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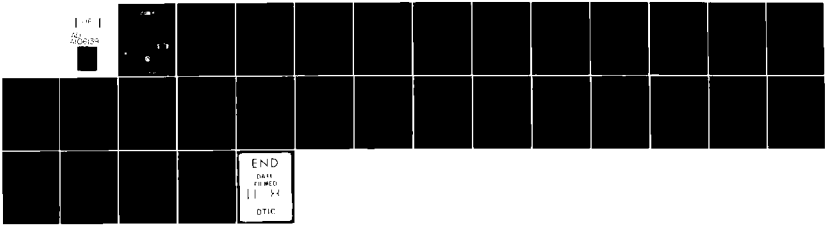

NRL Report 8498

Construction of Large Reaction Mechanisms

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An algorithm has been developed to systematically and objectively generate tractable reaction mechanisms using as input information the species present, and their enthalpies, entropies, number of atoms, and number of bonds. The algorithm generates all possible reactions subject to the constraints of mass balance, energy, entropy, and number of bonds broken and formed. Bimolecular, unimolecular decomposition, addition and isomerization reactions are considered. Even the most expert kineticist can err (by omission) with mechanisms involving 50 or more species. This method reduces that error and still allows for the application of chemical intuition by the researcher.

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CONTENTS

CONSTRUCTION OF LARGE REACTION MECHANISMS

INTRODUCTION

Researchers are currently studying combustion reactions in an effort to gain new insights into fuel combustion efficiency and fuel safety. The understanding of combustion systems is often greatly aided through the use of computational models. However, the complexity of multispecies systems makes the modeling task formidable. The methodology presented here demonstrates the logical formulation of a reaction mechanism for a multispecies combustion system.

For the combustion modeler and the chemical modeler in general, the formulation of a complex mechanism consists of two major steps:

1. Specification of the molecules and molecular fragments to be included in the system.

2. Selection of the chemical reactions to be considered and included in the proposed mechanism.

Subsequent steps to complete the overall modeling process include:

3. Assignment of the rate constants to the selected reactions.

4. Solution of the time dependent coupled differential equations of the model's full mechanism.

5. Comparison of the output from the model with experimental data.

6. Performance of sensitivity analysis on the parametric input to the model.

The six steps are usually performed in the order listed, but not necessarily. This report is concerned mostly with Step 2, the selection of the chemical reactions in the mechanism. We will assume that the species involved have been previously specified (Step 1) and we will use a sample species set for illustrative purposes.

Frequently chemical kinetic mechanisms are the product of a researcher's expertise and feelings. However, it can be very difficult for the modeler to consider each of the possible reactions when constructing a reaction set from a given set of reactive species. Even a small species set can give rise to an extremely large reaction scheme. Typically combustion systems can have more than 30 species. If the modeler does not or cannot consider all possible reactions involving the given species, then it is possible that potentially important reactions will not be considered.

Usually there is some agreement among modelers as to the rate constants to assign to various reactions (Step 3). Many models are attacked because of rate constants that are possibly incorrect by one or two orders of magnitude (typical units of cm^3 $molecule^{-1}$ s^{-1}). However, one quickly realizes that omitting a potentially important reaction underestimates that rate constant by 13 or 14 orders of magnitude. (Omission sets a rate constant of zero versus a typical bimolecular rate constant value of 10^{13} to 10^{14} cm^3 $molecule^{-1}$ s^{-1}.) It is for this reason that it is quite important to *consider* (not necessarily include, but consider) all possible reactions. Even the most expert kineticist can easily err when it comes to mechanisms of 50 or more species. It should be mentioned parenthetically here that the difficulty in the eventual solution of the coupled differential equations (Step 4) is in the number of species, not the number of reactions, because the number of coupled differential equations is dictated by the number of species. A model of 900 reactions of 55 species is tractable.

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If a systematic procedure, or algorithm, which allows for the consideration of all possible reactions can be followed when constructing a reaction set, some of the uncertainty associated with the proposed mechanism can be eliminated. The organization of the mechanism is also enhanced, and the time required to construct the complete reaction set is decreased. Therefore, in an effort to reduce the arbitrariness inherent in Step 2, we present in this report a convenient algorithm by which modelers can quickly and automatically construct a complete reaction set. We assume for this analysis that all the relevant species which play a significant role in the mechanism have been specified.

SAMPLE SYSTEM AND NOTATION

In order to understand the use of the proposed algorithm, it will be discussed here in the context of an example system. Specifically, we formulated and used our algorithm as part of our effort model understanding the low-temperature n-butane oxidation phenomenon. Some of the criteria explained in the following section are specific to the n-butane oxidation system; however, most considerations are generally valid.

The set of reactive species used as a sample in this report is listed in Table 1. The column titled "Species" gives each species an eight character name (four computer words on our 16-bit machine). The name is for the convenience of the users; no exclusion criterion is based on the *name* of the species. Columns 2 through 4, NC, NH, and NO designate the number of carbons, hydrogens, and oxygens in the original molecule. Remember that the system of interest here is a C, H, O system. The algorithm can be easily modified to include other atomic species. Column 5 entitled NZ gives a number to each species. This number is mostly for internal accounting in the program. It is shown in the next section how selective numbering can aid in generating an additional criterion. Columns 6 and 7 are the $\Delta H_f(298)$ in kcal/mole and S(298) cal/(deg·mole), respectively, of the input molecules. These numbers can be found in the literature [1] or estimated using conventional means [2].

It will be helpful to understand the following discussion of the algorithm and the program itself, to introduce some notation. The set of stable molecules and molecular fragments (radicals) shall be called R. There are N species in R including a special species M which is explained later in this report. Let R(I), R(J), R(K), and R(L) represent the I, J, K, and L species within the set of the N chosen species. Indices I, J, K and L range independently over the entire set of N species. There is nothing to prohibit these indices from being equal. Throughout the text, and the program, I and J will index reactants and K and L will index products. Thus, all possibilities of two reactants forming two products are:

$$R(I) + R(J) \rightarrow R(K) + R(L). \tag{1}$$

We can represent Eq. (1) using matrix notation. The reactants portion of Eq. (1) are represented by the N × N matrix whose entries consist of all possible combinations of R(I) and R(J). Since there are N possible R(I) and independently N possible R(J), there are N^2 possible species combinations of R(I) + R(J).

As a simple example, consider the species set consisting of only A, B and C. We can represent all possible combinations of reactants involving these species by the entries in the following symmetric matrix:

$$\begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix}.$$

Similarly, this matrix also represents all possible combinations of products of bimolecular reactions involving these species. The special species M is included in the reaction set so that addition and unimolecular decomposition reactions are also available.

Thus, all possible reactions in the form of Eq. (1) can be represented as a mapping from one entry of the reactant matrix onto any one entry of the product matrix. For the species set A, B, C, the following are equivalent for the set R:

$$\begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix} \longrightarrow \begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix}.$$

There are N^2 entries in each matrix and thus $N^2 \times N^2 = N^4$ total reaction possibilities. Even for a relatively small set of species, the total number of possible reactions is formidable. There is an obvious need, therefore, to formulate criteria to eliminate many of the possible reactions quickly and automatically.

CRITERIA IN MECHANISM GENERATION

Appendix A lists program RXNGN, a FORTRAN program for generation of a reaction mechanism. The many criteria appearing in the program RXNGN will be discussed in this section but not necessarily in the order that they appear in the program. Generally, the criteria in the program appear in order of decreasing exclusion. The sooner a reaction fails a criterion and can be removed, the less criteria must be applied to that reaction. The development of criteria in the text will be ordered more along the lines of a chemical deductive process.

One of the most important criteria for the reactions to satisfy is mass balance. The input information on the number of carbons, hydrogens, and oxygens (columns 2, 3, and 4 of Table 1) is used for the mass balance computation (lines 83 to 89 of the program). As a programming note, we parenthetically point out that carbon balance is checked first, then hydrogen balance, and then oxygen balance. If the carbon balance fails, there is no need to check the hydrogen or oxygen balance (see program).

The number of possible reactions that may be eliminated by the mass balance criterion is entirely dependent on the specific species list, and, therefore, cannot be denoted generally in terms of the number of original species, N. The following discussion indicates the number of reactions that are eliminated by the imposition of each criterion, but the number indicated does *not* exclude those already eliminated by the mass balance criterion. Note that the number of reactions that may be eliminated on the basis of any one criterion is highly dependent on the order in which the criteria are imposed.

The next criterion to consider is that of simple permutation. Since it does not matter, for example, if A reacts with B, or B with A, all of the following denote the same reaction chemically:

$$A + B \rightarrow C + D$$

$$A + B \rightarrow D + C$$

$$B + A \rightarrow C + D$$

$$B + A \rightarrow D + C.$$

This repetition needs to be eliminated systematically. To illustrate the systematic elimination, we use the simple matrix. Label the upper and lower triangular region of each symmetric matrix x_1, x_2, x_3, x_4 such that:

$$\begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix} \longrightarrow \begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix}$$

becomes

$$\begin{vmatrix} AA & & x_2 \\ & BB & \\ x_1 & & CC \end{vmatrix} \longrightarrow \begin{vmatrix} AA & & x_4 \\ & BB & \\ x_3 & & CC \end{vmatrix}.$$

Since the product and reactant matrices are symmetric about the main diagonal, x_1 and x_2 of the reactant matrix and x_3 and x_4 of the product matrix contain equivalent entries. To eliminate the repetition, we eliminate all the entries of either x_1 or x_2 and x_3 or x_4. If we arbitrarily choose to eliminate x_2 and x_4, we now have:

$$\begin{vmatrix} AA & & \\ & BB & \\ x_1 & & CC \end{vmatrix} \longrightarrow \begin{vmatrix} AA & & \\ & BB & \\ x_3 & & CC \end{vmatrix}.$$

By eliminating the entries of x_2 and x_4, we eliminate $(N-1)+(N-2)+(N-3)+\ldots+1=\frac{N(N-1)}{2}$ entries from each matrix. The number of reaction possibilities we have eliminated by imposing this criterion is:

$$\begin{bmatrix}\text{The number of entries eliminated}\\ \text{from the reactant matrix.}\end{bmatrix} \times \begin{bmatrix}\text{Total number of entries}\\ \text{in the product matrix.}\end{bmatrix}$$
$$+ \begin{bmatrix}\text{The number of entries remaining}\\ \text{in the reactant matrix.}\end{bmatrix} \times \begin{bmatrix}\text{The number of entries eliminated}\\ \text{from the product matrix.}\end{bmatrix},$$

which in terms of N is:

$$\frac{N(N-1)}{2}\cdot N^2 + N^2 - \frac{N(N-1)}{2}\cdot\left[\frac{N(N-1)}{2}\right] = \frac{N^2(N-1)}{4}(3N+1)$$

reaction possibilities eliminated. The number of entries remaining in each matrix is $N^2 - N(N-1)/2 = N(N+1)/2$. Since there are $(N)(N+1)/2$ entries remaining in each matrix, and since with the remaining entries all mappings are possible, there are

$$\frac{N(N+1)}{2}\cdot\frac{N(N+1)}{2} = \left[\frac{N(N+1)}{2}\right]^2$$

possible reactions remaining to be considered.

