       H  -     - H           H -     - H
                          H     -               H     O
                                NO2                     -
                                                        H
***
```

```
        0   0   0   0
                          H
                          -
                          -
H       N-------C--H
  -   - -       -
   - -    -     -
H--C   H--C--H  -
   -      -     -
   -      -     -
H--C   H--C--H  -
   - -    -     -
  -   - -       -
H       N-------C--H
                          -
                          -
                          H
***
```

Table 4-3 (Page 6 of 6)

LIST OF INPUT DATA FOR SAMPLE CALCULATIONS

```
                                                                  HYPOTHETICAL   MOLECULE
      0   0   0   0
H    H     H   H                    H          H
 - -       - -                  H - H      H - H   H      H
  C    H   --                     ---    H   ---   -      -
 - - -    C--H      H   H        C       -   C   C----C--H
H    C    -            - -      -      H--C - - -      -
   - - -               --      -          - ---    -      H
  H    C              H--C   C    H    H    C       H
     - -                - - = -            -
     -    C         N    --    C         H - H
H--C    ---        C     C      -          ---
  --   H - -    -        --       H          C
 - -     H   - -          - -                -
H   H          C      H--C   C--H            -
             - -        --   --        NC--C--CN
          NC    C    - -   - H            -                    H
                ---  -   H   H    H H    -                    -
    H     H    - - C            -    - -                    C--H
    -       - -   H --          O       C---C--H          - -
    -        C      - -       -       -    - -          -    H
H--C   H   --      OC   -   OC       -    H    -       -
   -- - - -         -    -    -    -            -    -       H
   - ---   H        O      -    - -                - -       -
   H   C            -   H--C---C              H--C-----C--H
       -            H      -     -                            -
       C                 -    H-C-H        H                 H
     ---            H--C        -          -
    H - H             -- H--C-C----C---C-H
      H              H -    -- -       =  -
                       H   - - C--H    C  H
                         H   H --      --
                                - -   H -
                                H   H    H
```

***

Section 5
LOGIC FRAMEWORK OF PROGRAM

The TGAP program is written in the proposed American Standard version of the FORTRAN IV interpretive language. No machine language routines nor nongeneralized FORTRAN statements that are unique to specific compilers are employed. The intent, of course, is to be able to run the program on essentially any computer system without the need of modification or revision.

The program is composed of 55 routines. These are listed in Appendix B. A complete glossary of the program variables is presented in Appendix C. TGAP is also the name of the main routine in the program which calls the principal subprograms into execution. Figure 5-1 gives the logic flow chart for TGAP.

There are three main divisions in the logic structure of the program. Each of these is discussed in some detail below. Described herein are also the basic rules and decisions which govern the calculation of the various nonring interaction corrections and symmetry contributions of the molecule.

5.1 PROCEDURE FOR GROUP IDENTIFICATION

Section 1 of the program is concerned with the identification of the groups and group components as well as the group weights, bond vectors, and bond types.

Subroutine STAND is the control subprogram for Section 1. There are a total of 12 routines employed in this section. The cross reference map is displayed in Figure 5-2. Several routines such as IDENT, ASSIGN, BOND, NUMBER, SUMATM perform different basic functions and are employed more than once.

Subroutine STAND controls the scanning of the graphic formula input array GRID (i, j) of the molecule. The scan order is first rows then columns, starting with the left uppermost location (1, 1) of the array. Unless an error was

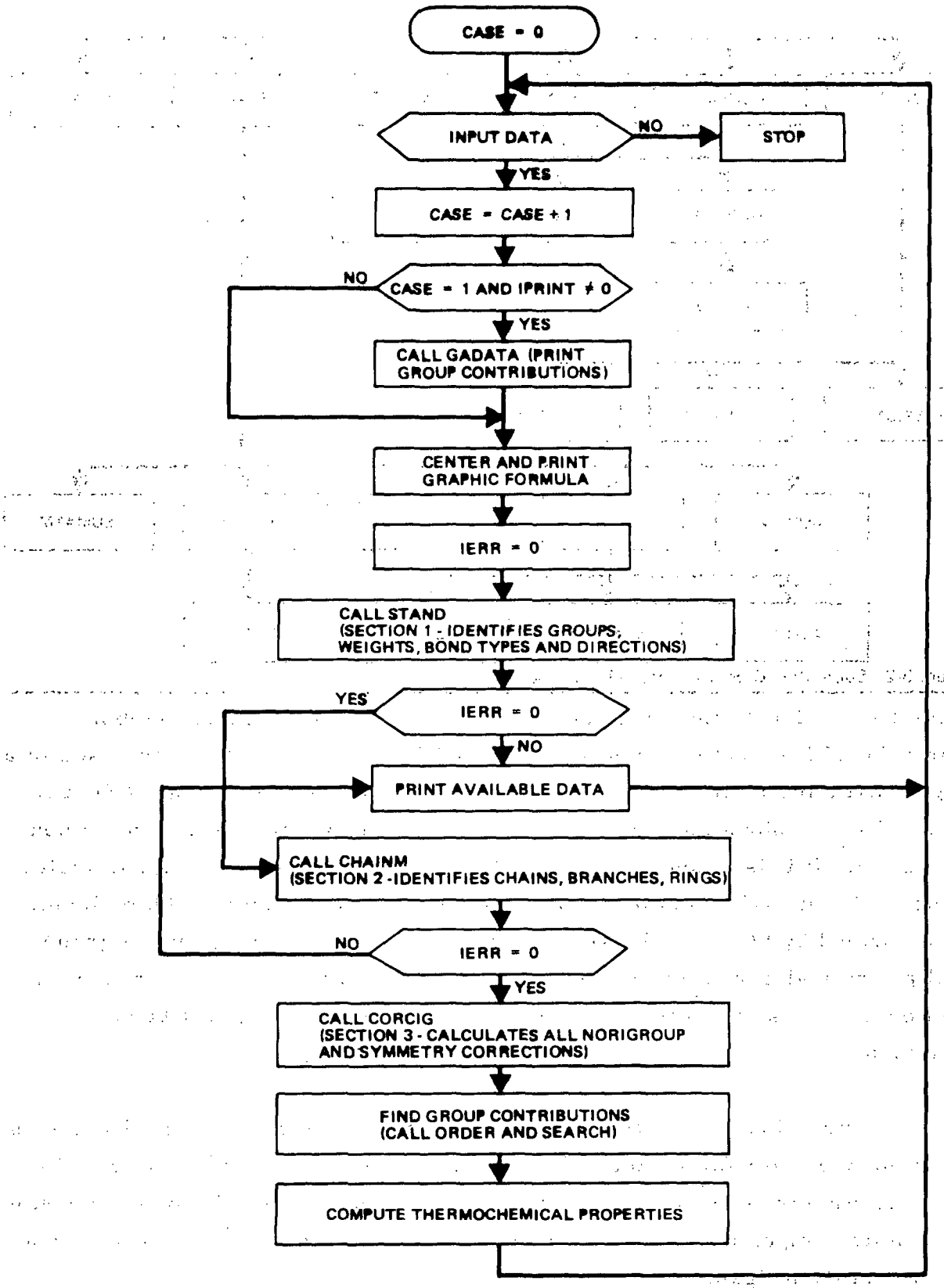


Figure 5-1. Flow Chart for Main Control Routine TGAP

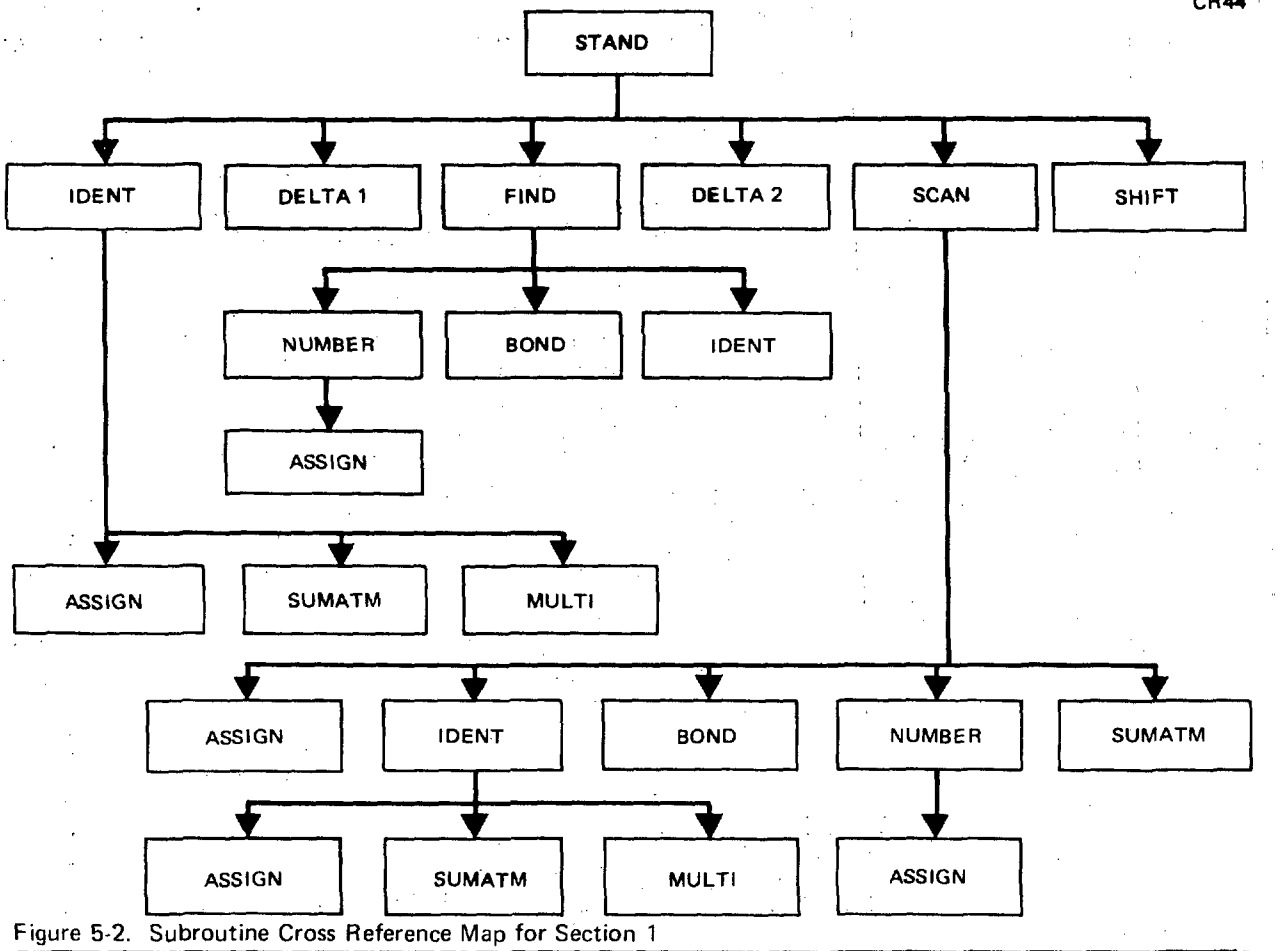
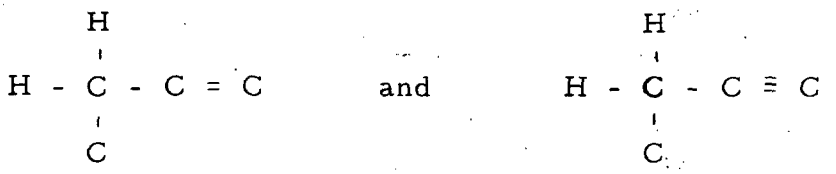


Figure 5-2. Subroutine Cross Reference Map for Section 1

committed on input, the first nonblank character is a chemical symbol. Subroutine IDENT determines if the symbol is valid and if it is composed of a single character or more than one character, such as the radicals CO, CN, NO and NO_2. Subroutine FIND ascertains if the first atom is a core or noncore atom. If it is a noncore atom, it finds the core atom of this particular group. The identification of all the other group components in the molecule is performed by SCAN. The scan operation proceeds from group to group until a terminal core atom is reached. If branch structures are present, the scan operation is then shifted to a new branch which has not yet been examined.

The scan directions are set by Subroutine ASSIGN. Subroutine BOND checks the validity of symbols used as chemical bonds and scans same until a different character is encountered. In Section 1, Subroutine SUMATM computes the atomic composition of the molecule and later in Section 3 the atomic composition of each ligand.

The identification weight for the core atom and all ligand atoms of a group is computed by Subroutine DELTA1. The group weight is modified by Subroutine DELTA2 when one or more of the ligand atoms is also bonded to a surrounding carbon atom by means of a double or triple bond, as for example in the groups



The group weight is altered once more in Section 3 of the program if aromatic carbon atoms are present in the molecule. In order to execute this operation, however, all ring structures must already have been classified.

The presence of a ring structure is manifested when the identity flag of a particular core atom about to be scanned registers 1000, thus indicating the atom has already been processed in a previous cycle. This will activate the ring identification operations in Sections 2 and 3.

Several important molecular property arrays and variables are generated in this section. These include array IX (i, j, k) which contains the basic structural data described in 3.2.3, the connectivity array KON(i), the core atom arrays NC(i) and NW(i), the group weight array MOLWT(i), the branch atom array IDBR(i), the total number of branch atoms NOBR and the total number of core atoms KCC.

5.2 PROCEDURES FOR CHAIN AND RING IDENTIFICATION

Section 2 of the program identifies all the chain segments and the components of each unique ring in the molecule. Subroutine CHAINM is the control subprogram for Section 2. A total of 8 routines are employed in this section. The cross reference map for these subroutines is presented in Figure 5-3.

Subroutine CHAINM monitors the calculation of the chain properties. For this purpose the first element in the first chain is set equal to the first terminal core atom in the molecule. If no such atom is present, each core

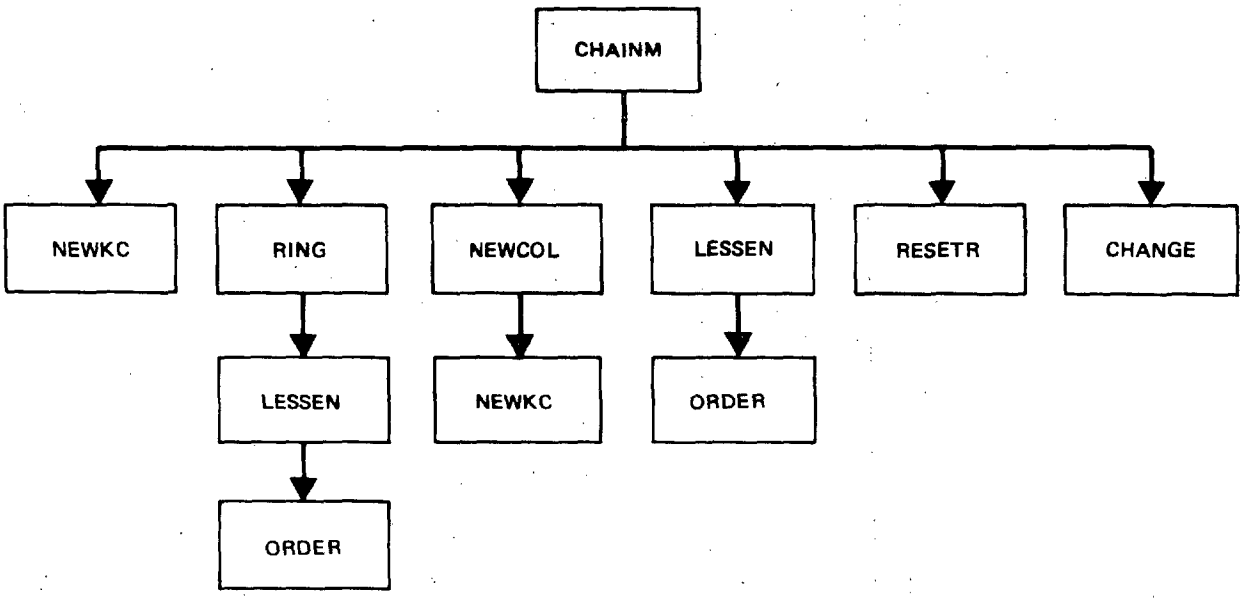


Figure 5-3. Subroutine Cross Reference Map for Section 2

atom in the molecule must be a component of a ring structure. In this case, the first element is set equal to the core atom of group number one. The core atom bonded to element one becomes the second element in the chain, and so on, until a ring closure or a terminal atom is reached. All linkage information is derived from the IX molecular property array.

If a terminal atom is reached and there are branch junctions in the molecule, Subroutine NEWCOL constructs the new chain by first locating the nearest branch atom with unused core ligands. Subroutine NEWKC finds the group number of the core ligand which is to replace the previous chain segment of the branch. The procedure is continued until all the core ligands of every branch atom have been processed. In this cycle the group numbers of the components of each chain are stored in array NBC(i, j), the locations of the branch atoms in each chain in array NBX (i, j), and the total number of components and branch atoms in each chain in array NBS(i, j).

In the event the presence of a ring was detected in Section 1, the program now checks each new element in the chain for ring closure. When this occurs, the particular chain is closed and a new chain is started by Subroutine NEW-COL providing, of course, there are still new chain segments to be formed. One advantage of this procedure is that the ring components are defined simultaneously with the chain elements. Subroutine RING copies the ring components and ring size in array IRING(i, j). When polycyclic fused ring structures are present, the same ring may be identified more than once with the ring elements stored in a different order. Subroutine RING also checks for situations such as this and eliminates the duplicate ring structures.

When all the chain segments have been constructed, three data checks are performed that may lead to a redefinition of the number and size of the ring structures and the length of the chains:

A. If more than one ring is present, each ring is checked by Subroutine LESSEN to determine whether it is a basic cyclic unit and not a composite of two or more ring units. All composite ring structures are discarded.

B. If the first atom in the first chain is a ring atom and two or more rings are present separated by a chain segment, it is likely the lengths of all the chains can be increased the same amount simply by shifting the initial scan location of the ring next to the branch point. This is accomplished by Subroutine RESETR. Case 15 in Section 4 is an example of this type of situation.

C. Subroutine CHANGE will also increase the lengths of all the chains an equal amount if there is a chain that contains only one branch atom and more "non-similar" atoms than "similar" atoms. The "similar" atoms are those atoms listed first in the chain and common to all the chains in the molecule. This type of situation is illustrated below with an example of a chain and ring identification procedure. The core atom group numbers that appear in the skeleton drawing of the molecule demonstrate the order in which the

graphic formula is scanned in Section 1. Each column contains the group numbers of the elements in the chain. Prior to the execution of CHANGE the "similar" atoms consisted of atoms 1, 2, and 3.

