ABSTRACT

An Elementary Reaction Model for Thermal Decomposition of CF_2Cl_2 in a H_2 Atmosphere
and
Experimental Studies on Oxidation of CH_3OH Plus CH_4 Under Fuel Rich, Stoichiometric and Fuel Lean Conditions

by
Cheng Guo

Pyrolysis of CF_2Cl_2 in an atmosphere of H_2, has been studied in a tubular flow reactor, 723 to 873 K. Overall reaction conversion proceeds via loss of Cl with CHF_2Cl formation, then loss of the second Cl atom and CH_2F_2 product. Initiation occurs by unimolecular Cl atom loss. Subsequent chain propagation steps rapidly generate active H atoms which abstract Cl atoms, but abstraction of fluorine atoms by atomic hydrogen is slow at the temperatures of this study.

A small mechanism, about 35 elementary reaction steps, and a thermodynamic data base were developed to model the reaction system. Agreement of the mechanism with the data at varied time and temperature is reasonable. Rate constants were determined to be in the fall-off regime for the unimolecular dissociation reactions, Cl elimination, and were evaluated by Quantum Kassel Theory coupled with Transition State Theory. HCl and HF molecular elimination paths (both 1,1 and 1,2) and insertion of $^1{:}CF_2$ are also projected to be important in the high temperature chemistry of chloro-fluoro carbons.

Carbene elimination, both $^1{:}CF_2$ and $^1{:}CFCl$ from

CHF_2Cl, and thermal reaction of CHF_2Cl as well as subsequent formation of CH_2F_2 via ^{1}:CF_2 into H_2 under reaction conditions similar to those utilized in this study can be important.

Part II of this study is the tubular flow reactor experiments on methanol oxidation in the presence of methane fuel at varied fuel equivalence ratios of 0.7-1.7, at 1 atmosphere pressure with residence times of 0.3 to 2.0 seconds and temperature range of 500-850 C.

The extensive experimental data will be used as a basis for developing a detailed elementary reaction model for methanol/methane oxidation. Intermediate products: dimethyl ether (CH_3OCH_3) and formaldehyde dimethyl acetal($CH_3OCH_2OCH_3$), are observed in the low temperature regime (550-650C) and reported for the first time in this study. These products arise from the combination and addition reactions of CH_3O and CH_3 radicals with themselves and with CH_2O or CH_2OH radical which are important and readily occur. It is a surprise that they have not been previously observed or anticipated. These observations reveal some new pathways in the methanol combustion process. The new reactions will be included in our reaction modeling studies so that the model can be extended to conditions outside our experimental validation range.

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AND
EXPERIMENTAL STUDIES ON OXIDATION OF CH_3OH PLUS CH_4 UNDER FUEL RICH, STOICHIOMETRIC AND FUEL LEAN CONDITIONS

by
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An Elementary Reaction Model for Thermal Decomposition of CF_2Cl_2 in a H_2 Atmosphere and Experimental Studies on Oxidation of CH_3OH Plus CH_4 Under Fuel Rich, Stoichiometric and Fuel Lean Conditions

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CHAPTER 1
INTRODUCTION

There is compelling evidence that the build up of Chloro-Fluoro Carbons (CFCs) in the troposphere and the stratosphere are effecting significant reduction in ozone levels in the stratosphere(1-3). This ozone reduction allows harmful radiation to reach the troposphere with predicted increases in skin cancer as a result. As a consequence the Montreal Protocol(4) was enacted banning certain chloro-fluoro carbons by 1995 and calling for significant reductions in others, with specific scheduled phase outs of CFCs harmful to the ozone layer over the first several decades of the 21 century. Due to the very valuable properties these chloro-fluoro carbons have as refrigerants, aerosol propellants, fire retardants, etc..., they have been produced in very significant amounts - about 109 Kg/year.

The technical community is now faced with finding alternatives to these valuable chemicals and with either converting the large CFC supplies already in the market into less or non harmful substitutes or destroying the CFCs to produce non harmful products.

The objective of this effort is to demonstrate feasibility for conversion of the CF_2Cl_2 to environmentally acceptable materials hopefully with commercial value through pyrolysis in a hydrogen atmosphere. There are presently vast stores of chlorofluorocarbons, which are in use as refrigerants, fire suppressants and foaming agent etc. Due to the proven ability of stable chlorinated organics to deplete stratospheric ozone, the chlorofluoro carbons are to be removed from service as specified in the Montreal Protocol and in new Federal Regulations. Consequently it may be of significant economic and environmental benefit if these materials can be converted into valuable and useful substances of lower Ozone Depletion Potential (ODP).

Thermodynamic analysis indicates the overall reactions of CFC'c with hydrogen to form hydrocarbons and HF plus HCl are very favorable over a wide range of temperature.

$CF_2Cl_2 + H_2 \rightarrow CHF_2Cl + HCl$ $\Delta H_{298} = -23.3$ Kcal/mole

$CF_2Cl_2 + 2H_2 \rightarrow CH_2F_2 + 2HCl$ $\Delta H_{298} = -38.1$ Kcal/mole

$CF_2Cl_2 + 4H_2 \rightarrow CH_4 + 2HF + 2HCl$ $\Delta H_{298} = -78.6$ Kcal/mole

Due to the relative strong C-H bonds (100 Kcal/mole), the weaker C-Cl bonds (70-80 Kcal/mole) are easier to cleave (initiation of reaction) to form fluorocarbon radicals and Cl.

$CF_2Cl_2 \rightarrow CF_2Cl + Cl$ $\Delta H_{298} = 77.0$ Kcal/mole

There is also the possibility of molecular elimination channels forming singlet fluoro and chlorofluoro carbenes:

$CF_2Cl_2 \rightarrow :CF_2 + Cl_2$ $\Delta H_{298} = 74.7$ Kcal/mole

$CF_2Cl_2 \rightarrow :CFCl + ClF$ $\Delta H_{298} = 97.1$ Kcal/mole

The chloro-fluoro radical CF_2Cl will react, in this reaction system, with the H_2 bath gas to form new C-H and H-Cl bonds plus H.

$CF_2Cl + H_2 \dashrightarrow CHF_2Cl + H$ $\quad \Delta H_{298} = 2.8$ Kcal/mole

$Cl + H_2 \dashrightarrow HCl + H$ $\quad \Delta H_{298} = 1.2$ Kcal/mole

The $:CF_2$ and :CFCl singlet carbenes may undergo insertion reactions with H_2 to form an energized adduct $[CH_2F_2]^{\#}$ and $[CH_2FCl]^{\#}$. These adducts may be stabilized or react to lower energy products or back to the initial reactants before stabilization occurs.

$:CF_2+H_2 \leftrightarrow [CH_2F_2]\# \rightarrow CH_2F_2$ $\quad \Delta H_{298} = -68.6$ Kcal/mole

(stabilized)

$\rightarrow :CHF + HF$ $\quad \Delta H_{298} = 0.1$ Kcal/mole

$:CFCl+H_2 \leftrightarrow [CH_2FCl]\# \rightarrow CH_2FCl$ $\quad \Delta H_{298} = -57.6$ Kcal/mole

(stabilized)

$\rightarrow :CHF + HCl$ $\quad \Delta H_{298} = 9.0$ Kcal/mole

If reaction conditions could be adjusted so as this process were occurring to a significant extent, then the insertion reactions of :CHF may continue with H_2, eventually forming all HF, HCl plus hydrocarbons.

Converting the C-F and H-H bonds into C-H and H-F is thermodynamically favorable. But due to the higher C-F bond energy, it is more difficult to initiate.

We therefore conclude one possible mechanism or conversion of a fully chlorinated/fluorinated chloro-fluoro carbons which thermolysis in hydrogen atmosphere to produce a partially hydrogenated chloro-fluoro carbon and HX. The partially hydrogenated chemical may then be useful and not harmful to the ozone layer.

Experimental results on the thermal conversion of CF_2Cl_2 in a H_2 atmosphere to CHF_2Cl and CH_2F_2 between 723-873 K were reported by M. L. Energia Inc.(5) In this study, a detailed chemical kinetic mechanism is developed from fundamental thermochemical principles to describe and help understand the reaction system. The model is applied to the observed reactant and product profiles and shows good agreement over a wide range of experimental data.

CHAPTER 2
PREVIOUS STUDIES

There are a limited number of studies on CF_2Cl_2 pyrolysis in the literature with only one on pyrolysis (actually CO_2 irradiation) in H_2 atmosphere that we are aware of. This one previous study$^{(6)}$ is a CO_2 photolysis/pyrolysis where up to 20 Torr of H_2 was added in some of the experiments, by the Grunwald research group. The results showed dramatic changes in stable product profiles when hydrogen was added; that is formation of partially and fully hydrogenated hydrocarbons occurred rapidly.

There is one preliminary report on pyrolysis of $CF_2ClCFCl_2$ (Freon 113) which illustrates experimental results comparing pyrolysis in helium versus pyrolysis in hydrogen, by E. Ritter$^{(7)}$. This data of Ritter show dramatic changes in both rates of reaction (exponential increases in overall rate of freon decomposition in the presence of H_2) as well in the product distribution - formation of hydrocarbons and partially hydrogenated chloro - fluoro carbons with H_2 present.

There is, in addition, one ultraviolet photochemistry study of Rebbert and Ausloos$^{(8)}$, 214-147 nm, on $CFCl_3$ and CF_2Cl_2 from 234 to 453 K, temperature range, where they added the hydrocarbon ethane to the reactant system. They concluded from results of stable product analysis and reactions with added ethane (a Cl atom Scavenger), that the primary mechanism in their photo chemical studies was atomic chlorine elimination. Specifically the proposed multiple chlorine atom eliminations are:

$$CFCl_3 \;\text{-->}\; 2\ Cl + :CFCl$$

$$CF_2Cl_2 \;\text{-->}\; 2\ Cl + :CF_2$$

where there was ample photon energy for this process to occur in their studies. Rebbert and Ausloos(8) considered chemical activation processes to explain their observed products in only two of the about forty reactions proposed. The possibility of alternate paths, involving insertion of $:CF_2$ or :CFCl, which could have been produced via Cl_2 elimination (reverse of insertion as the initiation steps), could however be postulated as the mechanism of formation for several of their observed products. Still their product distributions and proposed qualitative mechanism are in very good agreement and they concluded insertion molecular elimination was not an important initiation process.

The thermal decomposition of the chlorofluorocarbons (CF_3Cl, CF_2Cl_2 and $CFCl_3$) were initially studied in a 4 cm ID x 20 cm alumina vessel by Trenwith and Watson(9) in 1957 over the temperature range 400-900 K and at the pressure of about one atmosphere. They found that stability increases in proportion of fluorine atoms in the molecule.

The decomposition of CF_2Cl_2 in this study(9) was over the range 700-900 K. The CF_2Cl_2 itself was quite stable below 750 K and almost completely decomposed at 900 K. The principal products were chloro-trifluoro-methane and chlorine; in addition there were smaller amounts of trichloro-fluoro-methane and carbon tetrachloride. They proposed the following mechanism:

$CF_2Cl_2 = CF_2Cl + Cl$

$CF_2Cl_2 + Cl = CF_2Cl + Cl_2$

$CF_2Cl + CF_2Cl_2 = CF_3Cl + CFCl_2$

$CFCl_2 + CF_2Cl_2 = CFCl_3 + CF_2Cl$

In 1976, Dever and Grunwald$^{(6)}$, see above, found that photolysis of CF_3Cl with a pulsed CO_2 laser (1.5 MW/cm^2 irradiation of 60 Torr of CF_3Cl at frequency of 1090 cm^{-1}) resulted in the formation of C_2F_6, CF_4 and CF_2Cl_2 as detected products. In the presence of H_2, the principal one-carbon product becomes CHF_3; additional two-carbon products (molecular weight growth) are C_2F_4 and C_2H_2. Similar condition of 60 Torr of $CFCl_3$ at 1079 cm^{-1} yields $CCl_2{=}CF_2$ and cis- and trans-CFCl=CFCl as detected products either as the pure gas or in the presence of 0-20 Torr H_2. Above 20 Torr of H_2, formation of C_2H_2 becomes more important.

The decomposition of CF_2Cl_2 by a pulsed infrared CO_2 laser at 921 cm^{-1} and 1088 cm^{-1} was reported by Hill et al$^{(10)}$. Major reaction products were CF_2ClCF_2Cl and CF_3Cl, which account for about 83% of the decomposed CF_2Cl_2. Minor products formed initially were $CF_2ClCFCl_2$ and $CFCl_3$.

There was no evidence for C_2F_4. They also suggested a mechanism:

$CF_2Cl_2 = CF_2Cl + Cl$

$CF_2Cl + CF_2Cl$ ->[singlet collision complex]-> CF_2ClCF_2Cl

$CF_2Cl + CF_2Cl$ ->[triplet collision complex]-> $CF_3Cl + {}^3CFCl$

J. Hudgens(11) presented results obtained by a two stage differentially pumped molecular beam sampling mass spectrometer designed to allow in situ optical and mass spectral analysis of the photolysis products generated with infrared pulses from CO_2 TEA laser (irradiation wavelength were 9.24 um for CF_2Cl_2 and 9.27 um for $CFCl_3$). They reported that the dominant decomposition channel and reaction barriers of CF_2Cl_2 and $CFCl_3$ were

$CF_2Cl_2 = CF_2Cl + Cl$ Ea = 78 Kcal/mol

$CFCl_3 = CFCl_2 + Cl$ Ea = 77 Kcal/mol

During the 1970's, many scientists focused on the initial reaction steps of CF_3Cl, CF_2Cl_2 and $CFCl_3$ photo decomposition. They demonstrated that Cl elimination is the initial step by molecular beam experiments employing detection of fragments by mass spectrometry and/or chemical scavengers. Fluorine atom or Cl_2 elimination is negligibly small. In 1978 and 1979, Sudbo et al(12,13) presented two papers about multiphoto dissociation of chlorofluorocarbon molecules. The experiments clearly indicated that single halogen atom Cl or Br elimination is the major process of unimolecular dissociation for halogenated methanes. They estimated that less than 10% of the CF_2Cl_2

could have dissociated through the three center elimination channel:

$CF_2Cl_2 \rightarrow :CF_2 + Cl_2$

In 1981, Morrison et al$^{(14)}$ measured absolute conversions and branching ratios for simple bond scission versus diradical formation in the infrared CO_2 laser (927 cm^{-1}) multiphoto dissociation of methyl freons in a serious of scavenged product analysis experiments. The maximum yields of $:CF_2$ from CF_2Cl_2 were found to be 10%. They indicated that $:CF_2$ is formed from CF_2Cl_2 in competition with C-Cl scission via direct reaction to a low energy primary pathway, not the result of high energy secondary fragmentation.

Naegeli et al$^{(15)}$ studied pyrolysis and oxidation of CF_2Cl_2 and CHF_2Cl added to methane and propane air flames to observe effects on flame stability and speed. Varied ratios of freon to fuel showed complete loss of the freon and about 80% production of HCl for low ratios (0.1). At higher ratios - approaching 1.0, the parent freon was destroyed to near completion, but HX acid production could only account for less than 20% of the mass balance, before flame extinction occurred.

Tokuhashi et al$^{(16)}$ studied decomposition of CF_2Cl_2 in a Bunsen type burner and observed significant amounts of nonconverted parent freon in the products when the freon/methane ratio exceeded 0.2. While this is in contrast to the data of Naegeli et al, the studies used different types of burners and this could explain the differences.

The molecular beam experiments(12-14) employing mass spectrometry detection of decomposition fragments or analysis of radical scavengers have clearly demonstrated that photo dissociation by CO_2 laser irradiation proceeds by Cl atom elimination, not molecular elimination for these molecular systems - CF_2Cl_2, $CFCl_3$, and CF_3Cl.

Further kinetic studies on chlorofluorocarbon decomposition were reported in 1989 and 1990. Zitter et al(17,18) presented a detailed study of CO_2 laser initiated decomposition of $CFCl_3$ and CF_3Cl(17) plus CF_2Cl_2(18) experiments around 50 Torr of the freon, and also concluded that initial decomposition of these molecules occurs by Cl atom elimination from these molecules. They postulated a set of reaction mechanism:

$CF_2Cl_2 = CF_2Cl + Cl$

$CF_2Cl + CF_2Cl = CF_2ClCF_2Cl$

$Cl + Cl = Cl_2$

$CF_2Cl + CF_2Cl_2 = CF_3Cl + CFCl_2$

$CFCl_2 + CF_2Cl_2 = CFCl_3 + CF_2Cl$

$CFCl_2 + Cl = CFCl_3$

$CF_2Cl + CFCl_2 = CF_2ClCFCl_2$

$CFCl_2 + CFCl_2 = CFCl_2CFCl_2$

$CF_2Cl_2 + Cl = CF_2Cl + Cl_2$

Their research, as that of Ausloos, showed molecular weight growth from combination and possible insertion reactions of the initial radical species occurred. Both studies also emphasized that insertion reactions did not appear to be important processes. Both of Zitter's studies, however, also concluded that there were reaction products, which were not well explained by their qualitative mechanisms.

CHAPTER 3
RESEARCH BACKGROUND

3.1 Methods for The Estimation of Thermochemical Data

Thermochemical data are required to determine the energy balance in chemical reactions and in determining the Gibbs Free Energy of a reaction as a function of temperature. The data also provide a convenient way to determine reverse reaction rate constants from the calculated equilibrium constant of the reaction and the known forward rate. This thermodynamic property data set also serves as the foundation of our mechanism development.

The thermodynamic data base, entropy (S_{298}), enthalpy of formation (H_{f298}) and heat capacity $C_p(T)$, is based upon the best currently available thermochemical data. When experimentally based thermochemical data were not available, the values were estimated using the THERM computer code(19), which is based on the group additivity techniques(20).

3.1.1 Benson Group Additivity Method

The group-additivity method is applicable for C_p, H_{f298}, S_{298}. A group is defined as a polyvalent atom(ligancy ≥ 2), in a molecule together with all of its ligands. Molecules such as HOH, CF_2Cl_2, and CH_4 that contain only one such atom (i.e., only one group), are irreducible entities and do not need to be treated by group additivity. For each group, the key central atom is given then followed by notation specifying other atoms bonded to the key atom.

For radicals, an average C_p can be calculated from values for adjacent saturated and olefinic hydrocarbons to obtain a value for the intermediate radical, for example :

$C_p(CC.) = 1/2\ [C_p(CC) + C_p(C{=}C)]$

This is a method for an initial rough estimate. The hydrogen bond dissociation group method (see below) is more accurate and recommended.

In calculating entropies by using the group additivity method, correction factors are considered for: symmetry number, optical isomers, degenerate spin of the electron etc. For example:

$Sp = S_{(int.)} - R{*}\ln\sigma_p + R{*}\ln OI$

$Sr = Sp + R{*}\ln\sigma_p - R{*}\ln\sigma_r + R{*}\ln2 - 0.1 - 2.6$

Sp : Parent molecule entropy

$Sp_{int.}$: Intrinsic parent molecule entropy

σ_p : Number of parent molecule symmetry

σ_r : Number of radical symmetry

R : Gas constant

S_r : Radical entropy

OI : Optical Isomer

. Add R*ln2 for free radical electron spin

. Subtract 0.1 for loss of H atom

. Subtract 2.6, if loss of an O-H, N-H or C-H rotor, compare with parent molecule.

3.1.2 Method of Hydrogen Atom Bond Dissociation Group

A data base of H atom bond dissociation (BD) groups(21) is derived for calculating thermodynamic properties on generic classes of radical species relevant to combustion and atmospheric chemistry. It is based on: 1. evaluated literature bond energies; 2. calculated changes resulting from loss and/or change in vibration frequencies including inversion; 3. changes in barriers to internal rotation; 4. spin degeneracy; and 5. external rotational and translational effects. The BD groups, when coupled with thermodynamic properties of the corresponding generic class of stable molecules, yield accurate thermodynamic properties for the respective radicals.

A computer code, THERM, which can be used to estimate, edit, or enter thermodynamic property data for gas phase radicals and molecules using Benson's group additivity method has been developed and reported(19,22). One important aspect of THERM is its ability to accurately estimate thermodynamic properties for a wide range of organic species, knowing only a bond type and the thermodynamic properties of the stable parent. These properties for radical species are calculated by applying Hydrogen Atom Bond Dissociation Increments to the corresponding property of stable parent molecules to reflect loss of the H atom.

Benson's group estimation technique is an accurate method for the estimation of ideal gas phase heat capacities, heats of formation, and entropies of molecules. This method assumes that the properties for a chemical substance are the sum of the contributions from each group or poly-valence atom (central atom) in that molecule. It is referred to as a second order estimation technique since next-nearest-neighbor corrections, and to some extent, chemical structures are accounted for. Estimation based upon chemical bond contributions alone are known as first order estimation techniques, while those based upon atomic contributions alone are referred to as zero order techniques. The second order estimation techniques are naturally more accurate than lower order techniques, however, more information about the molecule is required. Several other estimation techniques based upon group contribution principles are presented in Reid, Prausnitz, and Sherwood(23). This method, however, has become the most widely accepted due, in part, to its ease of use and relative accuracy when compared with other techniques.

To use Benson's method, one must become familiar with the notation used to describe the groups. For example if we consider chlorobenzene(C_6H_5Cl) we say that it has one C_B-(Cl) group and five C_B-(H) groups. C_B-(Cl) refers to a carbon atom in a benzene ring which is attached to a Cl atom, while C_B-(H) refers to a carbon atom in a benzene ring which is attached to an H atom. THERM identifies C_B-

(Cl) as CB/Cl and C_B-(H) as CB/H. For a second example consider propane (C_3H_8). This molecule contains two C-(H3)(C) groups for the two terminal methyls, and one C-(H2)(C2) for the center CH_2 group. THERM identifies C-(H3)(C) as C/C/H3, with C-(H2)(C2) identifies as C/C2/H2. We feel alphabetical order is preferred for simplicity in remembering the order of atoms in the group id. In addition to the group's id, various corrections for symmetry, optical isomers, ring structure, steric effects must be included where necessary.

Properties for the radicals may be estimated two different ways. One may estimate thermodynamic properties directly with radical group contributions as described by Benson. A second method applies only a single bond dissociation (BD) increment to stable molecules reflecting loss of an H atom from that species.

Conceptually BD groups are based on specific bond energies (R-H) and differences in heat capacity $C_p(T)$ and entropy S_{298}, e.g.

$BD(C_{p500}) = C_{p500}\text{Radical} - C_{p500}\text{parent}$ or

$BD(S_{298}) = S_{298}\text{Radical} - S_{298}\text{parent}$,

for generic classes of molecules. This group, once obtained, can then be added to the corresponding property of other molecules in that generic class to obtain the property of radical corresponding to the H atom loss. The BD groups have one advantage over those of the radical groups developed by Benson in that only one BD group is needed for a given radical. In the Benson scheme a radical group is needed for each central atom radical, in addition to a group for each central atom group attached to the radical center. Thus the Benson method requires a larger and more complex data set for determination of radical species thermodynamic properties.

The bond dissociation(BD) groups incorporate the following:

1. Accurate bond energies (R-H) for specific classes of compounds.
2. Entropy corrections for electron spin and optical isomers.
3. Loss of vibrations and changes in vibration frequencies.
4. Entropy and heat capacity corrections for changes in rotational barriers for rotors connected to radical centers (Benson tables A.18-A.20).
5. Inversion frequencies of carbon centered radicals.
6. Corrections to translational and rotational entropy for small molecules where loss of H atom contributes are described.
7. Changes in Symmetry are included by THERM.

The calculation of heats of formation for radical species simply uses the literature values of the bond dissociation (BD) energy for the specific H atom which is removed to effect the desired radical, plus the definition of bond energy (BE):

$$BE = \Sigma H_f(\text{products}) - \Sigma H_f(\text{reactants})$$

for simple loss of a H atom from an organic molecule:

$$R\text{--}H \longrightarrow R. + H$$

$$BE = H_f(R.) + H_f(H) - H_f(R\text{-}H)$$

H_f of the radical: $H_f(R.) = BE - H_f(H) + H_f(R\text{-}H)$

The Bond Energy and H_f of the corresponding Parent(R-H) may be obtained from group additivity (THERM) or from the literature$^{(24-27)}$.

For radical entropies and heat capacities, we have examples for some BD groups below:

RC.H2 = PARENT - V/C-H/ - 2V/H-C-H/ - V/HCC,TR/ + V/INV-H2/ - IR/RCH2-CH3/ + R/RCH2-CH2/

R2C.H = PARENT - 2IR/CH3-C2H5/ + 2IR/CH3-C.HCH3/ - V/H-C-H/ - V/C-H/ - 2V/H-C-C/ + V/INV-CH/

R3C. = PARENT - 3IR/CH3-IPROP/ - 3IR/CH3-C.(CH3)2/ - V/C-H/ - 3V/H-C-C/ + V/INV-C2/

here V and IR indicate vibration and internal rotation respectively. The methods for calculation of entropies and heat capacities incorporate effects from both loss of vibrations and changes in vibration frequencies. Effects of changes in rotational barriers due to formation of the radical are also accounted for. For example, resonance stabilization usually increases rotational barriers, and radical centers on carbons adjacent to saturated HC groups usually decrease the internal rotational barrier.

$$S_{tot} = S_t + S_{er} + S_{ir} + S_{vib} + S_{elec}$$

$C_{ptot} = C_{pt} + C_{per} + C_{pir} + C_{pvib}$
where t is translation, er and ir are external internal rotation.

The radicals we calculated by this computer code are CF_2Cl, CH_2F, $CFCl_2$, CHFCl and CFCl. The input file is:

CF_2Cl = CHF_2Cl -V/C-H/ -2V/H-C-F/ -V/H-C-Cl/ +V/INV-F2Cl/
CH_2F = CH_3F - V/C-H/ - 2V/H-C-H/ - V/H-C-F/ + V/INV-H2F/
$CFCl_2$ = $CHFCl_2$ -V/C-H/ -V/H-C-F/ -2V/H-C-Cl/ +V/INV-Cl2F/
CHFCl=CH_2FCl-V/C-H/-V/H-C-H/-V/H-C-F/-V/H-C-Cl/+V/INV-HFCl
CFCl = CHFCl - V/C-H/ - V/H-C-F/ - V/H-C-Cl/

The output file and calculation as well as the current rotation and vibration data base are attached in the Appendix.

3.2 Quantum Kassel Theory

Energized Complex/Quantum Kassel and termed QRRK by Dean(28,30) and later modified by Ritter and Bozzelli(19) for the formation of energized complex was used for modeling reactions involving atom and radical addition to an unsaturated bond and atom plus radical or radical plus radical combination reactions. The modified Quantum Kassel algorithm by Ritter and Bozzelli used Gamma function evaluations for the energy dependent term instead of factorials.

This modification obviates the need to round up the barriers to the nearest integer, before summation with respect to the energy. As a result the summations are not stopped at integer values of energy. This modification improves the Quantum Kassel prediction, especially at lower temperature where a small change of barrier can give large effect.