Simple permutations are eliminated by the code on line 91 in the program in Appendix A.

Nonreactions or "identity" reactions (i.e., A + B → A + B or A + A → A + A, etc.) must be eliminated. Thus, our criterion is that if I = K and J = L, or I = L and J = L, or I = K and J = K, or I = L and J = K, then the reaction is eliminated from consideration. These reaction types are *exact* mappings from an entry in the reactant matrix onto the same entry in the product matrix. Since there are the same number of these *identity* reactions as there are remaining entries in each matrix, by eliminating these *identity* reactions from consideration, we eliminate $N(N+1)/2$ possible reactions. The number of remaining possible reactions is then

$$\left[\frac{N(N+1)}{2}\right]^2 - \frac{N(N+1)}{2} = \frac{(N-1)(N)(N+1)(N+2)}{4}.$$

The next applicable criterion is *no reactions with certain species* or, if on the basis of experimental evidence it can be determined that certain species appear in *negligible* relative concentrations or are unreactive, then one may want to consider those species as products only, or eliminate them from consideration. If a certain species is to be considered as a product only, it is necessary to eliminate all possible reactions involving that species as a reactant going to all possible products. For any given species there are exactly N remaining entries in the matrix which contain that species. For example, if we are interested in species A, we find that for the case where $N=3$, there are exactly 3 entries which contain at least one A.

$$\begin{bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{bmatrix}$$

The number of possible product entries to which a given reactant entry can go is the number of entries on the product side minus one. We subtract one from the number of entries on the product side to avoid double counting those reactions which we eliminated previously by imposing the *identity reaction* criterion. For example, if we wish to eliminate all reactions involving species A as a reactant, then we do not want to count the following reactions as being eliminated by this criterion:

$$A + A \rightarrow A + A$$

$$B + A \rightarrow B + A$$

$$C + A \rightarrow C + A.$$

Thus, removing a given species from consideration as a reactant eliminates:

$$N \cdot \begin{matrix}\text{Number of entries} \\ \text{on product side}\end{matrix} - 1$$

$$= N \cdot \frac{N(N+1)}{2} - 1$$

$$= N \cdot \frac{N^2 + N - 2}{2} \text{ possible reactions.}$$

If for some reason, after the species set has been chosen, we wish to to eliminate all possible reactions involving a given species as both products and reactants, then we eliminate the possible reactions involving:

$$\begin{bmatrix}\text{A reactant pair having at} \\ \text{least one of the pairs as} \\ \text{species to be eliminated.}\end{bmatrix} \begin{matrix}\text{going} \\ \longrightarrow \\ \text{to}\end{matrix} \begin{bmatrix}\text{All products minus} \\ \textit{exact mappings}\end{bmatrix}$$

$$\begin{bmatrix}\text{The remaining} \\ \text{reactant pairs.}\end{bmatrix} \begin{matrix}\text{going} \\ \longrightarrow \\ \text{to}\end{matrix} \begin{bmatrix}\text{Product pairs which have} \\ \text{at least one of the pairs} \\ \text{being the species to be} \\ \text{eliminated}\end{bmatrix}.$$

Or in terms of N we eliminate:

$$N \cdot \frac{(N+1)N}{2} - 1 + \frac{N(N+1)}{2} - 1 \cdot N = (N^2 - 1) \cdot N \text{ possible reactions.}$$

(For an example of this criterion see lines 112 and 113 in Appendix A.)

Because radicals usually are more reactive than stable species, reactions involving two radicals, or one radical and one stable species as reactants, are much more likely to occur at low temperatures than

reactions involving two stable species. A fifth possible criterion is to eliminate all possible reactions involving two stable species as reactants. This criterion is applicable to our low temperature oxidation of n-butane, but is not applicable in many other cases. Letting NSP represent the number of stable species in the species set, we find that the number of stable reactant pairs in the reactants matrix is NSP (NSP+1)/2. We now wish to eliminate all reactant pairs consisting of two stable species which go to all possible products minus *exact mappings*. In our simple example, let us assume A is the only stable species.

$$\begin{bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{bmatrix} \longrightarrow \begin{bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{bmatrix}$$

We wish to eliminate the following possible reactions:

$$A + A \rightarrow B + A$$
$$A + A \rightarrow B + B$$
$$A + A \rightarrow C + A$$
$$A + A \rightarrow C + B$$
$$A + A \rightarrow C + C.$$

(Note: A + A → A + A was eliminated under the *exact mapping* criterion.) Here (with N = 3 and NSP = 1) we eliminate five possible reactions. In general with NSP stable species and N total species, we eliminate

$$\frac{NSP(NSP + 1)}{2} \cdot \frac{N(N + 1)}{2} - 1$$

"possible reactions."

This criterion is applied in the program in Appendix A by line 104. The species in the input file were carefully grouped (column NZ) so that all stable species were numbered after all the radicals, and the special species M. In Table 1 there are 29 stable species.

It is useful to limit the reactions also on an enthalpy and free energy basis. With the input enthalpy ($\Delta H_f(298)$, column 6 of Table 1) and entropy S(298), column 7 of Table 1) it is easy to calculate ΔH_R and ΔG_R (lines 131 to 133 of program RXNGN in Appendix A):

$$\Delta H_R = \Delta H_p - \Delta H_r$$
$$\Delta S_R = \Delta S_p - \Delta S_r$$
$$\Delta G_R = \Delta H_R - T\Delta S_R,$$

where T represents temperature, and the subscripts R, p, r represent reaction, products, and reactants.

One can then set limits for acceptable ΔG_R and ΔH_R. Ideally, of course, ΔG_R should be less than or equal to zero. However, since measurements of $\Delta H_f(298)$ and S(298) are not perfect, and since some estimated values for those quantities were used, it is advisable to set the cutoff for ΔG_R above the theoretical limiting value of 0.0.

In large complex chemical systems, such as combustion, endothermic reactions occur. In our example program we used a cutoff value for ΔH_R of 35 kcal/mole (line 134 of program RXNGN in Appendix A).

The next two criteria we used involve a knowledge of the structure of each molecule. In a carbon, hydrogen, oxygen system there are five major types of bonds: 1) carbon-hydrogen (the number of

carbon-hydrogen bonds is designated NCH); 2) carbon-carbon (NCC); 3) carbon-oxygen (NCO); 4) oxygen-oxygen (NOO); and 5) oxygen-hydrogen (NOH). Oxygen-oxygen bonds are important in low-temperature *n*-butane oxidation because of the prevalence of peroxides; this bond type might be unimportant in other systems. Logically, three atomic species should give rise to six bond types. The sixth type here is hydrogen-hydrogen, and since that occurs in only one molecule in our system hydrogen (H_2), NHH is not included. A double bond would count as two bonds. For example, NCC of ethene is 2. Table 2 lists the numbers of each of these five-bond types for our input data set. The first column (NZ) corresponds to the NZ column of Table 1. (Note that Table 2 concatenated to Table 1 is essentially the input file to program RXNGN.)

Using the number of each type of bond as input data, there are two apparent restrictions to impose. First, limit the total bond change between products and reactants; and second, put limits on the change in each type of bond between products and reactants.

It must be kept in mind that the purpose is to generate a set of elementary (one-step) reactions. If the products have, for example, four carbon-carbon bonds and the reactants have nine, it is difficult to see how one elementary chemical step can break five carbon-carbon bonds. The number of each type of bond broken is subtracted from the number of each type of bond formed (lines 138 to 142 of program RXNGN in Appendix A). Specific limits are then imposed for the change in total number of bonds (lines 148 and 152 to 154) and the change in number of each type of bond (lines 157 to 161) (Appendix A).

A special species M, without any mass, (i.e., the number of carbons, hydrogens, and oxygens in it are all zero) is used to allow for unimolecular decompositions, addition reactions, and single counting of isomerization reactions.

Unimolecular decomposition: $A + M \rightarrow B + C$.

Addition Reaction: $A + B \rightarrow C + M$.

Isomerization: (if A and B are isomers then all of the following satisfy mass balance):

$$A + M \rightarrow B + M$$

$$A + B \rightarrow B + B$$

$$A + C \rightarrow B + C\ ,\ \text{etc.}$$

We eliminate all isomerizations except for the first reaction listed. So that the program is more general, M does not have to be a specific species number (NZ), thus when numbering the species, no special number is reserved for M. The program finds what the species number of M is (lines 117 to 122). The species number of M is not used for the unimolecular decompositions or additions. The redundancy of isomerizations is eliminated by the code on lines 124 and 125 of Appendix A.

CRITERIA APPLIED TO *n*-BUTANE OXIDATION

We now want to examine the results of applying our general criteria developed in the first section of this report to the species set which we considered in modeling the low-temperature oxidation of n-butane. Our species set consisted of 56 species (27 radicals, 28 stable species, and the special species M, see Table 1). As we noted earlier for the reaction R(I) + R(J) → R(K) + R(L) with the only restriction being that I, J, K, and L be members of our species list consisting of N species, there originally existed N^4 or in this case $(56)^4 = 9{,}8348{,}496$ possible reactions to be considered.