```
                    C 8                    12   14
                    C 5                    C = C
                                         /       \
C - C - C - C 4 - C - C - C                         C
1   2   3         6   9   11\             /16
                            C - C
                            13   15
                    C 7
                    C 10
                    C 17
                    C 18
```

Chain One: 18, 17, 10, 7, 4, 5, 8

Chain Two: 18, 17, 10, 7, 4, 6, 9, 11, 12, 14, 16, 15, 13 (ring components)

Chain Three: 18, 17, 10, 7, 4, 3, 2, 1

5.3 PROCEDURES FOR DETERMINATION OF NONGROUP INTERACTIONS AND SYMMETRY

Section 3 of the program is a multi-functional logic structure that computes the various nonbonded, nongroup molecular interaction corrections, the contributions for internal and external rotational symmetry and the entropy of mixing contribution associated with the asymmetry or optical activity of the molecule.

Subroutine CORCIG is the main or control subprogram of Section 3. A total of 33 subroutines compose the logic structure of this section. The subroutine cross reference map is depicted in Figure 5-4. The logic and computational procedures associated with the principal functions of this section are described below.

5.3.1 Gauche Interactions

The program identifies the gauche alkane, alkene and ether interactions of the molecule and computes the total contribution of each to the heat of

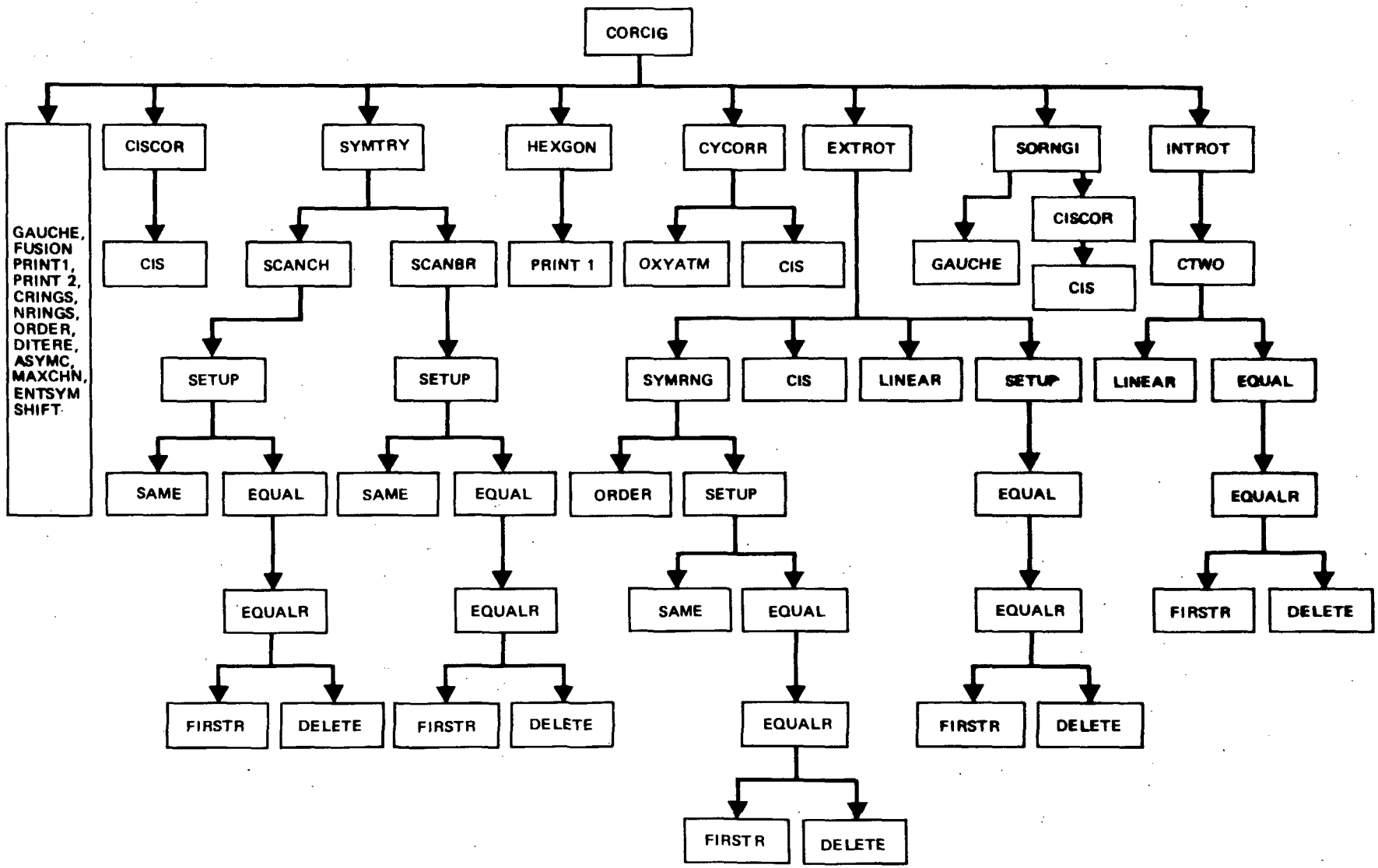


Figure 5-4. Subroutine Cross Reference Map for Section 3

formation. The individual gauche contributions are small as shown in Appendix A. In highly branched molecules, however, the sum of these contributions can amount to several kilocalories.

Table 5-1 depicts the various types of gauche interactions and gives the rules used to establish the presence or absence of gauche configurations. Actually the two central atoms M_1 and M_2 in the gauche alkane and gauche alkene type interactions can be either (a) two non-ring atoms or (b) one ring and one non-ring atom. An example of the latter is found in the compound cis-1-methyl, 2-ethyl cyclopentane. In the drawing below the two central carbon atoms involved in the interaction are labelled 1 and 2. Also refer to Case 12 in Section 4 for the thermochemical property calculations of this molecule.

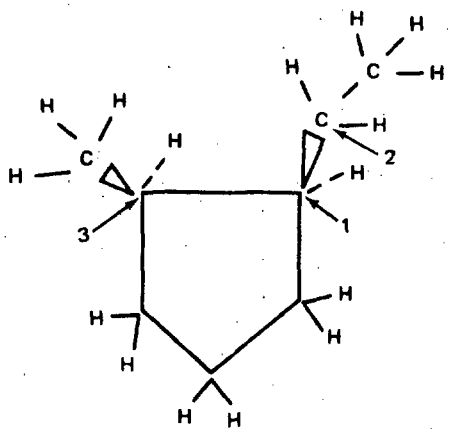


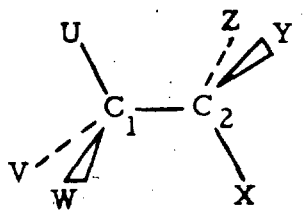
Table 5-2 gives the number of gauche interactions associated with the most stable configuration of each type which are not already included in the group value of M_1 or M_2. For example, in the linkage $(C)_3C\text{-}C(C)(=C)$ the gauche interaction between the double bonded carbon ligand and the ligands of the first carbon is taken into account by the group $C(C)_3(C_d)$, in which C_d represents a carbon atom double bonded to another carbon atom. Hence, this interaction is not included in the table. Furthermore, in accord with Reference 2, the gauche interaction for $(C)(H)_2C\text{-}C(C)(C_d)$ is ignored due to the small magnitude of this correction. The central atoms represented in the table are of the carbon-carbon, carbon-nitrogen, and ether types. The central atoms are not included in the ligand count. The columns entitled Type 2 give the number of ligands bonded to atoms one and two which are of the type designated by Rule 2 (cf. Table 5-1). Those configurations with a total of 6 ligands (3 and 3) are gauche alkane interactions whereas the 2-3

combination represent gauche alkene types. In the ethers, the maximum number of interactions is less since oxygen has only the one CO ligand in addition to the CO ligand that constitutes the central bond.

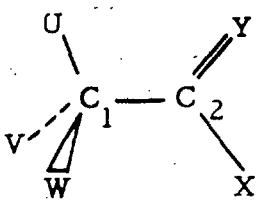
Table 5-1

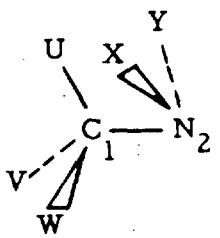
RULES FOR DETERMINATION OF GAUCHE INTERACTIONS

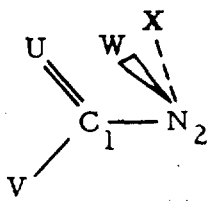
Alkane



Alkene

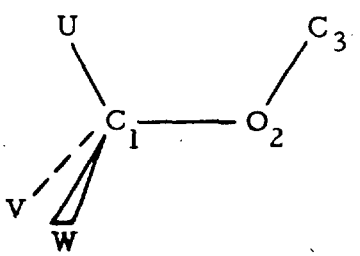






1. Atoms 1 and 2 must be carbon atoms or a carbon and a nitrogen atom of the indicated connectivities.
2. Ligand U, X etc. must be a heavy (non-hydrogen) atom.

Ether



1. Atoms 1 and 2 must be a carbon and oxygen atom of the indicated connectivities.
2. Ligand U, V, and W must be a heavy (non-hydrogen) atom. Atom 3 must be a carbon atom.

The gauche interaction configurations are identified by Subroutine GAUCHE. Each pair of carbon atoms in the molecule is checked for the presence of gauche formations according to the rules of Table 5-1. Use is also made of

Table 5-2

NUMBER OF GAUCHE INTERACTIONS FOR C-C, C-N AND C-O CENTRAL ATOMS

Atom(1)	Ligands	Type 2	Atom(2)	Ligands	Type 2	Interactions
C	1, 2, 3	0, 1, 2, 3	C	3	0	0
C	1, 2, 3	0	C	3	0, 1, 2, 3	0
C	3	1	C	3	1	0
C	3	2	C	3	1	1
C	3	3	C	3	1	2
C	3	2	C	3	2	2
C	3	3	C	3	2	4
C	3	3	C	3	3	6
C	2	1	C	3	1	0
C	2	2	C	3	1	0
C	2	1	C	3	2	0
C	2	2	C	3	2	2
C	2	1	C	3	3	0
C	2	2	C	3	3	2
C	1, 2	1, 2	C	1, 2	1, 2	0
C	1, 2, 3	0, 1, 2, 3	N	1, 2	0	0
C	1, 2, 3	0	N	1, 2	1, 2	0
C	3	1, 2	N	2	1	0
C	3	3	N	2	1	2
C	3	1	N	2	2	1
C	3	2	N	2	2	2
C	3	3	N	2	2	4
C	2	1	N	2	1	0
C	2	2	N	2	1	1
C	2	1	N	2	2	1
C	2	2	N	2	2	2
C	1	1	N	1, 2	1, 2	0
C	3	0	O	1	0	0
C	3	1	O	1	0	0
C	3	2	O	1	0	0
C	3	3	O	1	0	0
C	3	0	O	1	1	0
C	3	1	O	1	1	0
C	3	2	O	1	1	1
C	3	3	O	1	1	2
C	1, 2	1, 2	O	1	0, 1	0

Table 5-2 to compute the total contributions to the heat of formation. Subroutines CORCIG and SORNGI monitor the selection of the non-cyclic atom pair and the cyclic/non-cyclic atom pair, respectively.

5.3.2 Ditertiary Ether Contributions

In addition to the four gauche ether contributions, ditertiary-butyl ethers require an additional correction to the heat by formation of 8.4 kcal/mole. If gauche ether interactions are present, Subroutine DITERE determines whether the carbon atom in every two adjacent CO ether linkages has a tertiary butyl structure and applies the appropriate correction to the heat of formation.

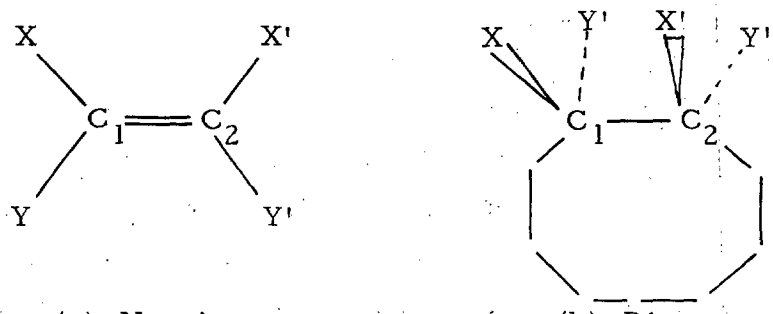
5.3.3 Cis Contributions

In some respects the identification and correction of cis effects is similar to that of gauche interactions. Each atom pair is examined individually, non-ring atoms and non-aromatic ring atoms may be involved, and the overall operation is monitored by Subroutines CORCIG and SORNGI, as before. There are however, some differences in the application of these two types of interactions in addition to the obvious dissimilarities in structure. In the case of cis configurations, the thermochemical corrections apply to the entropy (in specific cases) and the heat capacity as well as to the heat of formation. Furthermore, the corrections vary for certain structural groups. Lastly the rules for identifying the cis interactions are different. These rules and modifications are listed in Tables 5-3 and 5-4, respectively. The standard cis thermochemical corrections are listed in Appendix A. Table 5-4 lists only those corrections that are non-standard.

The calculation of the cis contributions is performed in two consecutive interphased steps. The first step, which is executed by Subroutine CIS, tests for the presence of the central carbon linkage and identifies the atom pairs on either side of the central bond. Subroutine CISCOR determines whether the composition and bonding properties of each ligand pair correspond to rule 2. If the criteria are satisfied, a search is initiated for the special structural configurations listed in Table 5-4. On the basis of these analyses, the appropriate cis corrections are selected and assigned to the pertinent functions.

Table 5-3

RULES FOR DETERMINATION OF CIS INTERACTIONS



(a) Nonring (b) Ring

1. C_1 and C_2 must be carbon atoms with a connectivity of 3(a) or 4(b).
2. X and X' or Y and Y' must also be carbon atoms with a connectivity ≥ 3. If all four ligands are carbon atoms with connectivities ≥ 3, there are two cis corrections for the atom pair.

The molecule cis-1-methyl-2-ethyl cyclopentane also provides an example of a cis interaction in a ring structure. The central atoms (1 and 3) are indicated in the graphic formula of the molecule presented in Section 5.3.1.

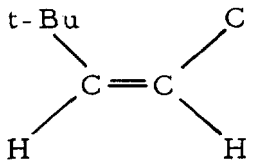
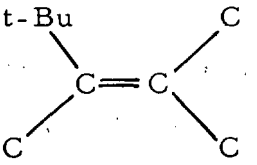
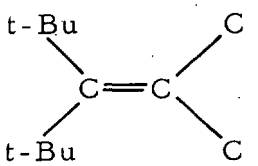
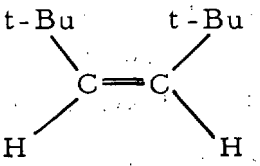
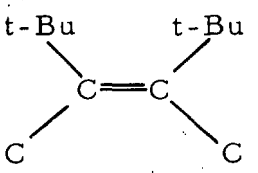
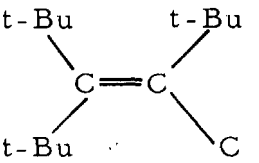
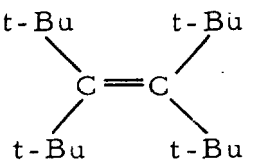
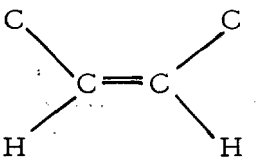
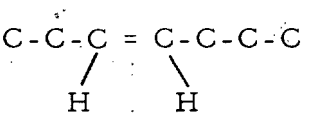
5.3.4 Ortho Corrections

In addition to the three aforementioned types of nongroup interactions, the program also corrects for still another type of nonbonded next-nearest neighbor interaction exhibited by aromatic structures - the ortho interaction. In the case of pyridine, there is a correction for para as well as ortho substitution in the ring.

The assignment of these corrections as well as those for the ring structures (see Sections 5.3.5) is preceded by a series of logistic tests and determinations that establish the identity of the ring structure itself. For this purpose, the program has to distinguish between simple and fused ring structures, aromatic and nonaromatic cyclic rings, and benzene, pyridine, and higher nitrogen - containing aromatics. In addition, it must establish the size composition, intra-ring bonding properties, and the types of nonring atoms bonded to the ring. A few of these properties, such as the size and

Table 5-4

NON-STANDARD CIS CORRECTIONS FOR SPECIFIC CONFIGURATIONS

	$\Delta H^{\circ}_{f,298}$ (kcal/mole)		$\Delta H^{\circ}_{f,298}$ (kcal/mole)
	4.0		6.0
	8.0		10.0
	12.0		14.0
			S (cal/° K-mole)
	20.0		1.2
Two cis interactions	3.0		-0.6

components of the individual ring units, are computed in Section 2 of the program, as described earlier. Subroutine FUSION initiates the entire ring calculation procedure of Section 3. FUSION is a dual function routine that identifies the set(s) of fused ring system(s) present in the molecule and determines certain symmetry characteristics of these polycyclic structures such as the number and type of atoms that are common to any and to all ring pairs in the set. This information is also used later in the symmetry calculations.