The Quantum Kassel approach assumes the formation of an activated complex $[AB]^{\#}$ due to the addition or combination of two species A and B. This activated complex has energy equal to the sum of $\Delta Hf_{[AB]o}$ (heat of formation of stabilized adduct AB^{o}) plus the bond energy for the formation of adduct. The following pathways are now available to the energized complex:

(i) It can dissociate back to reactants A and B.

(ii) It can stabilize to AB^{o} and lose the extra energy from the new bond formation in the adduct.

(iii) It can dissociate to new products, by unimolecular reaction which are viable, because of its extra energy.

$$\begin{tikzcd}
A + B \arrow[r, leftrightarrow, "k_1", "k_{-1}"'] & {[AB]^{\#}} \arrow[r, "k_2"] \arrow[d, dash, "k_{stab}"] & C + D \\
 & AB^{o} &
\end{tikzcd}$$

For condition of steady state: $(dAB^{\#}/dt = 0)$

$$[AB]^{\#} = k_1[A][B]/(k_{-1} + k_2 + k_{stab}) \tag{1}$$

$$\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{k_1\ k_2\ [A][B]}{k_{-1} + k_2 + k_{stab}} \qquad (2)$$

$$\frac{d(AB^o)}{dt} = \frac{k_{stab}\ k_1\ [A][B]}{k_{-1} + k_2 + k_{stab}} \qquad (3)$$

k_{stab} is calculated via the method of Troe$^{(31)}$ and uses the weak collision assumption and a "Troe" beta function for collision stabilization efficiency.

Eq.(2) and (3) provide apparent reaction rate constants to provide C + D and stabilized adduct, AB^o, by Quantum Kassel approach.

The k_1 and k_2 are functions of energy and are determined by an expression given by Dean.

In contrast to the above Quantum Kassel approach the more conventional thermal equilibrium analysis will consider the reaction as:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB \xrightarrow{k_2} C + D$$

For conditions of steady state

$$(AB)_{ss} = k_1\ [A][B]\ /\ (k_{-1} + k_2) \qquad (4)$$

$$\frac{d([C]+[D])}{dt} = \frac{k_1\ k_2\ [A][B]}{(k_{-1} + k_2)} = k_2\ K_{eq}\ [A][B] \qquad (5)$$

Eq. (5) in the limit $k_{-1} >> k_2$ reduces to

$$\frac{d([C]+[D])}{dt} = \frac{k_1\ k_2\ [A][B]}{k_{-1}} = k_2\ K_{eq}\ [A][B] \qquad (6)$$

where

$K_{eq} = k_1/k_{-1} = [AB]/([A][B])$

Eq. (3) and (6) demonstrate that substantial differences in the computed apparent rate constants for the formation of C + D can arise depending upon whether one uses a Quantum Kassel or chemical thermal approach. Dean, Ritter and Bozzelli showed that the two approaches become equivalent only at the high pressure limit, where all of the [AB]# is stabilized prior to reaction. Dean(28) found that the pressure required for complete stabilization varies extensively energy with species and temperature.

The present study of CF_2Cl_2/H_2 system was carried at temperature between 723 K and 873 K and pressure of 1 atm. The Quantum Kassel treatment of energized complex formation and considerations of its stabilization, plus forward and reverse reaction channels is a more accurate way to analyze the thermal reaction processes. Microreversibility for all reactions was also used in the mechanism to evaluate "reasonableness" of the reaction in each direction. Equilibrium could be established for any reaction should the necessary conditions exist via reverse reaction.

CHAPTER 4
EXPERIMENT

4.1 Experimental Apparatus

A schematic of the flow reactor is show in Figure 4.1. The high temperature tubular flow reactor was controlled isothermally and at atmosphere pressure in the study. The tubular flow reactor was made of quartz with ID of 1 cm^2 and maintained at a constant temperature by a brass block constant temperature oven.

The reactor heating block is machined from aluminum bronze alloy (CDA954), and insulated with a ceramic blanket. Heating is achieved by four Watlow J16A12 heating cartridges with Watlow 965 controller. Temperature is maintained constant to +/- 1 C by thermo-couple feed back to the proportional controller.

A reactant stream is created by mixing a flow of gaseous reactants (CF_2Cl_2) into a hydrogen flow stream (reducing bath gas) or by bubbling H_2 carrier through liquid CF_2Cl_2 which is held at a constant temperature 0 C (ice/salt bath). The gas mixture then flows through a preheat zone, then the quartz flow tube, which is heated by the temperature oven. After flowing through the preheat zone, the reactant gas mixture goes through the isothermal reaction zone. The gas mixture is held slightly above one atmosphere pressure (several cm of H_2O).

The CF_2Cl_2/H_2 stream exits the quartz reactor and is then vented to the hood. The outlet of the reactor has connections for syringe collection of the effluent gas, a bubbler for collection of HCl and to an evacuated glass bulb for collection of a batch gas sample for further GC or GC/MS analysis.

4.2 Quantitative Analysis of Reaction Products

Each experimental run was analyzed by conventional packed-column GC. Samples were drawn by syringe from the cooled exit stream of the reaction chamber. For selected runs, gas samples were passed into all all-glass sampling bulb for further analysis by GC/MS. .

Gas Chromatography was performed on a Perkin Elmer 900 GC with FID detector. The column is 1/8" OD x 2 meter length stainless steel tube packed with Supelco Graphpac 60/80 mesh with 5% Fluorcal coating. The operating conditions are: isothermal temperature is 50 C; flow rate of carrier gas N2 is 30 cc/min.

Some products could not be identified from GC retention times, and therefore GC/MS analysis was employed.

Organic hydrocarbon and chlorocarbon products were identified by using GC/MS Spectrometry on batch samples of reactor gas drown into evacuated Pyrex and stainless steel sample cylinders. A Finnigan 4000 quadrupole mass spectrometer equipped with an HP 5710A Gas Chromatograph and Techivent Vector-1 Data Station was used for these analysis. The GC was equipped with a 50 meter (OV101) 0.25 mm ID capillary column with methyl silicone stationary phase. Approximately 2 ml of reactor gas was injected into the GC using a 6-port sampling valve and cryofocused at the head of the column with liquid nitrogen for 10 minutes to trap the non-methane organics. The GC was held at 35 C for 4 minutes and then programmed at a rate of 16C/min. to 200C.

4.3 Hydrochloric Acid Analysis

Hydrochloric acid (HCl) analysis is performed for each experimental run. The sample for HCl were collected independently from the GC sampling. In the analysis, the effluent was bubbled through a two stage bubbler before exhaust to the fume hood. Each stage of bubbler contained 20ml of 0.01 M NaOH, plus 2-3 drops of phenolphthalien indicator. The gas passed through the two bubbler stages until the first stage solution reached the indicator endpoint. The time required for this to occur was recorded. At this point the bubbling was stopped, and the aliquots were combined and then titrated to their end point with standardized 0.01 M HCl.

Acknowledgment: The author acknowledge CF_2Cl_2 experiment done by S. Gulati, M. Lavid and A. Poulos at M. L. Energia, Inc., Princeton, NJ 08542(5).

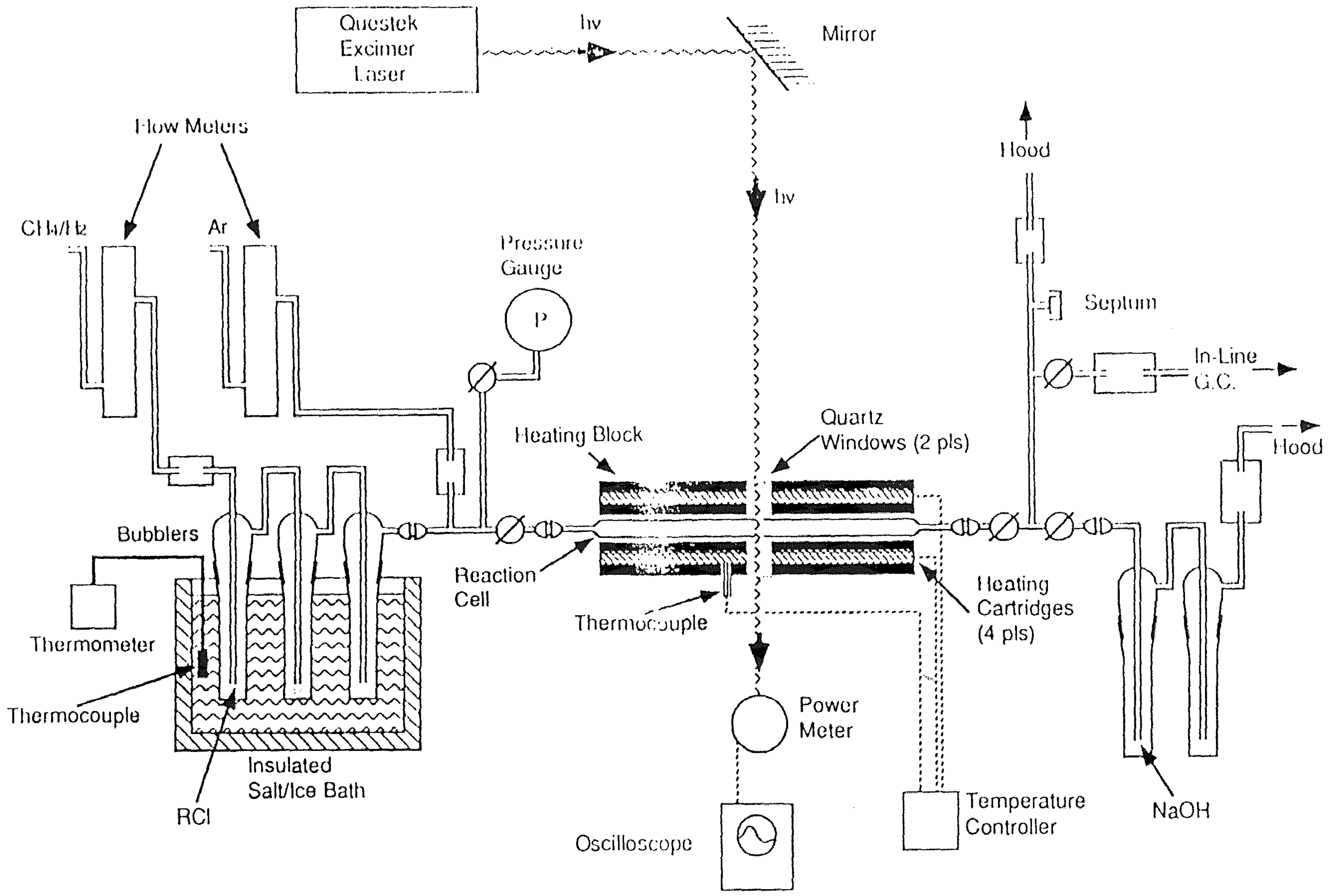


Figure 4.1 Experimental System

CHAPTER 5
RESULT AND DISCUSSION

5.1 Description

CF_2Cl_2 is observed to undergo thermal reaction with H_2 only at temperatures above 723 K. The temperature dependence of CF_2Cl_2 decomposition is illustrated in Figure 5.1, which plots fractional concentrations of CF_2Cl_2 relative to initial concentration, at nearly constant reactor residence time 2.6-3.2 seconds, versus reactor temperature at constant composition. The CF_2Cl_2 decomposition at a constant temperature (T = 823 K) vs different residence time is shown in Figure 5.2.

The major products in the thermal reaction systems of CF_2Cl_2/H_2 are CHF_2Cl and HCl(up to 93% selectivity). Secondary products are CH_2F_2 (up to 20%), and traces of CF_3CH_2F, C_2F_4 and CHF_2CHF_2. Small (trace) amounts (<1%) of $CHFCl_2$ and CF_2ClCF_2Cl are also measured. All these compounds were identified from GC retention times of standards and from GC/MS assignment.

The product distribution is a function of temperature, residence time and ratio of $CF_2Cl_2:H_2$. Table 5.1 lists the experimental data at residence time of 3 second and $CF_2Cl_2:H_2$ = 8:92. Extremely high selectivity toward CHF_2Cl is obtained in the temperature range 773-823 K. At 873 K, the selectivity drops to approximately 60% due to further reaction of CHF_2Cl in its conversion to CH_2F_2. Experimental results at different residence time at temperature of 823 K are also listed in Table 5.2.

The initiation step in this reaction system involves unimolecular decomposition of CF_2Cl_2:

CF_2Cl_2 --> CF_2Cl + Cl ▲ Hf = 77.0 Kcal/mole

Thermodynamic analysis for the other channels like

CF_2Cl_2 --> CFCl2 + F ▲ Hf = 115.57 Kcal/mole

CF_2Cl_2 --> :CFCl + ClF ▲ Hf = 97.08 Kcal/mole

indicate that these two reactions are not reasonable as initial reactions since higher energy barriers limit these processes. Our analysis of the dissociation of CF_2Cl_2 is in agreement with previous studies(12)-(14).

H atom is rapidly produced from Cl atom reaction with H_2

Cl + H_2 --> HCl + H

which serves to continue the chain reaction sequence.

The CF_2Cl will now react with H_2 bath gas.

CF_2Cl + H_2 --> CHF_2Cl + H ▲ Hf = 2.76 Kcal/mole

H atoms from reaction (2) and (4) as well as other similar reactions will abstract Cl from the parent CF_2Cl_2 forming additional CF_2Cl radicals.

CF_2Cl_2 + H --> CF_2Cl + HCl

The CF_2Cl radical can also rapidly react with itself to form a chemically activated adduct $[C_2F_4Cl_2]^{\#}$ as discussed in 5.2.2.

Further conversion from CHF_2Cl to CH_2F_2 can occur by the following different paths:

(i). $CHF_2Cl + H \rightarrow CHF_2 + HCl$

$CHF_2 + H_2 \rightarrow CH_2F_2 + H$

(ii). $CHF_2Cl \rightarrow :CF_2 + HCl$

$:CF_2 + H_2 \rightarrow CH_2F_2$

Sensitivity analysis show that both paths are important but path (i) is more important than the other one.

5.2 Quantum Kassel Calculations on combination and carbene ($:CF_2$, :CFCl, :CHF Insertion / Elimination Reactions)

The decomposition of the energized radical and molecular complexes was modeled using the Quantum Kassel calculations previously described. The details of the Quantum Kassel theory are presented in Chapter 3.

Figure 5. 3-20 illustrate the energy level diagrams and apparent rate constants versus temperature and pressure for

a. Unimolecular dissociation:
   - i. $CF_2Cl_2 \rightarrow$ products
   - ii. $CHF_2Cl \rightarrow$ products

b. Bimolecular chemical activation reactions:
   - i. $CF_2Cl + CF_2Cl \rightarrow$ products
   - ii. $:CF_2 + H_2 \rightarrow$ products
   - iii. $:CFCl + H_2 \rightarrow$ products
   - iv. $:CHF + H_2 \rightarrow$ products

The input rate parameters used in these calculations are listed in Table 5.3-5.8.

5.2.1 Unimolecular Dissociation

i. CF_2Cl_2 --> products

$$CF_2Cl_2 \xrightarrow{k_1} CF_2Cl + Cl \qquad \Delta H_{298} = 77.0 \text{ Kcal/mole} \qquad (1a)$$
$$\xrightarrow{k_2} :CF_2 + Cl_2 \qquad \Delta H_{298} = 74.7 \text{ Kcal/mole} \qquad (1b)$$
$$\xrightarrow{k_3} :CFCl + ClF \qquad \Delta H_{298} = 97.1 \text{ Kcal/mole} \qquad (1c)$$

The CF_2Cl_2 dissociation reaction is the most important reaction in this reaction system under initiation conditions. The energy level diagram and calculation results shown in Figure 5.3-5.5 indicate that the dominant channel is the dissociations to (CF_2Cl+Cl). The other possible dissociation channel is (:CF_2+Cl_2). These results are further verified by previously research of Sudbo et al(12,13) and Morrison et al(14).

ii. CHF_2Cl --> products

$$CHF_2Cl \xrightarrow{k_1} :CFCl + HF \qquad \Delta H_{298} = 45.0 \text{ Kcal/mole} \qquad (2a)$$
$$\xrightarrow{k_2} :CF_2 + HCl \qquad \Delta H_{298} = 53.9 \text{ Kcal/mole} \qquad (2b)$$
$$\xrightarrow{k_3} CHF_2 + Cl \qquad \Delta H_{298} = 87.1 \text{ Kcal/mole} \qquad (2c)$$

The CHF_2Cl is formed by

$$CF_2Cl + H_2 \longrightarrow CHF_2Cl + H \qquad \Delta Hf = 2.76 \text{ Kcal/mole}$$

which radical CF_2Cl is formed by decomposition of the parent CF_2Cl_2 in this study. Quantum Kassel calculations indicate that the two three-center elimination channels are dominant ones where the (2a) channel is more important as shown in Figure 5.6-5.8.

5.2.2 Bimolecular Chemical Activation Reactions.

i. CF_2Cl + CF_2Cl Reaction (combination)

The CF_2Cl radical can arise from dissociation of CF_2Cl_2 or from H atom abstracting Cl from CF_2Cl_2 to form CF_2Cl and HCl.

$CF_2Cl + CF_2Cl \leftrightarrow [C_2F_4Cl_2]^{\#}$

$\longrightarrow C_2F_4 + Cl_2 \quad \Delta H_{298} = -25.5$ Kcal/mole (3a)

$\longrightarrow C_2F_4Cl + Cl \quad \Delta H_{298} = -6.2$ Kcal/mole (3b)

$\longrightarrow C_2F_4Cl_2 \quad \Delta H_{298} = -87.0$ Kcal/mole (3c)

The fraction of activated $[C_2F_4Cl_2]^{\#}$ that decomposes to reactants, lower energy products $C_2F_4 + Cl_2$ or $C_2F_4Cl + Cl$, or is stabilized to $C_2F_4Cl_2$ is a function of energy distribution in the initially formed $[C_2F_4Cl_2]^{\#}$ adduct (temperature), stabilizing collisions (pressure), and unimolecular and stabilization rate constants.

Due to the high energy barrier (activation energy of Cl_2 elimination), channel (3a) does not occur. The channel (3b) and (3c) are both thermodynamically favorable relative to initial energy of the reactants. The energy level diagram for the above reaction system is shown in Figure 5.9. The Quantum Kassel calculations for the temperature range of 298 to 2000 K and pressure range of 0.1-7600 Torr indicate that the $C_2F_4Cl_2$ channel (stabilization) is dominant as shown in Figure 5.10-5.11.

ii. $:CF_2 + H_2$ Reaction

Carbene radicals (all singlets in lowest energy form for this study) such as $:CF_2$, $:CFCl$, $:CHF$ which can be formed by dissociation of CHF_2Cl will combine with bath gas H_2 via insertion reactions also forming energized complexes as with the $[C_2F_4Cl_2]^{\#}$ above. These adducts can react to lower energy products before stabilization.

$:CF_2 + H_2 \;<\!-\!> [CH_2F_2]^{\#}$

$-\!-\!>:CHF + HF \quad \Delta H_{298} = 0.1$ Kcal/mole (4a)

$-\!-\!> CHF_2 + H \quad \Delta H_{298} = 34.4$ Kcal/mole (4b)

$-\!-\!> CH_2F_2 \quad \Delta H_{298} = -68.6$ Kcal/mole (4c)

The Quantum Kassel calculations show that reaction (4a) and (4c) are important ones. CH_2F_2 channel is dominant. But when pressure decreases (as low as 1 Torr) and temperature increases (above 1000 K), the channel $:CHF+HF$ becomes more important. The energy level diagram and calculation results of $:CF_2+H_2$ are shown in Fig 5.12-5.14.

iii. $:CFCl + H_2$ Reaction

$:CFCl + H_2 \;<\!-\!> [CH_2FCl]^{\#}$

$-\!-\!> CH_2F + Cl \quad \Delta H_{298} = 25.9$ Kcal/mole (5a)

$-\!-\!>:CHF + HCl \quad \Delta H_{298} = 9.0$ Kcal/mole (5b)

$-\!-\!> CH_2FCl \quad \Delta H_{298} = -57.6$ Kcal/mole (5c)

The Quantum Kassel calculations show that stabilization (5c) is dominant reaction. Only at low pressure (1

Torr) and high temperature (above 1000 K), the other two channels CH_2F+Cl and :CHF+HCl become more important. The energy level diagram and Quantum kassel calculations of :CFCl+H_2 are shown in Fig 5.15-5.17.

iv. :CHF + H_2 Reaction

:CHF + H_2 <-> $[CH_3F]^{\#}$

--> CH_3 + F $\blacktriangle H_{298}$ = 27.7 Kcal/mole (6a)

--> CH2F + H $\blacktriangle H_{298}$ = 18.1 Kcal/mole (6b)

-->:CH_2 + HF $\blacktriangle H_{298}$ = 10.1 Kcal/mole (6c)

--> CH_3F $\blacktriangle H_{298}$ = -81.9 Kcal/mole (6d)

The energy diagram and Quantum Kassel calculations about reaction :CHF+H_2 are shown in Figure 5.18-5.20. The calculation results indicate that the stabilization channel (6d) is dominant reaction. The channel (6b) becomes important only at high temperature (above 1000 K) and low pressure (1 Torr).

5.3 Kinetic Mechanism and Modeling

A detailed kinetic mechanism (Table 5.9) was developed to describe the systems of reactions studied. This kinetic mechanism consists of 35 elementary reaction steps involving 28 radical and stable compounds. The thermochemical parameter of species which have not been previously measured or calculated are evaluated using the techniques of group additivity and the THERM computer code. Important dissociation, addition, insertion and combination reactions are analyzed by DISSOC and CHEMACT computer code.

Experimental data are compared with model predictions in Fig.5.22 for CF_2Cl_2 decomposition and product distribution (mainly CHF_2Cl) between 723 and 950 K. The calculated mole fractions of CF_2Cl_2 and CHF_2Cl are in excellent agreement with those experimental results.

The model predicts that the product CHF_2Cl will decrease and CH_2F_2 will dominate above 873 K at reaction time of 3 sec. The significant routes to CH_2F_2 in this study are:

$CHF_2Cl + H \text{--->} CHF_2 + HCl$

$CHF_2 + H_2 \text{--->} CH_2F_2 + H$

Sensitivity analysis shows that at higher temperature the above two reactions are important and contribute significantly to the formation of CH_2F_2.

Table 5.1 Selectivity and Conversion of CF_2Cl_2 by Thermolysis in Flow Reactor

T.K	t.sec	Conversion %	Selectivity(CHF_2Cl)%	CHF_2Cl%
773	3	5.6	93	5.2
823	2.8	12.7	93	11.8
873	2.7	60.1	65	39.1

Table 5.2 Thermal Decomposition of CF_2Cl_2 at 823 K

Time (sec)	C/Co		
	CF_2Cl_2	CHF_2Cl	CH_2F_2
2	0.897	0.079	0.003
2.8	0.872	0.100	0.004
5	0.543	0.382	0.040
8	0.376	0.489	0.082
10	0.193	0.498	0.239