With 56 species both the reactants matrix and the products matrix were originally 56 × 56 square symmetric matrices composed of 3136 entries each. By imposing the permutation criterion, (which

essentially eliminates all entries above or below the main diagonal from each matrix) we eliminated $N(N-1)/2 = 56(55)/2 = 1540$ entries from both the products and reactants matrix. The number of reaction possibilities which we eliminated was:

$$N^2 \frac{(N-1)}{4} [3N+1] = (56)^2 \cdot \frac{55}{4} [3(56)+1] = 7{,}287{,}280.$$

The number of reaction possibilities which remained was $(N(N+1))^2 = 2{,}547{,}216$.

By imposing the *identity* reaction criterion, we eliminated $N(N+1)/2$ possible reactions or, in this case, $56(57)/2 = 1596$ reactions. Thus by imposing the first two criteria, we eliminated 7,290,416 possible reactions.

For our particular system we selected three stable species to act as products only. As shown earlier, removing a given species from consideration as a reactant results in the elimination of $N(N^2+N-2)/2$ possible reactions or in this case:

$$\text{(three species) } (56)56^2 + 56 - 2)/2 = 267{,}960$$

possible reactions were eliminated.

We imposed the criterion to eliminate all possible reactions involving two stable species as reactants. Since in our particular species set there were 28 stable species, by applying this criterion we eliminated: $\frac{NSP(NSP+1)}{2} - \frac{N(N+1)}{2} - 1 = \frac{28(29)}{2} - \frac{56(57)}{2} - 1 =$ 647,975 possible reactions. Before taking the mass balance criterion into consideration and as a result of imposing these four criteria, our reaction set consisted of 1,628,145 possible reactions. In our example the mass balance criterion was, next to the permutation criterion, the most restrictive. Every species in our system was composed of some number and combination of H atoms, C atoms, and O atoms. The mass balance criterion was then, if one of the following was not true, the reaction was eliminated:

$$C(K) + C(L) - C(J) - C(I) = 0$$

$$H(K) + H(L) - H(J) - H(I) = 0$$

$$O(K) + O(L) - O(J) - O(I) = 0.$$

Using only three criteria, mass balance and elimination of permutation and redundancy reduced the set from $(56)^4 = 9{,}834{,}496$ to a much more manageable 13,092.

Imposition of the thermodynamic criteria (limiting value for ΔH_R and ΔG_R) reduced the reaction set by 3282 reactions. The bond breaking and forming criteria reduced the set by 2687 reactions. By allowing isomerizations to occur only with the special species M, the mechanism shortened by another 1080 reactions. The specific case criterion of no bimolecular reactions of stable species eliminated 539 reactions. The additional specific checks (see listing of program in Appendix A) eliminated 2255 reactions and brought the set down 3249 reactions. Remember, the amount each criterion reduces the total is dependent on the order in which the criteria are applied.

Thirty-two hundred reactions are still quite a lot, but few enough so that visual inspection is a realistic task. We examined the mechanism with the aid of the search programs which are described in the next section. Many of the remaining reactions were not one-step reactions. In fact, many reactions appeared to be two-step reactions and both of the individual steps were already in the mechanism. Below are three such examples where part (a) is an obvious two-step mechanism and parts (b) and (c) are the two individual reaction steps which were already part of the mechanism.

1) a. $CH_3CO + O_2 \rightarrow CH_3O_2 + CO$

   b. $CH_3CO + M \rightarrow CH_3 + CO$

   c. $O_2 + CH_3 \rightarrow CH_3O_2 + M$

2) a. $CH_3CO + n\text{-}C_3H_7 \rightarrow C_4H_{10} + CO$

   b. $CH_3CO + M \rightarrow CH_3 + CO$

   c. $CH_3 + n\text{-}C_3H_7 \rightarrow C_4H_{10} + M$

3) a. $CH_3OO + i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_7O_2 + CH_3$

   b. $CH_3OO + M \rightarrow CH_3 + O_2$

   c. $O_2 + i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_7O_2 + M$

The output of program RXNGN is not reproduced here because it is excessively long; however, the outputs of the two search programs described in the next section are formatted the same. (See Tables 3 and 4.) For each reaction, the reactants and products with their respective species numbers; the ΔH_R; the ΔG_R; the number of reactions tried, the number of reactions found; the net change of CH, CC, CO, OO, and OH bonds; and the total net bond change, are tabulated. The species numbers are for convenience and give the subsequent search programs something to key on. The number tried is the number of reactions that pass the mass balance, redundancy and permutation criteria. The number found represents those reactions that have passed all the imposed criteria. The bond change numbers represent the sum of that type of bond in the products minus the sum of that type of bond in the reactants. (Note that these numbers can be negative.) The column entitled NET is the sum of the absolute values of each of the preceding five columns.

From the original $(56)^4 = 9{,}834{,}496$ possible reactions, we were able to construct a reasonable reaction set by formulating a logically ordered set of general and specific rational criteria, and imposing these criteria upon all of the possible reactions. We are thus able, to a great extent, to remove the process of reaction set formulation out of the intuitive domain. Imposing the formulated rational criteria allowed us to systematically arrive at a reaction set consisting of about 850 reactions, after originally considering over nine million possible reactions.

SEARCH CAPABILITIES

Three programs were developed to assist in the examination of the mechanism. These three programs look at the file created by the program RXNGN (Appendix A).

The capability to search through the data file is very powerful. For example, program SELET (reproduced in Appendix B) searches the reaction file for all reactions in which a particular input species is found as a reactant, or as a product; or as either a reactant or a product. In this way, one can quickly see the formation and destruction pathways a particular species takes through the overall mechanism. If the user is, for example, interested specifically in methanol, the reaction set may be searched for the reaction in which methanol appears. Alternatively, one could search for those reactions that create hydroxy radicals. It is, of course, possible that from examination of this *edited* output from the search program, the chemist might feel that a reaction that is felt to be important intuitively is missing. This means that either (1) a key species has been omitted from the original data file input to RXNGN; or (2) one of the criteria used in RXNGN is too stringent and excludes important reactions. Chemical knowledge and intuition are still important in the use of these algorithms.

Table 3 shows some sample output of program SELET. All the reactions in which methanol (species number 28) occurred as a reactant, were found.

Program SLRXT (reproduced in Appendix C) permits the user to search for reactions of classes of reactants. For example, one could examine all the reactions that occur with alkyl radicals by inputting the species numbers of all the alkyl radicals. The program also allows complementary reactants, that is, one could examine all the reactions that occur between alkyl radicals and alcohols by specifying all the alkyl radicals and then specifying all the species numbers of all the alcohols as complementary reactants. Table 4 shows this situation as a sample output of SLXRT.

The last utility program is entitled RLIST (reproduced in Appendix D). This simple program allows the listing of the reaction file in a shortened version so that there is room (in the right hand *margin*) to annotate the file. The other two programs (SELET and SLRXT) reproduce the input file exactly as it is, merely selecting out certain reactions. Program RLIST is merely a convenience and is included as Appendix D for completeness.

CONCLUSION

We have formulated an algorithm to systematically produce tractable reaction mechanisms for computational modeling of complex chemical kinetic systems. The additional searching algorithms provide a very powerful observational and educational tool as they permit the user to study thoroughly the entire reaction mechanism.

REFERENCES

1. D.R. Stull and H. Prophet, editors, *JANAF Thermochemical Tables*, 2nd ed., NSRDS, NBS-37, U.S. Govt. Printing Office (1971).

2. Sidney W. Benson, *Thermochemical Kinetics*, 2nd edition, J. Wiley and Sons, N.Y., 1976.

LIST OF SYMBOLS

	Description	Units
A, B, C, D	Designation for arbitrary species	
I, J	Indices of reactant species	
K, L	Indices of product species	
M	Special species	
N	Number of species in set R	
NC	Number of carbon atoms	
NCC	Number of carbon-carbon bonds	
NCH	Number of carbon-hydrogen bonds	
NCO	Number of carbon-oxygen bonds	
NH	Number of hydrogen atoms	
NHH	Number of hydrogen-hydrogen bonds	
NO	Number of oxygen atoms	
NOO	Number of oxygen-oxygen bonds	
NOH	Number of oxygen-hydrogen bonds	
NSP	Number of stable species	
NZ	Species number of a specific species	
R	The set of all input species	
R(index)	The indexed species	
S(298)	Entropy at 298K	cal/(deg·mole)
T	Temperature	degrees K
$X_1X_2X_3X_4$	Areas of particular matrix under discussion	
ΔG_R	Free energy change of reaction	kcal/mole
$\Delta H_f(298)$	Heat of formation at 298K	kcal/mole
ΔH_R	Enthalpy change of reaction	kcal/mole
Subscript p	Products	
Subscript r	Reactants	
Subscript R	Reaction	