In order to maintain the nomenclature of the structural input as close to standard chemical notation as possible, no special symbols are assigned to aromatic carbon and nitrogen atoms. Instead the identification of these aromatic groups is performed directly by the program. Subroutine CYCORR executes the identification procedures. Figure 5-5 illustrates the various different types of aromatic groups in question. Once identification is achieved, Subroutine HEXGON alters the identification weights of all the conjugated aromatic groups in the molecule. The resultant weights correspond to the true identification weights assigned to the various

CR44

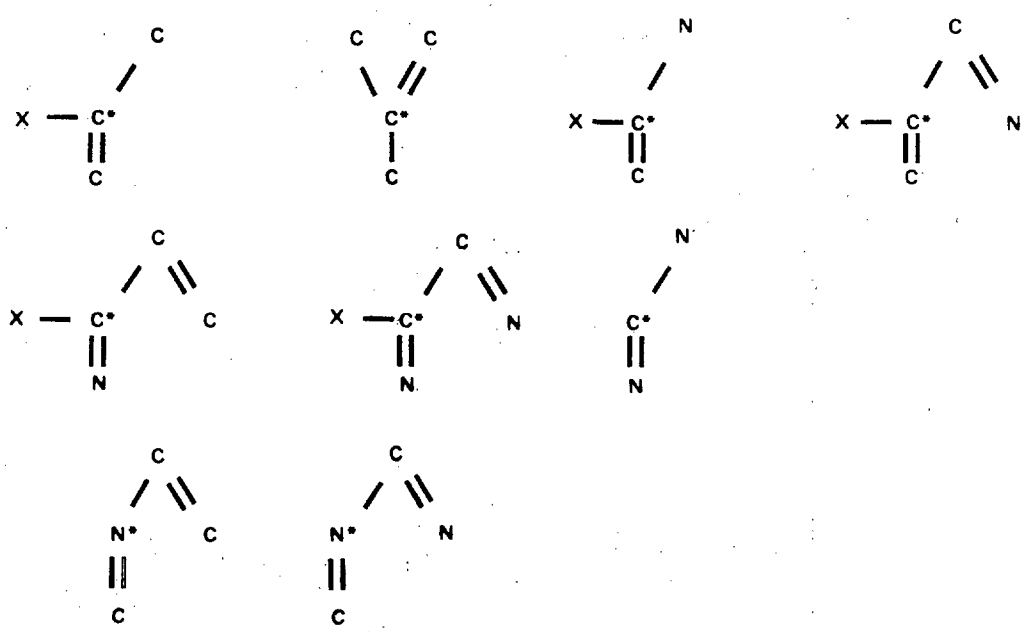


Figure 5-5. Carbon and Nitrogen-Containing Ring Groups Requiring Special Processing

aromatic groups. These weight modifications are performed on both monocyclic and polycyclic fused ring systems as well as on nonring groups bonded to these ring systems.

Subroutine HEXGON also determines the number of ortho corrections in benzene and pyridine-like rings as well as the number of para corrections in the latter. Both monocyclic and fused polycyclic ring systems are included. In order to qualify, the ortho and para substituted ligands can be any atom or group other than hydrogen (See Section 4, case 14).

5.3.5 Ring Contributions

The ring corrections to the thermochemical properties of the molecule are associated with the ring structure itself. In most cases the ring correction for the heat of formation equals the strain energy of the ring. These corrections are applied to all ring structures listed in Appendix A.

Subroutine CYCORR assigns the appropriate correction to single ring units. Subroutine CRINGS performs this function for spiropentane and the six bicyclo compounds and Subroutine NRINGS does it for the fused tricyclic nitrogen-containing ring. In each case, the procedure entails a check of the size, composition and bonding characteristics of the ring. In the case of fused ring systems, the number of rings, the properties of each, and the types and number of atoms in common have to be determined also.

A few of the sample calculations in Section 4 involve ring corrections. Aromatic systems appear to be exceptions. This is because in aromatic systems the ring correction is already included in the group thermochemical contributions.

5.3.6 Symmetry Logic Structure: Part I

The logic schemes for the determination of the symmetry of the molecule and of the individual groups thereof are the most extensive and complex of the logic structures of the program. These symmetry operations are divided into two parts. Part I, which is discussed in this section, performs the basic internal group by group symmetry evaluations of the molecule. In particular, the ligands of each group are compared one versus another and the similarity

or dissimilarity of their structures is determined. Here as before, the term ligand denotes all the atoms, one or more, which form the bond chain or "branch" of a particular core atom. A tetrahedral carbon atom, for example, has four ligands each composed of one, two or any number of atoms.

The principal steps in the logic framework of Part I are outlined in Figure 5-6. The figure lists only the control routines for the indicated steps. The names of the auxiliary subprograms are given in Figure 5-4.

The symmetry calculations of Part I are initiated and controlled by Subroutine SYMTRY The atomic composition calculations performed by SYMTRY and its auxiliary routines SCANCH and SCANBR serve as a screening medium. In this manner, complex ligand pairs with dissimilar atomic compositions are from the start automatically eliminated from the more time consuming structural identity tests. Groups in which the core atom of the group is also a ring atom are likewise exempt from undergoing additional symmetry analysis in Part I.

The structural similarity of two or more ligands which contain no core atoms, such as H, CN etc., is determined at once by directly comparing the atomic composition of the ligands. If the ligands are complex, that is they contain core atoms, the structural similarities of each ligand pair must be determined bond by bond and branch by branch. A pair of ligands is not considered dissimilar until all possible branch pair combinations of the two ligands have been tested. This operation is performed by Subroutine EQUAL. If ring structures are encountered during the structural analysis of a ligand pair, the equality of the ring structures is determined by Subroutine EQUALR and by auxiliary routines FIRSTR and DELETE. The program can actually handle several ring formations per ligand. The limits imposed on the various variables are those for ring formations in general, namely, 30 components per ring and a total of 40 ring units per molecule.

Once the structures of a ligand pair are found to be similar, several blocks of symmetry identification data pertinent to the particular ligands and groups are generated and stored by Subroutine SAME. These comprise: (a) the

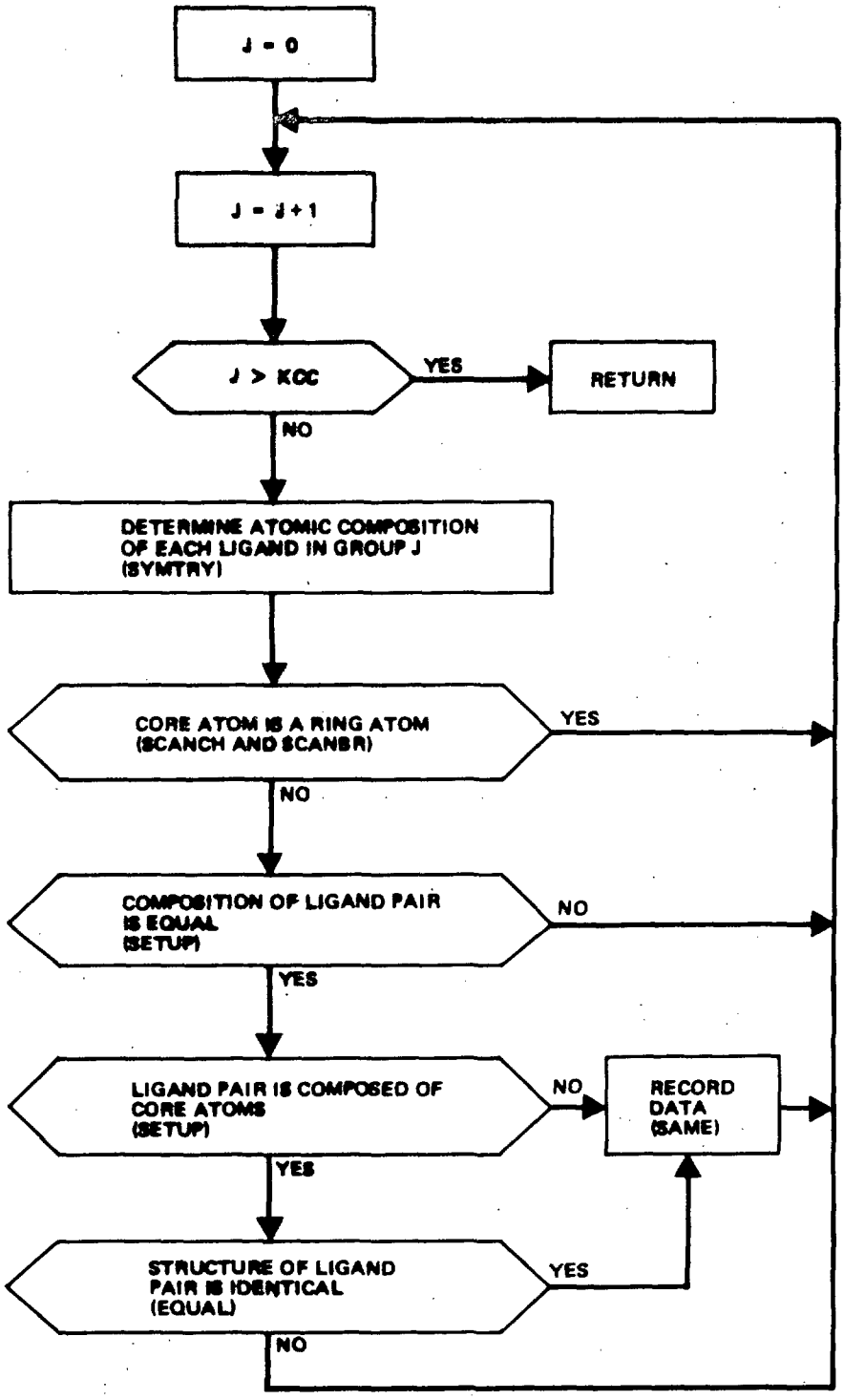


Figure 5-6. Main Logic Flow Chart for Symmetry Calculations: Part I

group numbers of the atoms in the ligand pair(s) which are bonded directly to the core atom. (KCSAME(i, j)); (b) the number of elements in (a), the number of different ligand pairs, and the code type assigned to each similar ligand (NOSAME(i, j)); and (c) the total number of similar ligands of each type in the group (NTOTAL(i, j)).

5.3.7 Symmetry Logic Structure: Part II

The symmetry data calculated in Part I are utilized in Part II to compute the various molecular properties listed in Figure 5-7. Each of these properties is discussed below.

5.3.7.1 Identification of Asymmetric Atoms

The first function in the final sequence of symmetry calculations consists of determining the total number of asymmetric atoms in the molecule and the group numbers of these atoms. The following are the criteria employed by the program for the selection of asymmetric atoms.

A. The core atom must be a carbon atom
B. It must be a nonring atom
C. It must have a connectivity equal to 4, i. e., tetrahedral.
D. The four ligands of the core atom must be dissimilar

These tests are conducted by Subroutine ASYMC. If all the aforementioned algorithms are satisfied by a particular atom, the asymmetry counter NASYMC is incremented by one and the group number of the atom is stored in array IOPATM.

The data are utilized later to compute the entropy effects arising from optical isomerism. These data are also used in the computation of the longest chain which is described next.

5.3.7.2 Determination of the Longest Chain

The calculation of the longest chain is a prerequisite to the computation of the external symmetry number. If asymmetric atoms are not present, the longest chain is simply taken as the longest of the chains in the molecular chain array which was identified and constructed in Section 2 of the program.

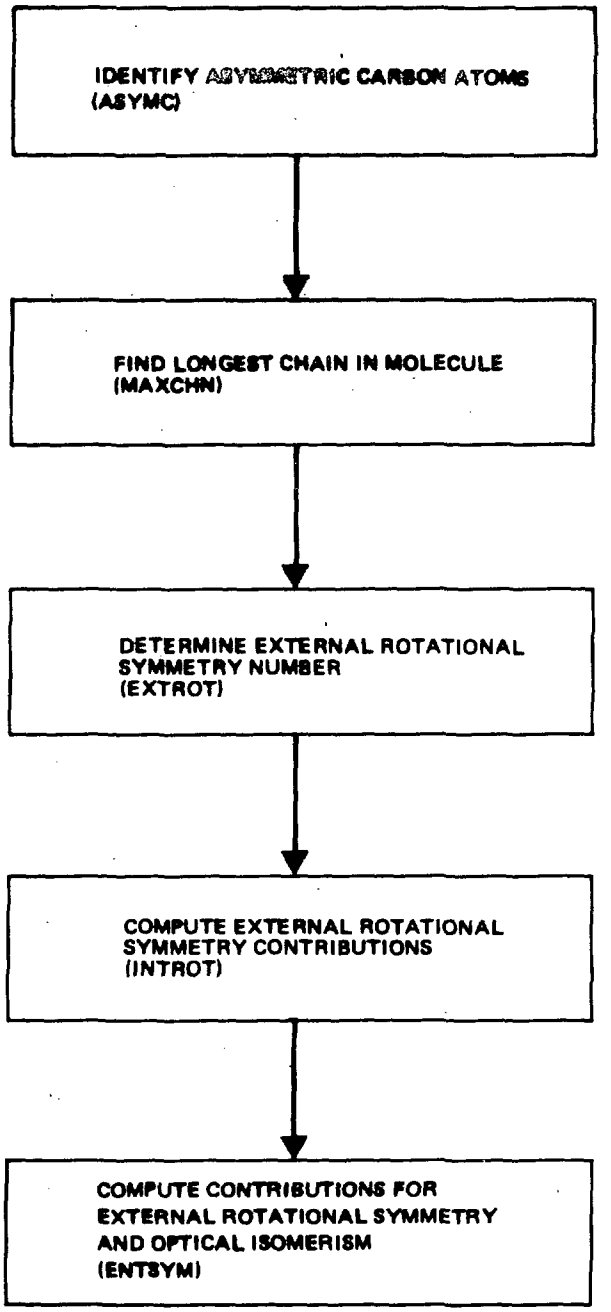


Figure 5-7. Main Logic Flow Chart for Symmetry Calculations: Part II

When there is more than one chain of maximum length, the one located first in the chain array is selected as the longest chain of the molecule.

In the event asymmetric atoms are present and there is more than one chain of maximum length available, the program computes the number of asymmetric atoms present in the first chain of maximum length identified. If all the asymmetric atoms are contained in this chain, no redefinition is necessary. If only some of these atoms are contained therein, all other chains equal to the longest chain in size are examined for their content of asymmetric atoms. That chain of maximum length containing the greatest number of asymmetric atoms is designated the longest chain in the molecule.

The above tests are executed by Subroutine MAXCHN. The number of the components and the chain number of the longest chain are stored in array MBS, and the group numbers of the chain components in array MBC. These data are also output by the routine.

5.3.7.3 Determination of the Symmetry Number

The computation of the symmetry number, a property that characterizes the external rotational symmetry of the molecule, is a multi-phase logic-controlled operation executed by Subroutine EXTROT. The principal steps involve finding the central atom or atoms in the molecule and the number of structurally identical ligands bonded to this atom or atoms.

For the purpose of this analysis, the central atom is defined as the atom in the center of the longest chain. If the chain contains an odd number of atoms the molecule has one central atom. If the number of chain constituents is even, there are two central atoms in the molecule whose ligands have to be analyzed for similarity of structure.

Once the even or odd multiplicity of the chain is established and with it the number of central atoms, additional classifications are made to determine the symmetry number of the molecule. These new classifications include the type and connectivity of the central atom(s) and the symmetry characteristics of the ligands. The principal algorithms of the classification scheme are listed below. The symmetry number of configurations not

listed therein is set equal to one. The symbol C_p refers to the axial rotational symmetry of the ligand.

Rules for the Assignment of the Symmetry Number

A. Odd Number of Atoms in the Longest Chain

1. Central Atom is a Carbon Atom

a. Two Ligands

(1) $X - C \equiv Y$

(a) X and Y are both linear, $\sigma = 1$

(b) X is linear and Y is symmetrical (or vice versa), σ = symmetry of Y

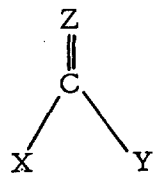
(c) X and Y both have the same axial rotational symmetry C_p, $\sigma = C_p$

(2) $X = C = Y$

(a) $X = Y$ $\sigma = 2 \times C_p$

(b) $X \neq Y$, same as (1)

b. Three Ligands



X = Y and Z is linear or has $C_p = C_2$, $\sigma = 2$

c. Four Ligands

(1) CX_2YZ, $\sigma = 1$

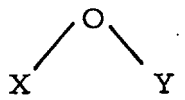
(2) CX_2Y_2, $\sigma = 2$

(3) CX_3Y, $\sigma = 3$

(4) CX_4 and X is linear or has $C_p = C_3$, $\sigma = 12$

CX_4 and X not linear or $C_p \neq C_3$, $\sigma = 6$

2. Central Atom is an Oxygen Atom



X = Y $\sigma = 2$

3. Central Atom is a Nitrogen Atom

a. Two Ligands

X - N = Y $\sigma = 1$

b. Three Ligands

NXYZ

X = Y = Z, $\sigma = 3$

B. Even Number of Atoms in the Longest Chain

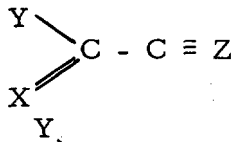
1. Two Central Atoms are Unique: $\sigma = 1$

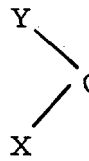
2. Two Central Atoms are Carbon Atoms

a. Two Ligands

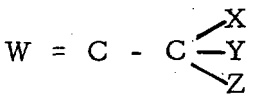
X = C - C = Y or X = C = C = Y Same as 1.2.

b. Three Ligands

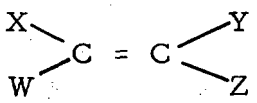
(1)  $\sigma = 1$

(2)  X = Y and Z is linear or has $C_p = C_2$, $\sigma = 2$

c. Four Ligands

(1) 

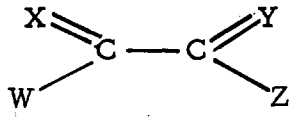
X = Y = Z and W is linear or has $C_p = C_3$, $\sigma = 3$

(2) 

(a) W = X = Y = Z $\sigma = 4$

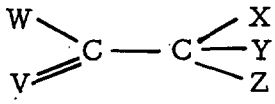
(b) W = Z and X = Y $\sigma = 2$

(c) W = X and Y = Z $\sigma = 2$

(3) 

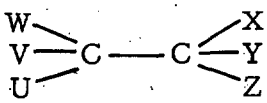
X = Y and W = Z $\sigma = 2$

d. Five Ligands



$\sigma = 1$

e. Six Ligands



(1) U = V = W = X = Y = Z $\sigma = 6$

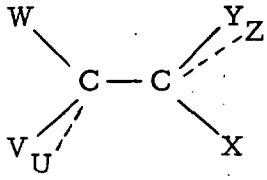
(2) U = V = Y = Z and W = X $\sigma = 2$

(3) U = V = W and X = Y = Z $\sigma = 1$

(4) W = X, V = Y, U = Z

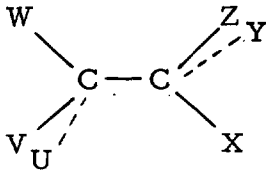
Two symmetry configurations are possible:

(a) Dissymmetric, nonasymmetric form



$\sigma = 2$

(b) Nondissymmetric form



$\sigma = 1$

3. Two Central Atoms are Oxygen Atoms

X - O - O - Y (assuming nonplanar structure)

X = Y $\sigma = 2$

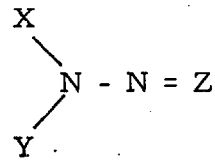
4. Two Central Atoms are Nitrogen Atoms

a. Two Ligands

X - N = N - Y

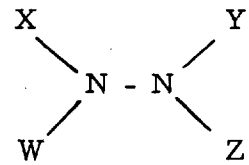
X = Y $\sigma = 2$

b. Three Ligands



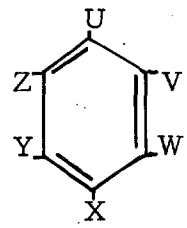
$\sigma = 1$

c. Four Ligands



$\sigma = 1$

As indicated in Section 2.2, the program does not determine the symmetry number of a molecule whose central atom(s) is(are) part of a ring structure unless the ring is a monocyclic benzene-type ring. In the latter case, the symmetry number assignments are made according to the following rules:



Condition	σ
U = V, X = Y, W = Z	2
U = W, X = Z, $C_p = C_2$ for V, Y	2
U = W, X = Z, V = Y, $C_p = C_2$ for V, Y	2
U = X, V = Y, W = Z	2
U = V = W, X = Z, $C_p = C_2$ for V, Y	2
U = V = W, X = Y = Z, $C_p = C_2$ for all ligands	2
U = W = Y, V = X = Z	3
U = W = Y, V = X = Z, $C_p = C_2$ for all ligands	6
U = V = W = X, Y = Z	2
U = V = W = Y, X = Z, $C_p = C_2$ for V	2
U = V = X = Y, $C_p = C_2$ for W, Z	2
U = V = X = Y, W = Z	2
U = V = X = Y, W = Z, $C_p = C_2$ for W, Z	4
U = V = W = X = Y, $C_p = C_2$ for all ligands	2
U = V = W = X = Y = Z	6
U = V = W = X = Y = Z, $C_p = C_2$ for all ligands	12

5.3.7.4 Calculation of Internal Rotation Contributions

The program computes the contributions to the entropy associated with the internal rotation of one or more groups of atoms in the molecule. The rotation about the bond axis can be either of C_3 or C_2 symmetry. Specifically, the program applies this correction to tetrahedral carbon atoms of C_3 symmetry aromatic rings (benzene and pyridine types) of C_2 symmetry, and $-NO_2$ groups.