C/Co : [Compound]/[CF_2Cl_2]o

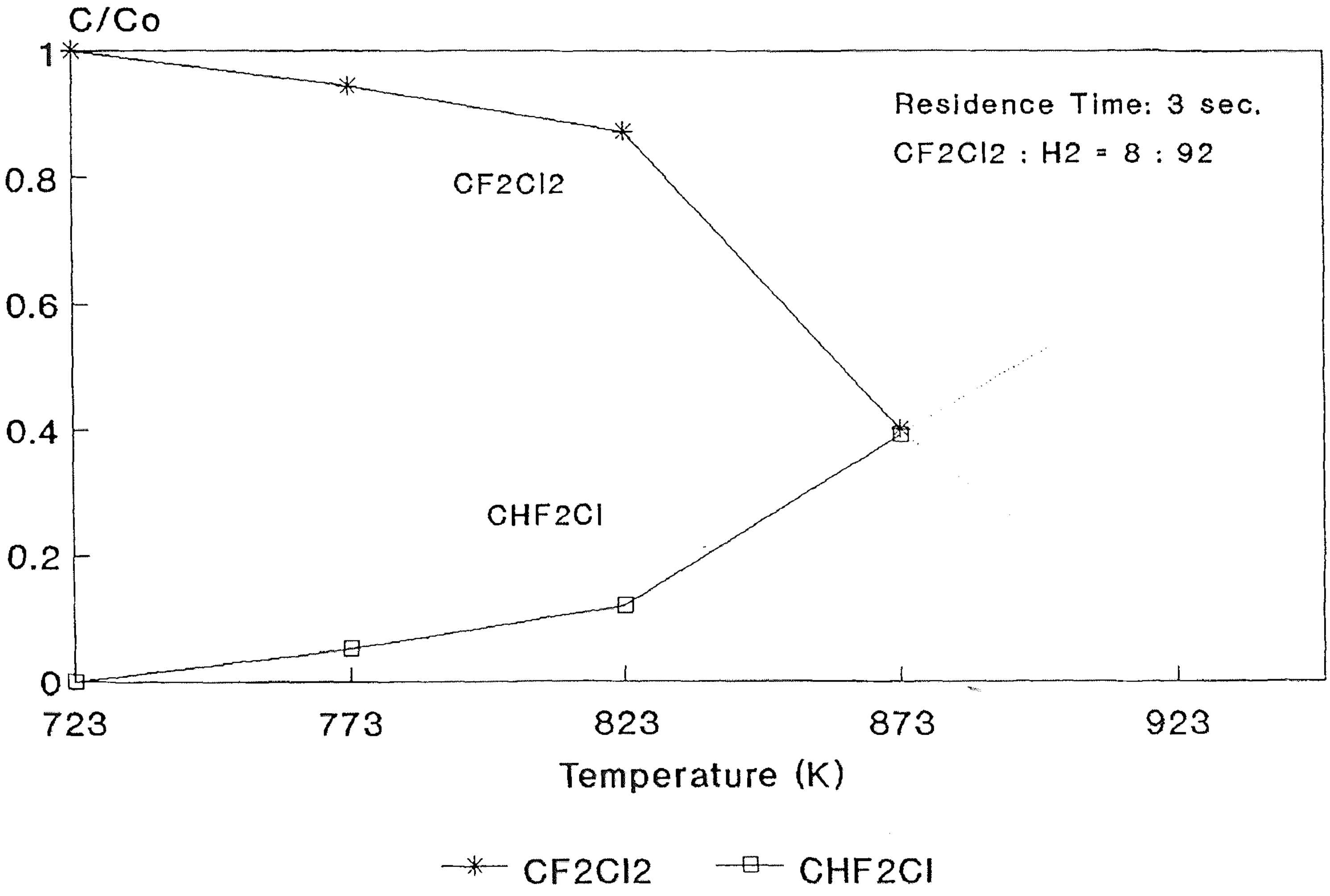


Figure 5.1 Product Distribution vs Temperature

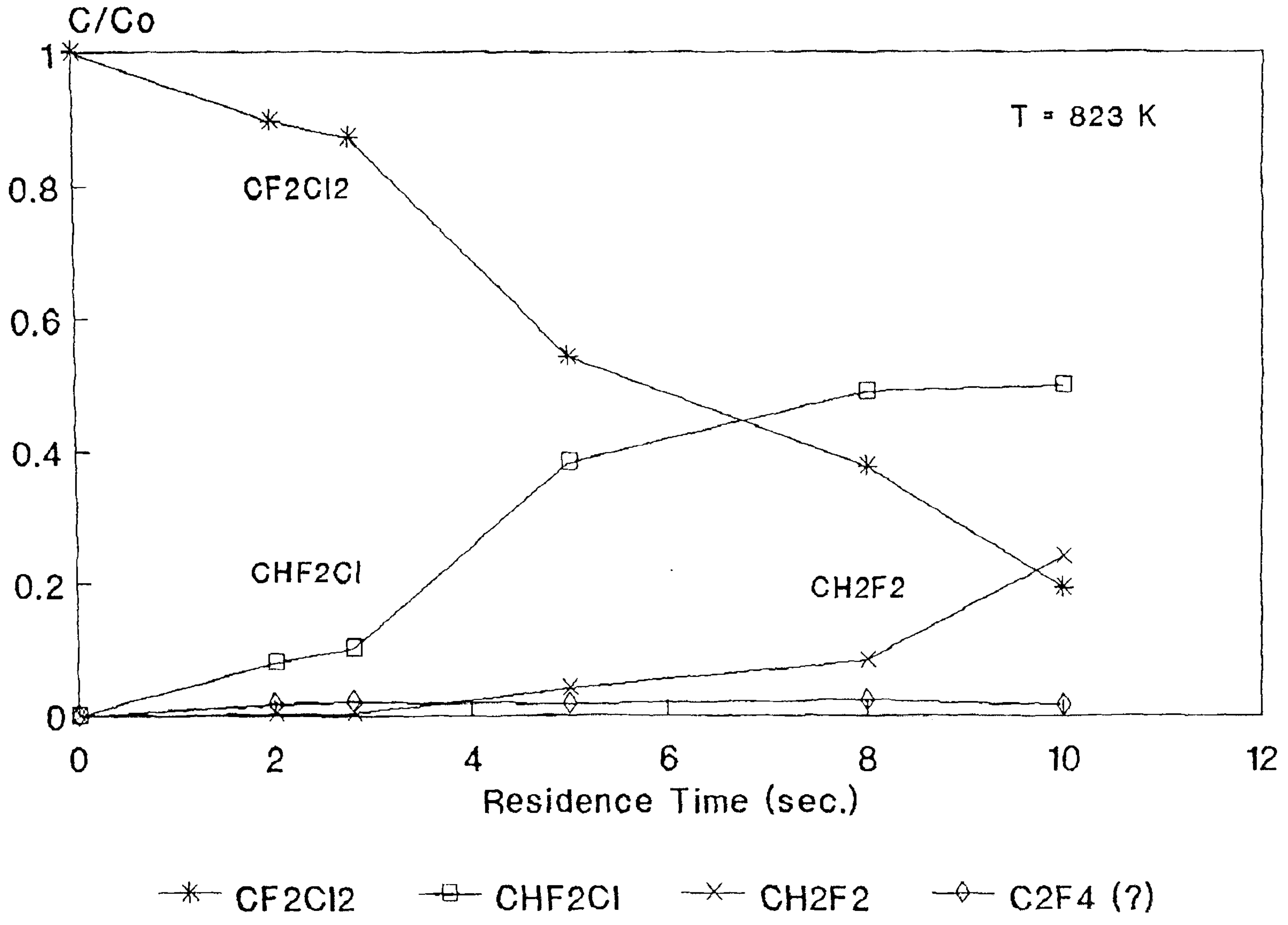


Figure 5.2 Product Distribution vs Time

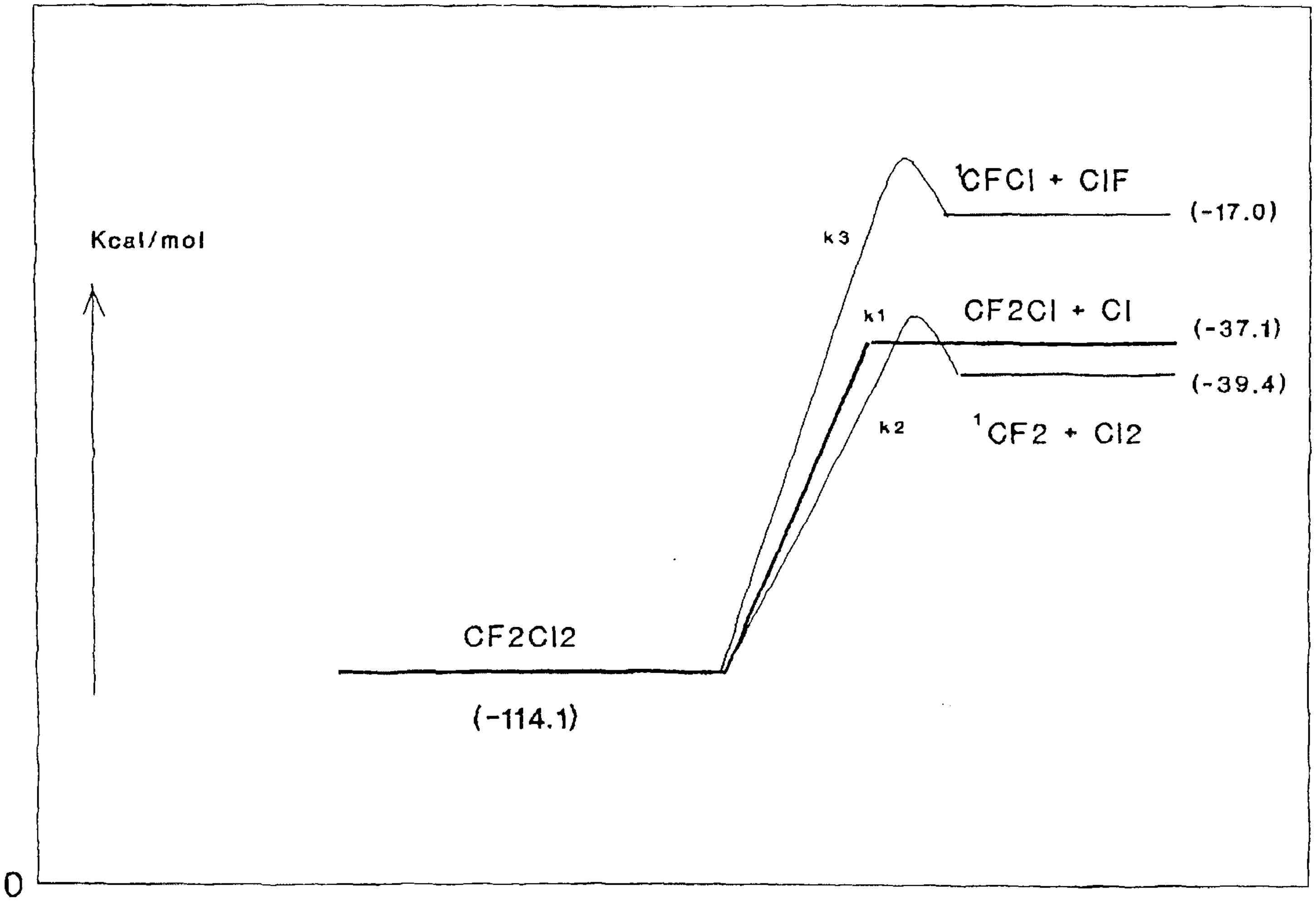


Figure 5.3 Potential Energy Diagram for CF2Cl2

Table 5.3 CF_2Cl_2 DISSOC Input Parameters

CF_2Cl_2 ----> PRODUCTS

	Reaction	A	n	E_a
k_1	CF_2Cl_2 --> CF_2Cl + Cl	1.00E16	0.0	75.0
k_2	CF_2Cl_2 --> ^{1}:CF_2 + Cl_2	4.00E13	0.0	82.7
k_3	CF_2Cl_2 --> ^{1}:CFCl + ClF	1.60E14	0.0	105.1

A's in sec^{-1} and cm^3/mole-sec E_a in Kcal/mole

<v> = 567 cm^{-1}, Evaluated from computer code Cpfit.
σ = 4.5 Å, e/k = 450 K. LJ parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1: A_1 from A_{-1} Microscopic Reversiblity, A_{-1} = 6.00 x 10^{13} taken from Cl + CHCl2, Danis, F., Caralp, F., Veyret, B., Loirat, H. and Lesclaux, R., Int. J. Chem. Kinet. 21, 715, (1989). Ea = ▲ H - RT.

k_2: A_2 = (ekT/h)exp$^{▲S/R}$ x Degeneracy (Transition State Theory, e = 2.7183, k = 1.38E-16 Boltzmann Constant, h = 6.62E-27 Planck Constant, below same), T = 800 K, ▲ S = 0.0, E_a = ▲ H_{rxn} + 8.0, energy barrier from Arunan,E.,Wategaonkar, S.J. and Setser, D.W., J. Phys. Chem. 1539, 95, (1991).

k_3: A_3 = (ekT/h)exp$^{▲S/R}$ x Degeneracy (Transition State Theory), T = 800 K, ▲ S = 0.0, E_a = ▲ H_{rxn} + 8.0, (see ref. to k_2).

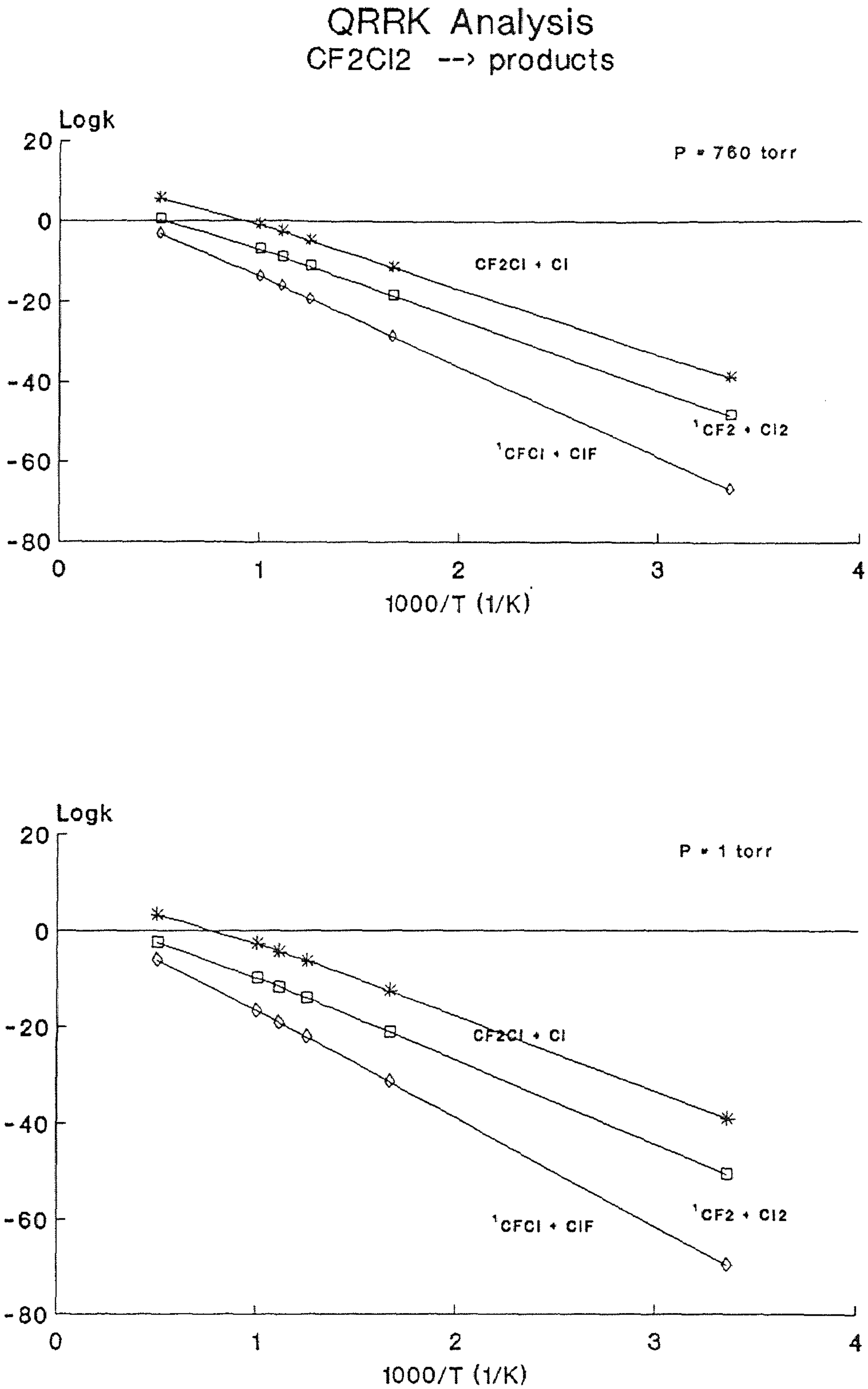


Figure 5.4 Log k vs 1000/T

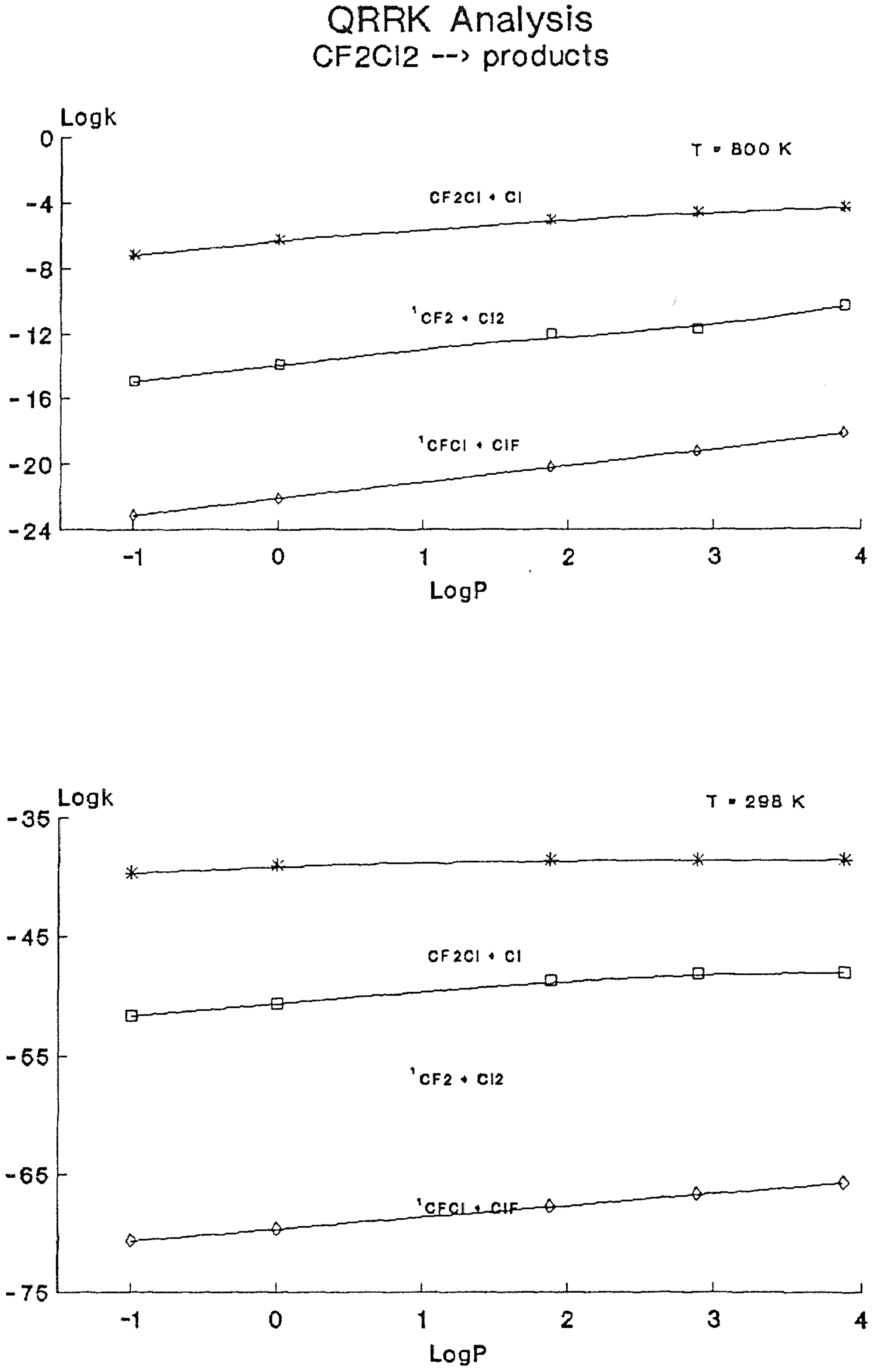


Figure 5.5 Log k vs Log P

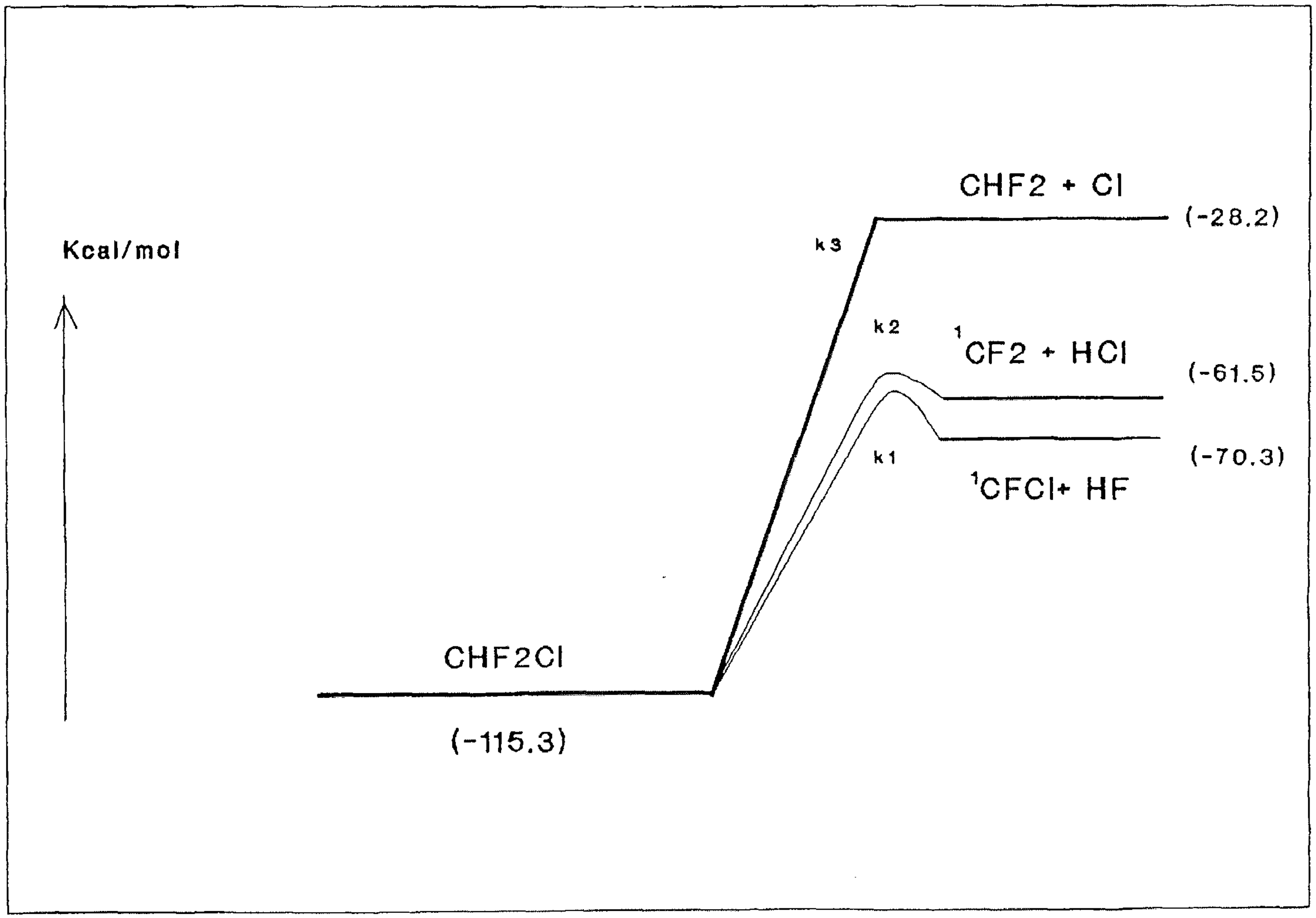


Figure 5.6 Potential Energy Diagram for CHF2Cl

Table 5.4 CHF_2Cl DISSOC Input Parameters

CHF_2Cl ----> PRODUCTS

	Reaction	A	n	E_a
k_1	CHF_2Cl --> ^{1}:CFCl + HF	8.00E13	0.0	59.8
k_2	CHF_2Cl --> ^{1}:CF_2 + HCl	4.00E13	0.0	61.8
k_3	CHF_2Cl --> CHF_2 + Cl	1.22E16	0.0	86.5

A's in sec^{-1} and cm^3/mole-sec E_a in Kcal/mole

<v> = 898 cm^{-1}, Evaluated from computer code Cpfit.
σ = 4.5 Å, e/k = 450 K. LJ parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1: A_1 = (ekT/h)exp$^{\blacktriangle S/R}$ x Degeneracy (Transition State has optical isomer here), T = 800 K, $\blacktriangle$ S = 0.0, E_a = $\blacktriangle$ H + 14.8, energy barrier from Arunan, E., Wategaonkar, S.J. and Setser, D.W., J. Phys. Chem. 1539, 95, (1991)

k_2: A_2 = (ekT/h)exp$^{\blacktriangle S/R}$ x Degeneracy (Transition State Theory), T = 800 K, $\blacktriangle$ S = 0.0, E_a = $\blacktriangle$ H_{rxn} + 8.0 (see ref. to k_1).

k_3: A_3 from A_{-3} Microscopic Reversiblity, A_{-3} = 8.0 x 10^{13} taken from Cl + CH2Cl, Danis, F., Caralp, F., Veyret, B., Loirat, H. and Lesclaux, R., Int. J. Chem. Kinet. 21, 715, (1989). Ea = $\blacktriangle$ H - RT.