Table 1 — Species and Parameters

SPECIES	NC	NH	NO	NZ	DELTA H	S
O*	0	0	1	24	59.5	38.5
O2	0	0	2	48	0.0	49.0
H*	0	1	0	1	52.1	27.4
OH*	0	1	1	2	9.4	43.9
HO2*	0	1	2	3	5.0	54.4
H2O	0	2	1	49	-57.8	45.1
CH4	1	4	0	50	-17.9	44.5
CO	1	0	1	44	-26.4	47.3
CO2	1	0	2	40	-94.0	51.2
CH3O*	1	3	1	5	3.5	55.2
CH3OH	1	4	1	28	-48.1	57.3
CH3O2*	1	3	2	6	6.7	65.3
C2H4	2	4	0	29	12.5	52.4
C2H5*	2	5	0	7	26.5	58.0
C2H6	2	6	0	30	-20.2	54.9
CH3CO*	2	3	1	8	-5.4	64.5
CH3CHO	2	4	1	31	-39.7	63.2
CH3CH2O*	2	5	1	9	-4.0	65.3
C2H5OO*	2	5	2	10	-5.0	76.4
C3H6	3	6	0	32	4.9	63.8
C3H7*-N	3	7	0	11	21.0	68.5
C3H7*-I	3	7	0	12	17.6	66.7
C2H3CHO	3	4	1	33	-17.7	69.1
CH3COCH3	3	6	1	34	-51.7	70.5
C3H7O-I*	3	7	1	13	-12.6	71.8
C4H8TBTE	4	8	0	35	-2.7	70.9
C4H81BTE	4	8	0	36	0.0	73.6
C4H9-N*	4	9	0	14	16.8	76.6
C4H9-S*	4	9	0	15	13.7	75.2
C4H10NBT	4	10	0	37	-30.2	74.1
C4H8OTHF	4	8	1	38	-44.0	73.6
C4H9OH	4	10	1	39	-65.6	86.8
C4H9O*	4	9	1	16	-14.0	76.5
C4H9O2*S	4	9	2	27	-17.8	93.5
M	0	0	0	4	0.0	0.0
H2O2	0	2	2	41	-32.6	56.0
HCHO	1	2	1	42	-26.0	52.3
HCO*	1	1	1	17	9.0	53.7
CH3OOH	1	4	2	43	-31.3	67.5
CH3*	1	3	0	26	34.3	46.4
MECHO*ET	4	9	1	18	-17.5	89.6
CH3COOOH	2	4	3	45	-80.9	80.4
CH3COO*	2	3	2	19	-49.6	66.6
MCHOOHET	4	10	2	46	-53.3	92.1
C4H9OOH	4	10	2	47	-49.0	94.1
C4H9OO*	4	9	2	20	-13.5	96.0
CH3COOO*	2	3	3	21	-29.0	78.9
C2H5OOH	2	6	2	51	-40.5	76.3
C3H7O*	3	7	1	25	-9.9	75.3
C3H7OO*	3	7	2	22	-8.5	88.2
MCHOO*M	3	7	2	23	-12.9	84.1
C3H7OOH	3	8	2	52	-44.0	84.6
MCHOOHM	3	8	2	53	-48.4	82.7
C3H8	3	8	0	54	-24.8	64.5
C4H823EB	4	8	1	56	-23.9	84.6
H2	0	2	0	55	0.0	31.2

Table 2 — Numbers of Bond Types

NZ	NCH	NCC	NCO	NOO	NOH
1	0	0	0	0	0
2	0	0	0	0	1
3	0	0	0	1	1
4	0	0	0	0	0
5	3	0	1	0	0
6	3	0	1	1	0
7	5	1	0	0	0
8	3	1	2	0	0
9	5	1	1	0	0
10	5	1	1	1	0
11	7	2	0	0	0
12	7	2	0	0	0
13	7	2	1	0	0
14	9	3	0	0	0
15	9	3	0	0	0
16	9	3	1	0	0
17	1	0	2	0	0
18	9	3	1	0	0
19	3	1	3	0	0
20	9	3	1	1	0
21	3	1	3	1	0
22	7	2	1	1	0
23	7	2	1	1	0
24	0	0	0	0	0
25	7	2	1	0	0
26	3	0	0	0	0
27	9	3	1	1	0
28	3	0	1	0	1
29	4	2	0	0	0
30	6	1	0	0	0
31	4	1	2	0	0
32	6	3	0	0	0
33	4	3	2	0	0
34	6	2	2	0	0
35	8	4	0	0	0
36	8	4	0	0	0
37	10	3	0	0	0
38	8	3	2	0	0
39	9	3	1	0	1
40	0	0	4	0	0
41	0	0	0	1	2
42	2	0	2	0	0
43	3	0	1	1	1
44	0	0	2	0	0
45	3	1	3	1	1
46	9	3	1	1	1
47	9	3	1	1	1
48	0	0	0	1	0
49	0	0	0	0	2
50	4	0	0	0	0
51	5	1	1	1	1
52	7	2	1	1	1
53	7	2	1	1	1
54	8	2	0	0	0
55	0	0	0	0	0
56	6	3	2	0	0

Table 3

REACTIONS INVOLVING SPECIES NUMBER 28 AS A REACTANT

REACTANTS				PRODUCTS			DELH	DELG	#TRD	#FND	NCHD	NCCD	NCOD	NOOD	NOHD	NET
O•	(24) + CH3OH	(28) ->	OH•	(2) + CH3O•	(5)		1.5	.5	22	8	0	0	0	0	0	0
H•	(1) + CH3OH	(28) ->	CH3O•	(5) + H2	(55)		-.5	-1.0	789	132	0	0	0	0	-1	1
OH•	(2) + CH3OH	(28) ->	H2O	(49) + CH3O•	(5)		-15.6	-15.3	1198	214	0	0	0	0	0	0
HO2•	(3) + CH3OH	(28) ->	CH3O•	(5) + H2O2	(41)		14.0	14.1	1662	278	0	0	0	0	0	0
CH3OH	(28) + CH3O2•	(6) ->	CH3O•	(5) + CH3OOH	(43)		13.6	13.6	3737	529	0	0	0	0	0	0
CH3OH	(28) + C2H5•	(7) ->	CH3O•	(5) + C2H6	(30)		4.9	6.4	3754	531	1	0	0	0	-1	2
CH3OH	(28) + CH3CO•	(8) ->	OH•	(2) + CH3COCH3	(34)		11.2	13.4	3762	532	0	1	-1	0	0	2
CH3OH	(28) + CH3CO•	(8) ->	CH3O•	(5) + CH3CHO	(31)		17.3	18.3	3765	533	1	0	0	0	-1	2
CH3OH	(28) + C2H5OO•	(10) ->	CH3O•	(5) + C2H5OOH	(51)		16.1	16.8	3802	534	0	0	0	0	0	0
CH3OH	(28) + C2H5OO•	(10) ->	CH3CH2O•	(9) + CH3OOH	(43)		17.8	18.1	3803	535	0	0	0	0	0	0
CH3OH	(28) + C3H7•-N	(11) ->	CH3O•	(5) + C3H8	(54)		5.8	7.6	3830	538	1	0	0	0	-1	2
CH3OH	(28) + C4H9-N•	(14) ->	CH3O•	(5) + C4H10NBT	(37)		4.6	6.0	3931	544	1	0	0	0	-1	2
CH3OH	(28) + C4H9-S•	(15) ->	CH3O•	(5) + C4H10NBT	(37)		7.7	8.7	3939	549	1	0	0	0	-1	2
CH3OH	(28) + C4H9O•	(16) ->	CH3O•	(5) + C4H9OH	(39)		-.0	-2.4	3973	554	0	0	0	0	0	0
CH3OH	(28) + HCO•	(17) ->	OH•	(2) + CH3CHO	(31)		8.8	10.0	4013	562	0	1	-1	0	0	2
CH3OH	(28) + HCO•	(17) ->	CH3O•	(5) + HCHO	(42)		16.6	17.6	4016	563	1	0	0	0	-1	2
CH3OH	(28) + CH3•	(26) ->	CH4	(50) + CH3O•	(5)		-.6	.6	4022	565	1	0	0	0	-1	2
CH3OH	(28) + C4H9OO•	(20) ->	CH3O•	(5) + C4H9OOH	(47)		16.1	17.3	4061	567	0	0	0	0	0	0
CH3OH	(28) + CH3COOO•	(21) ->	CH3O•	(5) + CH3COOOH	(45)		-.3	-.1	4072	574	0	0	0	0	0	0
CH3OH	(28) + C3H7OO•	(22) ->	CH3O•	(5) + C3H7OOH	(52)		16.1	17.8	4101	576	0	0	0	0	0	0
CH3OH	(28) + C3H7OO•	(22) ->	CH3OOH	(43) + C3H7O•	(25)		15.4	16.2	4108	578	0	0	0	0	0	0
CH3OH	(28) + NCH2OO•M	(23) ->	CH3O•	(5) + NCH2OOHM	(53)		16.1	17.1	4115	579	0	0	0	0	0	0
CH3OH	(28) + NCH2OO•M	(23) ->	C3H7O-I•	(13) + CH3OOH	(43)		17.1	17.7	4118	581	0	0	0	0	0	0

SELECTION PROCESS FINISHED. A TOTAL OF 21 SELECTED.

Table 4

REACTIONS INVOLVING SPECIES AS REACTANTS-> 7 11 12 14 15 26
COMPLEMENTARY REACTANTS -> 28 39

REACTANTS				PRODUCTS			DELH	DELG	#TRD	#FND	NCHD	NCCD	NCOD	NOOD	NOHD	NET
CH3OH	(28) + C2H5•	(7) ->	CH3O•	(5) + C2H6	(30)		4.9	6.4	3754	531	1	0	0	0	-1	2
CH3OH	(28) + C3H7•-N	(11) ->	CH3O•	(5) + C3H8	(54)		5.8	7.6	3830	538	1	0	0	0	-1	2
CH3OH	(28) + C4H9-N•	(14) ->	CH3O•	(5) + C4H10NBT	(37)		4.6	6.0	3931	544	1	0	0	0	-1	2
CH3OH	(28) + C4H9-S•	(15) ->	CH3O•	(5) + C4H10NBT	(37)		7.7	9.7	3939	549	1	0	0	0	-1	2
CH3OH	(28) + CH3•	(26) ->	CH4	(50) + CH3O•	(5)		-.6	.6	4022	565	1	0	0	0	-1	2
C2H5•	(7) + C4H9OH	(39) ->	C2H6	(30) + C4H9O•	(16)		4.9	8.9	5179	945	1	0	0	0	-1	2
C3H7•-N	(11) + C4H9OH	(39) ->	C4H9O•	(16) + C3H8	(54)		5.8	10.1	7800	1893	1	0	0	0	-1	2
C3H7•-I	(12) + C4H9OH	(39) ->	C4H9O•	(16) + C3H8	(54)		9.2	12.9	8175	2053	1	0	0	0	-1	2
C4H9-N•	(14) + C4H9OH	(39) ->	C4H10NBT	(37) + C4H9O•	(16)		4.6	8.4	9809	2385	1	0	0	0	-1	2
C4H9OH	(39) + CH3•	(26) ->	CH4	(50) + C4H9O•	(16)		-.6	3.0	10792	2600	1	0	0	0	-1	2

SELECTION PROCESS FINISHED. A TOTAL OF 10 SELECTED.