In the case of tetrahedral atoms, the rotation can involve a simple structure like $-CH_3$ or groups in which the structures of the identical ligands are highly complex. (For example, carbon group 12 of case calculation 17, Section 4.) Subroutine INTROT looks for core atoms which are carbon atoms with a connectivity of four and three structurally identical ligands. Each of these groups is assigned a threefold rotational axis and an entropy, correction equal to $-R \ln 3$. If the particular internal rotation has already been included in the external rotational symmetry of the molecule, it is eliminated from this calculation.

The auxiliary routine CTWO assigns a twofold axis of rotation and an entropy correction of $-R \ln 2$ to NO_2 groups and to aromatic rings of C_2 symmetry providing each of these structures is bonded to a nonlinear ligand. The linearity of the ligand is determined by Subroutine LINEAR. The twofold rotational symmetry of a ring is established by Subroutine EQUAL and its auxiliary subprograms. This calculation is feasible even when there are complex ligand subroutines present in the structure of the ring.

5.3.7.5 Calculation of Optical Isomer Contributions

In order for a molecule to be optically active, it must in general be dissymmetric, that is, it must lack an alternating (S_n) axis of symmetry (5). From the intramolecular point of view, the most frequently encountered albeit not necessary, condition for optical activity is the presence of an asymmetric carbon atom. The criteria used by the program to identify the presence of asymmetric carbon atoms were presented in Section 5.3.7.1.

Subroutine ENTSYM computes the optical properties (number of enantiomers and meso structures) of a molecule in which the optical activity is due to the

presence nonring asymmetric carbon atoms. The number of active conformations or enantiomers (a) and the number of meso structures (m) is computed directly from equations A, B, or C (6).

A. All asymmetric carbon atoms are different:

$$a = 2^{\gamma} \quad m = o$$

B. Like asymmetric carbon atoms are present and γ is even:

$$a = 2^{(\gamma-1)} \quad m = 2^{\left(\frac{\gamma-2}{2}\right)}$$

C. Like asymmetric carbon atoms are present and γ is add:

$$a = 2^{(\gamma-1)} - 2^{\left(\frac{\gamma-1}{2}\right)} \quad m = 2^{\left(\frac{\gamma-1}{2}\right)}$$

where γ is the total number of asymmetric carbon atoms including the pseudoasymmetric carbon atom (if any). The latter is defined as follows: If two like asymmetric carbon atoms are joined to a carbon atom attached to two different nonasymmetric groups, two active forms and two meso forms are possible. The central atom in such compounds is called a pseudoasymmetric carbon atom. The pseudoasymmetric carbon atom and meso structures are identified by Subroutine EXTROT. Only that asymmetric carbon atoms contained in a single chain of the molecule can be included in the above equations. The program takes into account all asymmetric carbon atoms contained in the longest chain where, if necessary, the latter is redefined in the manner described in Section 5.3.7.2.

Subroutine ENTSYM also computes the enthropy contribution due to external rotational symmetry

$$S = -R \, lu \, (\sigma)$$

and optical isomerism

$$S = R \ln (n)$$

where $n = a + m$. The assumption is made here that all isomers are present in equal amounts.

Section 6

REFERENCES

1. S. W. Benson. Thermochemical Kinetics. John Wiley & Sons, Inc., New York, 1968.

2. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh. Additivity Rules for the Estimation of Thermochemical Properties. Chemical Reviews, 1969; Vol. 69, p 279-313.

3. S. W. Benson and J. H. Buss. Additivity Rules for the Estimation of Molecular Properties. Thermodynamic Properties. Journal of Chemical Physics, 1958; Vol. 29, p 546-572.

4. D. R. Stull, E. F. Westrum, and G. C. Sinke. The Chemical Thermodynamics of Organic Compounds. John Wiley & Sonc, Inc., New York, 1969.

5. E. L. Eliel. Stereochemistry of Carbon Compounds. McGraw Hill Book Company, Inc., New York, 1962.

6. C. R. Noller. Chemistry of Organic Compounds. W. B. Saunders Company, London, 1951, p 329.

REPORT NO. MDC G4388

ESTIMATION OF GAS-PHASE THERMOKINETIC PARAMETERS

VOLUME II

DEFINITION OF REQUIREMENTS FOR
ESTIMATION OF KINETIC PARAMETERS

APRIL 1973

BY

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FOR

BALLISTIC RESEARCH LABORATORIES

PREPARED BY

MCDONNELL DOUGLAS ASTRONAUTICS COMPANY
HUNTINGTON BEACH, CALIFORNIA

PREPARED UNDER CONTRACT NO. DAAD05-72-C-0098

PREFACE

This document comprises the final report for the program "Automated Estimation of Gas Phase Thermokinetic Parameters for High Ignition Temperature Solid Gun Propellants." The work was performed for the Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland, by McDonnell Douglas Astronautics Company, under Contract DAAD05-72-C-0098. This final report covers the period 15 November 1971 to 15 January 1973.

The report is submitted in two volumes:

Volume I – A FORTRAN Program for Computing the Thermochemical Properties of Complex Gas Molecules by the Method of Group Additivity
(Books 1 and 2)

Volume II – Definition of Requirements for Estimation of Kinetic Parameters

ABSTRACT

Group additivity thermodynamic methods are applied to the calculation of Arrhenius parameters. Studies of several classes of unimolecular reactions are presented together with preliminary methods developed for the calculation of kinetic rate constants. The problems associated with bimolecular reactions are reviewed and some preliminary solutions suggested. Where required to support this work, thermodynamic functions of radical-containing groups, single bond strengths, and pi bond strengths for various compounds are calculated. A computer scheme to calculate the rate constants for simple unimolecular fission is presented.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Section 1 INTRODUCTION 1

Section 2 METHODS FOR ESTIMATING THE ACTIVATION ENERGY AND FREQUENCY FACTOR OF GAS PHASE CHEMICAL REACTIONS 3

2.1 Calculational method for ΔH_f^o of Radical Groups, Bond Strengths in Single Bonds and Pi Bonds 4

2.1.1 Method of Calculation of ΔH_f^o of Radical Groups 5

2.1.2 Method of Calculation of Single Bond Strengths 7

2.1.3 Method for Calculation of Pi Bond Strengths 7

2.2 Unimolecular Reactions 9

2.2.1 Simple Fission Reactions 10

2.2.2 Three Membered Ring Reactions 11

2.2.3 Six Centered Elimination Reactions 17

2.3 Bimolecular Reactions 26

2.3.1 Metathesis Reactions 27

2.3.2 Association Reactions 27

2.3.3 Displacement Reactions 28

Section 3 SCHEME FOR COMPUTER CALCULATION OF THE MOST PROBABLE REACTION RATE 30

Section 4 METHODS FOR HANDLING COMPLEX REACTION SYSTEMS 31

4.1 Successive Reaction Systems 31

4.1.1 Criterion for Favorable Chain Propagation Steps 32

4.1.2 Method for Determining Chain Propagators 32

4.1.3 Initiation Reactions 34

4.1.4 Termination Reactions 35

4.2 Additive Reaction Systems 36

Section 5 POTENTIAL PROGRAMMING METHODS FOR COMPUTER APPLICATION 39

5.1 Simple Fission Reactions 39
5.2 Reactions of Simple Fission with Resonance Stabilization 40

FIGURES

Number		
5-1	Flow Chart 1	41
5-2	Flow Chart 2	42

TABLES

2-1	Heat of Formation of Radical Groups	6
2-2	Single Bond Strengths	7
2-3	Pi Bond Strengths	9
2-4	Calculated and Observed Activation Energies	15
2-5	Activation Energies and End Interaction Correction	20
2-6	Activation Energies and Corrections for β Methyl Substituents	21
2-7	Activation Energies and Corrections for β Ethyl Substituents	22
2-8	Activation Energies and Corrections for α Methyl Substituents	23
2-9	Activation Energies and Corrections for α Ethyl Substituents	24
2-10	Activation Energy for Six Centered Reactions	24
4-1	Fission of Molecules into Two Radicals	34
4-2	Radical-Radical Association Reactions	36

Section 1
INTRODUCTION

Although the advantages of applying chemical kinetics to the solution of many physico-chemical problems are well recognized, the measurement of basic kinetic data is tedious and time-consuming. In addition, the sample size and sample purity required for such measurements are often prohibitive. This makes it especially difficult to evaluate new and potentially useful chemical compounds. A reliable method for estimating the kinetic parameters of as yet un-studied compounds would be particularly valuable.

Systematic exploration of current data on gas phase reactions by Benson[1] has revealed that for some reaction categories, the Arrhenius parameters can be fitted with the aid of some simple rules into the frame work of transition state theories. These rules involve in part the extension of the methods of group additivity to the calculation of kinetic parameters. The purpose of the present work was to investigate more thoroughly and improve upon those reaction categories to which these methods have been applied and to extend the group additivity methods to other reaction categories.

The first task of the kinetic investigation was to examine critically empirical methods of estimating activation energies for elementary chemical reactions. This has proved to be a fairly involved task because the problems associated with different reaction categories are very specific for each category. Before a systematic set of rules for the computation of kinetic parameters can be formulated and ultimately adopted to computer programming methods, it is necessary to understand fully the problems and techniques involved in calculating activation energies. Therefore, the majority of work on this project was devoted to the first task of estimating activation energies.

Several specific classes of reactions were investigated in depth. This approach was used rather than a general survey involving less detailed analysis of a

large number of reaction classes in order to understand more fully the problems associated with empirical methods of estimating activation energies.

The ultimate goal of this project is to develop uniform techniques to calculate rate constants of elementary chemical reactions rapidly.

Section 2

METHODS FOR ESTIMATING THE ACTIVATION ENERGY AND FREQUENCY FACTOR OF GAS PHASE CHEMICAL REACTIONS

For a simple unimolecular reaction

$$A \xrightarrow{k} B$$

the rate constant k can be described by the Arrhenius equation

$$k = Ae^{-E/RT}$$

where E is the activation energy, R is the gas constant, T is the reaction temperature in ^{o}K, and A is the frequency factor. Transition state theory postulates the participation of an "activated complex" or excited intermediate in chemical reactions. For the simple unimolecular reaction this is represented by

$$A \rightarrow A^{\dagger} \rightarrow B$$

where $A^{\dagger}$ is the excited intermediate of the transition state. The frequency factor A, as given by the transition state theory is

$$A = \frac{ekT}{h} \exp\ (\Delta S^{\dagger}/R)$$

where $\Delta S^{\dagger}$ is the entropy of activation, that is, the change in entropy in going from reactant A to the transition state $A^{\dagger}$. The other terms have their usual significance. Similarly the activation energy E is equal to

$$E = \Delta H^{\dagger} + RT$$

where $\Delta H^{\dagger}$ is the enthalpy of activation, namely, the difference in enthalpy between the transition state and reactant. These equations can easily be generalized to more complex elementary reactions with more than one reactant or product. In any case, the values of $\Delta S^{\dagger}$ and $\Delta H^{\dagger}$ are required to calculate the rate constant.

Benson[1a] has examined the experimentally determined Arrhenius parameters for the most common reaction categories and has derived fairly simple rules for estimating entropies of activation through consideration of the changes in molecular structure in going from reactants to transition state. The rules for computing the A factors are uniquely defined for each particular transition state model, and are based on changes in bond lengths, bond bending and stretching frequencies, and barrier heights to internal rotation. The method used by Benson is fairly general and can be applied with success to a wide variety of reaction categories.

In contrast, the problems encountered with the calculation of $\Delta H^{\dagger}$ for different reaction classes has proved to be specific, or nearly specific, for each reaction class. In practice, only those classes of reaction were chosen for the study of methods for calculating $\Delta H^{\dagger}$, for which methods have been well developed for calculating $\Delta S^{\dagger}$. There are several reasons for this approach. First, the transition state model adopted for these reaction classes has been shown to be accurate due to agreement of calculated and experimental A factors. Second, for these classes, in general, a large amount of experimental data is available for comparison of results. Finally, the methods for calculating $\Delta H^{\dagger}$ can be combined with those for $\Delta S^{\dagger}$ to generate reaction rate constants for those classes.

The methods applied to several classes of unimolecular and bimolecular reactions will be discussed in this section. In addition, the work performed to determine some bond energies and heats of formation required for this work will also be discussed.

2.1 CALCULATION METHOD FOR ΔH_f^o OF RADICAL GROUPS, BOND STRENGTHS IN SINGLE BONDS AND Pi BONDS

After the onset of this work, it was evident that group additivity thermodynamic functions were required for radical containing groups. The need for these values values arose several times during the course of this work. Benson and O'Neal[2] have given a partial tabulation, but additional data were required. In addition, their tabulation does not take into account delocalization in radical groups which possess multiple-bonded ligands. That is, Benson and O'Neal's formulation would give the same group value for the heat of formation of the

group $[\cdot C-(C_d)(H_2)]$ as for $[\cdot C-(C)(H_2)]$. In their calculation, a second step is required to account for the delocalization of the unpaired electron by the double bonded carbon. The present calculation incorporates the effect of delocalization into the group values. This is compatible with group values for non-radical groups and removes an additional step from the calculations. This is advantageous for machine calculations.

A second requirement for these calculations was a tabulation of bond strengths. Benson[1b] has given a fairly complete tabulation, but additional data were required. For example, previously in group additivity calculations, the same value of bond energy was assigned to a carbon-carbon single bond in a hydrocarbon chain as to a C-C bond alpha to a carbon-oxygen single bond. It was found to be necessary to differentiate between two cases such as this in order to accurately account for differences in activation energy. In addition, pi bond energies of C=C and C=O double bonds were required. It was possible to calculate all required bond strengths using group additivity thermodynamic methods and group values of radical groups.

2.1.1 Method of Calculation of ΔH_f^o of Radical Groups

The formula

$$\Delta H^o_f[\cdot R] = DH^o[C-H] + \Delta H_f^o[HR] - \Delta H_f^o[\cdot H]$$

is used to calculate the heat of formation ΔH_f^o of the radical group $\cdot R$. $DH^o[C-H]$ represents the bond strength of the carbon-hydrogen bond of the saturated group HR which on dissociation yields the radical $\cdot R$. $\Delta H_f^o[\cdot H]$ is the heat of formation of a hydrogen atom, namely, 52.1 kcal/mole. All heats of formation are for the standard state at 298°K.

It is necessary to use the value of $DH^o[C-H]$ which best reflects the ligand environment of the group HR. For example, the difference in the C-H bond strength for the CH_3 group of C_3H_8 and $CH_2=CH-CH_3$ is 10.5 kcal/mole. Therefore, the approximation will be used that the bond strengths given by Benson for saturated hydrocarbons can be corrected for the presence of a C_d ligand in the HR group by subtracting 10.5 kcal/mole. Similarly the C-H bond strength for the CH_3 group of propane is 98 kcal/mole compared to the value for acetone of 98.3 kcal/mole. A value of 0.3 kcal/mole is thus added to the

C-H bond strengths in saturated hydrocarbons to correct for the replacement of a carbon ligand by a carbonyl ligand. Finally, a value for the C-H bond of the CH_3 group of propyne of 91.5 kcal/mole and of methanol of 95.9 kcal/mole gives correction factors of -6.5 kcal/mole for C_t ligands and -2.1 kcal/mole for single bond oxygen ligands respectively.

Table 2-1 contains the ΔH_f^o for a series of radical groups ·R. Included in the table are the values of ΔH_f^o [HR] used as obtained from Benson[1c], and the C-H bond strength used. Also included is the model compound used for the bond strength along with the resultant correction factors. Where two or more ligands are present which require a correction factor, the correction factors are considered additive.

Table 2-1
HEAT OF FORMATION OF RADICAL GROUPS

·R	ΔH_f^o [·R] kcal/mole	ΔH_f^o [HR] kcal/mole	DH^o [C-H] kcal/mole	Model	Correction kcal/mole
$\cdot C-(C)(H_2)$	35.8	-10.08	98	$H-CH_2CH_3$	-
$\cdot C-(C_d)(H_2)$	25.5	-9.95*	87.5	$H-CH_2CHCH_2$	-
$\cdot C-(CO)(H_2)$	36.1	-10.08	98.3	$H-CH_2CH_3$	+0.3
$\cdot C-(C_2)(H)$	37.5	-4.95	94.5	$H-CH(CH_3)_2$	-
$\cdot C-(C_d)(C)(H)$	27.1	-4.76	84.0	$H-CH(CH_3)_2$	-10.5
$\cdot C-(CO)(C)(H)$	37.7	-5.0	94.8	$H-CH(CH_3)_2$	+0.3
$\cdot C-(C_3)$	37.0	-1.90	91	$H-C(CH_3)_3$	-
$\cdot C-(C_d)(C_2)$	26.9	-1.48	80.5	$H-C(CH_3)_3$	-10.5
$\cdot C-(H_2)(O)$	33.7	-10.08	95.9	$H-CH_2CH_3$	-2.1
$\cdot C-(H)(C)(O)$	31.8	-8.5	92.4	$H-CH(CH_3)_2$	-2.1
$\cdot C-(O)_2(C)$	17.5	-17.2	86.8	$H-C(CH_3)_3$	-4.2

*The value of H_f [$C-(C_d)*H_3$)] was not available from Benson[1a]. This value was calculated from the ΔH_f^o = 4.9 kcal/mole for CH_2CHCH_3.