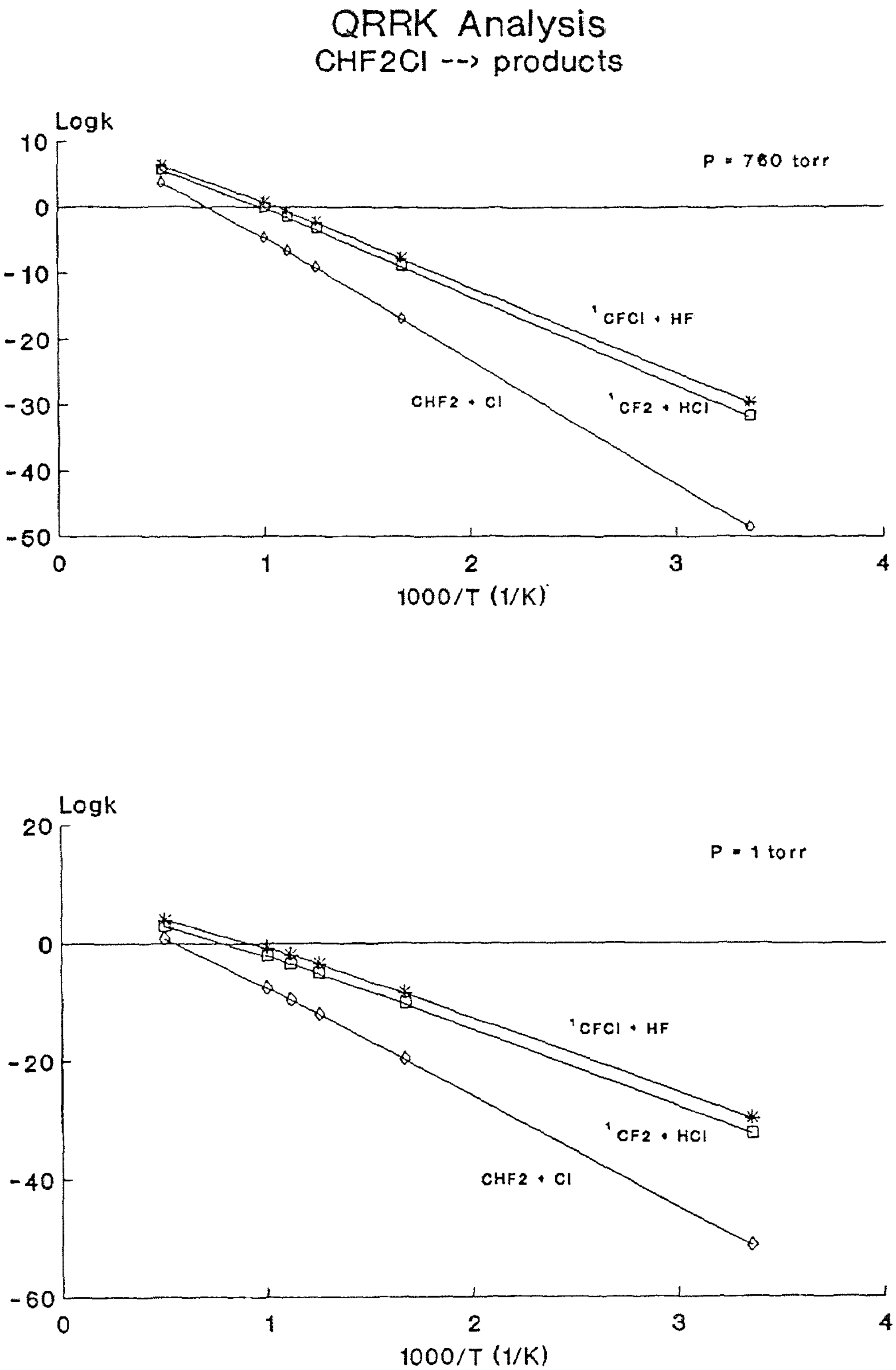


Figure 5.7 Log k vs 1000/T

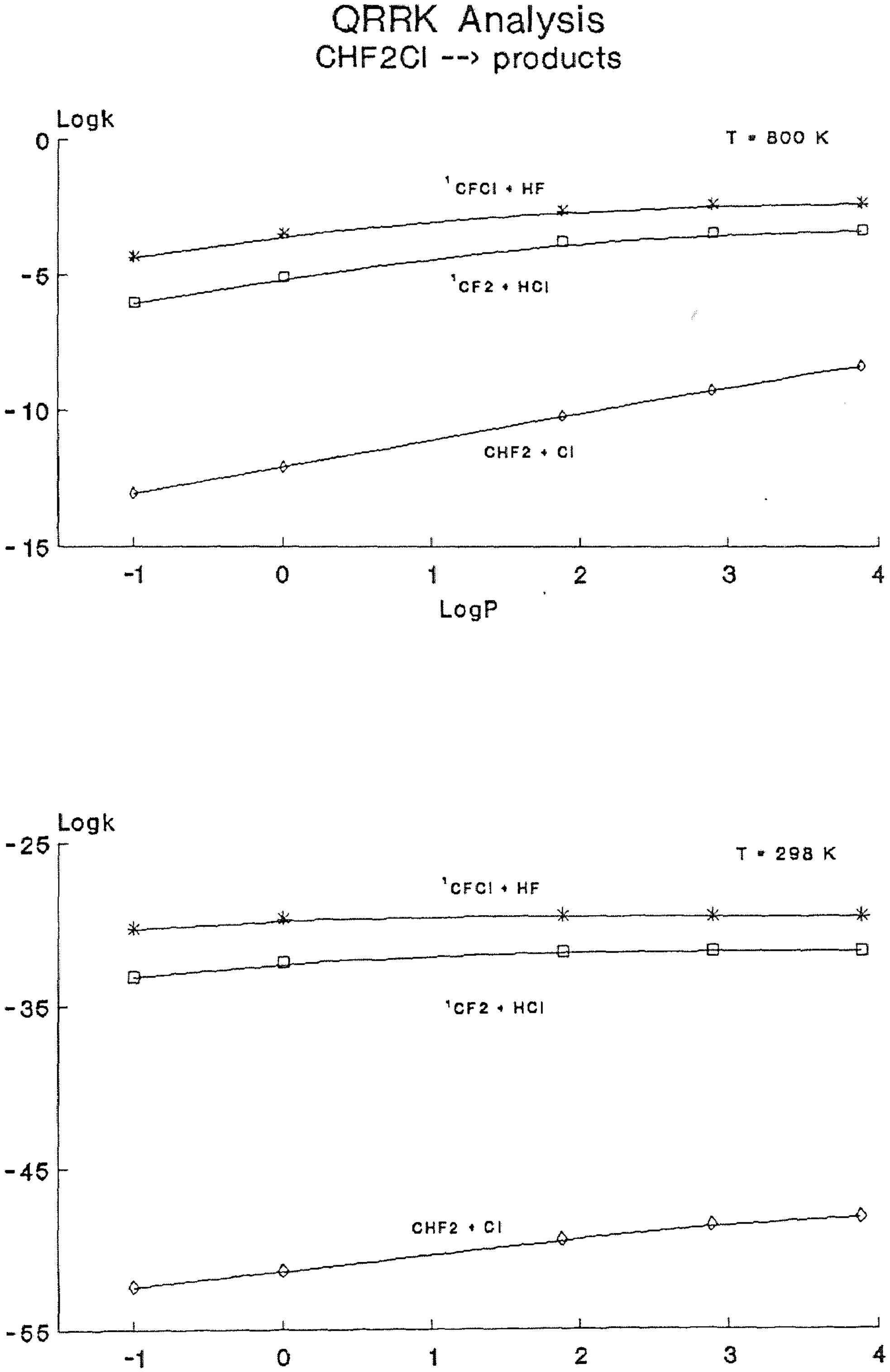


Figure 5.8 Log k vs Log P

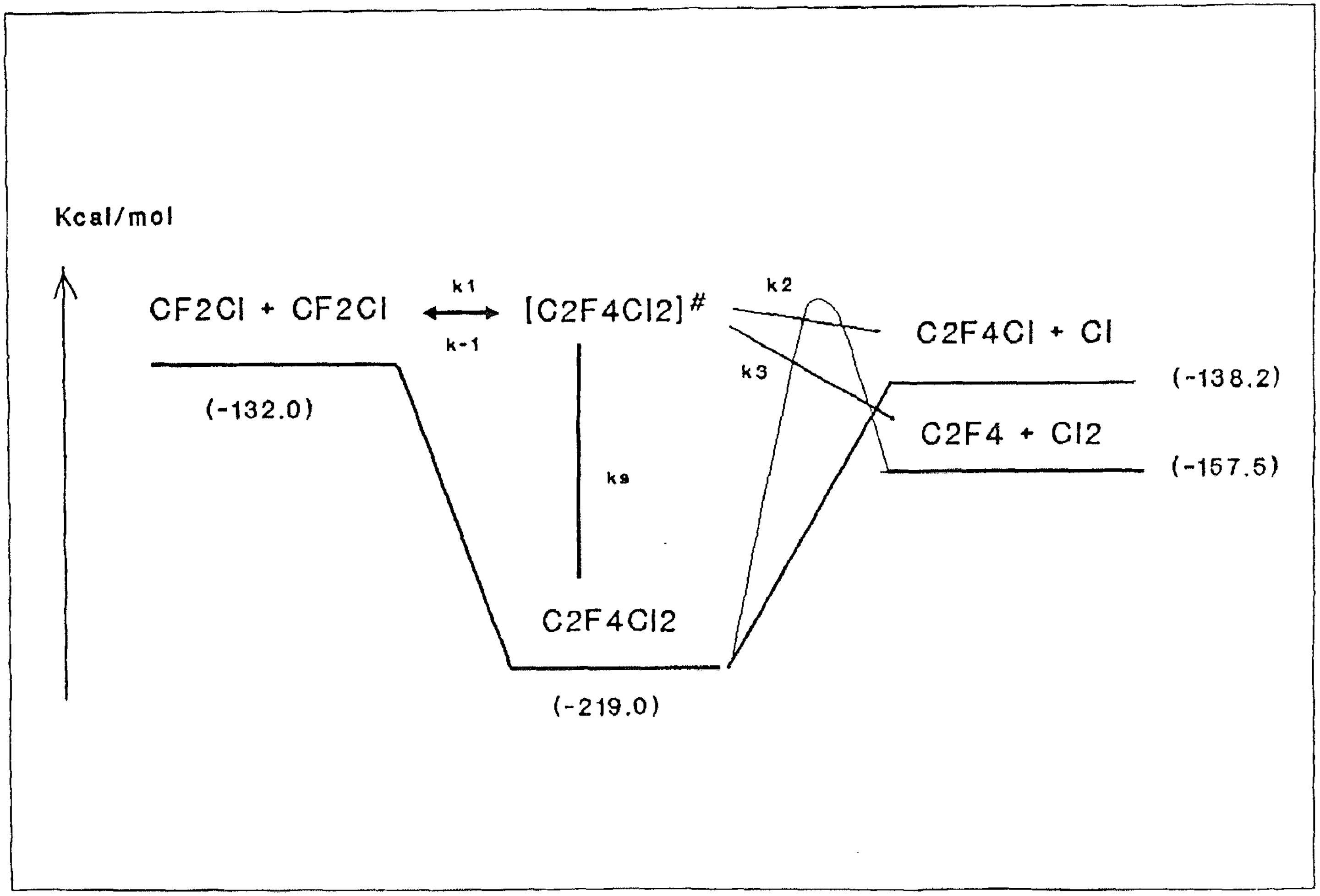


Figure 5.9 Potential Energy Diagram for CF2Cl + CF2Cl

Table 5.5 $CF_2Cl + CF_2Cl$ Chemact Input Parameters

$CF_2Cl + CF_2Cl$ ----> PRODUCTS

	Reaction	A	n	E_a
k_1	$2\ CF_2Cl \rightarrow C_2F_4Cl_2$	4.00E12	0.0	0.0
k_{-1}	$C_2F_4Cl_2 \rightarrow 2\ CF_2Cl$	2.50E17	0.0	86.4
k_2	$C_2F_4Cl_2 \rightarrow C_2F_4Cl + Cl$	1.50E15	0.0	80.2
k_3	$C_2F_4Cl_2 \rightarrow C_2F_4 + Cl_2$	4.30E12	0.0	104.5

A's in sec^{-1} and cm^3/mole-sec. E_a in Kcal/mole

$\langle v \rangle = 576\ cm^{-1}$, Evaluated from computer code Cpfit.
$\sigma = 5.1$ Å, $e/k = 500$ K, Lennard-Jones (LJ) parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1: A_1 from combination reactions of chloro methyl radicals vs number of Cl's. E_a is 0.0.

k_{-1}: Thermodynamics & Microscopic Reversiblity. Averaged over 300 - 1500 K.

k_2: A_2 from A_{-2} Microscopic Reversiblity, $A_{-2} = 2.0 \times 10^{13}$ taken from Danis, F., Caralp, F., Veyret, B., Loirat, H. and Lesclaux, R., Int. J. Chem. Kinet. 21, 715, (1989)

k_3: $A_3 = (ekT/h)\exp^{\blacktriangle S/R}$ x Degeneracy(Transition State Theory), T = 800 K, $\blacktriangle S = -4.0$ lower limit $E_a = \blacktriangle H_{rxn} + 43.0$, Karra, S.B. and Senkan, S.M., Ind. Eng. Chem. Res. Vol. 27, No.3, (1988)

(Actual Ea is probably much higher but this channel is unimportant. Increasing the Ea will not effect over all results.)

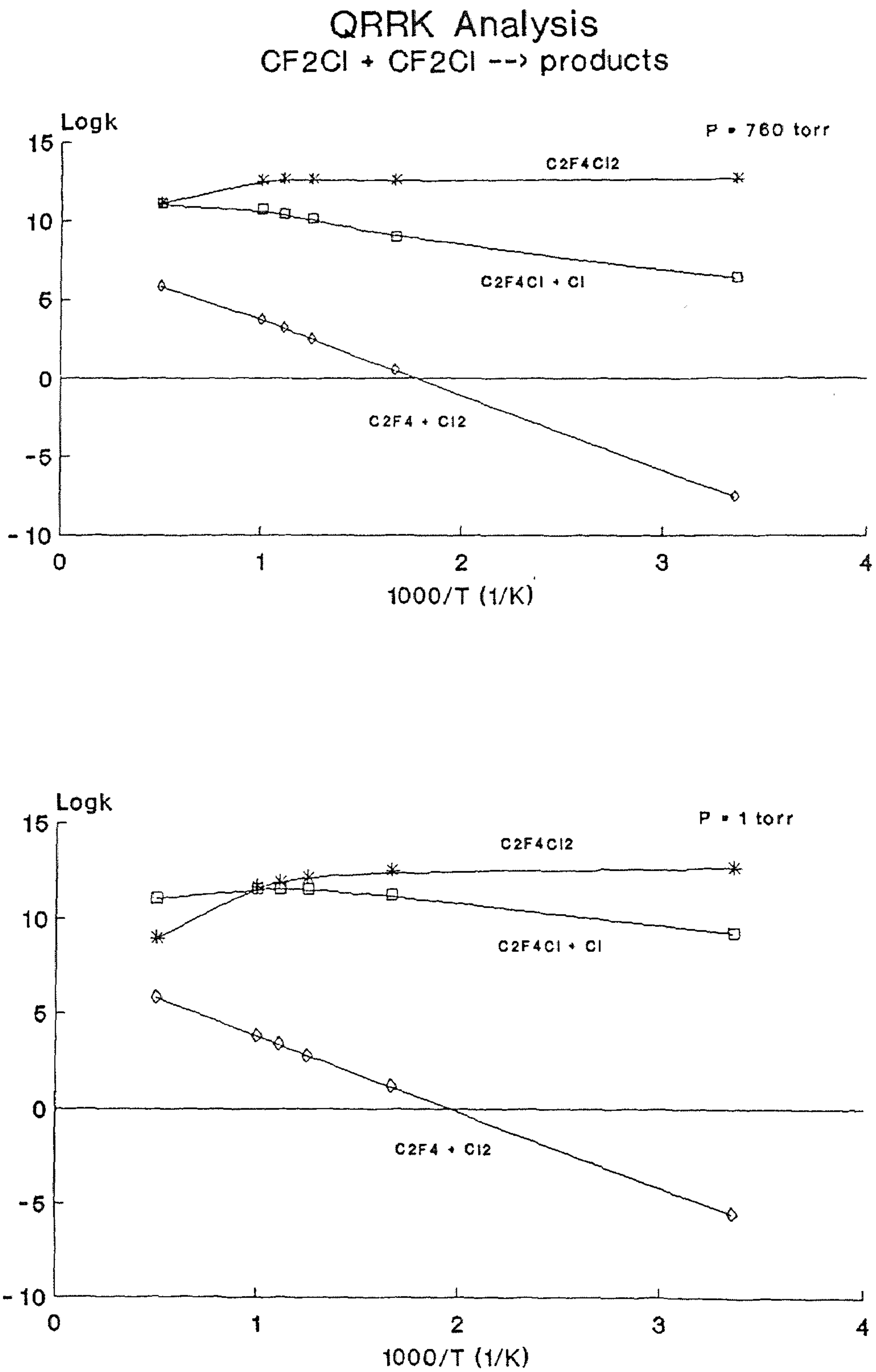


Figure 5.10 Log k vs 1000/T

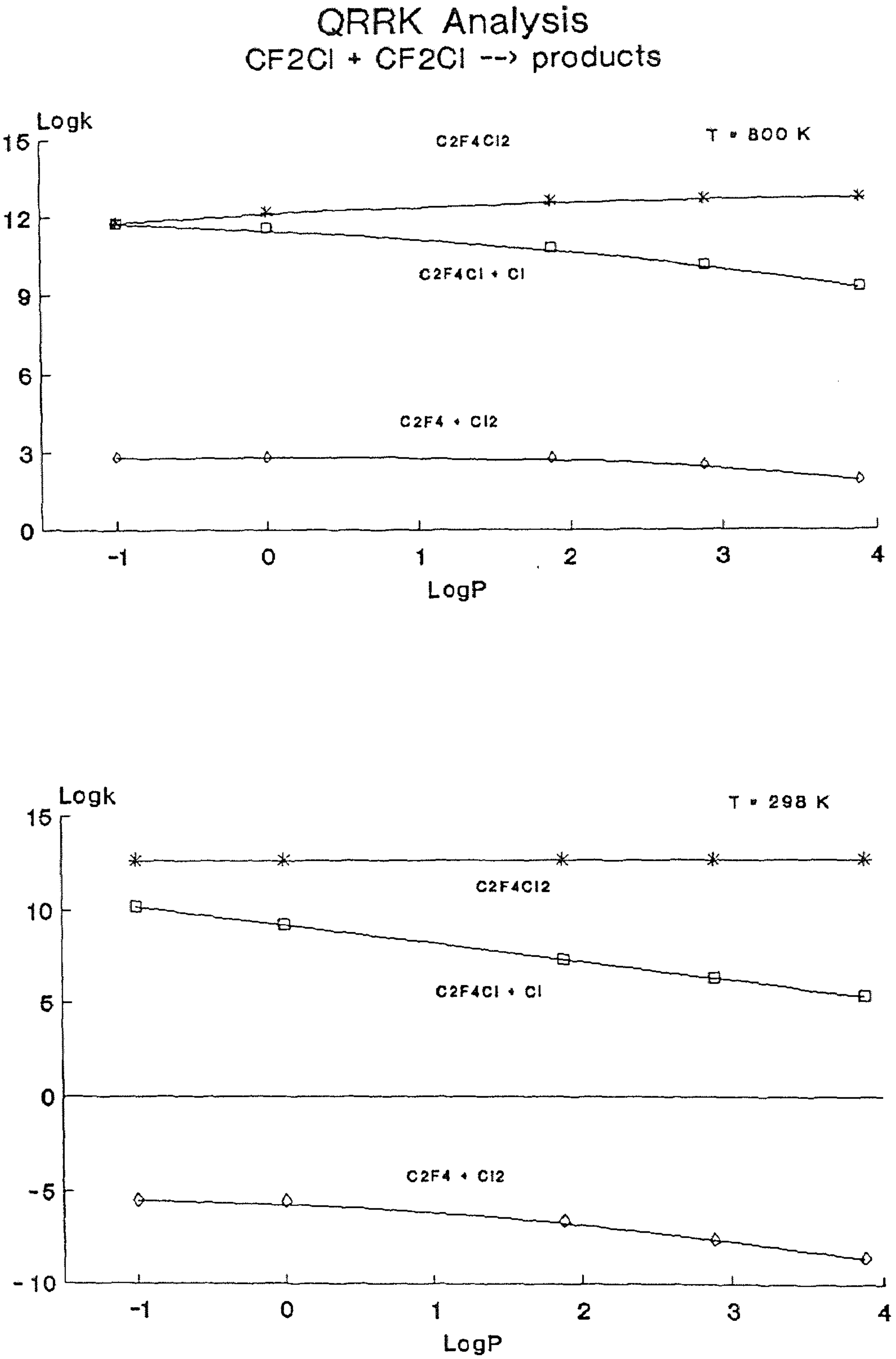


Figure 5.11 Log k vs Log P

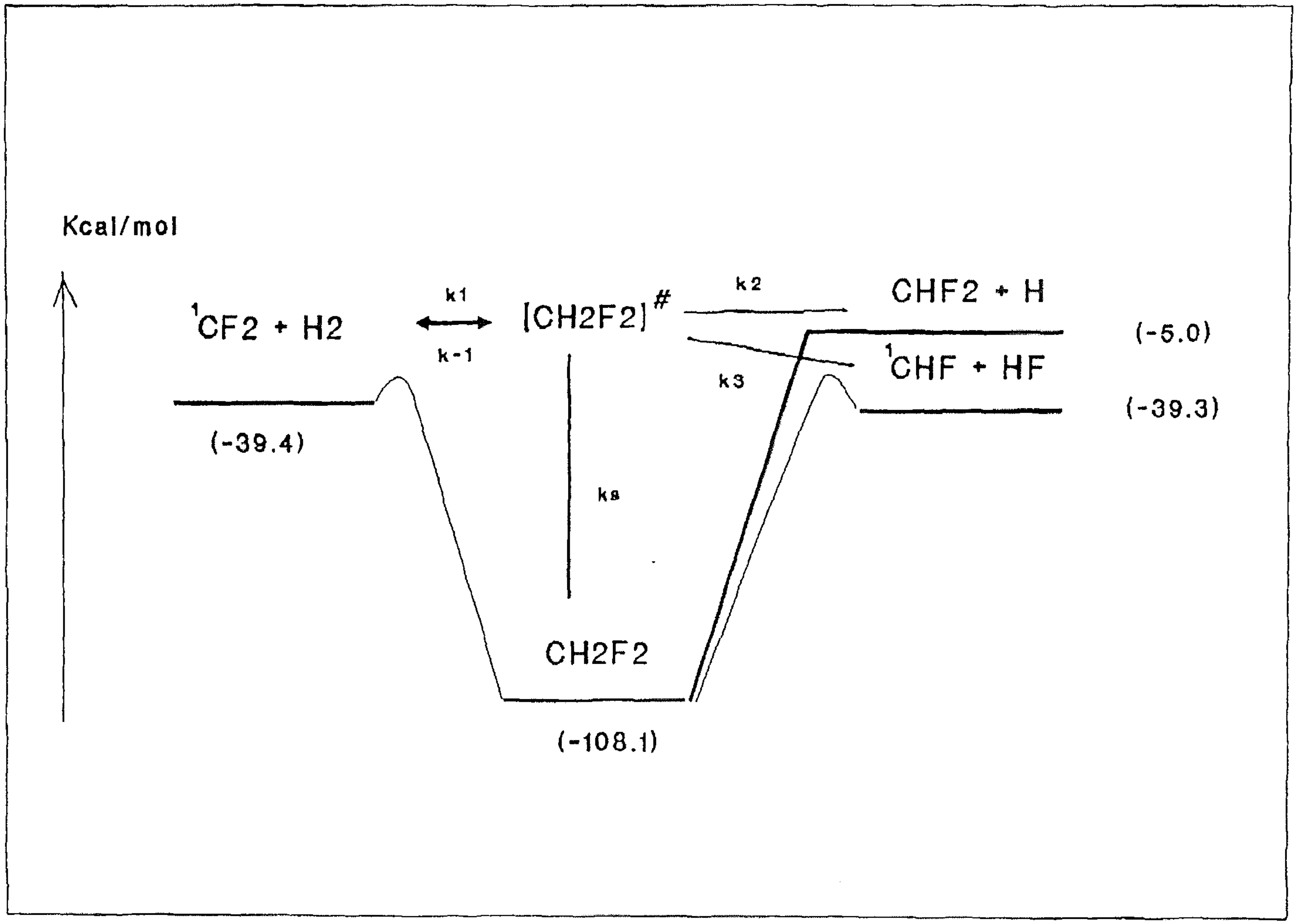


Figure 5.12 Potential Energy Diagram for CF2 + H2

Table 5.6 ^{1}:CF$_2$ + H$_2$ QRRK Input Parameters

^{1}:CF$_2$ + H$_2$ ----> PRODUCTS

	Reaction	A	n	E_a
k_1	^{1}:CF$_2$ + H$_2$ --> CH$_2$F$_2$	6.70E11	0.0	8.0
k_{-1}	CH$_2$F$_2$ --> ^{1}:CF$_2$ + H$_2$	3.20E13	0.0	76.7
k_2	CH$_2$F$_2$ --> CHF$_2$ + H	5.80E15	0.0	102.5
k_3	CH$_2$F$_2$ --> ^{1}:CHF + HF	1.30E14	0.0	83.6

A's in sec^{-1} and cm^3/mole-sec E_a in Kcal/mole

<v> = 1388 cm^{-1}, Evaluated from computer code Cpfit.
σ = 3.5 Å, e/k = 350 K. LJ parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1: A_1 from A_{-1} Microscopic Reversiblity, A_{-1} = (ekT/h) x exp$^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a evaluated HCl elimination from CHF2Cl,Arunan,E.,Wategaonkar, S.J. and Setser, D.W., J. Phys. Chem. 1539, 95, (1991)

k_{-1}: A_{-1} = (ekT/h)exp$^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 8.0 (see ref. to k_1).

k_2: A_2 from A_{-2} Microscopic Reversiblity, A_{-2} = 1.0 x 10^{14} taken from C$_3$H$_7$ + H, Allara, D. J. and Shaw, R. J., Phys. Chem. Ref. Data 9, 523, (1980)

k_3: A_3 = (ekT/h)exp$^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 14.8, evaluated HF elimination from CHF3, Setser et al., J. Phys. Chem. 1539, 95, (1991).