Appendix A
PROGRAM RXNGN

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 PAGE 0001  FTN    9:38 AM  THU., 16  JULY, 1981


0001   FTN4,L
0002         PROGRAM RXNGN(3,99), REV. 800709 DOREN INDRITZ
0003   C     VERSION 800709 FOR HEWLETT PACKARD MINICOMPUTER
0004   C      IDEA BUILT UPON WALT SHAUB'S REACTION GENERATOR.
0005   C
0006   C     PROGRAM GENERATES ALL POSSIBLE REACTIONS, GIVEN INPUT SPECIES
0007   C      (UP TO 100), SUBJECT TO VARIOUS CONSTRAINTS LISTED
0008   C      THROUGHOUT THE COMMENTS IN THE PROGRAM.
0009   C
0010   C      CURRENTLY DIMENSIONED FOR UP TO 100 INPUT SPECIES.
0011         DIMENSION NAME(4,100),ENTL(100),NZ(100),ENTR(100)
0012         DIMENSION NCH(100),NCC(100),NCO(100),NOO(100),NOH(100)
0013         INTEGER C(100),H(100),O(100),IP(5)
0014         DATA II,JJ,TEMP/0,0,298.0/
0015   C
0016   C     FORMATS
0017   C
0018    100   FORMAT(' ENTER LU OF DATA CASSETTE: ')
0019    101   FORMAT(1X,6I9)
0020    102   FORMAT(' IER = ',I8)
0021    103   FORMAT(I2)
0022    104   FORMAT(1X,4A2,4X,I1,3X,I2,4X,I1,4X,I2,2X,F10.3,2X,F10.3)
0023    105   FORMAT(2X,4A2,4X,I1,3X,I2,4X,I1,4X,I2,2X,F10.1,2X,F10.1)
0024    106   FORMAT('1 REACTION GENERATOR N-BUTANE COOL FLAME'///)
0025    107   FORMAT(2X,4A2,'(',I2,')',3H + ,4A2,'(',I2,')',4H -) ,
0026        +        4A2,'(',I2,')',3H + ,4A2,'(',I2,')',2X,F10.1,2X,
0027        +        F10.1,1X,I5,I6,6I5)
0028    108   FORMAT('1',9X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
0029       &        3X,'#TRD',2X,'#FND',2X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
0030       &        'NOOD',1X,'NOHD',2X,'NET')
0031    109   FORMAT(' LEN = ',I10)
0032    110   FORMAT(////' TOTAL REACTIONS EXAMINED = ',I10)
0033    111   FORMAT(6I3)
0034    112   FORMAT(1H1,7X,'NZ',6X,'NCH',6X,'NCC',6X,'NCO',6X,'NOO',6X,'NOH')
0035    113   FORMAT(' ENTER LU OF OUTPUT DEVICE')
0036    114   FORMAT(' RXNGN HAS FINISHED ',I8,' REACTIONS EXAMINED.' 'NUMBER FOUND
0037       &        = ',I6)
0038   C
0039   C      GET LOGICAL UNIT NUMBER (LU) OF DIALOGUE DEVICE.
0040         CALL RMPAR(IP)
0041   C
0042   C      OBTAIN LU OF INPUT DEVICE (CURRENTLY THE PROGRAM IS SET UP
0043   C       TO READ THE INPUT FILE OFF A CASSETTE.  THAT CAN BE CHANGED
0044   C       WITHOUT TOO MUCH DIFFICULTY.)
0045         WRITE(IP(1),100)
0046         READ(IP(1),*) IN
0047   C      OBTAIN LU OF LIST DEVICE
0048         WRITE(IP(1),113)
0049         READ(IP(1),*) LP
0050   C      NOTE THAT OUTPUT DEVICE CAN BE TO A MAG TAPE (LU = 8 OR 18
0051   C       ON THIS SYSTEM).  IF SO, A CONTROL WORD INTERNAL TO THE
0052   C       PROGRAM, IS NEEDED.
0053         ICNTL = 1000B + LP
0054   C      WRITE OUT TITLE
0055         WRITE(LP,106)
```

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 PAGE 0002  RXNGN  9:38 AM  THU., 16  JULY, 1981


0056  C      READ IN DATA FROM CASSETTE
0057  C      SEE SAMPLE DATA FILE FOR FORMAT.
0058         READ(IN,*) N
0059         DO 15 I=1,N
0060         READ(IN,104) (NAME(IZ,I),IZ=1,4),C(I),H(I),O(I),NZ(I),ENTL(I),
0061        +              ENTR(I)
0062         WRITE(LP,105)(NAME(IZ,I),IZ=1,4),C(I),H(I),O(I),NZ(I),ENTL(I),
0063        +              ENTR(I)
0064         ENTR(I) = ENTR(I)/1000.0
0065    15   CONTINUE
0066  C      READ IN NUMBER OF THE DIFFERENT TYPES OF BONDS FROM DATA FILE.
0067  C
0068         WRITE(LP,112)
0069         DO 200 I = 1, N
0070         READ(IN,111) NC,NCH(NC),NCC(NC),NCO(NC),NOO(NC),NOH(NC)
0071    200  CONTINUE
0072         WRITE(LP,101) (I,NCH(I),NCC(I),NCO(I),NOO(I),NOH(I),I=1,N)
0073  C
0074  C
0075         WRITE(LP,108)
0076  C
0077  C      LOOP THROUGH ALL POSSIBLE COMBINATIONS OF THE INPUT SPECIES.
0078  C
0079         DO 50 I=1,N
0080         DO 40 J=1,N
0081         DO 30 K=1,N
0082         DO 20 L=1,N
0083  C      CHECK FOR MASS BALANCE
0084         T1=(C(K)+C(L))-(C(J)+C(I))
0085         IF(ABS(T1).GT.0.01) GO TO 20
0086         T2=(H(K)+H(L))-(H(J)+H(I))
0087         IF(ABS(T2).GT.0.01) GO TO 20
0088         T3=(O(K)+O(L))-(O(J)+O(I))
0089         IF(ABS(T3).GT.0.01) GO TO 20
0090  C      CHECK IF REACTION HAS BEEN DONE BEFORE
0091         IF(K.GT.L.OR. I.GT.J) GO TO 20
0092  C      CHECK FOR SIMPLE PERMUTATIONS OF REACTANT/PRODUCT PAIRS
0093         IF(I.EQ.K.AND.J.EQ.L ) GO TO 20
0094         IF(I.EQ.L.AND.J.EQ.L ) GO TO 20
0095         IF(I.EQ.K.AND.J.EQ.K ) GO TO 20
0096         IF(I.EQ.L.AND.J.EQ.K ) GO TO 20
0097         II=II+1
0098  C      DON'T ALLOW REACTIONS OF STABLE SPECIES.
0099  C      THIS IS AN EXAMPLE OF A REASONABLE CRITERION THAT THE USER
0100  C       MIGHT IMPOSE BASED ON PRIOR KNOWLEDGE OF THE SYSTEM.
0101  C       NOTE: HERE THE DATA FILE HAS BEEN SET UP IN A SPECIAL WAY
0102  C         TO GROUP ALL STABLE SPECIES SEPARATELY FROM ALL RADICALS
0103  C         I.E., THE RADICALS HAVE SPECIE NUMBERS > 27.
0104         IF(NZ(I) .GT. 27 .AND. NZ(J) .GT. 27) GOTO 20
0105  C
0106         IA = NZ(I)
0107         JA = NZ(J)
0108         KA = NZ(K)
0109         LA = NZ(L)
0110  C
```

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 PAGE 0003  RXNGN  9:38 AM  THU., 16  JULY, 1981