2.1.2 Method of Calculation of Single Bond Strengths

Various C-C, C-O, C-H, and O-H bond strengths were required to compute the energies of activation. The general values of these bond strengths were not accurate enough since they do not take into account the effect of nearest neighbor environments in the compounds where these groups occur. Some of these bond values were already available but most values had to be calculated using group additivity methods. For example, for a C-C bond of the type $C\text{-}CH\text{—}CH_2\text{-}O$ (where the longer bond indicates the one to be broken) no value for the bond strength could be obtained. The model compound $CH_3CH_2CH_2OH$ was chosen and the bond energy calculated from the reaction

$$\Delta E + CH_3CH_2CH_2OH \rightarrow CH_3CH_2\cdot + \cdot CH_2OH$$

Group additivity thermodynamic calculations are applicable to this problem, and the ΔH_f^o of the radical groups previously derived can be used for this purpose. Two examples are given in Table 2-2.

Table 2-2
SINGLE BOND STRENGTHS

Bond Type	Bond Environment	Model Compound	Bond Strength kcal/mole
C-O	C-O —— CH_2-O	CH_3OCH_2OH	88.0
C-C	C-CH_2 —— CH_2-O	$CH_3CH_2CH_2OH$	83.0

2.1.3 Method for Calculation of Pi Bond Strengths

Values of the pi bond strength for various C=O and C=C bonds are required. For symmetric compounds such as ethylene, the pi bond strength is defined as the difference of the C-H bond strength in the cleavage of ethane.

i.e. $E_\pi[CH_2CH_2] = DH\ [CH_3CH_2\text{-}H] - D\ [\dot{C}H_2CH_2\text{-}H]$

$E_\pi[CH_2CH_2] = 98 - 38.5 = 57.7$ kcal/mole

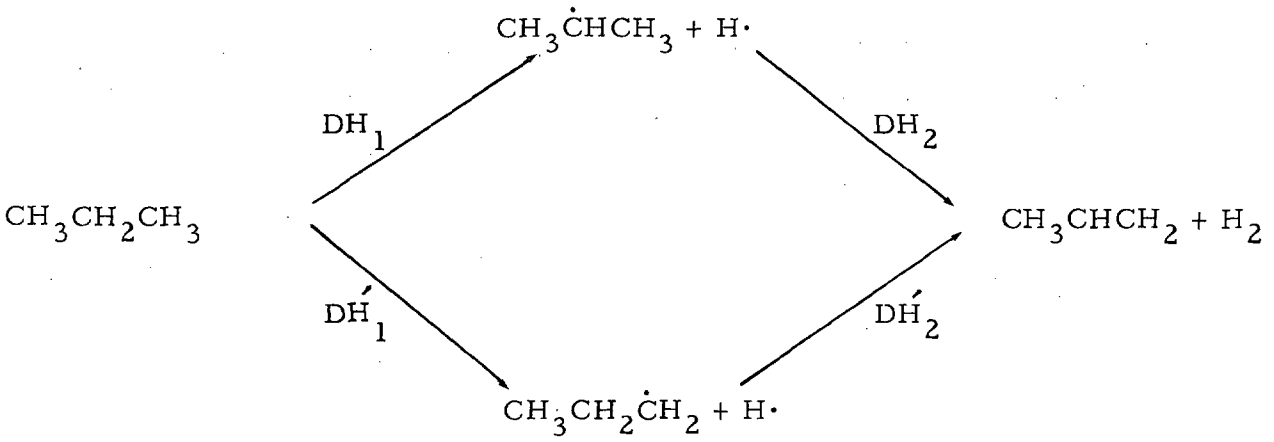
Experimental values are available for this example, but group additivity thermodynamic methods along with radical group values have been used to

calculate the pi bond energy of those compounds which lack such experimental data

e.g., $E_\pi[CH_3CH = CHCH_3] = DH\ [CH_3\overset{H}{\overset{|}{C}}HCH_2CH_3] - DH\ [CH_3\overset{H}{\overset{|}{C}}HCHCH_3]$

Experimental values are available for the first bond energy but the second bond energy is calculated by group additivity.

The same principle is applied to asymmetric compounds. The pi bond energy for propene is defined by the scheme:



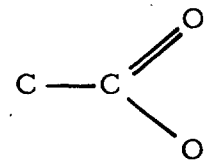
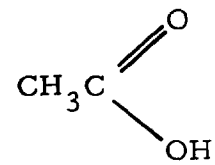
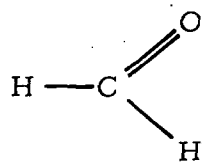
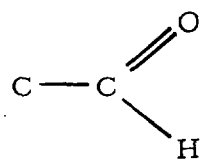
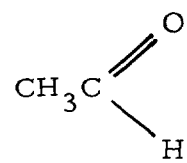
where

$$E_\pi[CH_3CHCH_2] = DH_1 - DH'_2 = DH'_1 - DH_2$$

In Table 2-3 are the pi bond energies along with the bond environment and model compound used in the calculations.

Table 2-3

PI BOND STRENGTHS

Bond Type	Bond Environment	Model Compound	Bond Strength kcal/mole
C = O			82.6
C = O		CH_2O	75.0
C = O			74.5
C = C	$CH_2 = CH - O$	CH_2CHOH	52.8
C = C	$CH_2 = CH_2$	CH_2CH_2	59.5
C = C	C-CH = CH-C	$CH_3CHCHCHCH_3$	57.7
C = C	C-CH = CH_2	CH_3CHCH_2	58.4

2.2 UNIMOLECULAR REACTIONS

The majority of work on individual reaction classes has centered on unimolecular reactions. The emphasis on unimolecular reactions was for two reasons. First, these reactions constitute the simplest reaction category, and if a trial method to calculate activation energies fails here, it is not likely to work for more complex classes of reactions. Second, many bimolecular reactions can be treated as the reverse of unimolecular reactions. Kinetic information calculated for the latter case can then be used, by means of detailed balance, to compute comparable data for the more complex bimolecular reactions.

2.2.1 Simple Fission Reactions

Simple fission of a molecule into an atom and molecule or two molecules is the simplest case of unimolecular reactions. The procedure for calculating the A factor for these types of reactions is well documented and straight forward. In addition, with the assumption that the back reaction for the association of two radicals or a radical and atom has zero activation energy, the activation energy for simple fission reactions is

$$E_a = \Delta H_R^o + RT$$

where ΔH_R^o is the endothermicity of the reaction defined as

$$\Delta H_R^o = \Delta H_f^o \text{ [products]} - \Delta H_f^o \text{ [reactant]}$$

these ΔH_f^o are easily calculated by group additivity thermodynamic methods using the radical group values given above. Two examples are:

1. $C_2H_6 \longrightarrow 2\ [\cdot CH_3]$

   Observed $E\hat{a} = 91.7$ kcal/mole at $T = 800^oK$

   Calculated from group additivity:

   $$\Delta H_R^o = 2\Delta H_{f,\ 800^oK}^o\ [\cdot CH_3] - \Delta H_{f,\ 800^oK}^o\ [C_2H_6] = 90.6 \text{ kcal/mole}$$

   $$E\hat{a} = \Delta H_R^o + RT = 92.2 \text{ kcal/mole}$$

2. $C_2H_3ONO_2 \longrightarrow C_2H_5O + NO_2$

   Observed $E\hat{a} = 41.2$ kcal/mole at $T = 420^oK$

   Calculated from group additivity

   $$\Delta H_R^o = \Delta H_{f,\ 298^oK}^o\ [C_2H_5O\cdot] + H_{f,\ 420^oK}^o\ [NO_2]$$

   $$- \Delta H_{f,\ 420^oK}^o\ [C_2H_5ONO_2] = 41.6 \text{ kcal/mole}$$

   $$E\hat{a} = \Delta H_R^o + RT = 42.4 \text{ kcal/mole}$$

The agreement in both cases is good, and even with this method only applied to a few examples, it seems fairly certain that the method is applicable to a wide variety of simple fission cases.

Some possible problems can be anticipated. In many cases there is a lack of group heat capacity values available to allow extrapolation of ΔH_f^o at 298°K to the appropriate reaction temperature. In the examples given above, this extrapolation has been made for the cases where heat capacity exists, but an important deficiency in the group value tables is this lack of heat capacity data. This may limit the effectiveness of higher temperature calculations.

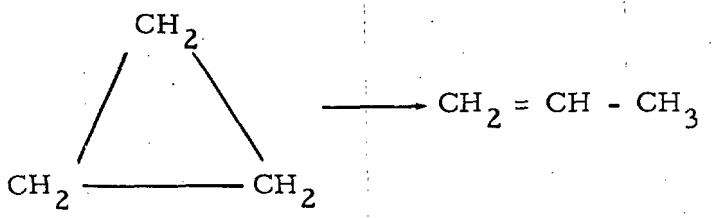
One advantage of this present method is that the use of the radical group values given above already accounts for resonance stabilization of the unshared electron in the free radical molecule. This is an improvement over earlier methods which had to account for resonance stabilization by a general correction factor in a separate calculation step. But some problems may be encountered when conjugated chains or rings are available to stabilize the free radical.

In any case, since the calculation for the A factors for these types of reactions is well established, the inclusion of this method to calculate the activation energy should provide a successful method to calculate rate constants for simple fission reactions without any great difficulty.

2.2.2 Three Membered Ring Reactions

This class of reactions represents a fairly involved reaction system. O'Neal and Benson[2] have postulated a biradical mechanism for these reactions, and they have developed a system to calculate $\Delta S^{\dagger}$ for individual reactions. In addition, they have done extensive work on a method to estimate activation energies for this class of reactions. This class of reactions was studied in this project so as to better understand the application of group additivity methods to the calculation of Arrhenius parameters for more complex classes of reaction and also to see what improvements could be offered on the present method.

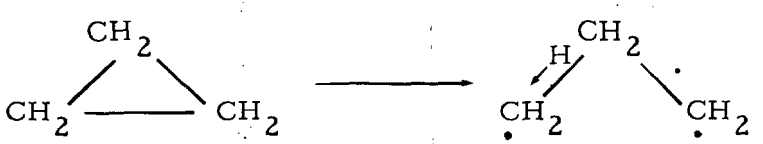
The simplest reaction of this class is the pyrolysis of cyclopropane to give propylene



Using a biradical mechanism, the reaction can be divided into several distinct steps.

1. Ring Opening. For ring openings to the corresponding biradical, $\Delta H_1^{\dagger}$ can be estimated directly using group additivity thermodynamic methods. Again, the group values of the radical groups are required for this step.
2. Temperature Correction. The ΔH_f^{o} given in the tables (1c) is for 298°K. Heat capacity data has to be used to correct this to the reaction temperature. There is an important lack of heat capacity data for radical groups, and this may prove to limit the effectiveness of some calculations.
3. Transition States. Modification of the bi-radical structure to the structure of the transition state must be made and the corresponding $\Delta H_3^{\dagger}$ deduced for this step. This is the important step since the value for $\Delta H_3^{\dagger}$ for this step can only be obtained by empirical methods. In addition, for a given cyclopropane ring reaction several transition states are possible, and all of these have to be accounted for in this step. As an example the cyclopropane decomposition is considered in detail.

   Step 1. Ring opening via a biradical mechanism



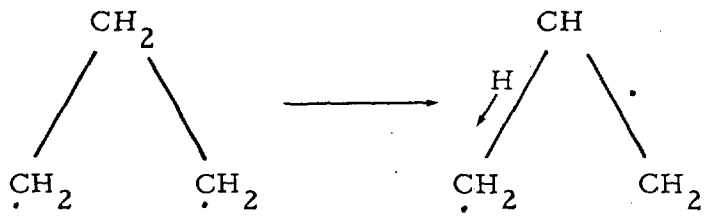
$$\Delta H_1^{\dagger} = 2\Delta H_f^{o}\ [\cdot C - (H_2)(C)] - 2\Delta H_f^{o}\ [C - (H_2)(C_2)] - \Delta H_f^{o}\ [\Delta]$$

$$= 54.0 \text{ kcal/mole}$$

where ΔH_f^{o} $[\Delta]$ is the three member ring strain energy as given by Benson[2].

Step 2. For a reaction temperature of 770°K a correction of 0.8 kcal/mole must be added to $\Delta H_{1,\ 298^{o}K}^{\dagger}$

Step 3. Transition State. The decomposition of cyclopropane yields propylene. The transition state involves a hydrogen atom migration:



The measured activation energy is 65.6 kcal/mole at 770°K. As calculated

$$Ea = \Delta H_1^{\dagger} + \Delta H_2^{\dagger} + \Delta H_3^{\dagger} + RT = 65.6 \text{ kcal/mole}$$

All the factors in this equation are known except $\Delta H_3^{\dagger}$, that is the correction factor for hydrogen atom migration in the transition state. Its value can be deduced to be

$$\Delta H_{Hmig}^{\dagger} = 9.3 \text{ kcal/mole}$$

The numerical values differ somewhat from those of O'Neal and Benson[2], due mainly to different values for the radical groups.

This deduced value for the energy associated with hydrogen atom migration in a 1, 3 biradical will be used for other 3-membered ring calculations. The assumption is made that this value can be used at all temperatures.

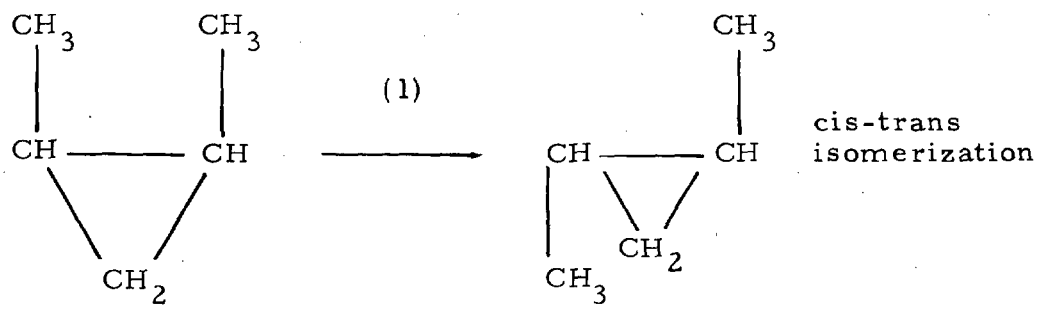
A second possibility is available in step 3 above, that is closure of the three membered ring. The reaction of the cis-trans isomerization of 1, 2-dideutero-cyclopropane has been studied and an experimental activation energy obtained of 64. 2 kcal/mole at 720°K. Therefore

$$\Delta H^{\dagger}_{C_3} = 8.0 \text{ kcal/mole}$$

Again, the assumption is made to use this value at all temperatures.

The biradical mechanism is demonstrated for the case of cis-1, 2 - dimethylcyclopropane.

The reactions are:

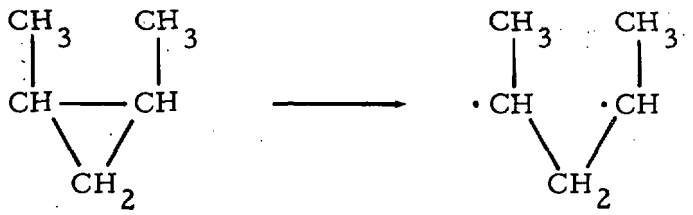


$$\xrightarrow{(2)} CH_3CHCHCH_2CH_3$$

$$\xrightarrow{(3)} CH_3CH_2\underset{\underset{CH3}{|}}{C}CH_2$$

$$\xrightarrow{(4)} CH_3CH\underset{\underset{CH_3}{|}}{C}CH_3$$

An important point in three membered ring reactions is that several sites are available for the biradical, for example,



The calculated and observed activation energies for the above reactions are shown in Table 2-4.

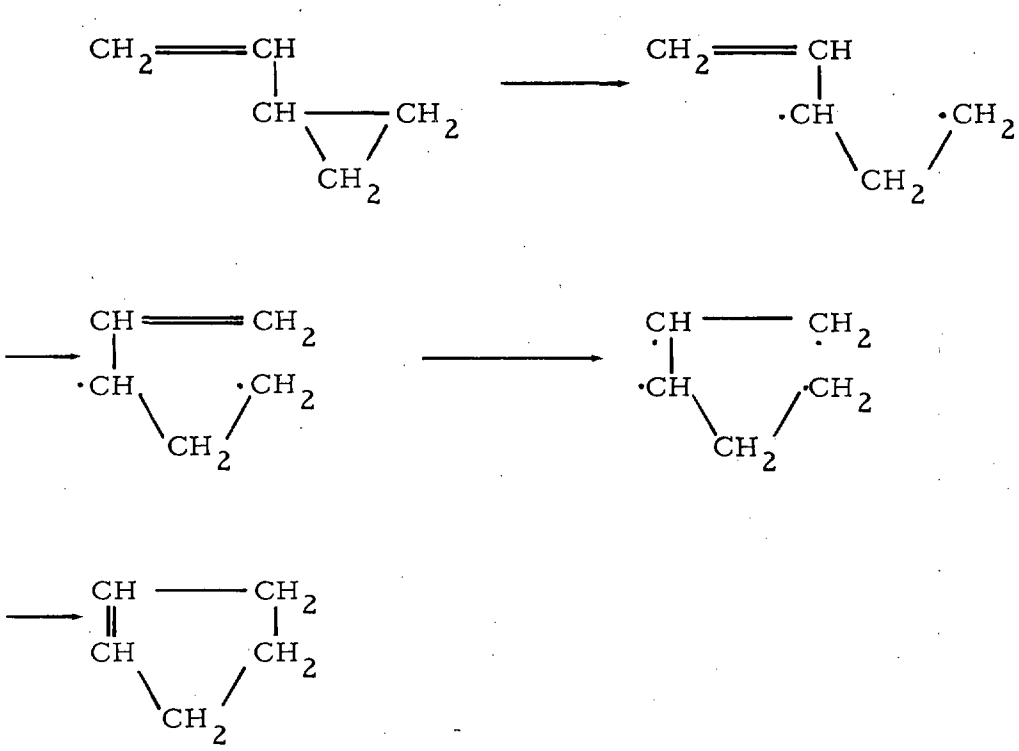
Table 2-4.