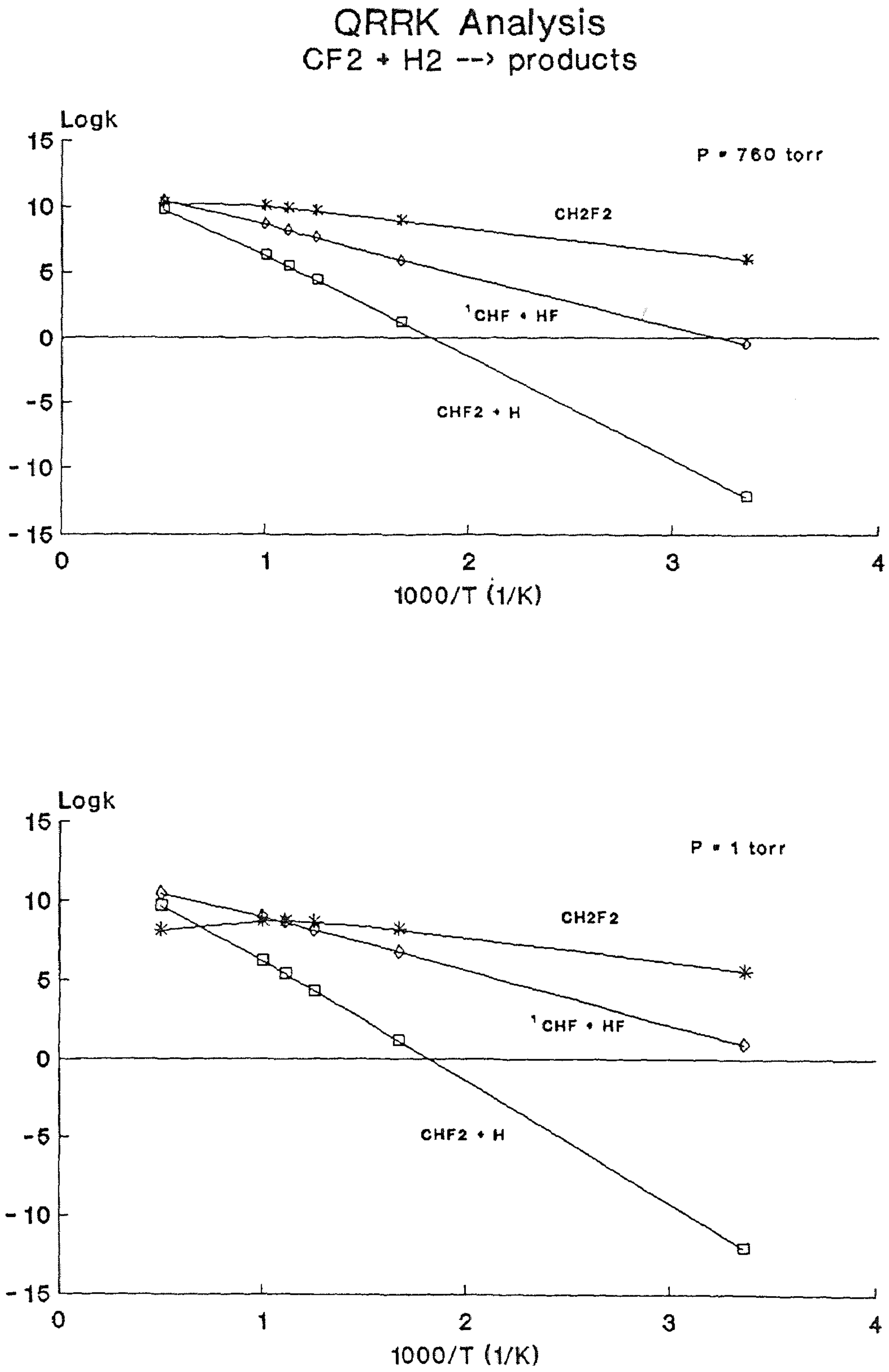


Figure 5.13 Log k vs 1000/T

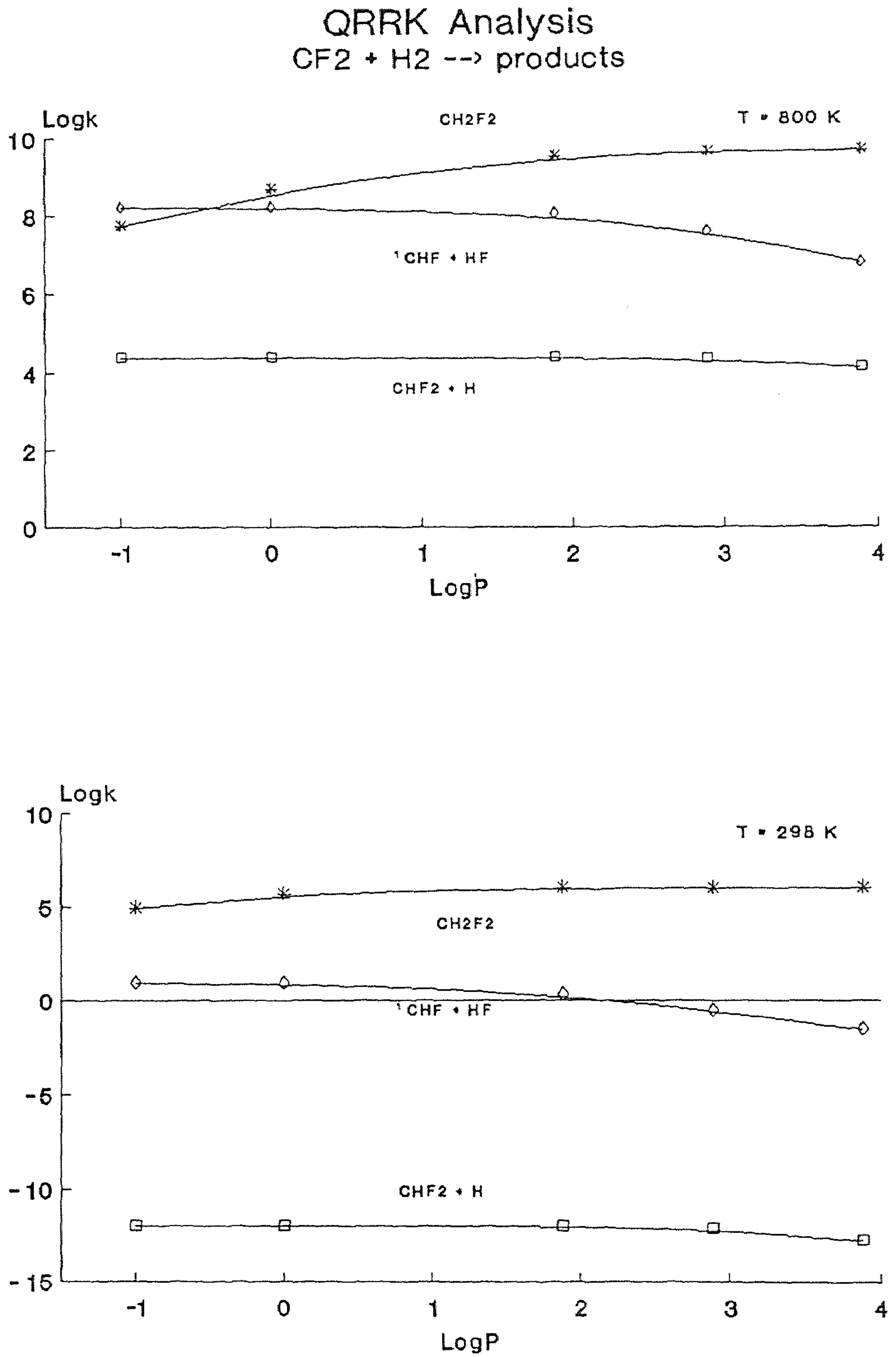


Figure 5.14 Log k vs Log P

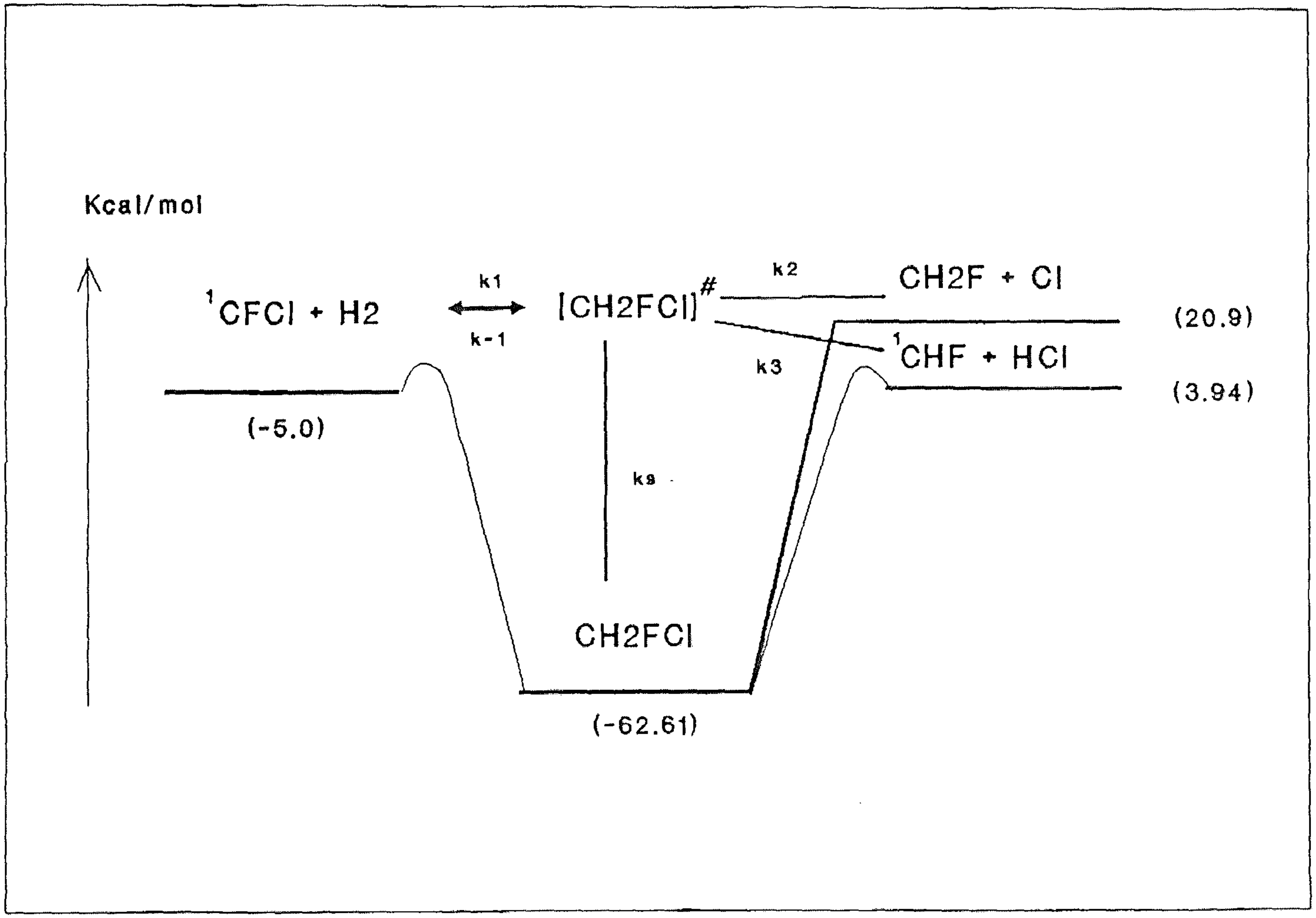


Figure 5.15 Potential Energy Diagram for CFCl + H2

Table 5.7 ^{1}:CFCl + H_2 CHEMACT Input Parameters

	^{1}:CFCl + H_2 ----> PRODUCTS Reaction	A	n	E_a
k_1	^{1}:CFCl + H_2 --> CH_2FCl	1.50E11	0.0	8.0
k_{-1}	CH_2FCl --> ^{1}:CFCl + H_2	3.20E13	0.0	65.6
k_2	CH_2FCl --> CH_2F + Cl	1.10E15	0.0	82.9
k_3	CH_2FCl --> ^{1}:CHF + HCl	6.30E13	0.0	74.6

A's in sec^{-1} and cm^3/mole-sec E_a in Kcal/mole

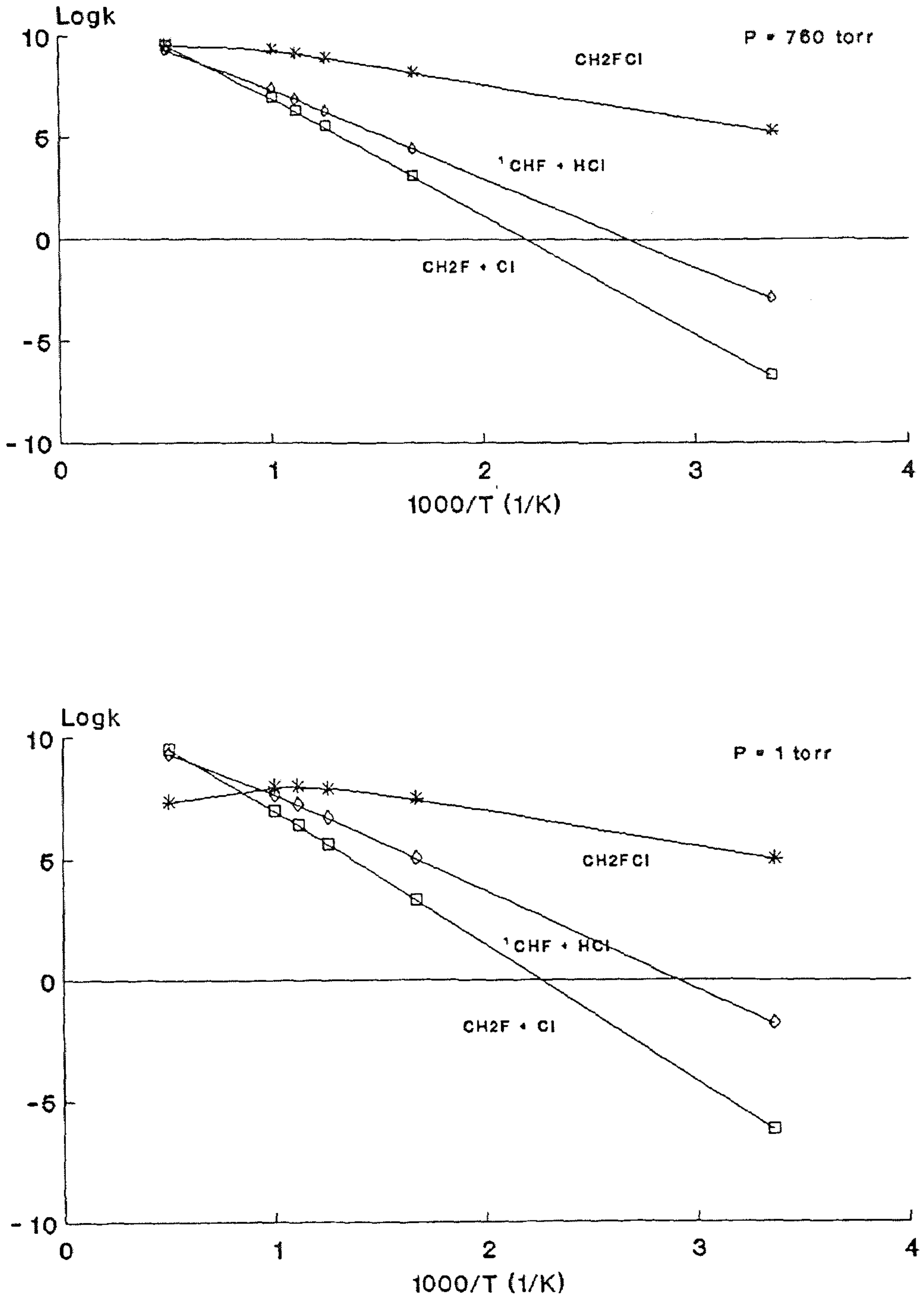
<v> = 1255 cm^{-1}, Evaluated from computer code Cpfit.
σ = 4.5 Å, e/k = 350 K. LJ parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1 : A_1 from A_{-1} Microscopic Reversiblity, E_a = 8.0, evaluated HCl elimination, Arunan, E., Wategaonkar, S.J. and Setser, D.W., J. Phys. Chem. 1539, 95, (1991)

k_{-1}: A_{-1}=(ekT/h)$\exp^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 8.0 (see ref. to k_1).

k_2: A_2 from A_{-2} Microscopic Reversiblity, A_{-2} = $2.0\text{x}10^{13}$ taken from Danis, F., Caralp, F., Veyret, B., Loirat, H. and Lesclaux, R., Int. J. Chem. Kinet. 21, 715, (1989)

k_3: A_3 = (ekT/h)$\exp^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 8.0, evaluated from HCl elimination, Setser et al., J. Phys. Chem. 1539, 95, (1991).



QRRK Analysis
CFCl + H2 --> products

Figure 5.16 Log k vs 1000/T

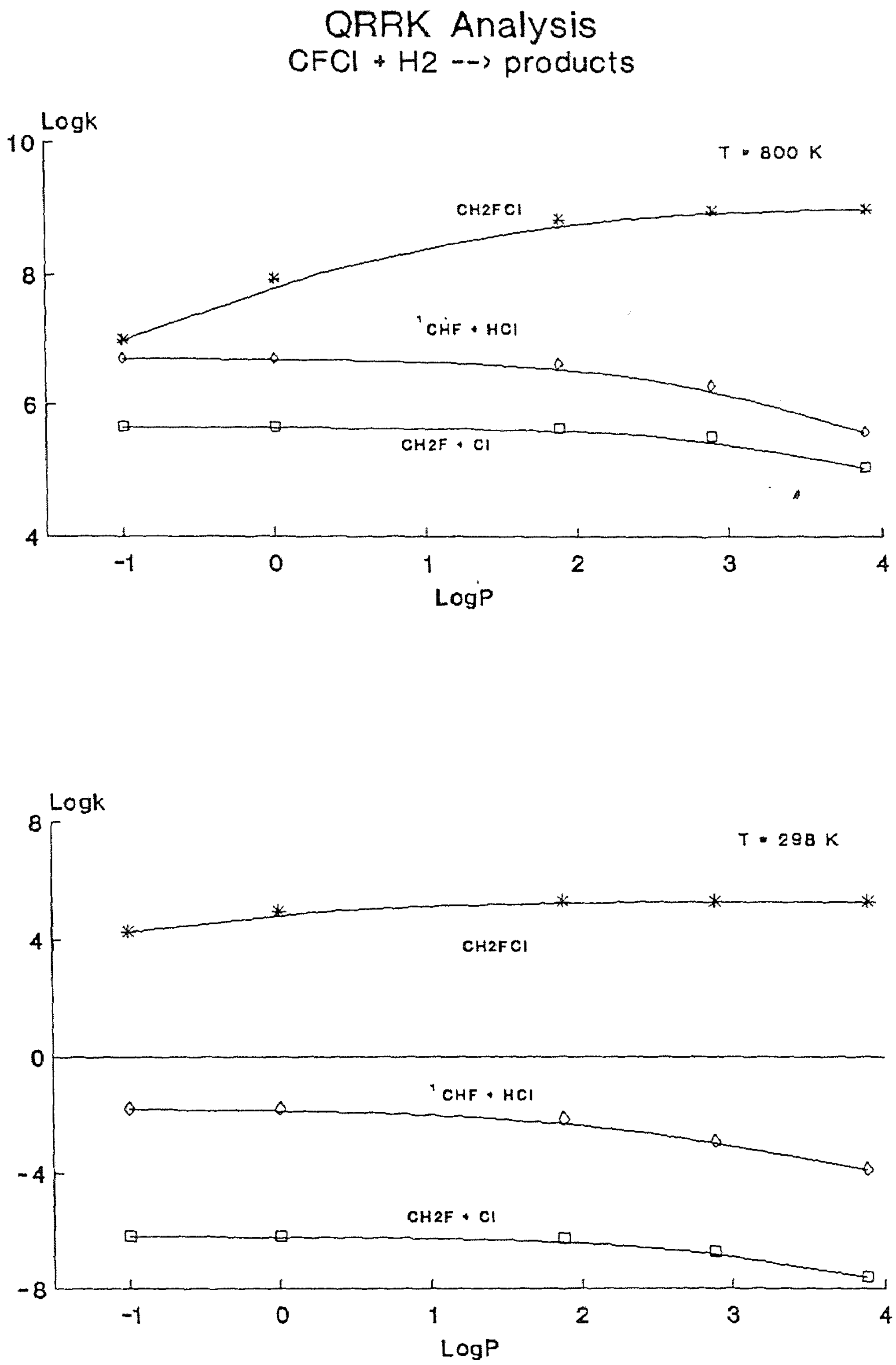


Figure 5.17 Log k vs Log P

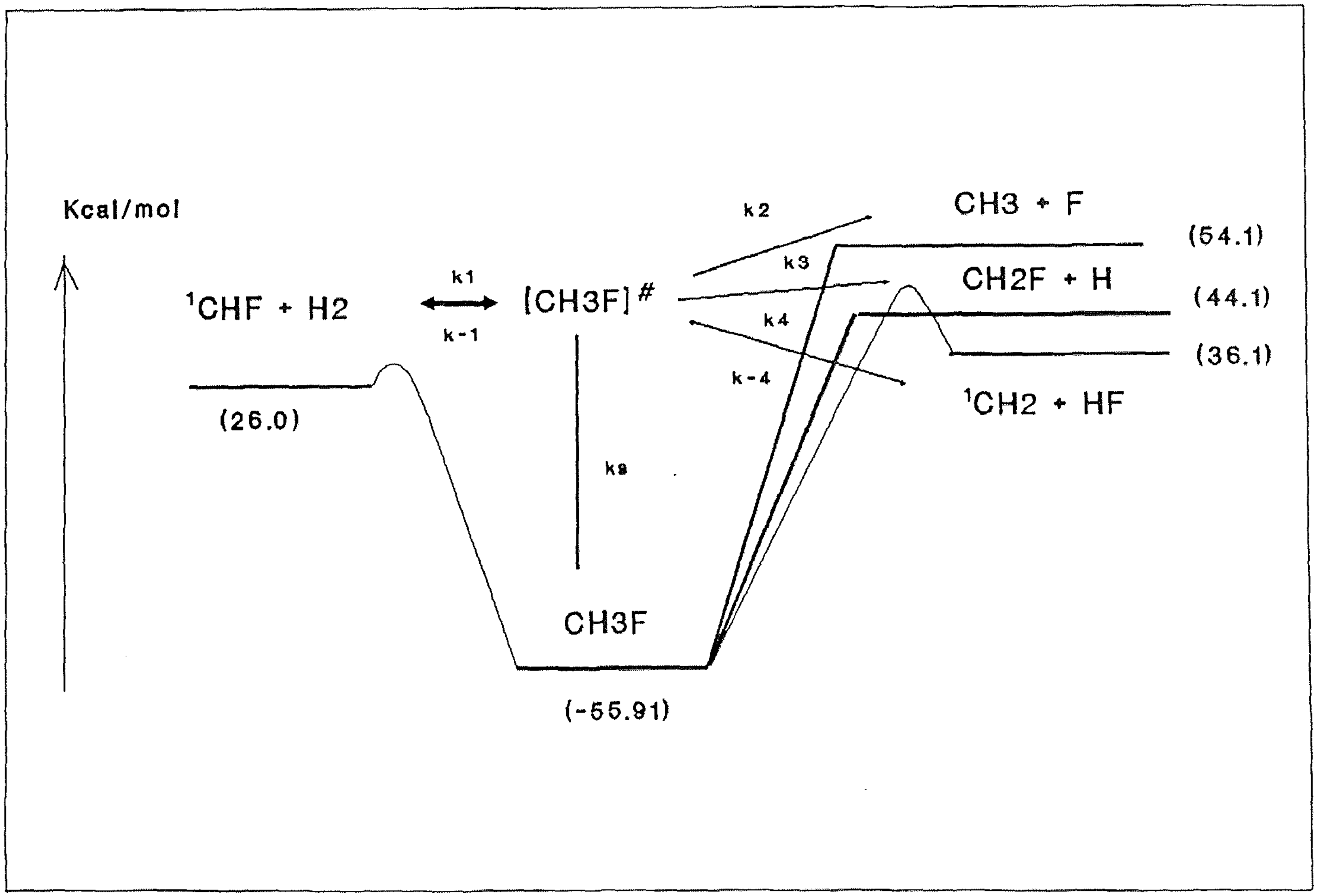


Figure 5.18 Potential Energy Diagram for CHF + H2

Table 5.8 ^{1}:CHF + H_2 CHEMACT Input Parameters

	^{1}:CHF + H_2 ---->	PRODUCTS		
	Reaction	A	n	E_a
k_1	^{1}:CHF + H_2 --> CH_3F	9.50E11	0.0	8.0
k_{-1}	CH_3F --> ^{1}:CHF + H_2	9.50E13	0.0	89.9
k_2	CH_3F --> CH_3 + F	4.30E15	0.0	109.1
k_3	CH_3F --> CH_2F + H	1.50E15	0.0	99.4
k_4	CH_3F --> ^{1}:CH_2 + HF	9.50E13	0.0	106.8
k_{-4}	^{1}:CH_2 + HF --> CH_3F	1.00E05	0.0	180.0

A's in sec^{-1} and cm^3/mole-sec E_a in Kcal/mole

<v> = 1704 cm^{-1}, Evaluated from computer code Cpfit.
σ = 3.8 Å, e/k = 350 K, LJ parameters from The Properties of Gases and Liquids, 3rd Ed., Reid, R. C., Prausnitz, J. M. and Sherwood, T. K.

k_1: A_1 from A_{-1} Microscopic Reversiblity, E_a = 8.0, evaluated from HCl elimination, Setser et al., J. Phys. Chem. 1539, 95, (1991)

k_{-1}: A_{-1}= (ekT/h)$exp^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 8.0 (see ref. to k_1).

k_2: A_2 from A_{-2} Microscopic Reversiblity, A_{-2} = 5.4x10^{13} taken from CH_3 + OH, Tsang, W. and Hampson, R.F., J. Phys. Chem. Ref. Data, 15,1087, (1986)

k_3: A_3 from A_{-3} Microscopic Reversiblity, A_{-3} = 4.0 x 10^{13} taken from C_2H_5 + H, Allara,D.J. and Shaw, R.J., Phys. Chem. Ref. Data 9, 523, (1980)

k_4: A_4 = (ekT/h)$exp^{\Delta S/R}$ x Degeneracy (Transition State Theory), T = 800 K, Δ S = 0.0, E_a = Δ H_{rxn} + 14.8, evaluated from HF elimination, Setser et al., J. Phys. Chem. 1539, 95, (1991).