0111   C      ALLOW H2(55), CO2(40) AND H2O(49) AS PRODUCTS ONLY
0112          IF( IA .EQ. 55 .OR. IA .EQ. 40 .OR. IA .EQ. 49) GOTO 20
0113          IF( JA .EQ. 55 .OR. JA .EQ. 40 .OR. JA .EQ. 49) GOTO 20
0114   C
0115   C      FIND NZ(SPECIES M) -- SPECIES NUMBER OF THE SPECIAL SPECIES M
0116   C
0117          DO 201 IFM = 1, N
0118          IF(C(IFM) .NE. 0 .OR. O(IFM) .NE. 0 .OR. H(IFM) .NE. 0) GOTO 201
0119          NM = NZ(IFM)
0120          GOTO 202
0121    201   CONTINUE
0122    202   CONTINUE
0123   C      ALLOW ISOMERIZATIONS ONLY WITH M
0124          IF((IA.NE.NM.AND.JA.NE.NM).AND.(IA.EQ.KA .OR. IA.EQ.LA .OR.
0125         &     JA.EQ.KA .OR. JA.EQ.LA)) GOTO 20
0126   C      ONLY ALLOW TMF(38),1-BUTENE(36) AND T-BUTENE(35) AS PRODUCTS
0127   C           OF ISOMERIZATIONS
0128          IF((KA.EQ.39 .OR. KA.EQ.36 .OR. KA.EQ.35 .OR. LA.EQ.38 .OR.
0129         & LA.EQ.36 .OR. LA.EQ.35)  AND. (IA.NE.NM  AND. JA.NE.NM)) GOTO20
0130   C
0131          DELH=(ENTL(K)+ENTL(L))-(ENTL(I)+ENTL(J))
0132          DELS = (ENTR(K)+ENTR(L)) - (ENTR(I)+ENTR(J))
0133          DELG = DELH - TEMP * DELS
0134          IF(DELG .GT. 20.0 .OR. DELH .GT. 35.0) GOTO 20
0135   C
0136   C      MAKE CHECKS BY THE NUMBER OF BONDS FORMED AND BROKEN
0137   C
0138          NCHD = NCH(KA) + NCH(LA) - NCH(IA) - NCH(JA)
0139          NCCD = NCC(KA) + NCC(LA) - NCC(IA) - NCC(JA)
0140          NCOD = NCO(KA) + NCO(LA) - NCO(IA) - NCO(JA)
0141          NOOD = NOO(KA) + NOO(LA) - NOO(IA) - NOO(JA)
0142          NOHD = NOH(KA) + NOH(LA) - NOH(IA) - NOH(JA)
0143          NET = IABS(NCCD)+IABS(NCHD)+IABS(NOOD)+IABS(NOHD)+IABS(NCOD)
0144   C
0145   C      SET SOME CRITERIA FOR MAXIMUM NUMBER OF BOND CHANGES ALLOWED
0146   C       IN A SPECIFIC REACTION.
0147   C
0148          IF(NET .GT. 3) GOTO 20
0149   C
0150   C      ALLOWS 3 BOND CHANGES IF CO2(40) IS FORMED OR IF 2 RADICALS
0151   C         FORM 2 STABLE SPECIES.
0152          IF((NET.EQ.3).AND.(KA.EQ.40.OR.LA.EQ.40)) GOTO 90
0153          IF((NET.EQ.3).AND.(IA.GT.27.OR.JA.GT.27.OR.KA.LT.28.OR.LA.LT.28))
0154         &   GOTO 20
0155       90 CONTINUE
0156   C
0157          IF(IABS(NCOD) .GT. 2) GOTO 20
0158          IF(IABS(NCCD) .GT. 1) GOTO 20
0159          IF(IABS(NCHD) .GT. 2) GOTO 20
0160          IF(IABS(NOOD) .GT. 2) GOTO 20
0161          IF(IABS(NOHD) .GT. 1) GOTO 20
0162   C      ADD SPECIFIC CHECKS
0163   C      ALLOW CO(44) TO GO TO ONLY CO2(40) OR M(4)
0164          IF((IA.EQ.44.OR.JA.EQ.44) AND.(KA.NE.40.AND.KA.NE.4.AND.LA.NE.4
0165         &     AND.LA.NE.40)) GOTO 20
```

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0166  C      ALLOW CH4(50) TO GO TO ONLY CH3(26)
0167         IF((IA.EQ.50 OR JA.EQ.50) AND. (KA NE.26 AND.LA NE 26)) GOTO 20
0168  C      ALLOW C2H6(30) TO GO TO ONLY C2H5(7)
0169         IF((IA EQ.30.OR.JA.EQ 30).AND. (KA NE.7 .AND.LA.NE.7 )) GOTO 20
0170  C      ALLOW C3H8(54) TO GO TO ONLY CH3CH2CH2(11) OR CH3CHCH3(12)
0171         IF((IA.EQ.54 OR JA.EQ.54) AND. (KA.NE.11 AND KA NE.12 .AND.
0172        &    LA NE.11.AND.LA.NE.12)) GOTO 20
0173  C      ALLOW C4H10(37) TO GO TO ONLY CH3CH2CHCH3(15) OR CH3CH2CH2CH2(14)
0174         IF((IA.EQ.37.OR.JA.EQ.37).AND. (KA NE 14.AND.KA NE.15 .AND.
0175        &    LA.NE.14.AND.LA.NE.15)) GOTO 20
0176  C      ALLOW CH3O(5) TO GO TO SOMETHING WITH ZERO OR ONE CARBON
0177         IF((IA.EQ.5.OR.JA.EQ.5).AND. ((C(K).NE.0.AND.C(K) NE.1.AND.
0178        &    C(L) NE.0 .AND. C(L).NE.1)) GOTO 20
0179  C      ALLOW M(1) TO GO TO ONLY M(4), H2(55), H2O(49), OR H2O2(41)
0180         IF((IA.EQ.1.OR.JA.EQ.1).AND.(KA NE.4.AND.KA.NE.55.AND.KA.NE.49
0181        &     AND. KA NE.41 AND.LA.NE.4 AND.LA NE 55 AND.LA NE 49
0182        &     .AND. LA.NE.41))GOTO 20
0183  C      ALLOW OH(2) TO GO TO ONLY M(4), H2O(49), HO2(3), AND H2O2(41)
0184         IF((IA EQ.2 OR JA EQ.2).AND.(KA NE.4 AND.KA NE.49 AND.KA NE.3.AND.
0185        &    KA NE 41.AND LA.NE.4 AND LA NE 49 AND.LA NE 3.AND LA NE.41))
0186        &    GOTO 20
0187  C      DON'T ALLOW CERTAIN GROUPS OF ISOMERS TO INTERCONNECT UNLESS M(4)
0188  C      IS INVOLVED.  GROUP I (11, 52, 25, 22) WILL NOT CONNECT WITH
0189  C      GROUP II (12, 53, 13, 23).  GROUP III (14, 16, 20, 47) WILL
0190  C      NOT CONNECT WITH GROUP IV (15, 18, 27, 46).
0191         IF((IA.EQ 11 OR.IA EQ.52 OR IA EQ.25 OR.IA.EQ.22.OR.JA.EQ.11.OR.
0192        &     JA.EQ.52.OR.JA.EQ.25 OR JA EQ.22) .AND. (KA.EQ.12.OR.KA.EQ.53
0193        &      OR.KA.EQ.13.OR.KA.EQ.23.OR.LA.EQ.12.OR.LA.EQ 53 OR.LA.EQ.13
0194        &      OR.LA.EQ.23) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
0195         IF((IA.EQ.12.OR.IA.EQ 53.OR.IA EQ.13.OR.IA.EQ.23.OR.JA.EQ.12.OR.
0196        &     JA.EQ 53.OR.JA.EQ.13 OR.JA.EQ.23) .AND. (KA.EQ.11.OR.KA.EQ.52
0197        &      OR.KA.EQ.25.OR.KA.EQ.22.OR.LA.EQ.11.OR.LA.EQ.52.OR.LA.EQ.25
0198        &      OR.LA.EQ.22) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
0199         IF((IA EQ.14.OR.IA.EQ 16.OR.IA.EQ.20 OR IA.EQ.47 OR.JA.EQ.14.OR.
0200        &     JA EQ.16.OR.JA EQ.20.OR.JA.EQ.47).AND.(KA.EQ.15.OR.KA.EQ.18
0201        &      OR.KA.EQ.27 OR.KA EQ 46.OR LA.EQ.15.OR.LA EQ 18 OR.
0202        &     LA.EQ.27.OR.LA.EQ.46) .AND. (IA.NE.NM .OR. JA NE.NM)) GOTO 20
0203         IF((IA EQ.15.OR.IA.EQ 18.OR.IA.EQ.27 OR.IA.EQ.46 OR.JA.EQ.15.OR.
0204        &     JA EQ 18.OR.JA.EQ 27 OR.JA.EQ.46) .AND. (KA.EQ.14 OR.KA.EQ.16
0205        &      OR.KA.EQ.20.OR.KA.EQ.47.OR.LA.EQ.14 OR LA.EQ.16.OR.LA.EQ.20
0206        &      OR LA.EQ.47) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
0207  C      ALLOW METHANE (50) TO COME FROM METHYL (26) ONLY
0208         IF((KA.EQ.50.OR.LA.EQ 50) .AND. (IA.NE.26 AND.JA NE 26)) GOTO 20
0209         JJ = JJ + 1
0210         WRITE(LP,107)(NAME(IZ,I),IZ=1,4),IA,(NAME(IZ,J),IZ=1,4),JA,
0211        &(NAME(IZ,K),IZ=1,4),KA,(NAME(IZ,L),IZ=1,4),LA,
0212        &DELH,DELG,II,JJ,NCHD,NCCD,NCOD,NOOD,NOHD,NET
0213       20 CONTINUE
0214       30 CONTINUE
0215       40 CONTINUE
0216       50 CONTINUE
0217  C
0218  C      WRITE OUT TOTAL COMBINATIONS TRIED
0219  C
0220         WRITE(LP,110) II
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0221  C      IF WRITING TO TAPE WRITE EOF
0222         IF(LP.EQ.8  OR. LP .EQ.18) CALL EXEC(3,ICNTL)
0223  C      INDICATE END
0224         WRITE(IP(1),114) II,JJ
0225         END


  FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)


  **  NO WARNINGS **  NO ERRORS **   PROGRAM = 04084      COMMON = 00000
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Appendix B

PROGRAM SELET

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 PAGE 0001  FTN.   9:46 AM  FRI., 17  JULY, 1981


0001  FTN4,L
0002        PROGRAM SELET(3,99), REV. 800710 DOREN INDRITZ
0003  C     VERSION 800710 FOR HEWLETT PACKARD MINICOMPUTER
0004  C     PROGRAM TO READ A SELECTED DATA FILE FOR SPECIFIED
0005  C             REACTANT AND/OR PRODUCT (ONE SPECIES ONLY)
0006  C      THIS ALLOWS THE CHEMIST TO FOLLOW THE REACTIONS OF
0007  C       A PARTICULAR SPECIES IN A LARGE MECHANISM.
0008  C
0009  C     LOGICAL LOG TELLS TRUTH OF MATCHES
0010        LOGICAL LOG
0011        DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),
0012       &          ISLCT(9),IMAS(8)
0013  C     ICR IS THE CARTRIDGE THAT THE DATA FILE IS ON.
0014  C     NMAT IS THE NUMBER OF SUCCESSFUL MATCHES.
0015  C     IPL IS ASCII "+", USED TO LOCATE POSITION IN FILE.
0016  C     ISLCT ARE THE COLUMNS IN THE DATA FILE CORRESPONDING TO
0017  C      THE SPECIES NUMBERS
0018        DATA ICR,ISC,NMAT,IPL,IL/27,0,0,25400B,132/
0019        DATA ISLCT/12,13,27,28,43,44,58,59/
0020  C
0021  C     FORMATS
0022  C
0023     100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
0024     101 FORMAT(3A2)
0025     102 FORMAT(' IER = ',I8)
0026     103 FORMAT(' WHICH SPECIES NUMBER ARE YOU INTERESTED IN?')
0027     104 FORMAT(132H1)
0028     105 FORMAT(' ',132H1)
0029     106 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,
0030        &       ' AS A PRODUCT'///)
0031     107 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,
0032        &       ' AS A REACTANT'///)
0033     108 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,' AS A REACTANT',
0034        &       ' OR A PRODUCT'///)
0035     109 FORMAT(' DO YOU WISH TO EXAMINE SPECIES NUMBER',I3,' AS ',
0036        &       /' A REACTANT ONLY? = 1'/' A PRODUCT ONLY? = 2'/
0037        &       ' OR AS A PRODUCT AND A REACTANT? = 3')
0038     110 FORMAT(//' SELECTION PROCESS FINISHED. A TOTAL OF ',I3,
0039        &       ' SELECTED.')
0040     111 FORMAT(10X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
0041        &       4X,'#TRD',2X,'#FND',3X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
0042        &       'NOOD',1X,'NOHD',2X,'NET'//)
0043  C
0044  C
0045  C     GET LOGICAL UNIT NUMBER(LU) OF DIALOGUE DEVICE
0046        CALL RMPAR(IP)
0047  C     SET LU FOR LIST DEVICE
0048        LP = 06
0049  C     GET NAME OF DATA FILE
0050        WRITE(IP(1),100)
0051        READ(IP(1),101) (NAMF(K),K = 1, 3)
0052  C     GET THE NUMBER OF THE SPECIES TO DO THE SEARCH ON
0053        WRITE(IP(1),103)
0054  C     NOTE "*" FORMAT IS FREE FORM INPUT.
0055        READ(IP(1),*) INATCH
```