CALCULATED AND OBSERVED ACTIVATION ENERGIES

Product	Reaction Temperature °K	E_a (Calculated) kcal/mole	E_a (Observed) kcal/mole
1	689	61.4	59.4
2	689	62.7	61.3*
3	689	64.1	61.9
4	689	64.1	62.3

*Average of 61.2 and 61.4 for cis and trans form form of pent-2-ene.

The agreement is good for the activation energies. This methods appears to be generally applicable to these small ring compounds. O'Neal and Benson[2] have also investigated cyclobutane reactions and these methods also are applicable in that case. Nevertheless, several problems are evident. First, if a multiple bond is available alpha to an unshared pair of electrons, delocalization will occur. Presumably, since the group values for radical groups

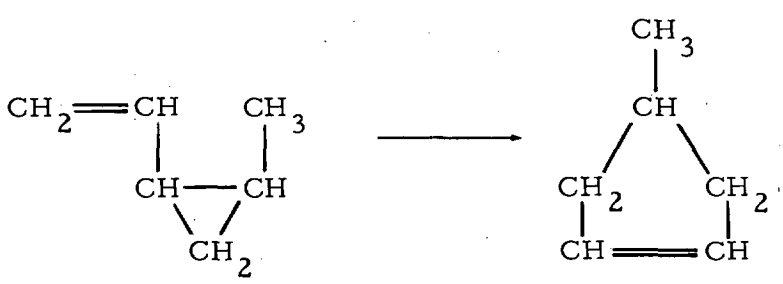
already account for this delocalization, this can be handled in a straightforward manner. The problem of conjugated chains or rings being available for further stabilization of the free radical has not been studied. More important though, double bonds can allow for migration of the unshared pair. This can lead to new mechanisms with different transition states. For example, the major product of vinyl cyclopropane decomposition is cyclopentene.



This five membered ring closure mechanism can also be treated in a manner similar to the three membered ring closure. This results in

$$\Delta H^{\dagger}_{C_5} = 8.3 \text{ kcal/mole}$$

Applying this value of $\Delta H^{\dagger}_{C_5}$ to the reaction



yields an activation energy of 47.8 kcal/mole. The observed E_a is 48.6 kcal/mole. Again the agreement is good, but this simple example does give some indication of the problems associated with complex side chains. They greatly increase the total number of possible products and provide new transition states. Extensive experimental data will be required to provide model systems for many possible transition states.

2.2.3 Six Centered Elimination Reactions

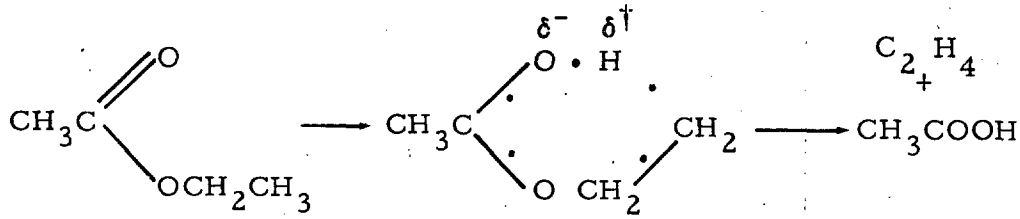
A large fraction of unimolecular gas phase reactions appear to take place by way of four centered and six centered cyclic activated complexes. The vast majority of the four centered reactions are the elimination of hydrogen halides from the alkyl halides to produce olefins. Losses of water, ammonia and H_2S from tertiary alcohols, amines, and mercaptans have been observed in only a few cases. Since this program is not concerned with halogen containing compounds we will not investigate four centered reactions at this time. Instead we will investigate six centered reactions which involve esters, alcohols and ketones. These reactions are more applicable to the interests of this program, and it is believed that the techniques developed for six centered reactions will be equally applicable to four centered reactions.

Methods have been developed for calculating $\Delta S^{\dagger}$ for different classes of six centered elimination reactions but little work has been done on estimating $\Delta H^{\dagger}$ for these types of reactions[3].

The information and experience gained in the study of the two previous categories of unimolecular reactions were applied to several six-centered elimination reactions.

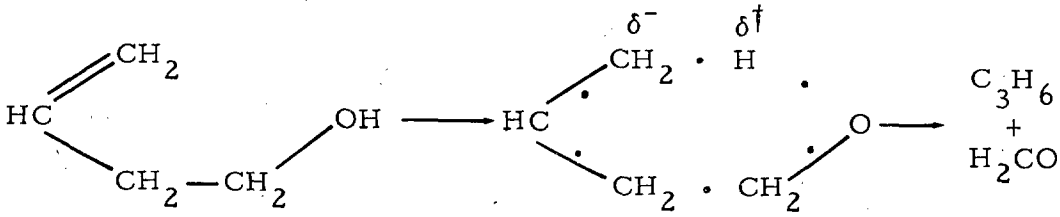
Below are given model reactions for the various categories of six centered reactions which were studied. In all cases, the transition state involves a six membered ring containing bonds of fractional order. This results in an overall polarization of the molecule between the two reacting ends.

1. Esters



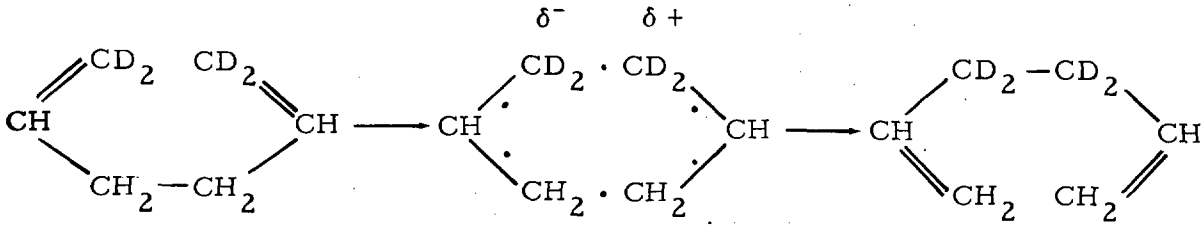
Ethyl acetate

2. α - Unsaturated Alcohols



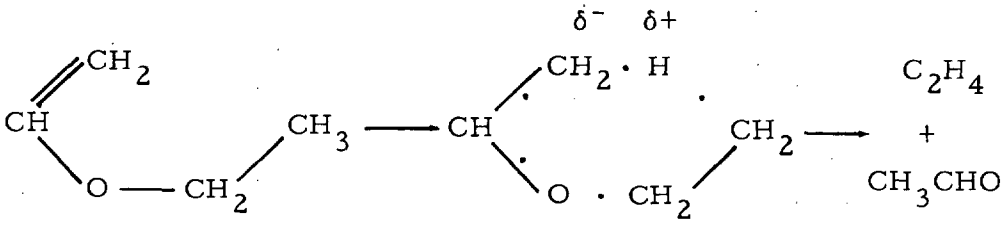
But-3-ene-1-ol

3. Allylic Rearrangement



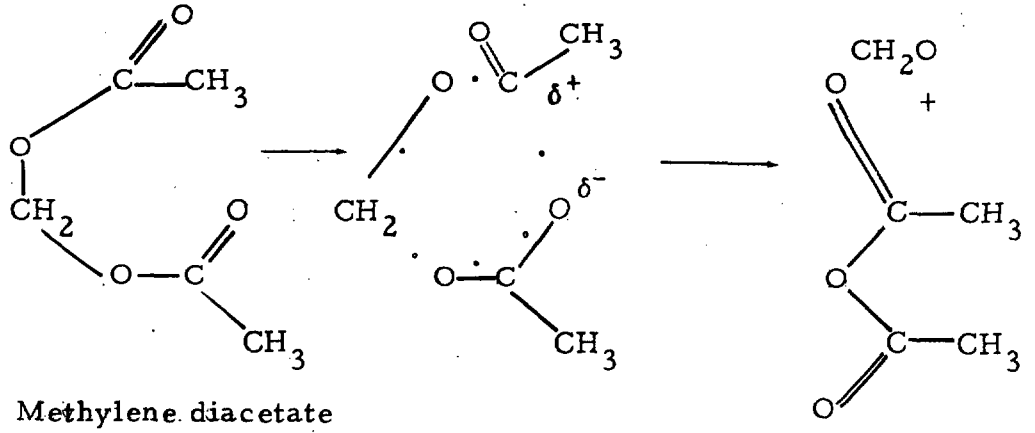
1, 1, 6, 6 - Tetradeutero -1, 5 - hexadiene

4. Allylic Ethers



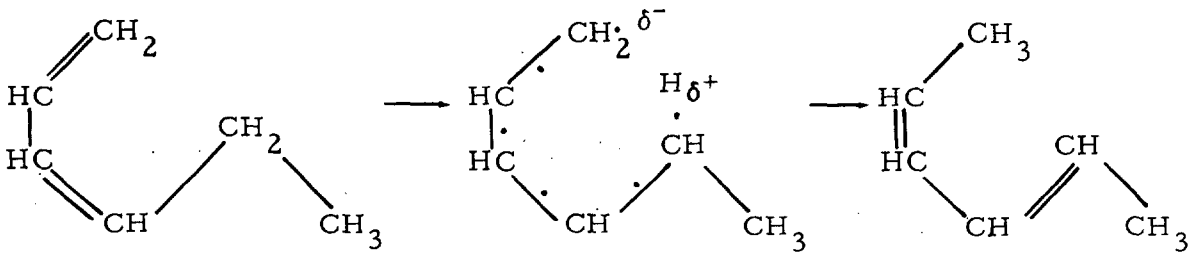
Ethyl vinyl ether

5. Diesters



Methylene diacetate

6. H - atom transfer



1, 3 - hexadiene (cis)

The assumption was made that all bonds formed or broken in the transition state of the model compound are of order one-half. The energy involved is equated to one-half the appropriate bond strength. The various bond strengths required were calculated by group additivity thermodynamic methods as outlined above.

The six-membered ring of partial bonds produces a polarization of the reacting ends of the six membered chain. The polarization energy is the difference involved in the energy required to produce the partial bonds and the observed activation energy.

The various model compounds listed above were chosen as the simplest examples for which experimental data were available. The experimentally observed activation energies are listed in Table 2-5 along with the correction for end interaction $\Delta H_p^{\dagger}$ deduced by this method.

Table 2-5

ACTIVATION ENERGIES AND END INTERACTION CORRECTION

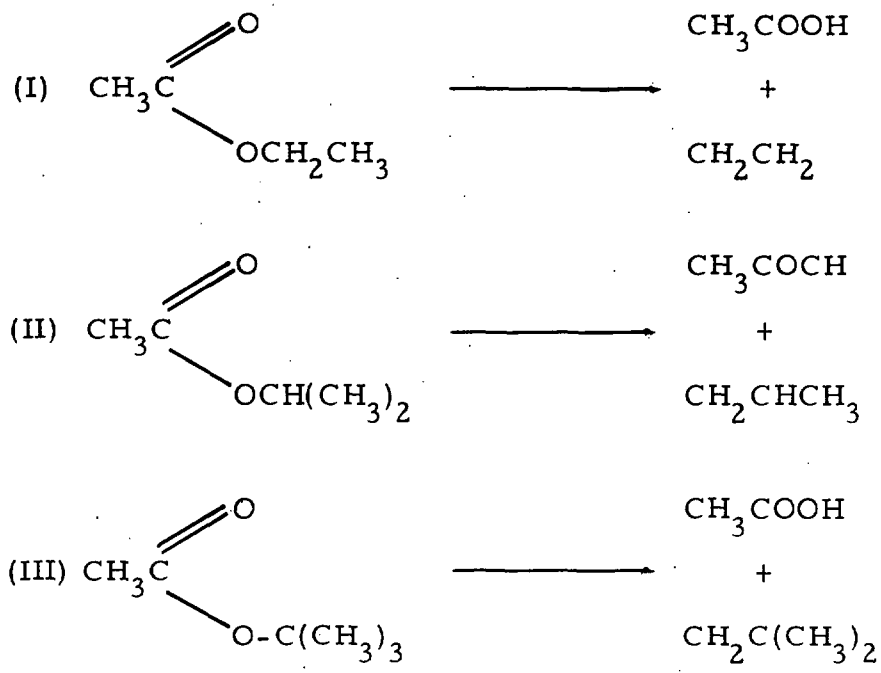
Reaction Category	Model Compound	E_a kcal/mole	T°K	$\Delta H_p^\dagger$ kcal/mole
Esters	Ethyl Acetate	48.0	725-876	13.8
α - unsaturated alcohols	But-3-ene-1-ol	41.0	643-685	13.2
Allylic Rearrangement	1,1,6,6 - tetra - deutero - 1,5 - hexadiene	35.5	530	4.4
Allylic Ethers	ethyl vinyl ethers	44.4	640-721	3.5
Diesters	methylene diacetate	36.4	493-578	17.2
H-atom transfers	1,3 - hexadiene (cis)	32.5	474-518	14.1

E_a was calculated from the summation of one-half the bond energies of those bonds being broken in the transition state, and the subtraction of (1) one-half the bond energies of those bonds being formed, and (2) $\Delta H_p^\dagger$, to account for the stabilization of the transition state due to the end polarization.

One important consideration for these reactions is the effect of substituent groups attached to the six membered ring. These groups do not enter directly into the transition state, but have the effect of adding or withdrawing electron density from the ring, thereby increasing or decreasing the magnitude of the end interaction. The class of ester reactions was chosen to investigate substituent effects since they encompass a large amount of experimental data.

The model compound for ester reactions is the decomposition of ethyl acetate into ecetic acid and ethylene. In studying compounds with hydrocarbon substitution at the α or β position of the transition state ring, account must be taken of the changing bond environment as well as the change in electron density of the ring.

The two cases of methyl substitution at the β position of the ester along with the nonsubstituted model compound, ethyl acetate are illustrated below.



The calculated and observed activation energies are given in Table 2-6 along with the correction per methyl group.

Table 2-6

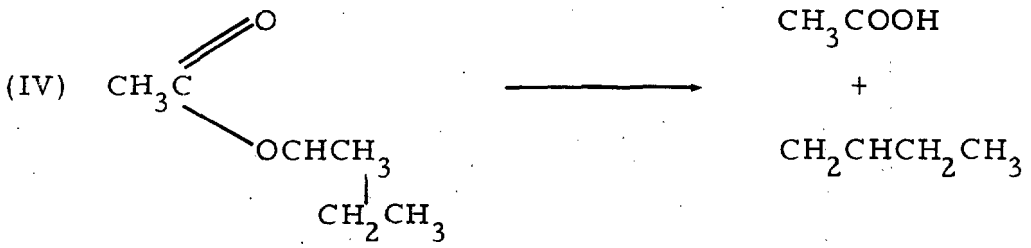
ACTIVATION ENERGIES AND CORRECTIONS FOR β METHYL SUBSTITUENTS

Reaction Number	Observed ΔE-kcal	Calculated ΔE-kcal	Number CH_3 groups	Correction per CH_3 group-kcal
I	48.0	48.0	0	——
II	45.0	48.8	1	-3.8
III	40.0	49.4	2	-4.7

Therefore an average correction of -4.3 kcal per CH_3 group will be applied.

In a similar manner, the following are examples of ethyl substituents at the β position; and the corresponding calculated corrections per ethyl group. The

activation energies and the calculated corrections per ethyl group are presented in Table 2-7.



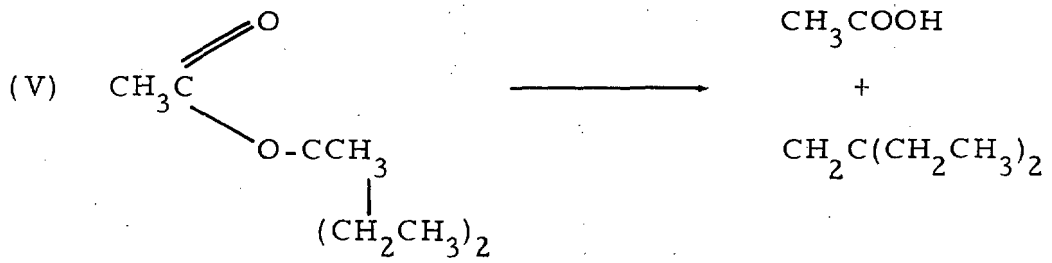


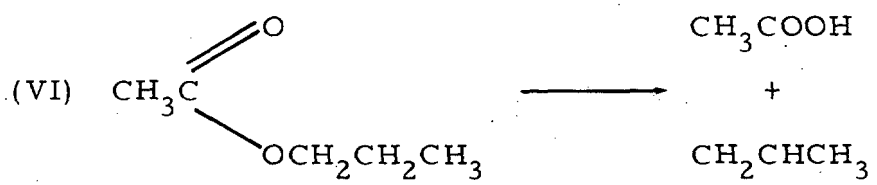
Table 2-7

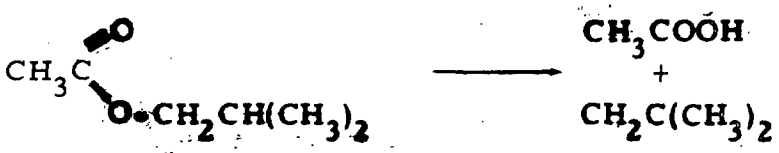
ACTIVATION ENERGIES AND CORRECTIONS FOR β ETHYL SUBSTITUENTS

Reaction Number	Observed ΔE-kcal	Calculated ΔE-kcal	Number of Ethyl Groups	Correction per Ethyl group-kcal
I	48.0	48.0	0	——
IV	45.2	48.8	1	-3.6
V	38.0	49.4	2	-5.7

The average correction is -4.7 kcal per ethyl group.

Methyl substituents at the α position are shown in (VI) and (VII):



(VII) 

The data for these substituents are shown in Table 2-8.