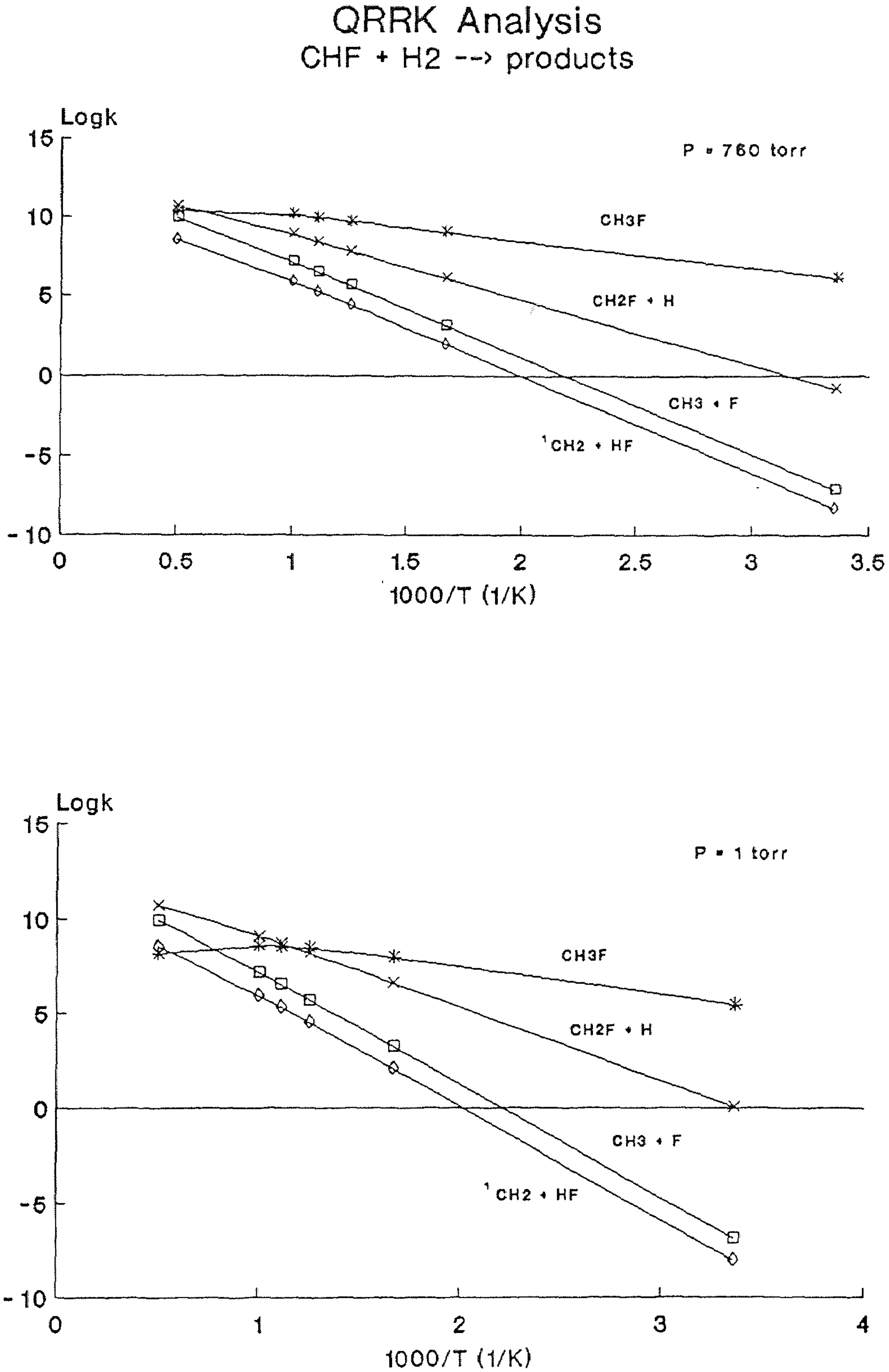


Figure 5.19 Log k vs 1000/T

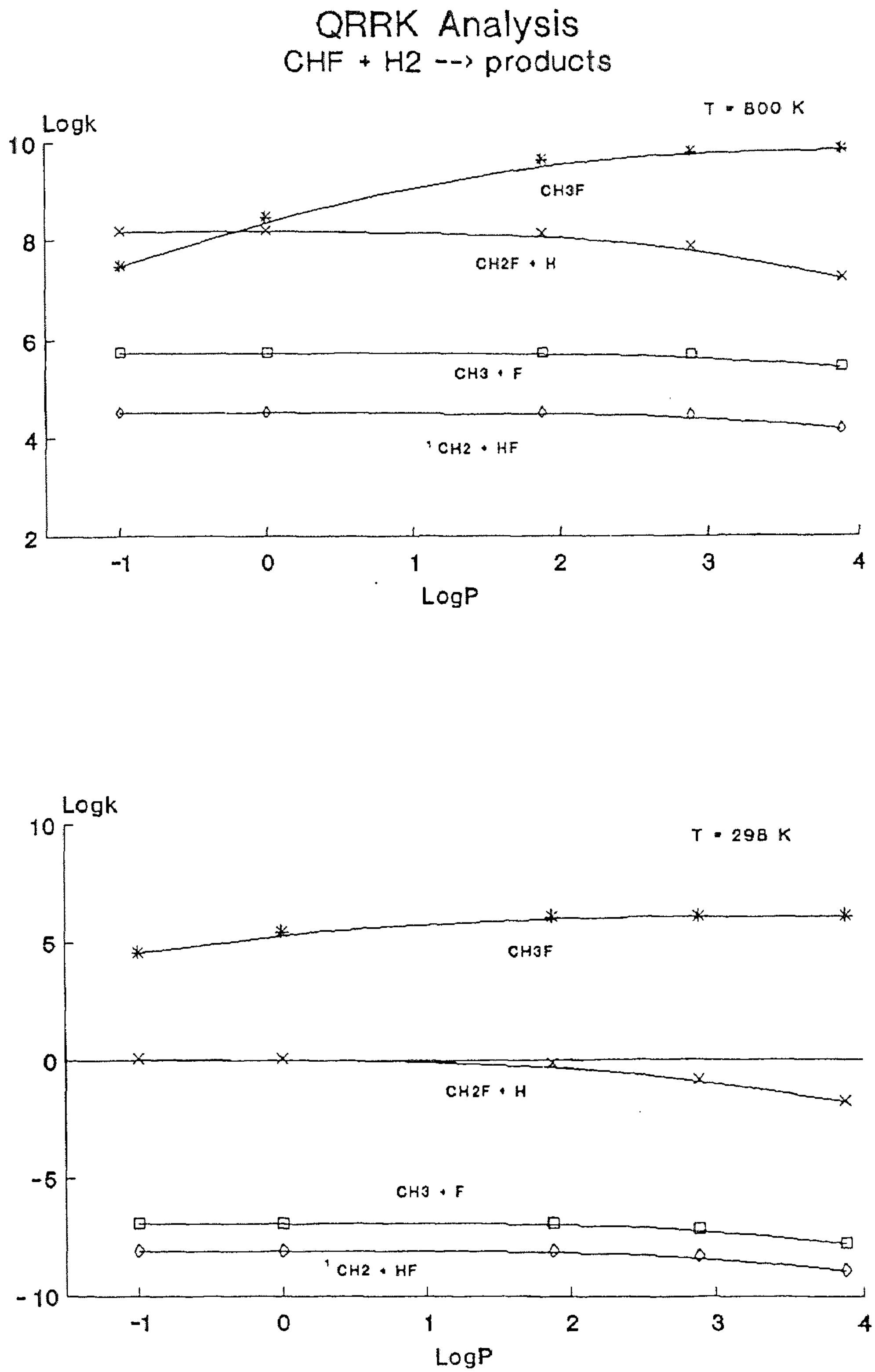


Figure 5.20 Log k vs Log P

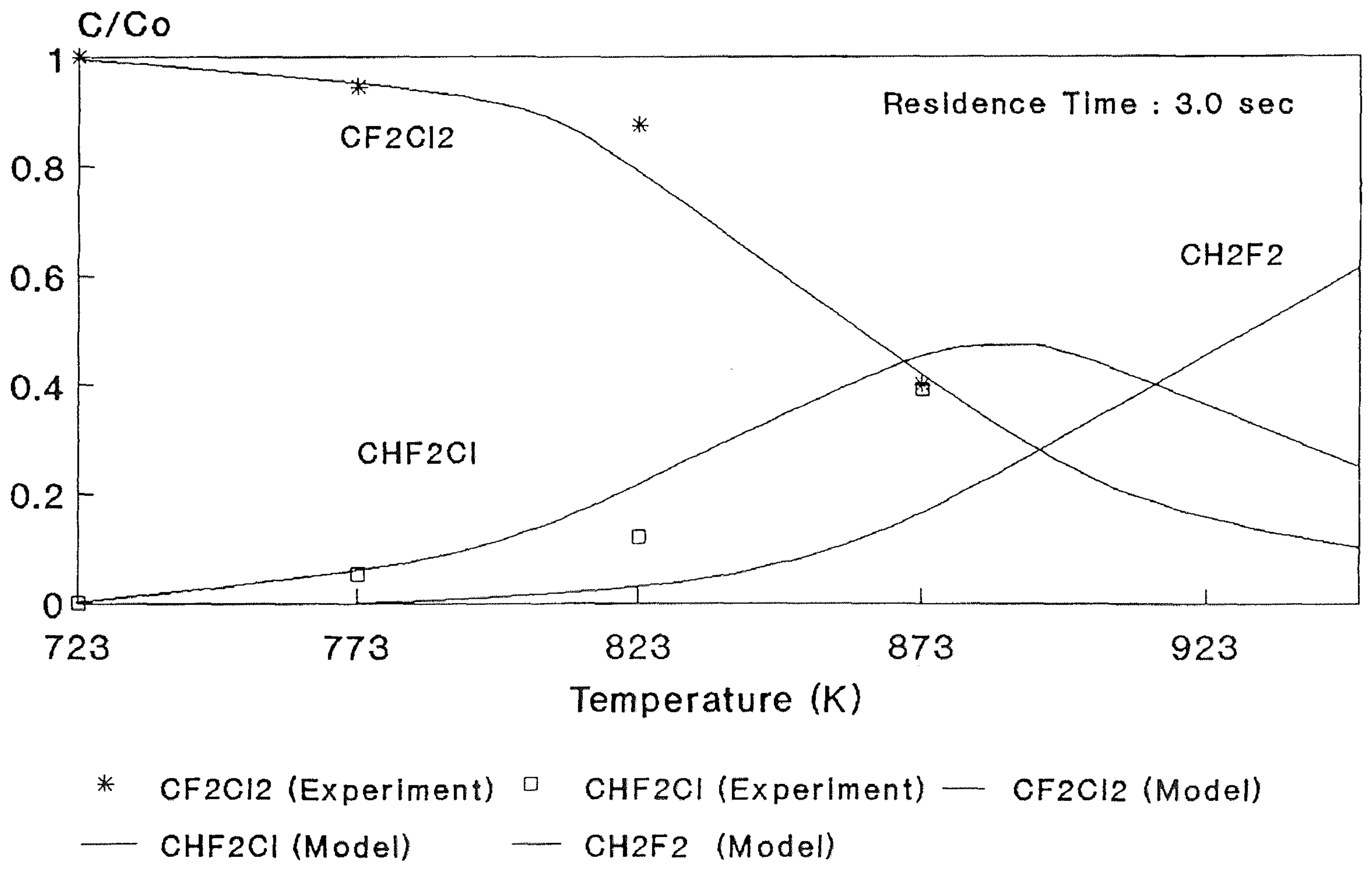


Figure 5.21 Comparison of Model with Experiment vs Temp.

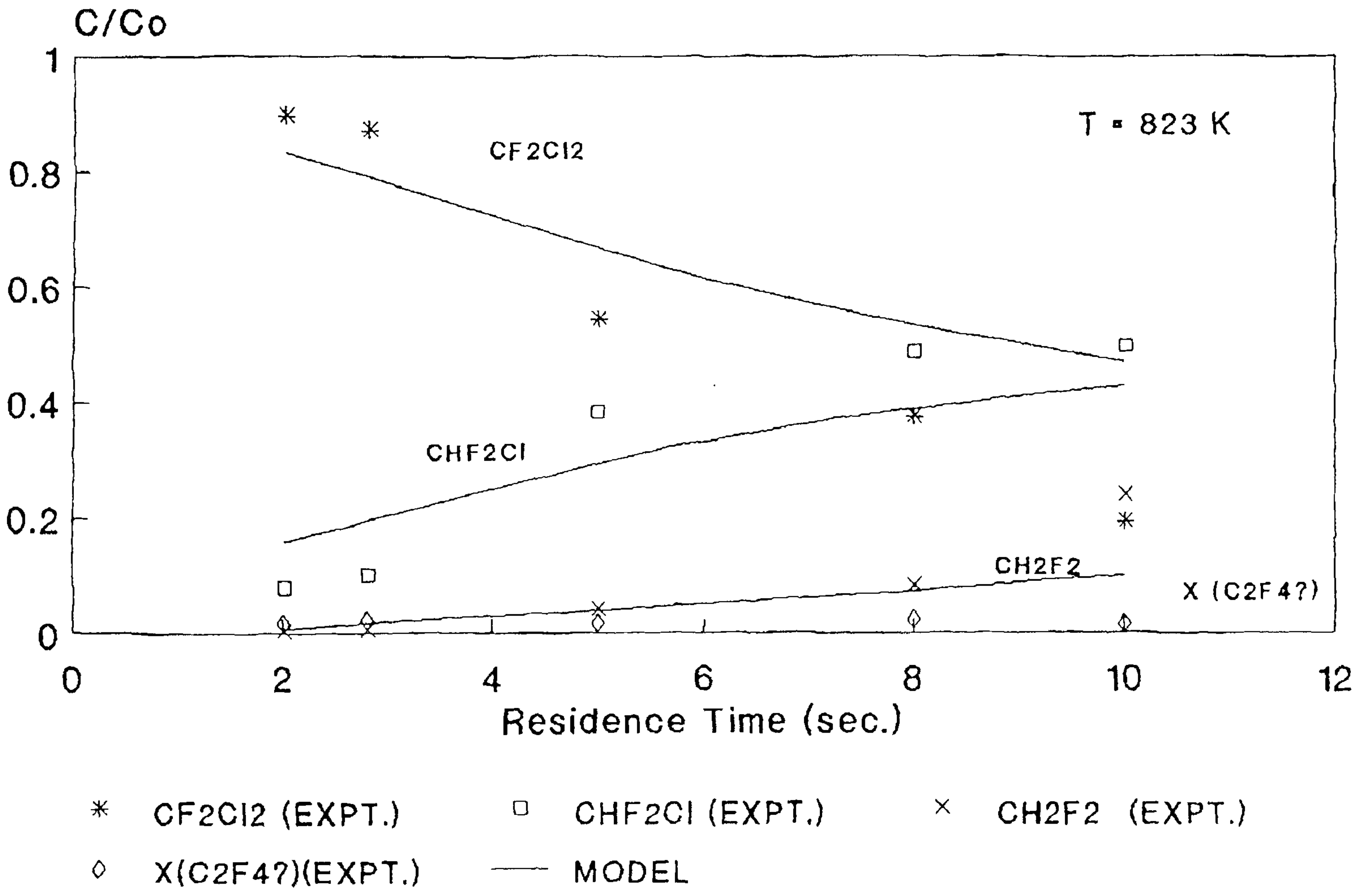


Figure 5.22 Comparison of Model with Experiment vs Time

Table 5.9 Mechanism for CF_2Cl_2/H_2 Reaction System

REACTIONS	A	n	E_a	Source
1. $CF_2Cl_2 = CF_2Cl + Cl$	1.39E37	-6.75	81.5	DISSOC
2. $CF_2Cl_2 = CF_2(S) + Cl_2$	2.20E31	-6.47	86.9	DISSOC
3. $CF_2Cl_2 = CFCl + ClF$	1.06E21	-3.80	107.0	DISSOC
4. $CF_2Cl + H_2 = CHF_2Cl + H$	8.00E12	0.0	13.7	1
5. $CF_2Cl_2 + H = CF_2Cl + HCl$	3.16E13	0.0	9.0	2
6. $Cl + H_2 = HCl + H$	7.94E13	0.0	5.5	3
7. $CHF_2Cl + Cl = CF_2Cl + HCl$	1.00E13	0.0	3.5	4
8. $CHF_2Cl + H = CHF_2 + HCl$	1.58E13	0.0	9.0	2
9. $CHF_2 + H_2 = CH_2F_2 + H$	8.00E12	0.0	13.7	1
10. $CHF_2 + CHF_2 = CHF_2CHF_2$	1.00E12	0.0	0.0	5
11. $CF_2(S) + C_2F_4 = C_3F_6$	7.94E09	0.0	7.0	6
12. $CHF_2Cl = CHF_2 + Cl$	1.48E28	-4.43	89.7	DISSOC
13. $CHF_2Cl = CF_2(S) + HCl$	5.19E32	-5.94	69.1	DISSOC
14. $CHF_2Cl = HF + CFCl$	5.44E31	-5.51	66.3	DISSOC
15. $CF_2Cl + CHF_2 = CHF_2CF_2Cl$	1.00E12	0.0	0.0	5
16. $CF_2(S) + CF_2(S) = C_2F_4$	3.98E11	0.0	0.0	6
17. $CH_2F_2 + Cl = CHF_2 + HCl$	1.58E13	0.0	3.5	7
18. $Cl + Cl + M = Cl_2 + M$	3.16E15	0.0	0.0	3
19. $CF_2Cl + CF_2Cl = C_2F_4Cl_2$	4.30E22	-3.08	4.04	CHEMACT
20. $CF_2Cl + CF_2Cl = C_2F_4 + Cl_2$	4.10E34	-7.66	36.11	CHEMACT
21. $CF_2Cl + CF_2Cl = C_2F_4Cl + Cl$	2.04E19	-1.84	14.28	CHEMACT
22. $C_2F_4Cl = C_2F_4 + Cl$	1.58E13	0.0	37.91	8,9

23. $CF_2(S) + H_2 = CH_2F_2$	3.31E16	-1.45	9.8	CHEMACT
24. $CF_2(S) + H_2 = CHF_2 + H$	2.20E20	-1.94	37.94	CHEMACT
25. $CF_2(S) + H_2 = CHF(S) + HF$	1.23E11	0.49	18.02	CHEMACT
26. $CFCl + H_2 = CH_2FCl$	5.56E16	-1.73	10.12	CHEMACT
27. $CFCl + H_2 = CH_2F + Cl$	3.64E17	-1.47	28.47	CHEMACT
28. $CFCl + H_2 = CHF(S) + HCl$	4.82E14	-0.85	21.62	CHEMACT
29. $CHF(S) + H_2 = CH_3F$	2.63E17	-1.69	10.06	CHEMACT
30. $CHF(S) + H_2 = CH_3 + F$	1.09E17	-1.18	29.1	CHEMACT
31. $CHF(S) + H_2 = CH_2F + H$	1.85E15	-0.66	20.12	CHEMACT
32. $CHF(S) + H_2 = CH_2(S) + HF$	1.01E18	-1.86	29.79	CHEMACT
33. $CF_2Cl_2 = CFCl_2 + F$	7.26E15	0.0	114.91	9,10
34. $ClF + M = Cl + F + M$	1.20E16	0.0	59.21	9,11
35. $H_2 + F = HF + H$	1.15E14	0.0	1.13	12

Temperature: 723 - 873 K

DISSOC: Apparent rate constant by DISSOC computer code.

CHEMACT: Apparent rate constant from CHEMACT computer code.

Sources of Rate Constants:

1. Evaluated from $CCl_3 + H_2 = CHCl_3 + H$ (A=5.01E12, Ea=14.3) Hautecloque,S., J. Chim. Phys., 67,771 (1970)
2. Evaluated from $CH_3Cl + H = CH_3 + HCl$ (A=3.7E13, Ea= 9.3) Westenberg,A.A and deHaas, N., J. Chem. Phys., 62, 3321 (1975)
3. V. N. Kondratiev, Rate Constant of Gas Phase Reactions, Moscow (1970)

4. Evaluated from $CH_3Cl+Cl=CH_2Cl+HCl$ (A=2.05E13, Ea=2.5) Atkinson, R. et al, J. Phys. Chem. Ref. Data, 18, 881 (1989)
5. From $CH_2Cl + CH_2Cl=CH_2ClCH_2Cl$ (A=1.0E13, Ea=0.0), Weissman, M. and Benson, S.W., Int. J. Chem. Kinet., 16, 307 (1984)
6. NIST Kinetic Data Base, (1990)
7. Okabe, H., Photochemistry of Small Molecules, J. Wiley, pp301, 305, 308. (1978)
8. Evaluated from $CHCl_2CCl_2=C_2HCl_3 +Cl$ (A=2.5E13, Ea=19.8) Benson, S.W. and Weissman, M., Int. J. Chem. Kinet. 14, 1287 (1982)
9. $E_a = \blacktriangle H_{rxn} - RT_m$.
10. A factor based on thermodynamics and microreversibility. A_{-1} taken as that for $CH_3 + C_3H_7$ ($A=2.0x10^{13}$), Allara,D.L. and Shaw, R.J., J. Phys. Chem. Ref. Data 9, 523, (1980)
11. A factor based on thermodynamics and microreversibility. A_{-1} taken as that for Cl + Cl ($A = 3.0x10^{15}$)
12. Atkinson, R. et.al, J. Phys. Chem. Ref. Data. 18, 881. (1989)

CHAPTER 6
CONCLUSION

Experiments on thermal reaction of CF_2Cl_2 in H_2 bath gas at 723-873 K and 2 to 3 second residence time were performed to determine reaction products and conversion efficiency to hydrogenated chlorofluorocarbons.

Results indicate that CF_2Cl_2 will be converted to CHF_2Cl with high selectivity (up to 93%) in temperature range 723-823 K and lower selectivity of 60% at 873 K. The observed decay of CF_2Cl_2 is about 80% at 873 K and time of 3 sec. Further conversion of the initial stable product CHF_2Cl to CH_2F_2 is observed above 873 K. Products from the reaction process are CHF_2Cl and CH_2F_2; these hydrogenated chlorofluorocarbons offer potentially less destruction potential to the stratospheric ozone layer and are of industrial values as chlorofluorocarbon substitutes. The organic chlorine is removed as HCl.

Detailed kinetic reaction mechanism based upon fundamental thermochemical and kinetic principles and literature data was developed. This mechanism includes 35 elementary reaction steps. Quantum Kassel theory was used to analyze those reactions involving dissociation, addition, insertion and recombination for pressure and temperature effects.

Appendix I Thermochemical Database

			Cp							
SPECIES	Hf(298)	S(298)	300	400	500	600	800	1000	1500	COMMENTS
Ar	0.00	36.98	4.97	4.97	4.97	4.97	4.97	4.97	4.97	JANAF
CF2Cl	-66.00	68.39	13.12	14.80	16.00	16.86	17.96	18.59	19.28	CALC
CH3F	-55.91	53.31	8.99	10.56	12.26	13.83	16.45	18.44	21.55	STULL
CH2F	-8.00	55.34	8.65	9.66	10.83	11.93	13.65	14.99	17.06	CALC
CHF(S)	26.00	53.37	8.28	8.82	9.41	9.97	10.89	11.59	12.61	TRC
CHF(T)	37.50	55.23	8.43	9.06	9.67	10.19	11.01	11.62	12.58	TRC
CHF2	-57.10	61.74	10.32	11.74	13.05	14.11	15.66	16.68	18.11	TRC
CH2F2	-108.08	59.03	10.27	12.22	14.09	15.72	18.22	19.98	22.54	PED.&JANAF
CHF3	-166.20	62.12	12.24	14.58	16.56	18.13	20.33	21.74	23.62	PED.&STULL
CF4	-223.14	62.60	14.73	17.41	19.43	20.91	22.84	23.91	24.80	PED.&STULL
CF3	-112.40	63.43	11.94	13.73	15.13	16.17	17.50	18.25	19.10	JANAF
CF2(S)	-39.40	57.55	9.32	10.29	11.09	11.71	12.50	12.95	13.45	SOU.& TRC
CF2(T)	5.40	59.97	9.64	10.55	11.31	11.88	12.61	13.02	13.49	TRC
CF	61.00	50.96	7.19	7.43	7.71	7.95	8.31	8.54	0.0	JANAF
CH2FCl	-62.61	63.27	11.28	13.28	15.07	16.56	18.80	20.39	22.73	JANAF
CHFCl2	-67.71	70.18	14.62	16.78	18.45	19.70	21.41	22.51	24.01	JANAF
CHF2Cl	-115.34	67.24	13.70	16.04	17.85	19.22	21.09	22.29	23.90	JANAF
CFCl3	-64.13	74.17	18.70	20.83	22.21	23.12	24.18	24.73	25.32	PED.&JANAF
CF2Cl2	-114.10	72.03	17.36	19.68	21.28	22.37	23.68	24.39	25.16	PED.&JANAF
CF3Cl	-168.81	68.30	16.04	18.53	20.32	21.59	23.16	24.02	24.98	PED.&JANAF
C2F4	-157.48	71.82	19.29	21.97	23.99	25.53	27.61	28.86	30.35	JANAF
C2H3F	-33.17	60.41	11.90	14.76	17.01	19.00	21.87	23.97	0.0	PED.&THERM
CH2CF2	-80.07	63.53	14.80	17.36	19.51	21.20	23.87	25.77	0.0	PED.&THERM
CHFCHF	-71.00	64.22	13.60	16.80	19.00	21.00	23.60	25.40	0.0	PED.&THERM
C2HF3	-117.21	70.10	16.50	19.40	21.50	23.20	25.60	27.20	0.0	PED.&THERM
C2F6	-321.27	79.55	25.53	30.01	33.26	35.54	38.32	39.79	41.38	PED.&JANAF
C2H5F	-61.70	63.63	14.29	17.84	21.40	23.79	28.22	31.37	0.0	THERM
CH3CHF2	-118.79	67.33	16.09	19.84	23.10	25.89	29.72	32.57	0.0	PED.&THERM
CH3CF3	-177.96	68.54	18.89	22.84	25.80	28.69	32.32	34.77	0.0	PED.&THERM
C2F2	5.00	58.42	13.64	15.12	16.24	17.11	18.31	19.05	19.96	JANAF
C2HF	26.00	55.43	12.54	13.91	14.85	15.57	16.66	17.49	18.85	LIAS&JANAF
CHF2CHF2	-218.60	78.20	19.80	24.00	27.40	30.20	33.40	35.60	0.0	THERM
CHF2CF2Cl	-215.60	79.60	23.60	28.10	31.20	33.70	36.50	38.20	0.0	THERM
C2F4Cl2	-219.00	86.00	27.40	32.20	35.00	37.20	39.60	40.80	0.0	PED.STU.THER
Cl	28.90	39.50	5.20	5.34	5.40	5.41	5.35	5.30	5.20	BENSON
Cl2	.00	53.30	8.10	8.38	8.59	8.74	8.91	8.99	9.10	BENSON
H	52.10	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97	JANAF
HCl	-22.06	44.64	6.96	6.95	6.99	7.07	7.29	7.56	8.10	STULL
H2	.00	31.21	6.90	6.95	6.99	7.02	7.10	7.21	7.72	JANAF
C3F6	-269.00	65.30	25.99	30.56	33.44	35.90	38.94	40.57	0.0	THERM
CFCl2	-17.50	69.95	14.04	15.54	16.60	17.34	18.28	18.81	19.39	CALC.
CH2CFCl	-41.99	67.71	15.42	18.21	20.39	22.06	24.47	26.12	28.59	TRC
CHFCHCl	-40.39	68.12	14.77	17.57	19.81	21.58	24.14	25.88	28.42	TRC
CHFCFCl	-80.81	72.71	17.54	20.20	22.28	23.88	26.10	27.53	29.47	TRC
CHClCF2	-79.40	72.39	17.28	20.08	22.23	23.85	26.08	27.53	29.47	TRC

Appendix I (Cont'd)

			Cp							
SPECIES	Hf(298)	S(298)	300	400	500	600	800	1000	1500	COMMENTS
CHFCCl2	-40.01	75.19	18.38	20.98	22.94	24.43	26.48	27.82	29.61	TRC
CHClCFCl	-42.59	75.02	18.28	20.98	22.99	24.50	26.55	27.87	29.64	TRC
C2F3Cl	-120.79	77.10	20.12	22.73	24.67	26.10	28.04	29.16	30.52	TRC
CF2CCl2	-80.31	77.84	20.84	23.37	25.24	26.60	28.37	29.42	30.64	TRC
CFClCFCl	-84.20	78.04	20.98	23.52	25.36	26.72	28.47	29.49	30.69	TRC
C2FCl3	-43.50	81.86	21.82	24.26	26.00	27.25	28.85	29.78	30.81	TRC
C2F5	-213.00	81.33	22.22	25.77	28.39	30.28	32.65	33.96	35.43	TRC
C3F7	-309.03	97.13	32.56	38.08	42.04	44.82	48.19	49.99	51.95	TRC
C4F9	-407.50	113.74	42.53	49.74	54.93	58.58	63.05	65.49	68.16	TRC
C5F11	-505.98	130.35	52.50	61.41	67.81	72.34	77.92	80.98	84.38	TRC
C6F13	-604.45	146.96	62.47	73.07	80.70	86.10	92.79	96.47	100.59	TRC
C6F6	-228.35	91.46	37.29	43.65	48.61	52.42	57.54	60.56	64.15	PED.&TRC
C6H5F	-27.72	72.33	22.70	29.96	36.00	40.79	47.68	52.32	58.99	PED.&TRC
12C6H4F2	-70.22	77.00	25.65	32.77	38.56	43.13	49.63	53.94	59.99	PED.&TRC
13C6H4F2	-73.90	76.82	25.60	32.75	38.57	43.13	49.63	53.94	59.99	PED.&TRC
14C6H4F2	-73.30	75.42	25.59	32.73	38.54	43.11	49.61	53.92	59.97	PED.&TRC
C6HF5	-192.76	90.27	34.32	40.94	46.12	50.12	55.58	58.94	63.12	PED.
F	18.97	37.94	5.43	5.36	5.28	5.22	5.13	5.08	5.02	TRC
F2	.00	48.47	7.49	7.89	8.19	8.41	8.68	8.89	9.13	JANAF
FO	26.05	51.95	7.32	7.68	7.99	8.22	8.53	8.72	8.95	TRC
FO2	3.20	60.65	10.64	11.33	11.85	12.25	12.80	13.13	13.53	TRC
F2O	5.90	59.11	10.37	11.40	12.12	12.62	13.22	13.56	14.00	TRC
F2O2	4.30	66.24	14.86	16.31	17.26	17.90	18.65	19.05	19.49	TRC
HF	-65.32	41.53	6.96	6.97	6.97	6.99	7.06	7.21	7.71	TRC
HFO	-23.50	55.33	8.59	9.19	9.75	10.21	10.91	11.45	12.36	TRC
HCOF	-93.80	58.92	9.68	11.08	12.35	13.43	15.08	16.22	17.85	ZHAO&JANAF
COF	-41.00	59.39	9.32	10.11	10.77	11.31	12.10	12.61	13.25	JANAF
COF2	-152.70	61.88	11.33	13.09	14.46	15.51	16.92	17.79	18.83	JANAF
CF3OF	-182.80	77.09	19.03	21.76	23.87	25.45	27.37	28.45	29.70	JANAF
ClF	-12.02	52.09	7.68	8.07	8.33	8.51	8.73	8.85	9.01	JANAF
ClF3	-37.97	67.30	15.30	16.88	17.80	18.36	18.98	19.29	19.61	JANAF
ClF5	-57.00	74.27	23.30	26.29	28.01	29.06	30.19	30.75	31.32	JANAF
C2F4Cl	-167.06	79.95	22.82	26.91	29.58	31.61	33.49	34.40	0.0	THERM
CFCl	-5.00	65.59	10.21	10.88	11.42	11.84	12.45	12.86	13.37	LIAS&CALC
CH	142.00	43.72	6.97	6.97	7.03	7.12	7.41	7.77	8.74	JANAF
CH2(S)	101.44	44.15	8.28	8.62	8.99	9.37	10.15	10.88	12.22	
CH2(T)	92.35	46.32	8.28	8.62	8.99	9.37	10.15	10.88	12.22	JANAF
CH3	34.82	46.38	9.26	10.05	10.81	11.54	12.90	14.09	16.26	JANAF
CH4	-17.90	44.48	8.51	9.77	11.10	12.44	15.00	17.20	20.61	JANAF
CF3CN	-118.41	71.31	18.67	21.31	23.40	25.04	27.28	28.62	30.21	JANAF
FCN	8.60	53.87	10.13	10.93	11.54	12.03	12.78	13.31	14.05	JANAF
NF	59.50	51.45	7.26	7.60	7.91	8.16	8.48	8.67	8.92	JANAF
NF2	10.10	59.74	9.82	10.85	11.62	12.16	12.82	13.18	13.57	JANAF
NF3	-31.57	62.33	12.80	14.78	16.15	17.07	18.16	18.73	19.34	JANAF
N2F2(CIS)	16.40	62.10	11.98	13.90	15.31	16.32	17.59	18.31	19.13	JANAF