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 PAGE 0002  SELET  9:46 AM  FRI., 17  JULY, 1981


0056   C      ASK IF USER WISHES SEARCH AS REACTANT ONLY, PRODUCT ONLY OR
0057   C       OR AS REACTANTS AND PRODUCTS
0058     1    WRITE(IP(1),109) IMATCH
0059          READ(IP(1),*) IBR
0060   C      MAKE SURE USER GAVE A LEGITIMATE RESPONSE
0061          IF(IBR.LT.1 .OR. IBR .GT. 3) GOTO 1
0062   C      ASSIGN CORRECT FORMAT FOR OUTPUT DEPENDING ON RESPONSE
0063          IF(IBR .EQ. 1) ASSIGN 107 TO ITIT
0064          IF(IBR .EQ. 2) ASSIGN 106 TO ITIT
0065          IF(IBR .EQ. 3) ASSIGN 108 TO ITIT
0066          WRITE(LP,ITIT) IMATCH
0067          WRITE(LP,111)
0068   C
0069   C      OPEN DATA FILE ON DISK #ICR
0070          CALL OPEN(IDCB,IER,NAMF,0,ISC,ICR)
0071   C      CHECK FOR ERROR RETURN
0072          IF(IER .LT. 0) WRITE(IP(1),102) IER
0073   C
0074   C      READ IN A LINE OF DATA
0075     7    CALL READF(IDCB,IER,IBUFR,IL,LEN)
0076   C      CHECK FOR ERROR RETURN
0077          IF(IER .LT. 0) WRITE(IP(1),102) IER
0078   C      CHECK FOR END OF FILE (EOF)
0079          IF(IER .EQ. -12) GOTO 25
0080   C
0081   C      CALL CODE READ DOES A FORMATTED READ OF THE FILE.
0082          CALL CODE
0083          READ(IBUFR,104) (IBUF(I), I = 1, 132)
0084   C
0085   C      LOOK FOR FIRST REACTION (LOOK FOR A PLUS SIGN)
0086   C
0087          IF(IAND(IBUF(16),IPL) .NE. IPL) GOTO 7
0088   C
0089   C      CONVERT SELECTED PORTIONS FROM ASCII TO NUMBERS INTERNAL TO THE
0090   C       COMPUTER   ISLCT POINTS TO CORRECT COLUMNS OF DATA FILE.
0091   C
0092          DO 10 I = 1, 8
0093          IMAS(I) = IBUF(ISLCT(I))
0094          IMAS(I) = IAND(IMAS(I),37400B)/400B
0095          IF(IMAS(I) .EQ. 40B) IMAS(I) = IMAS(I) + 20B
0096          IMAS(I) = IMAS(I) - 60B
0097     10   CONTINUE
0098   C      RECONSTRUCT NUMBERS IA & JA FOR REACTANTS, KA & LA FOR PRODUCTS.
0099          IA = 10 * IMAS(1) + IMAS(2)
0100          JA = 10 * IMAS(3) + IMAS(4)
0101          KA = 10 * IMAS(5) + IMAS(6)
0102          LA = 10 * IMAS(7) + IMAS(8)
0103   C
0104   C       LOOK FOR MATCHES
0105   C
0106          GOTO(11,12,13), IBR
0107   C
0108   C      REACTANT ONLY
0109   C
0110     11   LOG = IMATCH .EQ. IA  .OR. IMATCH .EQ. JA
```

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 PAGE 0003  SELET  9:46 AM  FRI., 17  JULY, 1981


0111          GOTO 20
0112   C
0113   C      PRODUCTS ONLY
0114   C
0115       12 LOG = IMATCH .EQ. KA  .OR.  IMATCH  .EQ. LA
0116          GOTO 20
0117   C
0118   C      REACTANT &/OR PRODUCT
0119   C
0120       13 LOG = IMATCH .EQ. IA .OR. IMATCH .EQ. JA .OR. IMATCH .EQ. KA
0121         &       .OR.  IMATCH .EQ. LA
0122   C
0123   C      OUTPUT TO LIST DEVICE
0124   C
0125       20 IF(LOG) WRITE(LP,105) (IBUF(I), I = 1, 126)
0126          IF(LOG) NMAT = NMAT + 1
0127   C
0128   C      CHECK FOR EOF
0129   C
0130          IF(IER .NE. -12) GOTO 7
0131    25    CONTINUE
0132   C
0133   C      EOF
0134   C
0135   C      WRITE NUMBER OF MATCHES TO LIST DEVICE AND TO DIALOGUE DEVICE.
0136          WRITE(LP,110) NMAT
0137          WRITE(IP(1),110) NMAT
0138          END


 FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)

 **  NO WARNINGS **  NO ERRORS **   PROGRAM = 01228      COMMON = 00000
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Appendix C
PROGRAM SLRXT

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 PAGE 0001  FTN.   9:57 AM  FRI., 17  JULY, 1981


0001   FTN4,L
0002         PROGRAM SLRXT(3,99), REV. 800813 DOREN INDRITZ
0003   C     VERSION 800813 FOR HP MINICOMPUTER
0004   C
0005   C     PROGRAM TO READ A SELECTED DATA FILE FOR SPECIFIED
0006   C              REACTANTS &/OR PRODUCTS
0007   C     THIS PROGRAM ALLOWS ONE TO SELECT MULTIPLE INPUTS (<=20) AS
0008   C      REACTANTS.  THUS ALLOWING ONE TO SELECT CLASSES OF
0009   C      REACTIONS.  (DIFFERS FROM &SELET, WHICH ALLOWS ONLY ONE.)
0010   C
0011   C     LOG IS LOGICAL FOR REACTANT SPECIES MATCH
0012   C     LOG2 IS LOGICAL FOR COMPLEMENTARY REACTIONS
0013         LOGICAL LOG,LOG2
0014         DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),
0015        &          ISLCT(8),IHAS(8),IIH(20),JIH(20)
0016         DATA ICR,ISC,NMAT,IPL,IL/27,0,0,254008,132/,IYES/2HYE/
0017         DATA ISLCT/12,13,27,28,43,44,58,59/
0018   C
0019   C     FORMATS
0020   C
0021     100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
0022     101 FORMAT(3A2)
0023     102 FORMAT(' IER = ',I8)
0024     103 FORMAT(' HOW MANY "IA" REACTANTS ARE YOU INTERESTED IN?')
0025     104 FORMAT(132A1)
0026     105 FORMAT(' ',132A1)
0027     106 FORMAT(' ENTER SPECIES -> ')
0028     107 FORMAT('1REACTIONS INVOLVING SPECIES AS REACTANTS-> ', ,1X,20I3)
0029     108 FORMAT(' DO YOU WANT TO SPECIFY COMPLEMENTARY REACTANTS?')
0030     109 FORMAT(A2)
0031     110 FORMAT(//' SELECTION PROCESS FINISHED. A TOTAL OF ',I3,
0032        &        ' SELECTED.')
0033     111 FORMAT(10X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
0034        &       4X,'#TRD',2X,'#FND',3X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
0035        &       'NOOD',1X,'NOHD',2X,'NET'//)
0036     112 FORMAT(' THIS PROGRAM ALLOWS YOU TO SELECT UP TO 20 REACTANTS')
0037     113 FORMAT(' HOW MANY "JA" REACTANTS ARE YOU INTERESTED IN?')
0038     114 FORMAT(' COMPLEMENTARY REACTANTS -> ',20I3)
0039   C
0040   C
0041   C     OBTAIN LOGICAL UNIT NUMBER(LU) OF INPUT DEVICE FOR DIALOGUE.
0042         CALL RMPAR(IP)
0043   C     LP IS LU FOR OUTPUT LISTING
0044         LP =  06
0045         WRITE(IP(1),112)
0046   C     OBTAIN NAME OF DATA FILE
0047         WRITE(IP(1),100)
0048         READ(IP(1),101) (NAMF(K),K = 1, 3)
0049   C     OBTAIN NUMBER OF REACTANTS
0050         WRITE(IP(1),103)
0051         READ(IP(1),*) NII
0052   C     OBTAIN NUMBERS OF THOSE REACTANTS
0053   C     HAVE TO REFER TO ORIGINAL DATA INPUT FILE TO SEE SPECIES NUMBERING
0054         WRITE(IP(1),106)
0055         READ(IP(1),*) (IIH(LL), LL = 1, NII)
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 PAGE 0002  SLRXT  9:57 AM  FRI., 17  JULY, 1981


0056  C      SEE IF USER WANTS TO SPECIFY COMPLEMENTARY REACTANTS
0057         WRITE(IP(1),108)
0058         READ(IP(1),109) IANS
0059         IF(IANS  EQ  IYES) LOG2 = .TRUE.
0060         IF( .NOT. LOG2) GOTO 9
0061  C      OBTAIN NUMBER OF COMPLEMENTARY REACTANTS
0062         WRITE(IP(1),113)
0063         READ(IP(1),*) NJJ
0064  C      OBTAIN THE NUMBERS OF THOSE REACTANTS
0065         WRITE(IP(1),106)
0066         READ(IP(1),*) (JIN(LL), LL = 1, NJJ)
0067     9   CONTINUE
0068  C      WRITE HEADER WHICH INCLUDES REACTANT SPECIES NUMBERS
0069         WRITE(LP,107) (IIN(L),L=1,NII)
0070         IF(LOG2) WRITE(LP,114) (JIN(L), L = 1, NJJ)
0071         WRITE(LP,111)