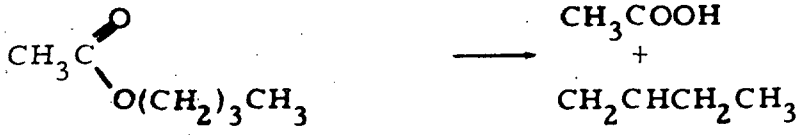
Table 2-8

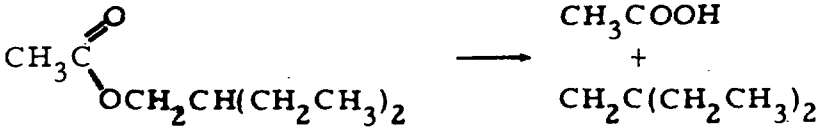
ACTIVATION ENERGIES AND CORRECTIONS FOR α METHYL SUBSTITUENTS

Reaction Number	Observed ΔE-kcal	Calculated ΔE-kcal	Number of Methyl Groups	Correction per Methyl group-kcal
I	48.0	48.0	0	——
VI	47.7	46.8	1	+0.9
VII	47.3	46.1	2	+0.6

The average correction is therefore +0.7 kcal per CH_3 group.

Examples of ethyl substitution at the α position are:

(VIII) 

(IX) 

Data for the ethyl substituents at the α position are shown in Table 2-9.

Table 2-9

ACTIVATION ENERGIES AND CORRECTIONS FOR α ETHYL SUBSTITUENTS

Reaction Number	Observed ΔE-kcal	Calculated ΔE-kcal	Number of Ethyl groups	Correction per Ethyl group-kcal
I	48.0	48.0	0	—
VIII	46.0	46.8	1	-0.8
IX	45.8	46.1	2	-0.2

This results in an average correction of -0.5 kcal per ethyl group at the α position.

This method for hydrocarbon substituents can be applied to other classifications of groups as well. The limiting factor is the lack of sufficient experimental data for model compounds.

Table 2-10 lists a variety of ester reactions to which our six-centered reaction method was applied to calculate the activation energy. The observed values of ΔE are from a tabulation of experimental values by Benson[3]. The values in parentheses are activation energies calculated from observed rate constants and Benson's tabulation of A factors. In most cases where a wide discrepancy exists between experimental values and Benson's "calculated" activation energies, Benson's values are probably more accurate. The values of ΔE calculated by the present method are in good agreement with the observed values.

Table 2-10

ACTIVATION ENERGY FOR SIX CENTERED REACTIONS

	ΔE-kcal Observed	ΔE-kcal Calculated
1. $C_2H_5COOC_2 \rightarrow$ $C_2H_4 + C_2H_5COOH$	48.5	48.0
2. Isopropyl acetate $\rightarrow$ $C_3H_6 + CH_3COOH$	45.0 46.3	44.5

Table 2-10

ACTIVATION ENERGY FOR SIX CENTERED REACTIONS (Continued)

		ΔE-kcal Observed	ΔE-kcal Calculated
3.	t - Butyl acetate → $(CH_3)_2C = CH_2 + CH_3COOH$	40.5 40.0	40.8
4.	sec - Butyl acetate → cis-trans-2butene + CH_3COOH 1-butene + CH_3COOH	46.6 (45.2) (45.2)	 43.8 44.1
5.	t-Butyl propionate → isobutene + C_2H_5COOH	39.16	40.8
6.	N-Propyl acetate → $C_3H_6 + CH_3COOH$	47.7 48.3	47.5
7.	N-Butyl acetate → 1-butene + CH_3COOH	46.0	46.3
8.	N-Pentyl acetate → 1-pentene + CH_3COOH	46.4	46.3
9.	3-Methylbutyl acetate → $CH_3COOH + CH_2 = CHCH(CH_3)_2$	47.9	46.3
10.	2-Methylpropyl acetate → isobutene + CH_3COOH	48.8	47.5
11.	2-Methylbutyl acetate → $CH_3COOH + CH_2 + C(CH_3)C_2H_5$	45.7	46.3
12.	2-Ethylbutyl acetate → $CH_3COOH + CH_2 = C(C_2H_5)_2$	49.7 (45.8)	 45.1
13.	2-Pentyl acetate → CH_3COOH + 2-pentenes (cis, trans) CH_3COOH + 1-pentene	43.7 (43.8) (43.8)	 42.6 44.1
14.	3-Pentyl acetate → CH_3COOH + 2-pentenes (cis, trans)	44.7	43.4
15.	2-Heptyl acetate → CH_3COOH + 2-heptenes (cis, trans) CH_3COOH + 1-heptenes	45.3 (43.6) (43.6)	 42.6 44.1

Table 2-10

ACTIVATION ENERGY FOR SIX CENTERED REACTIONS (Continued)

		ΔE-kcal Observed	ΔE-kcal Calculated
16.	3-Heptyl acetate →	46.9	
	CH_3COOH + 2-heptenes (cis, trans)	(42.8)	43.4
	CH_3COOH + 3-heptenes (cis, trans)	(42.8)	42.2
17.	4-Heptyl acetate →	44.9	42.2
	CH_3COOH + 3-heptenes (cis, trans)	42.7	
18.	3-Methyl - 2-pentyl acetate →	43.2	44.1
	3-Methylpent - 1-ene + CH_3COOH	(43.5)	
	3-Methylpent - 2-enes (cis, trans)		
	+ CH_3COOH	(43.5)	43.3
19.	2, 4 - Dimethyl - 3-pentyl acetate →	44.7	44.1
	$(CH_3)_2 C = CH(i = C_3H_7)$	(43.0)	
20.	2, 3 - Dimethyl - 2-butyl acetate →	41.3	41.7
	CH_3COOH + tetra methylethylene	(37.9)	
	$CH_3COOH + CH_2 = C(CH_3)CH(CH_3)_2$	(37.9)	40.4
21.	3-Methyl - 3-pentyl acetate →	42.4	
	CH_3COOH + 3-methylpent - 2-ene (cis, trans)	(38.0)	39.7
	CH_3COOH + 2-ethylbut - 1-ene	(38.0)	40.0
22.	2-Methyl - 2-pentyl acetate →	40.6	
	CH_3COOH + 2-methylpent - 1-ene	(38.3)	40.4
	CH_3COOH + 1-methylpent - 2-ene	(38.3)	38.9

The above results demonstrate the systematic method as applied to substituent effects for ester reactions. A similar method can be used to gain correction factors for oxygen, nitrogen, and halogen containing substituents. Similarly, it is expected that this method can be applied to the other classes of six centered reactions.

2.3 BIOMOLECULAR REACTIONS

In general, biomolecular reactions can be separated into three classes — metathesis or atom transfer, association reactions, and displacement

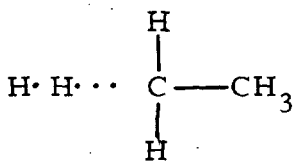
reactions. Some of the inherent problems and tentative solution methods for each of these reaction categories are described below.

2.3.1 Metathesis Reactions

An example of hydrogen atom transfer is:

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

The transition state for this type of reaction involves some structure such as:



The method of partial bond orders used in the six centered elimination reactions may be applied here to calculate activation energies. Problems are sure to be encountered in these atom transfer systems due to unequal sharing of the atom in question in the transition state. But a large set of data exist for many classes of metathesis reactions so empirical correction factors may be deduced.

A first step in calculating an entropy of activation for atom transfer reactions may be to assume a constant A factor for any one class of atom transfer. The A factors appear to be fairly constant within any one class.

Since most atom transfer reactions involve only two bonds being simultaneously made or broken, this category of reactions may prove to be successfully handled by group additivity methods. Most certainly some empirical correction factors will be needed nevertheless.

2.3.2 Association Reactions

Such association reactions as radical-radical recombination may be best handled by calculating the back rate for unimolecular decomposition and using the principle of detailed balance to calculate the desired rate. But

more complicated processes of association will require careful consideration of the vibrationally excited intermediate produced. For the general type of reaction:

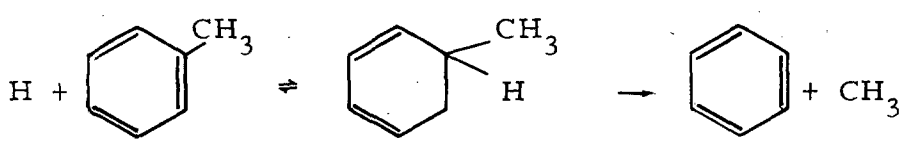
$$A + B \rightleftharpoons AB^* \rightleftharpoons AB$$

the intermediate AB* is usually vibrationally excited and unless this energy can be transferred to other degrees of freedom, the intermediate will decompose back to reactants. The rate of deactivation of this type of excited intermediate will be an important step in solving reaction rate calculations for these bimolecular reactions. A potential approach for estimating the rate of decomposition of larger intermediates is in the Rice-Ramsperger-Kassel model which treats the decomposition rate of an activated molecule in terms of transition probability and the density of vibrational quantum states. These, in turn, are a function of certain estimated or assigned variables such as the critical energy or minimum quanta of vibrational energy required for decomposition. The low-pressure limit for deactivation can also be calculated.

For small (di- or triatomic) intermediates, it may be possible and indeed desirable to utilize the more accurate Rice-Ramsperger-Kassel-Marcus model.

2.3.3 Displacement Reactions

This type of reaction appears frequently in the chemistry of unsaturated compounds. For example:



It may be possible to calculate activation energies for these reactions by assuming a stable structure for the transition state and using group additivity methods to calculate the ΔH of this species. Free radical group additivity data, such as that estimated during the course of this study, would be utilized to compute the heat of formation. In order to account for differences in bond strengths, chemical environments, etc., correction factors

will most probably have to be determined for various classes of compounds, as in our treatment of unimolecular reactions. These calculations may be hindered by the fact that little quantitative data seem to be available for this type of reaction.

Section 3

SCHEME FOR COMPUTER CALCULATION OF THE MOST PROBABLE REACTION RATE

For any elementary reaction to which there are several possible reaction paths, and therefore, several possible products, the most straightforward way to compute the most probable path would be to calculate the rate constant for all paths, and eliminate any paths which have a rate of less than 10 percent of the fastest path. This appears to be a reasonable criterion by which to predict the major products of a reaction. To save computer calculation time a preliminary screening method may be possible. Since many reactions of a given molecule along similar paths should have similar $\Delta S^{\dagger}$, it may be possible to calculate $\Delta H^{\dagger}$ and eliminate all but the most important paths having the smallest activation energies. Then the $\Delta S^{\dagger}$ could be calculated for only these most important paths.

Section 4
METHODS OF HANDLING COMPLEX REACTION SYSTEMS

Complex reaction systems involve multiple, parallel, or successive elementary reaction steps. For this study, complex reaction systems are divided into two general categories: Additive Reaction Systems and Successive Reaction Systems.

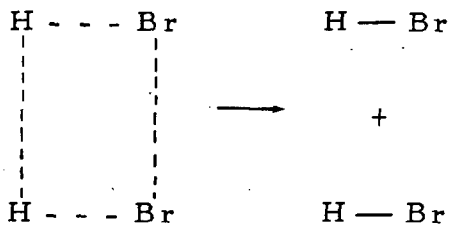
4.1 SUCCESSIVE REACTION SYSTEMS

These systems are defined as reaction systems which require one or more successive elementary steps to go from reactant to product. This is represented by:

$$A \longrightarrow A_1 \longrightarrow A_2 \longrightarrow A_n \longrightarrow A' \qquad (1)$$

This reaction group can be very complicated due to the fact that at each elementary step different products may be possible. This will produce branching reaction systems leading to different products. Parallel processes are also possible. In addition, the different products at each individual step may influence other steps.

Fortunately there are some basic considerations which make it possible to sort out those pathways which are important. In any chain reaction of the sort described in (1) it is necessary that the intermediate or chain propagation steps be very fast. This is necessary if the chain reaction is to compete favorably with the concerted mechanism. For example in the decomposition of H_2 and Br_2, the following concerted mechanism is possible:



(2)

The chain reaction would be

$$H_2 + Br \longrightarrow HBr + H \tag{3}$$

$$H + Br_2 \longrightarrow HBr + Br \tag{4}$$

In order that several successive steps can compete with a concerted mechanism, the chain propagation steps must have low activation energies. In addition, the intermediates (A_1, A_2, -- A_n, in reaction (1)) must be highly reactive intermediates, i. e., atoms and free radicals. This now limits somewhat the possible pathways.

4. 1. 1 Criterion for Favorable Chain Propagation Steps

Following the recommendations of Benson [1d], we will limit the possible chain propagation steps to three types of elementary reactions: addition, atom abstration, and unimolecular fission. In addition, Benson has proposed a criterion for the activation energies of chain propagation reactions. For bimolecular steps $\Delta E/\theta \leq 5.5$ and unimolecular steps $\Delta E/\theta \leq 14$ where $\theta = 2.303$ RT kcal/mole. This is an estimation of the activation energy required so that the chain propagation steps will be rapid enough to compete with a concerted mechanism.

4. 1. 2 Method for Determining Chain Propagators

In order for a chain reaction to proceed, some catalytic agent must be produced and then used to propagate the chain, the overall concentration of the propagator not increasing with time. Benson has proposed a general method to find the chain propagator. We have tested this for the decomposition of ethyl chloride and found that it successfully predicts the correct reaction mechanism.

The procedure is the following: Some radical R is chosen. It can only abstract an atom:

$$\begin{aligned} & \longrightarrow \cdot CH_2CH_2Cl + RH \\ R\cdot + C_2H_5Cl & \longrightarrow \cdot CH_3\dot{C}HCl + RH \\ & \longrightarrow CH_3\dot{C}H_2 + RCl \end{aligned} \tag{5}$$

There are three possible propagation steps. The exothermicity of the reactions is given in kcal/mole.

$$\cdot CH_2CH_2Cl \longrightarrow CH_2CH_2 + Cl\cdot \quad 21.3 \tag{6}$$

$$CH_3\dot{C}HCl \longrightarrow CH_2CHCl + H\cdot \quad 43.1 \tag{7}$$

$$CH_3\dot{C}H_2 \longrightarrow CH_2CH_2 + H\cdot \quad 39.0 \tag{8}$$

Clearly, considering that activation energy $E_a \geq \Delta H$, reactions (7) and (8) are too slow to be considered only reaction (6) will be the propagation step. Reaction (6) produces the radical Cl, so in order for this to be a chain process, the unspecified chain carrier R in reaction (5) must be Cl. The possible reactions with their ΔH are given below.

$$Cl\cdot + C_2H_5Cl \longrightarrow \cdot CH_2CH_2Cl + HCl \quad -5.0 \tag{9}$$

$$Cl\cdot + C_2H_5Cl \longrightarrow CH_3\dot{C}HCl + HCl \quad -8.4 \tag{10}$$

$$Cl\cdot + C_2H_5Cl \longrightarrow CH_3CH_2 + Cl_2 \quad +21.3 \tag{11}$$

Again only reactions (9) and (10) can compete, and as shown above only the decomposition of $\cdot CH_2CH_2Cl$ can compete. The final reaction system is given.

$$Cl\cdot + CH_3CH_2Cl \longrightarrow \cdot CH_2CH_2Cl + HCl \tag{12}$$

$$\cdot CH_2CH_2Cl \longrightarrow CH_2CH_2 + Cl\cdot \tag{13}$$

Therefore, the only products of CH_3CH_2Cl decomposition are CH_2CH_2 and HCl, and we have deduced the important elementary steps needed to calculate the overall rate. Unfortunately it has been found difficult to apply this method to more complex systems. A fair amount of chemical knowledge seems necessary to make a preliminary choice of important reactions; otherwise the number of possible reactions becomes difficult to handle. It is necessary to include the chemistry of initiation and termination reactions to develop a realistic list of possible reactions.

4.1.3 Initiation Reactions

For homogeneous systems, monoradicals must appear and disappear two at a time. It will be necessary to test all possible sources of radicals in a given system, the most rapid formation being the one observed. It is possible to develop an appropriate criterion to test some of the possibilities.

Shown in Table 4-1 are a factors and activation energies for a variety of unimolecular reactions involving the fission of a molecule into two radicals. While there is considerable range for the activation energies, $\log A = 16 \pm 1\ sec^{-1}$ for many systems. In contrast, bimolecular reactions of two molecules to two radicals (the reverse of radical disproportionation) have $\log A = 9 \pm 1$ liter/mole.sec.

Table 4-1

FISSION OF MOLECULES INTO TWO RADICALS

Reaction	Log A	E(kcal/mole)	T(^{o}K)
$C_2H_6 \longrightarrow 2CH_3$	16.0	86.0	850
$C_4H_{10} \longrightarrow 2C_2H_5$	17.4	82	400
$CH_3OOCH_3 \longrightarrow 2CH_3O$	15.4	36.1	410
$C_2H_5ONO \longrightarrow C_2H_5O + NO$	14.2	37.7	430
$C_2H_5ONO_2 \longrightarrow C_2H_5O + NO_2$	16.9	41.2	420
$CH_3N = NCH_3 \longrightarrow CH_3 + NNCH_3$	17.2	55.5	600
$C_6H_5 - CH_2C_2H_5 \longrightarrow C_6H_5 - CH_2 + C_2H_5$	14.9	68.6	950
$C(NO_2)_4 \longrightarrow C(NO_2)_3 + NO_2$	17.5	40.9	470

Considering these values of pre-exponential factors Benson[1e] has shown that for the rates of unimolecular and bimolecular fission to be equal, $E_1 - E_2 = (9.4 \pm 2)\ \theta$, where $\theta = 2.303$ RT kcal/mole, and E_1 is the activation energy for the unimolecular step and E_2 is the activation energy of the bimolecular process. At 2000°K $E_1 - E_2 = 88 \pm 18$ kcal. This is so high that bimolecular initiations will almost never happen. At 1000°K $E_1 - E_2 = 44 \pm 9$ kcal. It will be necessary to test possible bimolecular and unimolecular processes with this criterion.

In most case, the bimolecular initiation process will never occur, except with few exceptions. One example given by Benson [1e] is the pyrolysis of olefins.

$$C_3H_6 \longrightarrow C_3H_5 + H \quad \Delta H_1 = 87 \text{ kcal/mole}$$

$$2C_3H_6 \longrightarrow C_3H_5 + C_3H_7 \quad \Delta H_2 = 48 \text{ kcal/mole}$$

In this case near 1000°K the bimolecular process must be included in the kinetics.

4.1.4 Termination Reactions

The rates for several representative radical recombination reactions are given in Table 4-2.