Appendix I (Cont'd)

			Cp							
SPECIES	Hf(298)	S(298)	300	400	500	600	800	1000	1500	COMMENTS
N2F2(TR)	19.40	62.78	12.81	14.39	15.58	16.47	17.64	18.32	19.12	JANAF
N2F4	-2.00	71.99	19.00	22.58	25.05	26.72	28.68	29.72	30.83	JANAF
ONF	-15.70	59.29	9.90	10.65	11.23	11.69	12.35	12.78	13.34	JANAF
NO2F	-26.00	62.20	11.95	13.63	14.90	15.88	17.19	17.99	18.94	JANAF
FONO2	2.50	70.01	15.64	17.95	19.69	20.97	22.65	23.63	24.76	JANAF
NF3O	-39.00	66.56	16.28	18.82	20.53	21.72	23.19	24.02	24.96	JANAF
CHFCl	-25.00	64.44	11.17	12.94	14.40	15.51	16.95	17.75	18.34	CALC.
CH2FCF2	-106.60	74.34	17.71	20.72	23.29	25.37	28.39	30.42	33.25	CRT
CHF2CF2	-157.80	78.48	20.16	23.17	25.66	27.62	30.35	32.06	34.24	CRT
CH2FCHF	-56.28	70.11	16.64	19.42	21.82	23.79	26.68	28.63	31.39	CRT
CHF2CHF	-108.01	74.24	18.20	21.28	23.80	25.80	28.66	30.59	33.31	CRT
CF3CHF	-164.51	77.97	20.52	23.73	26.22	28.11	30.67	32.27	34.36	CRT
CH2FCH2	-10.65	66.86	13.90	16.68	19.20	21.36	24.78	27.33	31.29	CRT
CHF2CH2	-66.26	71.17	16.03	19.03	21.57	23.64	26.75	28.96	32.28	CRT
CF3CH2	-123.60	72.32	18.49	21.79	24.32	26.26	28.99	30.80	33.40	CRT
CH3CHF	-17.30	65.48	14.06	16.63	19.08	21.23	24.68	27.27	31.29	CRT
CH3CF2	-72.30	69.39	16.10	18.89	21.33	23.40	26.59	28.88	32.39	CRT

Unit: Hf: Kcal/mol, S and Cp : Cal/mol.K

References for Thermodynamic Properties

CALC: Calculated by Radicalc computer code. CF_2Cl from CHF_2Cl, CH_2F from CH_3F, $CFCl_2$ from $CHFCl_2$ and ^1CFCl from CH_2FCl.

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LIAS: Lias,S.G., Bartmess,J.E., Liebman,J.F., Holmes,J.L., Levin, R.D. and Mallard, W.G., J. Phy. Chem. Ref. Data, Supplement No.1, Vol.17 (1988)

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ROUX: Tschuikow-Roux, E., and Paddison, S., Inter. J. Chem. Kinet. 19, 15 (1987)

SQU: Paulino, J.A. and Squires, R.R., J. Am. Chem. Soc., 5573 (1991).

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THERM: Computer Code for Thermodynamic Properties Estimation, Ritter, E.R., and Bozzelli, J.W., Inter. J. Chem. Kinet., 23, 767 (1991)

TRC: TRC Thermodynamic Tables, Texas A&M University.

ZHAO: Zhao, Y, and Francisco, J.S., Chem. Phys. Letters, Vol. 173 No. 5.6 (1990)

Appendix II Vibration Assigned to Normal and Partial Bond Bending and Stretching Motions

Mode	Frequency (cm^{-1})	Comments	Mode	Frequency (cm^{-1})	Comment
inv-ch3	600	CH3 radical inversion	H-C-N	1150	
inv-h2	550	C-CH2 group inversion	H-C-O	1050	
inv-hc	570	C2-CH group inversion	H.C-C	800	
inv-c2	600	C3-C group inversion	H-O-C	1400	
inv-clh2	750	CClH2 radical inversion	H-O-O	1050	
inv-cl2h	780	CCl2H radical inversion	H-O-N	1200	
inv-cl3	500	CCl3 radical inversion	H.O-C	840	
inv-hcl	730	C-CHCl group inversion	H.O-N	840	
inv-ho	730	C-CHO group inversion	H-C#C,W	730	-CH triple bond wag
inv-cl2	750	C-CCl2 group inversion	H-C#C,R	610	-CH triple bond rock
inv-f2cl	600	C-F2Cl group inversion	H-C=C	1050	
C=O	1700	stretch	H-C=N	1150	
C-.O	1400		H-C=O	1150	
C-O,ETH	1100	C-O stretch in ethanol	H.C=C	790	
C-O,ACID	1200	C-O stretch in acid	H.C=N	790	
C.O	710		H-C-.C	1150	
C=C	1650		C-C=C	420	
C-.C	1300		C.C=C	290	
C-C	1000		C-C-.C	420	
C.C	675		O-.N-O	420	
CD-H	3100		O-C=O	420	
ct-h	3400		O-.C-.O	420	
C-H	3000		O-.N-.O	360	
c-I	500		C=C=C	850	
O-H	3400		C=C-.C	635	
N-H	3100		H-C-C,R	720	-CH2-, rock
S-H	3100		H-C-C,TR	850	terminal -CH3 rock
C.H	2200		H-C-.C,R	700	
O.H	2200		H-C=C,OP	700	out-of-plane bend
C-F	1100		C-C-Cl	400	
C.F	820		C-C.Cl	280	
C-Cl	700		Cl-C-Cl	280	
C.Cl	490		C-C-BR	360	
C-I	500		C-C.BR	250	
C.I	375		C-C-I	320	
C-BR	560		C-C.I	220	
C.BR	420		C-C-C	420	
H-C-H	1400		C-C.C	300	
H.C-H	1000		C-O-C	400	
H-C-CO	1150		C-O.C	280	
H-O-CD	1150		C-C-O	400	
H-C-C	1150		C-C.O	280	
H-C-Cl,tw	1150	-CH2Cl, -CHCl2 wag/twist	O-C-O	400	
H-C-Cl,R	1050	-CH2Cl, -CHCl2, ROCK	C=C,TR	500	torsion frequency
H-C-C,TW	1150	-CH3, -CH2- wag/twist	CC=CC,TR	400	torsion frequency
H-C-F	1250		HC=CC,TR	600	torsion frequency

Appendix III Moments of Inertia (I), Torsion Barriers (V)and Symmetry Numbers (S) to Free Rotation about Single Bonds

Rotors (A-B)	I_a	I_b	V/R	S_b	S_a	Reference
CH3-CH2	3.2	1.8	80	2	3	2
RCH2-CH2	36.5	1.8	80	2	1	Assigned
CH3-CCH	3.2	17.0	100	1	3	Assigned
CH2-C2H5	1.8	17.0	100	1	2	1
CH3-C.HCH3	1.8	56.0	370	1	3	4
CH3-C.(CH3)2	1.8	100.0	760	1	3	4
CH3-CF3	3.2	87.3	1660	3	3	1
CH3-CH3	3.2	3.2	1600	3	3	1
RCH2-CH3	36.5	3.2	1600	3	1	Assigned
CH3-C2H5	3.2	17.0	1655	1	3	1
CH3-IPROP	3.2	56.0	1950	1	3	1
RIPROP-CH3	83.0	3.2	1950	3	1	Assigned
CH3-TBUT	3.2	00.0	2365	1	3	1
CH3-PHENYL	3.2	88.0	0	2	3	1
CH3-OH	3.2	1.0	500	1	3	1
RCH2-OH	36.5	1.0	500	1	1	Assigned
C2H5-OH	17.0	1.0	600	1	1	1
CH2-OH	1.8	1.0	0	1	2	Assigned
CH3-OCH3	3.2	17.0	1409	1	3	1
CH3-OCH2R	3.2	36.5	1409	1	3	Assigned
CH2-OCH3	1.8	17.0	0	2	3	Assigned
CH3-CH2OH	3.2	17.0	1676	1	3	3
IPROP-OH	56.0	1.0	600	1	1	Assigned
CC-OC	17.0	25.6	1273	1	1	Assigned
CC-OCH2R	17.0	36.5	273	1	1	Assigned
IPROP-OC	56.0	25.6	1500	1	1	Assigned
VIN-OH	15.0	1.0	404	1	1	3
RVIN-OH	36.5	1.0	404	1	1	Assigned
VIN-OR	15.0	36.5	404	1	1	Assigned
CH3-OOH	3.2	34.7	598	1	3	3
RCH2-OOH	36.5	34.7	598	1	1	Assigned
CH2-OOH	1.8	34.7	0	1	2	Assigned
CCO-OH	55.0	1.0	330	1	1	Assigned
RCH2O-OH	55.0	1.0	330	1	1	Assigned
CH3O-OH	17.0	1.0	330	1	1	3
CC-OOH	17.0	34.7	598	1	1	Assigned
IPROP-OOH	56.0	34.7	598	1	1	Assigned
CH3-CHO	3.2	17.0	635	1	3	1
CH3-COCH3	3.2	34.0	635	1	3	1
CH2-COCH3	1.8	34.0	0	1	2	Assigned
CC-CHO	17.0	17.0	635	1	1	Assigned
CH3-C.*O	3.2	1.0	190	1	3	Assigned
CH2-VIN	1.8	15.0	0	1	2	Assigned
CH3-VIN	3.2	15.0	634	1	3	1
CH3-VINR	3.2	36.5	634	1	3	Assigned

Appendix III (Cont'd)

Rotors (A-B)	I_a	I_b	V/R	S_b	S_a	Reference
CH3-C.*CHR	3.2	18.0	0	1	3	Assigned
CC-VINR	17.0	36.5	634	1	1	Assigned
IPROP-VIN	56.0	15.0	634	1	1	Assigned
IPROP-VINR	56.0	36.5	634	1	1	Assigned
CH3-C=CC,TRA	3.2	16.0	377	1	3	1
CH3-C=CC,CIS	3.2	16.0	981	1	3	1
CH3-PH	3.2	88.0	0	2	3	1
CH2-PH	1.8	88.0	0	2	3	Assigned
CC-PH	17.0	88.0	0	2	1	Assigned
IPROP-PH	56.0	88.0	0	2	1	Assigned
CH3-BENZYL	3.2	170.0	1600	1	3	1
PHENYL-PHENYL	89.2	89.2	754.9	2	2	3
PH-BENZYL	89.2	170.0	0	1	2	Assigned
OH-PHENYL	1.0	89.2	0	2	1	3
CF3-CF3	87.9	87.9	1992	3	3	1
CH3-CH2Cl	3.2	103	1887	1	3	1
CH3-C.HCl	3.2	103	400	1	3	Roux 1992
CH2-CH2Cl	1.8	103	150	1	2	Assigned
CH3-CHCl2	3.2	203	2300	1	3	Assigned
CH3-C.Cl2	3.2	203	1000	2	3	Roux 1992
CH2-CHCl2	1.8	203	200	1	1	Assigned
CH2Cl-CH2Cl	103	103	2700	1	1	Assigned
C.HCl-CH2Cl	102	103	400	1	1	Assigned
CH3-CCl3	3.2	303	2500	3	3	1
CH2-CCl3	1.8	303	550	3	2	Assigned
CH2Cl-CHCl2	103	203	2900	1	1	Assigned
C.HCl-CHCl2	102	203	600	1	1	Assigned
CH2Cl-C.Cl2	103	202	600	2	1	Assigned
CHCl2-CHCl2	203	203	5500	1	1	Assigned
C.Cl2-CHCl2	202	203	800	1	2	Assigned
CH2Cl-CCl3	103	303	5000	3	1	Assigned
C.HCl-CCl3	103	303	850	3	1	Assigned
CHCl2-CCl3	203	303	6000	3	1	Assigned
C.Cl2-CCl3	203	302	1000	3	2	Assigned
CCl3-CCl3	303	303	6492	3	3	1
CH3-C#C	3.2	1.0	190	1	1	3
C2-C#C	17.0	1.0	190	1	1	Assigned
IPROP-C#C	56.0	1.0	190	1	1	Assigned

*** Symbols noted :**

1. Rotors (A-B) presents two rotors, A and B, along the single bond, A-B.
2. I_a and S_a: moments of inertia, amu-Å², and symmetry number for rotor A.
3. I_b and S_b: moments of inertia, amu-Å², and symmetry number for rotor B.
   For I_a and I_b, the moments are taken along the A-B axis.
4. V: torsion barrier, here divided by R (ideal gas constant), expressed as V/R, V/R unit = °K.

*** Reference :**

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Acknowledgment: The author acknowledge the Rotation and Vibration data base constructed by Lay, T. H.

Appendix IV Output File of Some Radical Species by RADICALC Computer Code

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CF2CL = CHF2CL - V/C-H/ - 2V/H-C-F/ - V/H-C-CL/ + V/INV-F2CL/

HEAT CAPACITY INCREMENTS
-1 * V/C-H           .000      .000     -.005     -.026     -.077     -.264     -.507    -1.039
-2 * V/H-C-F        -.347     -.357     -.914    -1.488    -1.972    -2.650    -3.055    -3.530
-1 * V/H-C-CL       -.609     -.617     -.999    -1.267    -1.448    -1.659    -1.769    -1.886
     V/INV-F2CL     1.030     1.039     1.366     1.559     1.677     1.805     1.868     1.933
ENTROPY INCREMENTS
-1 * V/C-H           .000      .000      .000     -.003     -.012     -.058     -.142     -.455
-2 * V/H-C-F        -.067     -.069     -.245     -.512     -.828    -1.496    -2.135    -3.480
-1 * V/H-C-CL       -.187     -.191     -.424     -.678     -.926    -1.375    -1.758    -2.502
     V/INV-F2CL      .448      .455      .803     1.130     1.426     1.928     2.338     3.111

Temperature(K)  heat capacity  entropy
                cal/mol K      cal/mol K
 298.0000         .0741          .1944
 300.0000         .0644          .1949
 400.0000        -.5523          .1334
 500.0000       -1.2224         -.0626
 600.0000       -1.8208         -.3398
 800.0000       -2.7682        -1.0005
1000.0000       -3.4628        -1.6968
1500.0000       -4.5217        -3.3264
```

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CH2F=CH3F-V/C-H/-2V/H-C-H/-V/H-C-F/+V/INV-H2F/

HEAT CAPACITY INCREMENTS
-1 * V/C-H           .000      .000     -.005     -.026     -.077     -.264     -.507    -1.039
-2 * V/H-C-H        -.210     -.217     -.662    -1.188    -1.673    -2.402    -2.863    -3.426
-1 * V/H-C-F        -.174     -.178     -.457     -.744     -.986    -1.325    -1.527    -1.765
     V/INV-H2F       .735      .744     1.119     1.366     1.527     1.711     1.805     1.903
ENTROPY INCREMENTS
-1 * V/C-H           .000      .000      .000     -.003     -.012     -.058     -.142     -.455
-2 * V/H-C-H        -.036     -.037     -.156     -.361     -.621    -1.210    -1.799    -3.086
-1 * V/H-C-F        -.033     -.035     -.123     -.256     -.414     -.748    -1.067    -1.740
     V/INV-H2F       .251      .256      .525      .803     1.067     1.535     1.928     2.682

Temperature(K)  heat capacity  entropy
                cal/mol K      cal/mol K
 298.0000         .3508          .1821
 300.0000         .3482          .1844
 400.0000        -.0053          .2453
 500.0000        -.5921          .1830
 600.0000       -1.2087          .0202
 800.0000       -2.2799         -.4806
1000.0000       -3.0928        -1.0811
1500.0000       -4.3264        -2.5987
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```
CFCL2=CHFCL2-V/C-H/-2V/H-C-CL/-V/H-C-F/+V/INV-CL2F/

HEAT CAPACITY INCREMENTS
-1 * V/C-H           .000      .000     -.005     -.026     -.077     -.264     -.507    -1.039
-2 * V/H-C-CL      -1.217    -1.235    -1.998    -2.534    -2.896    -3.318    -3.538    -3.773
-1 * V/H-C-F        -.174     -.178     -.457     -.744     -.986    -1.325    -1.527    -1.765
     V/INV-CL2F     1.138     1.146     1.448     1.619     1.722     1.832     1.886     1.941
ENTROPY INCREMENTS
-1 * V/C-H           .000      .000      .000     -.003     -.012     -.058     -.142     -.455
-2 * V/H-C-CL       -.374     -.382     -.848    -1.355    -1.851    -2.749    -3.516    -5.003
-1 * V/H-C-F        -.033     -.035     -.123     -.256     -.414     -.748    -1.067    -1.740
     V/INV-CL2F      .543      .550      .926     1.269     1.574     2.086     2.502     3.279

Temperature(K)  heat capacity  entropy
                cal/mol K      cal/mol K
 298.0000        -.2531         .1350
 300.0000        -.2673         .1333
 400.0000       -1.0126        -.0454
 500.0000       -1.6851        -.3458
 600.0000       -2.2369        -.7035
 800.0000       -3.0745       -1.4687
1000.0000       -3.6858       -2.2237
1500.0000       -4.6347       -3.9195
```

```
CHFCL=CH2FCL-V/C-H/-V/H-C-H/-V/H-C-F/-V/H-C-CL/+V/INV-HFCL/

HEAT CAPACITY INCREMENTS
-1 * V/C-H           .000      .000     -.005     -.026     -.077     -.264     -.507    -1.039
-1 * V/H-C-H        -.105     -.109     -.331     -.594     -.836    -1.201    -1.432    -1.713
-1 * V/H-C-F        -.174     -.178     -.457     -.744     -.986    -1.325    -1.527    -1.765
-1 * V/H-C-CL       -.609     -.617     -.999    -1.267    -1.448    -1.659    -1.769    -1.886
     V/INV-HFCL      .735      .744     1.119     1.366     1.527     1.711     1.805     1.903
ENTROPY INCREMENTS
-1 * V/C-H           .000      .000      .000     -.003     -.012     -.058     -.142     -.455
-1 * V/H-C-H        -.018     -.019     -.078     -.180     -.311     -.605     -.900    -1.543
-1 * V/H-C-F        -.033     -.035     -.123     -.256     -.414     -.748    -1.067    -1.740
-1 * V/H-C-CL       -.187     -.191     -.424     -.678     -.926    -1.375    -1.758    -2.502
     V/INV-HFCL      .251      .256      .525      .803     1.067     1.535     1.928     2.682

Temperature(K)  heat capacity  entropy
                cal/mol K      cal/mol K
   298.0000        -.1527         .0128
   300.0000        -.1607         .0117
   400.0000        -.6734        -.1004
   500.0000       -1.2650        -.3142
   600.0000       -1.8201        -.5948
   800.0000       -2.7379       -1.2502
  1000.0000       -3.4301       -1.9392
  1500.0000       -4.4996       -3.5575
```

```
CFCL=CHFCL-V/C-H/-V/H-C-F/-V/H-C-CL/

 HEAT CAPACITY INCREMENTS
-1 * V/C-H         .000      .000     -.005     -.026     -.077     -.264     -.507    -1.039
-1 * V/H-C-F      -.174     -.178     -.457     -.744     -.986    -1.325    -1.527    -1.765
-1 * V/H-C-CL     -.609     -.617     -.999    -1.267    -1.448    -1.659    -1.769    -1.886
ENTROPY INCREMENTS
-1 * V/C-H         .000      .000      .000     -.003     -.012     -.058     -.142     -.455
-1 * V/H-C-F      -.033     -.035     -.123     -.256     -.414     -.748    -1.067    -1.740
-1 * V/H-C-CL     -.187     -.191     -.424     -.678     -.926    -1.375    -1.758    -2.502

Temperature(K)  heat capacity  entropy
                cal/mol K      cal/mol K
   298.0000         -.7825       -.2205
   300.0000         -.7960       -.2258
   400.0000        -1.4612       -.5471
   500.0000        -2.0371       -.9370
   600.0000        -2.5111      -1.3517
   800.0000        -3.2480      -2.1805
  1000.0000        -3.8032      -2.9676
  1500.0000        -4.6898      -4.6970
```

Appendix V Thermodynamic Analysis for the Mechanism

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                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx          CF2CL2      = CF2CL      + CL
                     Hf (Kcal/mol) -114.100     -66.000     28.900
                     S (cal/mol K)   72.000      68.300     39.500

dHr (kcal/mol)     (298K) =       77.00      dHr avg (298., 1500. K) =        76.83
dU (dE) (kcal/mol) (")    =       76.41      dUr avg (298., 1500. K) =        75.04
dSr (cal/mol K)   ( " )   =       35.80      dSr avg (298., 1500. K) =        35.73
dGr  (kcal/mol)   ( " )   =       66.33      dGr avg (298., 1500. K) =        44.70
         Af/Ar    ( " )   =   1.004E+03     Af/Ar avg (298., 1500. K ) = 3.212E+02

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00    7.700E+01    7.641E+01    3.581E+01    1.002E+03    6.626E+01
   400.00    7.708E+01    7.628E+01    3.603E+01    8.408E+02    6.267E+01
   500.00    7.711E+01    7.611E+01    3.610E+01    6.956E+02    5.906E+01
   600.00    7.710E+01    7.591E+01    3.609E+01    5.778E+02    5.545E+01
   800.00    7.704E+01    7.545E+01    3.600E+01    4.137E+02    4.824E+01
  1000.00    7.694E+01    7.495E+01    3.589E+01    3.131E+02    4.105E+01
  1200.00    7.683E+01    7.444E+01    3.579E+01    2.480E+02    3.388E+01
  1500.00    7.665E+01    7.367E+01    3.566E+01    1.857E+02    2.317E+01
  2000.00    7.634E+01    7.236E+01    3.548E+01    1.272E+02    5.386E+00
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```
                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx          CF2CL2      = CF2S       + CL2
                     Hf (Kcal/mol) -114.100     -39.400      0.000
                     S (cal/mol K)   72.000      57.500     53.300

dHr (kcal/mol)     (298K) =       74.70      dHr avg (298., 1500. K) =        74.17
dU (dE) (kcal/mol) (")    =       74.11      dUr avg (298., 1500. K) =        72.98
dSr (cal/mol K)   ( " )   =       38.80      dSr avg (298., 1500. K) =        37.95
dGr  (kcal/mol)   ( " )   =       63.13      dGr avg (298., 1500. K) =        40.05
         Af/Ar    ( " )   =   4.546E+03     Af/Ar avg (298., 1500. K ) = 9.852E+02

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00    7.470E+01    7.410E+01    3.880E+01    4.518E+03    6.306E+01
   400.00    7.465E+01    7.385E+01    3.866E+01    3.154E+03    5.919E+01
   500.00    7.452E+01    7.352E+01    3.837E+01    2.181E+03    5.533E+01
   600.00    7.433E+01    7.314E+01    3.804E+01    1.538E+03    5.151E+01
   800.00    7.389E+01    7.230E+01    3.739E+01    8.348E+02    4.397E+01
  1000.00    7.339E+01    7.141E+01    3.684E+01    5.066E+02    3.655E+01
  1200.00    7.289E+01    7.050E+01    3.638E+01    3.344E+02    2.923E+01
  1500.00    7.219E+01    6.920E+01    3.586E+01    2.057E+02    1.840E+01
  2000.00    7.128E+01    6.730E+01    3.533E+01    1.184E+02    6.112E-01
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```
                         THERMODYNAMIC ANALYSIS for REACTION
                      Rx           CF2CL2      = CFCL        + CLF
                     Hf {Kcal/mol} -114.100      -5.000     -12.000
                     S {cal/mol K}   72.000      65.500      52.000

dHr {kcal/mol}    (298K) =       97.10     dHr avg (298., 1500. K) =        96.57
dU (dE) {kcal/mol} (")   =       96.51     dUr avg (298., 1500. K) =        95.38
dSr (cal/mol K)   ( " )  =       45.50     dSr avg (298., 1500. K) =        44.69
dGr  {kcal/mol}   ( " )  =       83.53     dGr avg (298., 1500. K) =        56.39
       Af/Ar      ( " )  =   1.324E+05    Af/Ar avg (298., 1500. K ) = 2.922E+04

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    9.710E+01    9.650E+01    4.550E+01    1.319E+05    8.345E+01
   400.00    9.709E+01    9.629E+01    4.548E+01    9.769E+04    7.890E+01
   500.00    9.697E+01    9.598E+01    4.522E+01    6.872E+04    7.436E+01
   600.00    9.679E+01    9.560E+01    4.489E+01    4.832E+04    6.986E+01
   800.00    9.630E+01    9.471E+01    4.419E+01    2.556E+04    6.095E+01
  1000.00    9.576E+01    9.378E+01    4.359E+01    1.512E+04    5.217E+01
  1200.00    9.522E+01    9.283E+01    4.309E+01    9.809E+03    4.351E+01
  1500.00    9.439E+01    9.141E+01    4.248E+01    5.758E+03    3.067E+01
  2000.00    9.316E+01    8.919E+01    4.177E+01    3.019E+03    9.624E+00
```