0072  C
0073  C      OPEN DATA FILE FROM DISK
0074         CALL OPEN(IDCB,IER,NAME,0,ISC,ICR)
0075  C      CHECK FOR ERROR RETURN
0076         IF(IER .LT. 0) WRITE(IP(1),102) IER
0077  C
0078  C      READ IN DATA LINE AT A TIME
0079     7   CALL READF(IDCB,IER,IBUFR,IL,LEN)
0080  C      CHECK FOR ERROR RETURN
0081         IF(IER .LT. 0) WRITE(IP(1),102) IER
0082  C      CHECK FOR END OF FILE (EOF)
0083         IF(IER .EQ. -12) GOTO 25
0084  C
0085  C      READ FILE WITH FORMAT.  NOTE THAT A READF CALL GETS RECORD
0086  C      FROM FILE AS IS.  CALL CODE READ DOES A FORMATTED READ OF THE
0087  C      FILE.  HP IS SUPPOSED TO COME OUT WITH A SOFTWARE REVISION
0088  C      THAT ALLOWS FOR DIRECT READING OF A NAMED FILE.
0089         CALL CODE
0090         READ(IBUFR,104) (IBUF(I), I = 1, 132)
0091  C
0092  C      LOOK FOR FIRST REACTION (LOOK FOR A PLUS SIGN)
0093  C
0094         IF(IAND(IBUF(16),IPL)  NE  IPL) GOTO 7
0095  C
0096  C      CONVERT SELECTED PORTIONS FROM KNOWN FORMAT INTO NUMBERS
0097  C      INTERNAL TO THE COMPUTER.
0098  C
0099         DO 10 I = 1, 8
0100  C      FOLLWING LINE TOGETHER WITH DATA STATEMENT FOR ISLCT GETS
0101  C      CHARACTERS FROM SPECIFIC COLUMNS OF DATA FILE
0102         IMAS(I) = IBUF(ISLCT(I))
0103         IMAS(I) = IAND(IMAS(I),37400B)/400B
0104         IF(IMAS(I)  EQ. 40B) IMAS(I) = IMAS(I) + 20B
0105         IMAS(I) = IMAS(I) - 60B
0106    10   CONTINUE
0107         IA = 10 * IMAS(1) + IMAS(2)
0108         JA = 10 * IMAS(3) + IMAS(4)
0109  C      KA AND LA ARE THE NUMBERS OF THE PRODUCTS FOR EACH REACTION.
0110  C      THEY ARE NOT USED IN THIS PROGRAM.  THE INFORMATION IS INCLUDED
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 PAGE 0003  SLRXT  9:57 AM  FRI., 17  JULY, 1981


0111   C      HERE SO THAT ONE CAN EASILY SEE HOW TO IMPLEMENT A SEARCH FOR
0112   C      SPECIFIC PRODUCTS.
0113   C      KA = 10 * IMAS(5) + IMAS(6)
0114   C      LA = 10 * IMAS(7) + IMAS(8)
0115   C
0116   C
0117   C      IF WE ARE LOOKING FOR REACTIONS OF SPECIES WITH SPECIFIED
0118   C       COMPLEMENTARY REACTANTS, JUMP AHEAD TO LINE 21.
0119          IF(LOG2) GOTO 21
0120          DO 15 II = 1, NII
0121          LOG = .FALSE.
0122   C      SEE IF SPECIFIED REACTANTS OCCUR IN POSITION IA OR JA.
0123          IF(IIN(II) .NE. IA .AND. IIN(II) .NE. JA ) GOTO 15
0124          LOG = .TRUE.
0125          GOTO 20
0126     15   CONTINUE
0127          GOTO 22
0128   C
0129   C      LOOK FOR MATCHES OF BOTH SPECIES AND COMPLEMENTARY REACTANTS
0130     21   CONTINUE
0131          DO 30 II = 1, NII
0132          DO 30 JJ = 1, NJJ
0133          LOG = .FALSE.
0134          IF((IIN(II) .EQ. IA .AND. JIN(JJ) .EQ. JA) .OR. (IIN(II) .EQ. JA
0135         &    .AND. JIN(JJ) .EQ. IA)) LOG = .TRUE.
0136          IF(LOG) GOTO 20
0137       30 CONTINUE
0138   C
0139   C      OUTPUT REACTION MATCHED
0140   C
0141       20 IF(LOG) WRITE(LP,105) (IBUF(I), I = 1, 126)
0142   C      COUNT NUMBER OF MATCHES
0143          IF(LOG) NMAT = NMAT + 1
0144   C
0145   C      CHECK FOR EOF, IF NOT EOF, CONTINUE READING
0146   C
0147       22 CONTINUE
0148          IF(IER .NE. -12) GOTO 7
0149    25    CONTINUE
0150   C
0151   C      EOF
0152   C
0153   C      IF EOF WRITE NUMBER OF MATCHES TO LISTING DEVICE AND TO DIALOGUE
0154   C      DEVICE.
0155          WRITE(LP,110) NMAT
0156          WRITE(IP(1),110) NMAT
0157          END


  FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)

  **  NO WARNINGS **  NO ERRORS **   PROGRAM = 01357      COMMON = 00000
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Appendix D
PROGRAM RLIST

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 PAGE 0001  FTN.   9:12 AM  WED., 22  JULY, 1981


0001   FTN4,L
0002         PROGRAM RLIST(3,99), REV. 810420 DOREN INDRITZ
0003   C     VERSION 810420 FOR HEWLETT PACKARD MINICOMPUTER
0004   C     TO LIST REACTION FILE, DOUBLE SPACED.
0005   C      IN SHORTENED FORMAT (ONLY FIRST 60 COLUMNS PLUS THE
0006   C      NUMBER LISTED UNDER "#FND")   THIS GIVES A LISTING
0007   C      THAT HAS ROOM TO MAKE COMMENTS IN THE RIGHT HAND "MARGIN",
0008   C      BUT STILL KEEPS REQUISITE IDENTIFIERS.
0009   C      ECHOS DATA AT HEAD OF FILE UNTIL FINDS FIRST REACTION.
0010   C      PROGRAM COUNTS NUMBER OF REACTIONS FOUND IN THE FILE.
0011   C
0012         DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),IMAS(5)
0013         DATA ICR,ISC,NMAT,IPL,IL,IBLBL/27,0,0,25400B,132,2H   /
0014   C     ICR IS THE CARTRIDGE THAT THE DATA FILE IS ON
0015   C     IPL IS ASCII FOR "+" IN THE LEFT BYTE.
0016   C
0017   C     FORMATS
0018   C
0019     100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
0020     101 FORMAT(3A2)
0021     102 FORMAT(' IER = ',I8)
0022     103 FORMAT(132A1)
0023     104 FORMAT(1H0,60A1,1X,I4)
0024     105 FORMAT(' FINISHED   A TOTAL OF ',I3,' WRITTEN.')
0025   C
0026   C     OBTAIN LOGICAL UNIT NUMBER(LU) OF DIALOGUE DEVICE.
0027         CALL RMPAR(IP)
0028   C     SET LU FOR LIST DEVICE
0029         LP = 9
0030   C     OBTAIN NAME OF DATA FILE
0031         WRITE(IP(1),100)
0032         READ(IP(1),101) (NAMF(K), K = 1, 3)
0033   C
0034   C     OPEN DATA FILE FOR READING.
0035         CALL OPEN(IDCB,IER,NAMF,0,ISC,ICR)
0036         IF(IER .LT. 0) WRITE(IP(1),102) IER
0037       7 DO 10 I = 1, 132
0038         IBUFR(I) = IBLBL
0039      10 CONTINUE
0040         CALL READF(IDCB,IER,IBUFR,IL,LEN)
0041         IF(IER .LT. 0) WRITE(IP(1),102) IER
0042         IF(IER .EQ. -12) GOTO 25
0043   C
0044   C      CALL CODE READ DOES A FORMATTED READ OF A SPECIFIED BUFFER.
0045         CALL CODE
0046         READ(IBUFR,103) (IBUF(I), I = 1, 132)
0047   C
0048   C     LOOK FOR FIRST REACTION (" + " SIGN)
0049   C
0050         IF(IAND(IBUF(16),IPL) .EQ. IPL) GOTO 8
0051         WRITE(LP,103) (IBUF(L),L=1,132)
0052         GOTO 7
0053   C
0054   C     GET #FND, THIS WILL BE PART OF THE OUTPUT
0055   C
```

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0056      8   DO 20 I = 1, 5
0057          IMAS(I) = IAND(IBUF(85+I),37400B)/400B
0058          IF(IMAS(I) .EQ. 40B) IMAS(I) = IMAS(I) + 20B
0059          IMAS(I) = IMAS(I) - 60B
0060     20   CONTINUE
0061          NFND = 10000*IMAS(1)+1000*IMAS(2)+100*IMAS(3)+10*IMAS(4)+IMAS(5)
0062   C
0063          WRITE(LP,104) (IBUF(I),I = 1, 60), NFND
0064   C      KEEP TRACK OF THE NUMBER OF MATCHES.
0065          NMAT = NMAT + 1
0066   C
0067   C      CHECK FOR EOF
0068          IF(IER .NE. -12) GOTO 7
0069     25   CONTINUE
0070   C
0071          WRITE(LP,105) NMAT
0072          WRITE(IP(1),105) NMAT
0073          END


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  **  NO WARNINGS **  NO ERRORS **    PROGRAM = 00815       COMMON = 00000
```

END

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