Table 4-2
RADICAL-RADICAL ASSOCIATION REACTIONS

Reaction	Log k (Liter/mole sec)	T(°K)
$2CH_3 \longrightarrow C_2H_6$	10.5	400
$2C_2H_5 \longrightarrow C_4H_{10}$	10.4	400
$CH_3 + C_2H_5 \longrightarrow C_3H_8$	10.7	400
$CH_3 + n\text{-}C_3H_7 \longrightarrow n\text{-}C_4H_{10}$	10.7	400
$2\ i\text{-}C_3H_7 \longrightarrow C_6H_{14}$	10.8	400
$2\ t\text{-}C_4H_9 \longrightarrow C_8H_{18}$	9.5	373
$2\ t\text{-}C_4H_9O \longrightarrow C_8H_{19}O_2$	8.8	420
$CH_3 + NO \longrightarrow CH_3NO$	8.8	300

Most of these reactions fall in the range of Log k = 9.8 ± 0.5 liters/mole sec. Disproportionation reactions for large radicals also have the same rate range. To a first approximation all radical-radical recombinations or disproportionations will be considered to have nearly the same rate. As the radical chain carriers build up in concentration, the termination reactions will be governed by this rate.

The only exception to this case is the recombination of two small radicals (CH_3, NO, Cl). In certain pressure regions these reactions will be third order. These molecules will have to be treated as special cases. Possibly the number of small radical reactions involved in most reactions can be minimized, and specific experimental data used for these reactions.

4.2 ADDITIVE REACTION SYSTEMS

These systems are defined by a molecule or molecules in which two or more distinct elementary steps are possible with the initial reactants. This can be represented by the following: If reactive center A can undergo an elementary step to produce A', and similarly B to B', then an additive reaction system would contain both A and B, that is:

$$A - B \longrightarrow A' - B'$$

This represents the additive reaction class in its simplest form. If both reactive center A and B are present in a molecule, then the product of the reaction is just the sum of the reactions of the two reactive centers. An additional mechanism may be possible. We will term this the interference mechanism. That is to say with both A and B present in the same molecule, the possible elementary steps which lead to products will be something different than A to A' and B to B'. In other words, the simultaneous occurrence of both A and B may interfere with the "usual" elementary reactions. For instance B to B' may be blocked by the presence of A.

$$A - B \longrightarrow A' - B$$

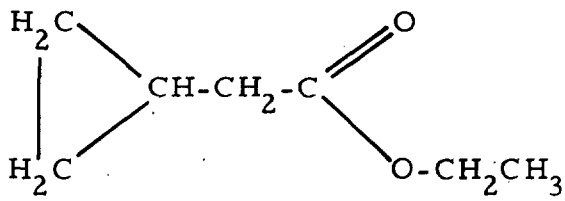
Or another possibility is that A and B together may produce some different elementary step.

$$A - B \longrightarrow A' - C$$

It is clear that in such cases as two carbon-carbon double bonds widely separated in a hydrocarbon chain so that there is no conjugation, the appropriate chemical entities will undergo their usual reaction, unhindered by the presence of each other. This would be a simple additive case. As long as we are able to calculate the individual elementary steps, the simple additive case will just be the sum of the possible elementary steps. But it will

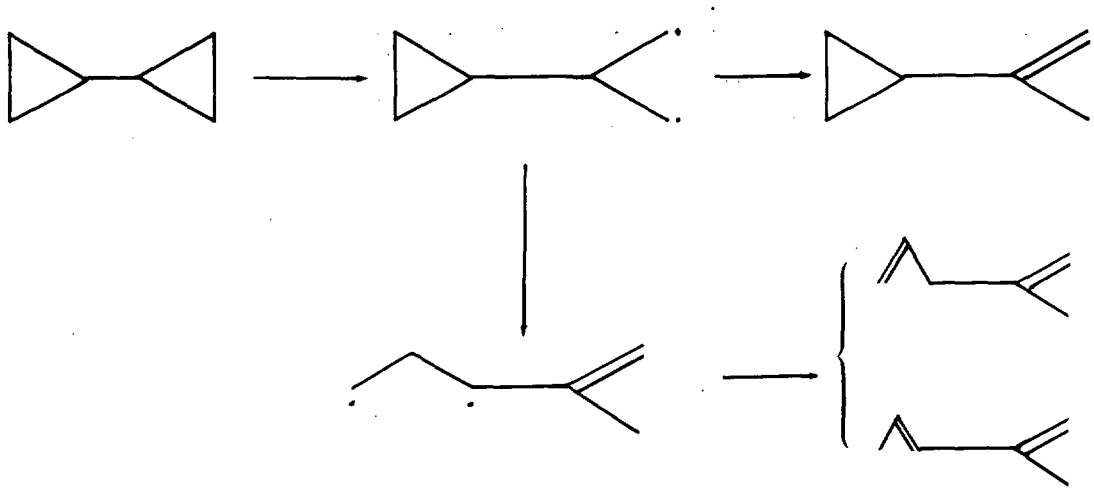
be necessary to investigate more thoroughly the possible "interference" mechanism possible for different combinations of A and B.

For example the molecule

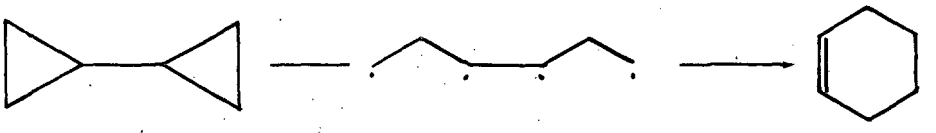


would be expected to undergo reactions specific to both 3-membered rings and to esters. The presence of the ring will not influence to any great extent the six centered elimination pathway of the ester; nor will the ester group interfere with the biradical mechanism of the small ring. The final product distribution depends only on the relative rates of the two independent pathways and the reaction conditions. This is a simple example of the additive reaction class.

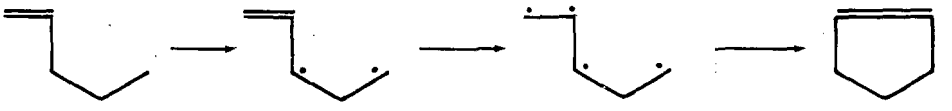
A more complex situation arises when "interference" between two distinct reaction centers can occur. An example of this type are the reactions of bicylopropyl. The usual biradical mechanism is present for each ring separately and 4 mono- and 9 di-ene products are found. Some examples are given below.



All these products arise due to "addition" of the pathways possible from the two distinct reactive centers. But several pathways are possible only if both reactive centers are present. These reactive pathways are not due to simple "addition" of reactive pathways. For example



This pathway in fact produces the major product for the bicyclopropyl molecule. Another example of an interference process is when a double bond is adjacent to a 3-membered ring. The usual reactive pathways of the ring and double bond are available, but the following reaction produces one of the major products.



This five-membered ring closure mechanism is not possible unless both the 3-membered ring and double bond are present together.

We have not investigated the possible interference mechanisms for a wide variety of systems. But these few examples indicate that they are of major importance. Some complex molecules which contain more than one reactive center will be able to be treated by simple addition of our present methods. But additional study will be required to locate important classes of interference mechanisms. Due to all the possible combinations between reaction categories, there may be many special cases which require special treatment.

Section 5
POTENTIAL PROGRAMMING METHODS FOR COMPUTER APPLICATION

Two examples have been chosen to demonstrate the application of computer methods to the reaction kinetics technique. These are simple fission reactions and reactions of simple fission with resonance stabilization.

5.1 SIMPLE FISSION REACTIONS

The conditions for this reaction category are that the products of a unimolecular reaction are radicals and/or atoms: and no concerted reaction path with a much lower activation energy is available. The activation energy at temperature T, is defined by $E = D_{A-B} + RT$, where D_{A-B} is the bond dissociation energy of the reaction coordinate. For the reaction

$$A\text{-}B \longrightarrow A\cdot + \cdot B$$

$D_{A-B} = -\Delta H_f(A\text{-}B) + \Delta H_f(A\cdot) + \Delta H_f(B\cdot)$. The assumption here is that the back reaction for the recombination of two radicals has zero activation energy.

The calculation for the entropy of activation is straightforward. The various contributions to the entropy of activation are (a) reaction path degeneracy, $R \ln(g)$ (b) external rotation which can be shown to be $R \ln(6D_{A-B}/RT)^{1/3}$ except for the case of H or D atom cleavage where it is zero, (c) hindered internal rotation to free rotation in the transition state, $\Delta S_{fr} = S_f - S_h$ (these values are tabulated by Benson[5]), (d) reduction in frequency of bending modes, $S_{bf} = 5$ e.u. for the case of atomic and free radical products, $S_{bf} = 10$ e.u. when the products are two radicals, (e) entropy associated with reaction coordinate, $\Delta S_{rc} = S_{st}$, where S_{st} is the entropy of stretching of a bond undergoing cleavage.

The entropy of activation, therefore is

$$\Delta S^{\dagger} = RLng + RLn\ (6D_{A-B}/RT)^{1/3} + \Delta S_{rc} + S_{bf} + \Delta S_{fr}$$

and the calculated rate constant is

$$k = (\frac{ekT}{h})\ \exp\ (\Delta S^{\dagger}/R)\ \exp\ (-E/RT)$$

This method for the calculation of the rate constant of a simple fission reaction can be adapted to computer programming. This is represented below in Figure 5-1.

5.2 REACTIONS OF SIMPLE FISSION WITH RESONANCE STABILIZATION

This case is very similar to the simple fission case with some exceptions. The conditions are the same with the addition of the fact that a C-C pi bond is one C-C single bond removed from the reaction site. This means that cleavage results in an atom and olefin or radical and olefin. The carbon-carbon double bond stabilizes the radical product by resonance delocalization. This mechanism produces changes in both activation energy and entropy from that in the simple fission case.

The activation energy is calculated in the same way as in the simple fission case, but it is necessary to use the group values for the radical groups developed earlier in this program. These group values already account for resonance stabilization of the radical.

The entropy calculation is similar, but the participation of the π bond in the transition state must be accounted for. This bond contributes mainly to the internal rotation where a 1/2 pi bond torsion is assigned -3.5 e.u. Also the entropy decrease for the tightening of the C-C single bond due to resonance is obtained by increasing its normal vibrational frequency by about 1.3. The resulting computer flow diagram is given below in Figure 5-2.

It would be a simple matter to integrate these two schemes together to treat simple fission cases with and without resonance stabilization.

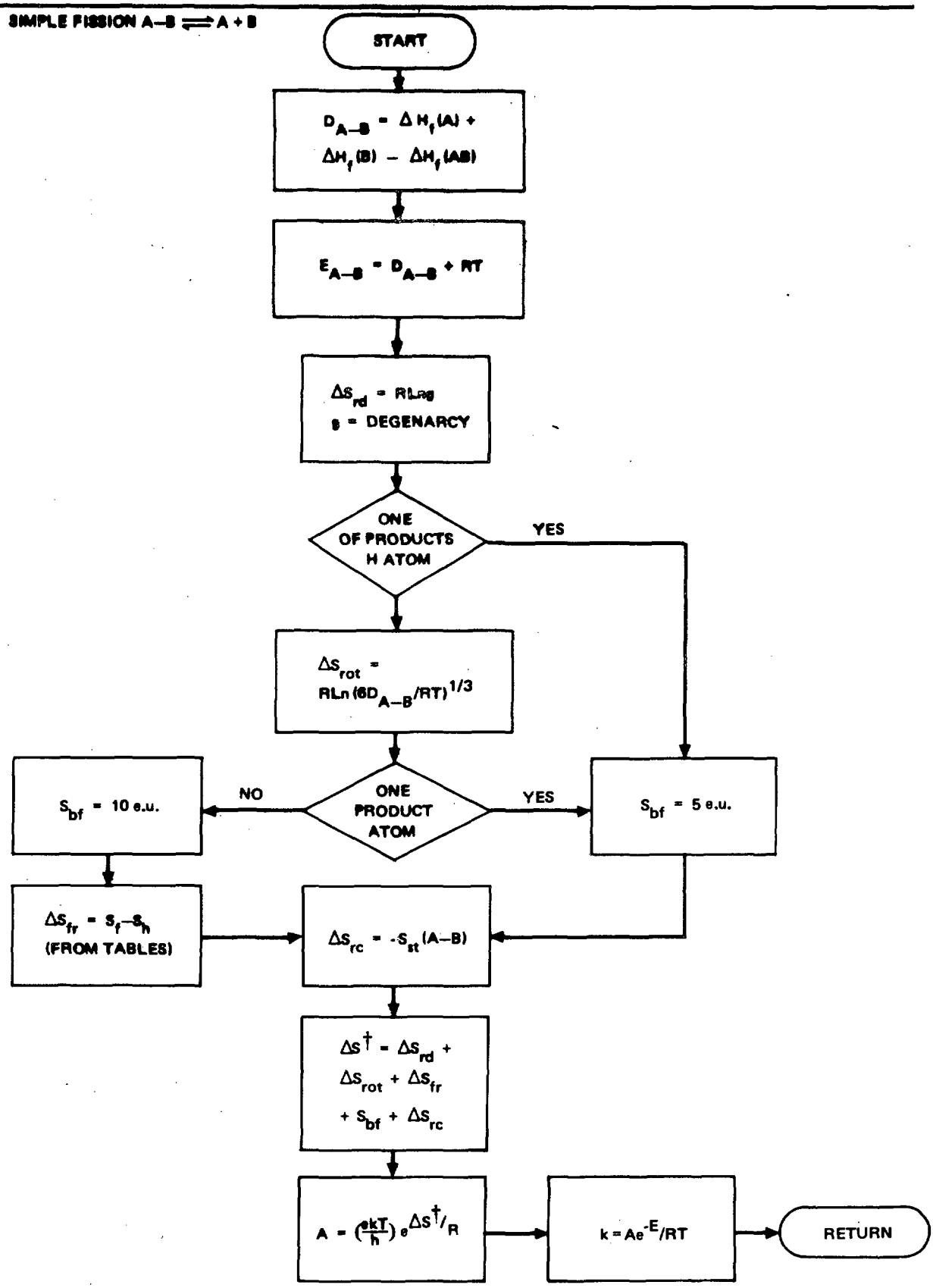


Figure 5-1. Flow Chart 1

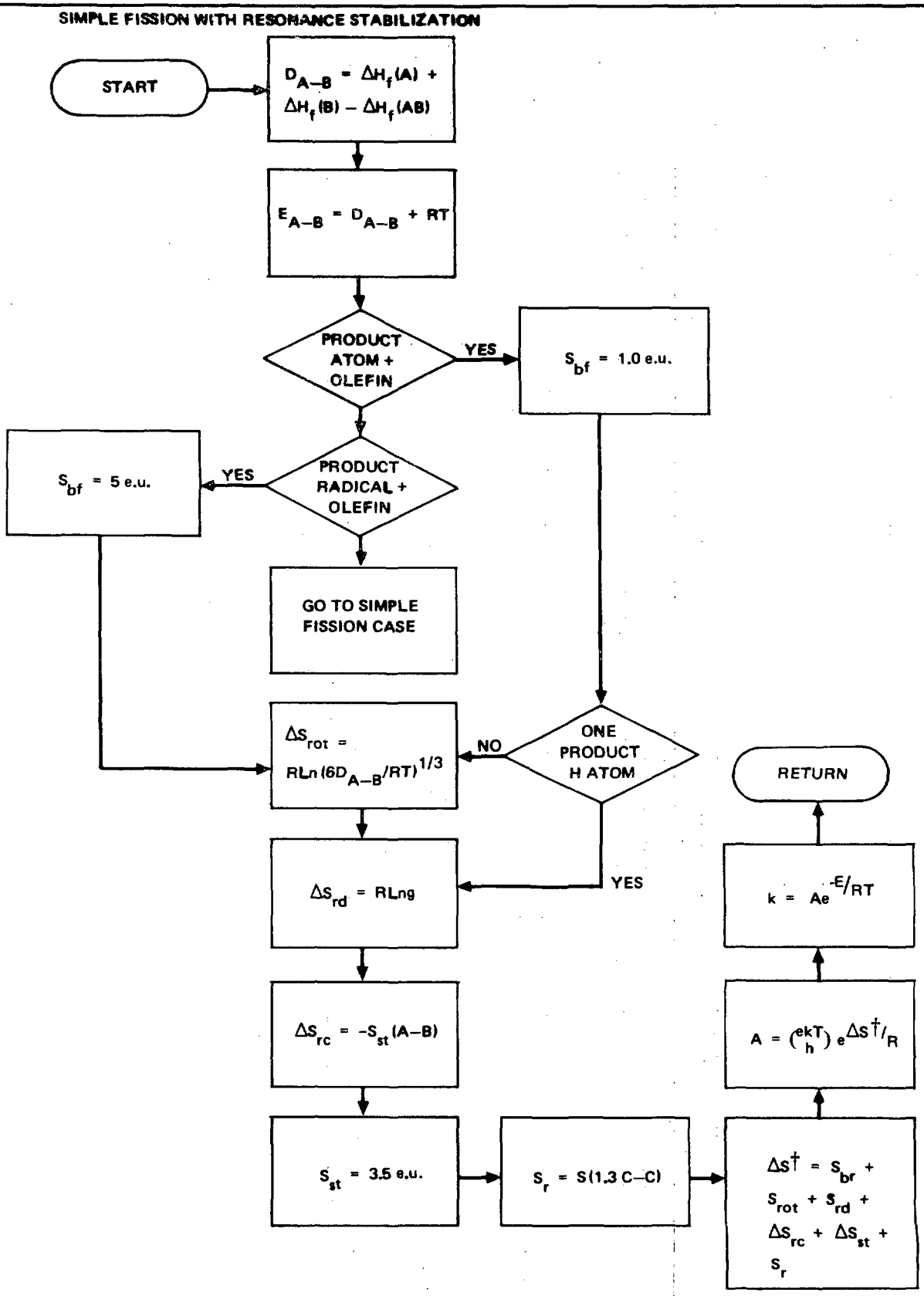


Figure 5-2. Flow Chart 2

REFERENCES

1. S. W. Benson. Thermochemical Kinetics. John Wiley & Sons, Inc., New York, 1958. (a) pp 55-19; (b) p 215; (c) pp 178-193; (d) pp 120-175; (e) pp 131-135.

2. H. E. O'Neal and S. W. Benson. J. Phys. Chem., 72, 1866 (1968).

3. H. E. O'Neal and S. W. Benson, J. Phys. Chem., 71, 2903 (1967).

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13. ABSTRACT

A FORTRAN program for calculating the thermodynamic properties of complex gas molecules by the method of group additivity is documented herein. Included are descriptions of the computational method, characteristics, functions, input/output formats, and logic structure of the program. Seventeen case calculations for diversely structured molecules are presented. Also depicted are a listing of the program, a complete glossary of the program variables and the tables of data comprising the data library input.

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