```
                         THERMODYNAMIC ANALYSIS for REACTION
                      Rx           C2F4CL      = C2F4        + CL
                     Hf {Kcal/mol} -167.000    -157.400      28.900
                     S {cal/mol K}   79.900      71.800      39.500

dHr {kcal/mol}    (298K) =       38.50     dHr avg (298., 1500. K) =        38.43
dU (dE) {kcal/mol} (")   =       37.91     dUr avg (298., 1500. K) =        37.24
dSr {cal/mol K}   ( " )  =       31.40     dSr avg (298., 1500. K) =        31.39
dGr  {kcal/mol}   ( " )  =       29.14     dGr avg (298., 1500. K) =        10.21
       Af/Ar      ( " )  =   1.097E+02    Af/Ar avg (298., 1500. K ) = 3.617E+01

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    3.850E+01    3.791E+01    3.141E+01    1.096E+02    2.908E+01
   400.00    3.860E+01    3.781E+01    3.171E+01    9.550E+01    2.592E+01
   500.00    3.861E+01    3.762E+01    3.173E+01    7.717E+01    2.275E+01
   600.00    3.857E+01    3.737E+01    3.165E+01    6.176E+01    1.958E+01
   800.00    3.843E+01    3.684E+01    3.145E+01    4.192E+01    1.327E+01
  1000.00    3.832E+01    3.633E+01    3.132E+01    3.149E+01    6.993E+00
  1200.00    3.826E+01    3.587E+01    3.127E+01    2.552E+01    7.344E-01
  1500.00    3.821E+01    3.523E+01    3.123E+01    2.005E+01   -8.640E+00
  2000.00    3.820E+01    3.422E+01    3.122E+01    1.497E+01   -2.425E+01
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```
                         THERMODYNAMIC ANALYSIS for REACTION
                    Rx            CF2CL       + H2          = CHF2CL      + H
                    Hf (Kcal/mol)  -66.000       0.000     -115.300     52.100
                    S (cal/mol K)   68.300      31.200       67.200     27.300

dHr (kcal/mol)    (298K) =        2.80     dHr avg (298., 1500. K) =        2.83
dU (dE) (kcal/mol) (")   =        2.80     dUr avg (298., 1500. K) =        2.83
dSr (cal/mol K)  ( " )   =       -5.00     dSr avg (298., 1500. K) =       -5.07
dGr  (kcal/mol)  ( " )   =        4.29     dGr avg (298., 1500. K) =        7.39
        Af/Ar    ( " )   =   8.075E-02    Af/Ar avg (298., 1500. K ) = 7.778E-02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
    300.00    2.797E+00    2.797E+00   -5.009E+00   8.041E-02    4.300E+00
    400.00    2.691E+00    2.691E+00   -5.318E+00   6.882E-02    4.819E+00
    500.00    2.642E+00    2.642E+00   -5.430E+00   6.505E-02    5.357E+00
    600.00    2.642E+00    2.642E+00   -5.432E+00   6.498E-02    5.901E+00
    800.00    2.758E+00    2.758E+00   -5.270E+00   7.050E-02    6.974E+00
   1000.00    2.988E+00    2.988E+00   -5.015E+00   8.016E-02    8.003E+00
   1200.00    3.293E+00    3.293E+00   -4.737E+00   9.216E-02    8.978E+00
   1500.00    3.828E+00    3.828E+00   -4.340E+00   1.125E-01    1.034E+01
   2000.00    4.808E+00    4.808E+00   -3.778E+00   1.494E-01    1.236E+01
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```
                         THERMODYNAMIC ANALYSIS for REACTION
                    Rx           CF2CL2      + H            = CF2CL       + HCL
                    Hf (Kcal/mol) -114.100      52.100      -66.000     -22.000
                    S (cal/mol K)   72.000      27.300       68.300      44.600

dHr (kcal/mol)    (298K) =      -26.00     dHr avg (298., 1500. K) =      -26.95
dU (dE) (kcal/mol) (")   =      -26.00     dUr avg (298., 1500. K) =      -26.95
dSr (cal/mol K)  ( " )   =       13.60     dSr avg (298., 1500. K) =       11.91
dGr  (kcal/mol)  ( " )   =      -30.05     dGr avg (298., 1500. K) =      -37.66
        Af/Ar    ( " )   =   9.387E+02    Af/Ar avg (298., 1500. K ) = 4.016E+02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
    300.00   -2.600E+01   -2.600E+01    1.359E+01   9.320E+02   -3.008E+01
    400.00   -2.626E+01   -2.626E+01    1.285E+01   6.426E+02   -3.140E+01
    500.00   -2.656E+01   -2.656E+01    1.218E+01   4.597E+02   -3.265E+01
    600. 0   -2.688E+01   -2.688E+01    1.159E+01   3.416E+02   -3.384E+01
    800.00   -2.756E+01   -2.756E+01    1.062E+01   2.094E+02   -3.606E+01
   1000.00   -2.823E+01   -2.823E+01    9.875E+00   1.440E+02   -3.81+01
   1200.00   -2.886E+01   -2.886E+01    9.300E+00   1.078E+02   -4.002E+01
   1500.00   -2.973E+01   -2.973E+01    8.651E+00   7.778E+01   -4.271E+01
   2000.00   -3.100E+01   -3.100E+01    7.918E+00   5.379E+01   -4.683E+01
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```
                         THERMODYNAMIC ANALYSIS for REACTION
                   Rx            CL          + H2         = HCL         + H
                 Hf (Kcal/mol)   28.900       0.000      -22.000      52.100
                 S (cal/mol K)   39.500      31.200       44.600      27.300

dHr (kcal/mol)    (298K) =         1.20     dHr avg (298., 1500. K) =         1.10
dU (dE) (kcal/mol) (")   =         1.20     dUr avg (298., 1500. K) =         1.10
dSr (cal/mol K)   ( " )  =         1.20     dSr avg (298., 1500. K) =         1.00
dGr  (kcal/mol)   ( " )  =         0.84     dGr avg (298., 1500. K) =         0.20
        Af/Ar     ( " )  =    1.829E+00    Af/Ar avg (298., 1500. K ) = 1.658E+00

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00    1.199E+00    1.199E+00    1.197E+00   1.827E+00    8.400E-01
    400.00    1.155E+00    1.155E+00    1.071E+00   1.714E+00    7.270E-01
    500.00    1.116E+00    1.116E+00    9.830E-01   1.640E+00    6.245E-01
    600.00    1.081E+00    1.081E+00    9.190E-01   1.588E+00    5.296E-01
    800.00    1.024E+00    1.024E+00    8.361E-01   1.523E+00    3.549E-01
   1000.00    9.830E-01    9.830E-01    7.903E-01   1.488E+00    1.927E-01
   1200.00    9.569E-01    9.569E-01    7.663E-01   1.471E+00    3.733E-02
   1500.00    9.403E-01    9.403E-01    7.536E-01   1.461E+00   -1.901E-01
   2000.00    9.557E-01    9.557E-01    7.619E-01   1.467E+00   -5.681E-01
```

```
                         THERMODYNAMIC ANALYSIS for REACTION
                 Rx            CHF2CL       + CL         = CF2CL       + HCL
                 Hf (Kcal/mol) -115.300      28.900      -66.000     -22.000
                 S (cal/mol K)   67.200      39.500       68.300      44.600

dHr (kcal/mol)    (298K) =        -1.60     dHr avg (298., 1500. K) =        -1.73
dU (dE) (kcal/mol) (")   =        -1.60     dUr avg (298., 1500. K) =        -1.73
dSr (cal/mol K)   ( " )  =         6.20     dSr avg (298., 1500. K) =         6.08
dGr  (kcal/mol)   ( " )  =        -3.45     dGr avg (298., 1500. K) =        -7.20
        Af/Ar     ( " )  =    2.265E+01    Af/Ar avg (298., 1500. K ) = 2.132E+01

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -1.598E+00   -1.598E+00    6.206E+00   2.272E+01   -3.460E+00
    400.00   -1.536E+00   -1.536E+00    6.389E+00   2.491E+01   -4.092E+00
    500.00   -1.526E+00   -1.526E+00    6.413E+00   2.521E+01   -4.733E+00
    600.00   -1.561E+00   -1.561E+00    6.351E+00   2.444E+01   -5.371E+00
    800.00   -1.734E+00   -1.734E+00    6.106E+00   2.161E+01   -6.619E+00
   1000.00   -2.005E+00   -2.005E+00    5.805E+00   1.857E+01   -7.810E+00
   1200.00   -2.336E+00   -2.336E+00    5.504E+00   1.596E+01   -8.941E+00
   1500.00   -2.888E+00   -2.888E+00    5.094E+00   1.298E+01   -1.053E+01
   2000.00   -3.852E+00   -3.852E+00    4.540E+00   9.822E+00   -1.293E+01
```

```
                      THERMODYNAMIC ANALYSIS for REACTION
              Rx            CHF2CL      + H          = CHF2        + HCL
              Hf (Kcal/mol) -115.300     52.100     -57.100     -22.000
              S (cal/mol K)   67.200     27.300      61.700      44.600

dHr (kcal/mol)    (298K) =      -15.90    dHr avg (298., 1500. K) =      -16.72
dU (dE) (kcal/mol) (")   =      -15.90    dUr avg (298., 1500. K) =      -16.72
dSr (cal/mol K)  ( " )   =       11.80    dSr avg (298., 1500. K) =       10.37
dGr  (kcal/mol)  ( " )   =      -19.42    dGr avg (298., 1500. K) =      -26.04
         Af/Ar   ( " )   =   3.794E+02   Af/Ar avg (298., 1500. K ) = 1.846E+02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -1.590E+01   -1.590E+01    1.179E+01   3.776E+02   -1.944E+01
    400.00   -1.609E+01   -1.609E+01    1.125E+01   2.873E+02   -2.059E+01
    500.00   -1.634E+01   -1.634E+01    1.069E+01   2.176E+02   -2.169E+01
    600.00   -1.663E+01   -1.663E+01    1.018E+01   1.677E+02   -2.273E+01
    800.00   -1.724E+01   -1.724E+01    9.298E+00   1.077E+02   -2.468E+01
   1000.00   -1.785E+01   -1.785E+01    8.616E+00   7.640E+01   -2.646E+01
   1200.00   -1.843E+01   -1.843E+01    8.086E+00   5.852E+01   -2.813E+01
   1500.00   -1.924E+01   -1.924E+01    7.479E+00   4.311E+01   -3.046E+01
   2000.00   -2.045E+01   -2.045E+01    6.781E+00   3.035E+01   -3.402E+01
```

```
                      THERMODYNAMIC ANALYSIS for REACTION
              Rx            CHF2        + H2         = CH2F2       + H
              Hf (Kcal/mol)  -57.100      0.000    -108.000      52.100
              S (cal/mol K)   61.700     31.200      59.000      27.300

dHr (kcal/mol)    (298K) =        1.20    dHr avg (298., 1500. K) =        1.03
dU (dE) (kcal/mol) (")   =        1.20    dUr avg (298., 1500. K) =        1.03
dSr (cal/mol K)  ( " )   =       -6.60    dSr avg (298., 1500. K) =       -7.05
dGr  (kcal/mol)  ( " )   =        3.17    dGr avg (298., 1500. K) =        7.37
         Af/Ar   ( " )   =   3.610E-02   Af/Ar avg (298., 1500. K ) = 2.880E-02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00    1.196E+00    1.196E+00   -6.613E+00   3.586E-02    3.180E+00
    400.00    1.018E+00    1.018E+00   -7.129E+00   2.765E-02    3.870E+00
    500.00    8.946E-01    8.946E-01   -7.407E+00   2.405E-02    4.598E+00
    600.00    8.225E-01    8.225E-01   -7.540E+00   2.249E-02    5.346E+00
    800.00    8.137E-01    8.137E-01   -7.558E+00   2.229E-02    6.860E+00
   1000.00    9.482E-01    9.482E-01   -7.411E+00   2.400E-02    8.359E+00
   1200.00    1.180E+00    1.180E+00   -7.200E+00   2.668E-02    9.820E+00
   1500.00    1.626E+00    1.626E+00   -6.870E+00   3.151E-02    1.193E+01
   2000.00    2.494E+00    2.494E+00   -6.372E+00   4.049E-02    1.524E+01
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                         THERMODYNAMIC ANALYSIS for REACTION
                          Rx          2 CHF2      = CHF2CHF2
                          Hf (Kcal/mol) -114.200   -218.600
                          S (cal/mol K)  123.400     78.200

dHr (kcal/mol)    (298K) =     -104.40     dHr avg (298., 1500. K) =     -103.86
dU (dE) (kcal/mol) (")   =     -103.81     dUr avg (298., 1500. K) =     -102.67
dSr (cal/mol K)   ( " )  =      -45.20     dSr avg (298., 1500. K) =      -44.37
dGr  (kcal/mol)   ( " )  =      -90.92     dGr avg (298., 1500. K) =      -63.97
        Af/Ar     ( " )  =   8.781E-06    Af/Ar avg (298., 1500. K ) = 4.030E-05

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00   -1.044E+02   -1.038E+02   -4.520E+01   8.820E-06   -9.084E+01
   400.00   -1.044E+02   -1.036E+02   -4.517E+01   1.194E-05   -8.632E+01
   500.00   -1.043E+02   -1.033E+02   -4.490E+01   1.710E-05   -8.181E+01
   600.00   -1.041E+02   -1.029E+02   -4.455E+01   2.448E-05   -7.734E+01
   800.00   -1.036E+02   -1.020E+02   -4.384E+01   4.664E-05   -6.850E+01
  1000.00   -1.030E+02   -1.011E+02   -4.325E+01   7.877E-05   -5.980E+01
  1200.00   -1.025E+02   -1.001E+02   -4.276E+01   1.204E-04   -5.120E+01
  1500.00   -1.017E+02   -9.875E+01   -4.218E+01   2.015E-04   -3.846E+01
  2000.00   -1.004E+02   -9.644E+01   -4.143E+01   3.933E-04   -1.756E+01



                         THERMODYNAMIC ANALYSIS for REACTION
                      Rx          CF2S        + C2F4       = C3F6
                      Hf (Kcal/mol)  -39.400   -157.400   -269.000
                      S (cal/mol K)   57.500     71.800     65.300

dHr (kcal/mol)    (298K) =      -72.20     dHr avg (298., 1500. K) =      -72.42
dU (dE) (kcal/mol) (")   =      -71.61     dUr avg (298., 1500. K) =      -71.23
dSr (cal/mol K)   ( " )  =      -64.00     dSr avg (298., 1500. K) =      -64.54
dGr  (kcal/mol)   ( " )  =      -53.12     dGr avg (298., 1500. K) =      -14.40
        Af/Ar     ( " )  =   6.831E-10    Af/Ar avg (298., 1500. K ) = 1.568E-09

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00   -7.220E+01   -7.161E+01   -6.401E+01   6.822E-10   -5.300E+01
   400.00   -7.240E+01   -7.161E+01   -6.459E+01   6.806E-10   -4.657E+01
   500.00   -7.253E+01   -7.154E+01   -6.488E+01   7.355E-10   -4.009E+01
   600.00   -7.261E+01   -7.142E+01   -6.502E+01   8.217E-10   -3.360E+01
   800.00   -7.266E+01   -7.107E+01   -6.510E+01   1.055E-09   -2.058E+01
  1000.00   -7.261E+01   -7.063E+01   -6.505E+01   1.351E-09   -7.564E+00
  1200.00   -7.250E+01   -7.011E+01   -6.495E+01   1.708E-09    5.436E+00
  1500.00   -7.229E+01   -6.931E+01   -6.479E+01   2.310E-09    2.490E+01
  2000.00   -7.197E+01   -6.799E+01   -6.460E+01   3.381E-09    5.724E+01
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                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx           CHF2CL      = CHF2        + CL
                     Hf (Kcal/mol) -115.300      -57.100      28.900
                     S (cal/mol K)   67.200       61.700      39.500

dHr (kcal/mol)    (298K) =       87.10      dHr avg (298., 1500. K) =       87.22
dU (dE) (kcal/mol) (")   =       86.51      dUr avg (298., 1500. K) =       86.03
dSr (cal/mol K)  ( " )   =       34.00      dSr avg (298., 1500. K) =       34.33
dGr  (kcal/mol)  ( " )   =       76.96      dGr avg (298., 1500. K) =       56.36
          Af/Ar  ( " )   =   4.060E+02     Af/Ar avg (298., 1500. K ) = 1.588E+02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00    8.710E+01    8.651E+01    3.401E+01    4.058E+02    7.690E+01
    400.00    8.725E+01    8.645E+01    3.443E+01    3.759E+02    7.348E+01
    500.00    8.733E+01    8.633E+01    3.461E+01    3.292E+02    7.002E+01
    600.00    8.736E+01    8.617E+01    3.468E+01    2.837E+02    6.656E+01
    800.00    8.736E+01    8.577E+01    3.468E+01    2.128E+02    5.962E+01
   1000.00    8.732E+01    8.533E+01    3.463E+01    1.661E+02    5.269E+01
   1200.00    8.726E+01    8.487E+01    3.457E+01    1.346E+02    4.577E+01
   1500.00    8.713E+01    8.415E+01    3.448E+01    1.029E+02    3.541E+01
   2000.00    8.688E+01    8.291E+01    3.434E+01    7.177E+01    1.820E+01


                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx           CHF2CL      = CF2S        + HCL
                     Hf (Kcal/mol) -115.300      -39.400     -22.000
                     S (cal/mol K)   67.200       57.500      44.600

dHr (kcal/mol)    (298K) =       53.90      dHr avg (298., 1500. K) =       53.85
dU (dE) (kcal/mol) (")   =       53.31      dUr avg (298., 1500. K) =       52.66
dSr (cal/mol K)  ( " )   =       34.90      dSr avg (298., 1500. K) =       35.01
dGr  (kcal/mol)  ( " )   =       43.49      dGr avg (298., 1500. K) =       22.38
          Af/Ar  ( " )   =   6.386E+02     Af/Ar avg (298., 1500. K ) = 2.234E+02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00    5.390E+01    5.331E+01    3.491E+01    6.392E+02    4.343E+01
    400.00    5.407E+01    5.328E+01    3.541E+01    6.142E+02    3.991E+01
    500.00    5.414E+01    5.315E+01    3.556E+01    5.307E+02    3.636E+01
    600.00    5.413E+01    5.294E+01    3.554E+01    4.384E+02    3.280E+01
    800.00    5.395E+01    5.236E+01    3.529E+01    2.889E+02    2.572E+01
   1000.00    5.362E+01    5.164E+01    3.493E+01    1.931E+02    1.870E+01
   1200.00    5.322E+01    5.083E+01    3.456E+01    1.335E+02    1.175E+01
   1500.00    5.259E+01    4.961E+01    3.409E+01    8.460E+01    1.454E+00
   2000.00    5.175E+01    4.777E+01    3.360E+01    4.956E+01   -1.546E+01
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                          THERMODYNAMIC ANALYSIS for REACTION
                         Rx           CHF2CL      = CFCL       + HF
                       Hf (Kcal/mol) -115.300      -5.000    -65.300
                       S (cal/mol K)   67.200      65.500     41.500

dHr (kcal/mol)    (298K) =        45.00     dHr avg (298., 1500. K) =        44.99
dU (dE) (kcal/mol) (")   =        44.41     dUr avg (298., 1500. K) =        43.80
dSr (cal/mol K)  ( " )   =        39.80     dSr avg (298., 1500. K) =        40.05
dGr  (kcal/mol)  ( " )   =        33.13     dGr avg (298., 1500. K) =         8.98
         Af/Ar   ( " )   =    7.520E+03    Af/Ar avg (298., 1500. K ) = 2.823E+03

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00    4.501E+01     4.441E+01     3.982E+01   7.552E+03    3.306E+01
    400.00    4.526E+01     4.446E+01     4.055E+01   8.191E+03    2.904E+01
    500.00    4.537E+01     4.437E+01     4.080E+01   7.421E+03    2.497E+01
    600.00    4.537E+01     4.417E+01     4.081E+01   6.197E+03    2.088E+01
    800.00    4.515E+01     4.356E+01     4.050E+01   3.991E+03    1.275E+01
   1000.00    4.476E+01     4.277E+01     4.007E+01   2.569E+03    4.690E+00
   1200.00    4.428E+01     4.189E+01     3.963E+01   1.716E+03   -3.280E+00
   1500.00    4.345E+01     4.047E+01     3.902E+01   1.008E+03   -1.508E+01
   2000.00    4.211E+01     3.814E+01     3.824E+01   5.125E+02   -3.438E+01




                          THERMODYNAMIC ANALYSIS for REACTION
                      Rx           CF2CL        + CHF2        = CHF2CF2CL
                       Hf (Kcal/mol)  -66.000     -57.100    -215.600
                       S (cal/mol K)   68.300      61.700      79.600

dHr (kcal/mol)    (298K) =       -92.50     dHr avg (298., 1500. K) =       -91.77
dU (dE) (kcal/mol) (")   =       -91.91     dUr avg (298., 1500. K) =       -90.58
dSr (cal/mol K)  ( " )   =       -50.40     dSr avg (298., 1500. K) =       -49.21
dGr  (kcal/mol)  ( " )   =       -77.47     dGr avg (298., 1500. K) =       -47.52
         Af/Ar   ( " )   =    6.412E-07    Af/Ar avg (298., 1500. K ) = 3.512E-06

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -9.250E+01    -9.190E+01    -5.040E+01   6.454E-07   -7.738E+01
    400.00   -9.242E+01    -9.162E+01    -5.017E+01   9.653E-07   -7.235E+01
    500.00   -9.223E+01    -9.124E+01    -4.975E+01   1.488E-06   -6.735E+01
    600.00   -9.197E+01    -9.078E+01    -4.929E+01   2.259E-06   -6.240E+01
    800.00   -9.136E+01    -8.977E+01    -4.841E+01   4.692E-06   -5.263E+01
   1000.00   -9.071E+01    -8.872E+01    -4.769E+01   8.431E-06   -4.303E+01
   1200.00   -9.008E+01    -8.770E+01    -4.711E+01   1.351E-05   -3.355E+01
   1500.00   -8.915E+01    -8.617E+01    -4.642E+01   2.390E-05   -1.952E+01
   2000.00   -8.764E+01    -8.366E+01    -4.555E+01   4.945E-05    3.458E+00
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                         THERMODYNAMIC ANALYSIS for REACTION
                           Rx            2 CF2S      = C2F4
                         Hf (Kcal/mol)  -78.800    -157.400
                         S (cal/mol K)  115.000      71.800

dHr (kcal/mol)    (298K) =       -78.60     dHr avg (298., 1500. K) =       -77.99
dU (dE) (kcal/mol) (")   =       -78.01     dUr avg (298., 1500. K) =       -76.80
dSr (cal/mol K)   ( " )  =       -43.20     dSr avg (298., 1500. K) =       -42.18
dGr  (kcal/mol)   ( " )  =       -65.72     dGr avg (298., 1500. K) =       -40.07
        Af/Ar     ( " )  =    2.403E-05     Af/Ar avg (298., 1500. K ) = 1.212E-04

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   -7.860E+01   -7.800E+01   -4.320E+01   2.424E-05   -6.564E+01
   400.00   -7.849E+01   -7.769E+01   -4.288E+01   3.783E-05   -6.134E+01
   500.00   -7.833E+01   -7.734E+01   -4.253E+01   5.650E-05   -5.706E+01
   600.00   -7.813E+01   -7.694E+01   -4.217E+01   8.123E-05   -5.283E+01
   800.00   -7.765E+01   -7.606E+01   -4.148E+01   1.533E-04   -4.447E+01
  1000.00   -7.708E+01   -7.509E+01   -4.084E+01   2.642E-04   -3.624E+01
  1200.00   -7.643E+01   -7.405E+01   -4.025E+01   4.262E-04   -2.813E+01
  1500.00   -7.554E+01   -7.256E+01   -3.959E+01   7.439E-04   -1.616E+01
  2000.00   -7.451E+01   -7.054E+01   -3.899E+01   1.341E-03    3.469E+00
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                         THERMODYNAMIC ANALYSIS for REACTION
                Rx            CH2F2      + CL        = CHF2      + HCL
                Hf (Kcal/mol) -108.000    28.900    -57.100    -22.000
                S (cal/mol K)   59.000    39.500     61.700     44.600

dHr (kcal/mol)    (298K) =         0.00     dHr avg (298., 1500. K) =         0.07
dU (dE) (kcal/mol) (")   =         0.00     dUr avg (298., 1500. K) =         0.07
dSr (cal/mol K)   ( " )  =         7.80     dSr avg (298., 1500. K) =         8.05
dGr  (kcal/mol)   ( " )  =        -2.33     dGr avg (298., 1500. K) =        -7.17
        Af/Ar     ( " )  =    5.068E+01     Af/Ar avg (298., 1500. K ) = 5.758E+01

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    2.983E-03    2.983E-03    7.810E+00   5.093E+01   -2.340E+00
   400.00    1.375E-01    1.375E-01    8.201E+00   6.200E+01   -3.143E+00
   500.00    2.215E-01    2.215E-01    8.390E+00   6.820E+01   -3.974E+00
   600.00    2.584E-01    2.584E-01    8.459E+00   7.060E+01   -4.817E+00
   800.00    2.101E-01    2.101E-01    8.394E+00   6.835E+01   -6.505E+00
  1000.00    3.484E-02    3.484E-02    8.201E+00   6.201E+01   -8.166E+00
  1200.00   -2.232E-01   -2.232E-01    7.967E+00   5.511E+01   -9.783E+00
  1500.00   -6.856E-01   -6.856E-01    7.623E+00   4.637E+01   -1.212E+01
  2000.00   -1.538E+00   -1.538E+00    7.134E+00   3.624E+01   -1.581E+01
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                    THERMODYNAMIC ANALYSIS for REACTION
                 Rx             2 CL       = CL2       + H2
               Hf (Kcal/mol)   57.800      0.000      0.000
               S (cal/mol K)   79.000     53.300      0.000

dHr (kcal/mol)    (298K) =      -57.80    dHr avg (298., 1500. K) =      -58.40
dU (dE) (kcal/mol) (")   =      -57.21    dUr avg (298., 1500. K) =      -57.21
dSr (cal/mol K)   ( " )  =      -25.70    dSr avg (298., 1500. K) =      -26.84
dGr  (kcal/mol)   ( " )  =      -50.14    dGr avg (298., 1500. K) =      -34.27
         Af/Ar    ( " )  =   1.606E-01   Af/Ar avg (298., 1500. K ) = 2.722E-01

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -5.780E+01   -5.721E+01   -2.572E+01   1.603E-01   -5.009E+01
    400.00   -5.804E+01   -5.724E+01   -2.639E+01   1.521E-01   -4.748E+01
    500.00   -5.826E+01   -5.726E+01   -2.688E+01   1.490E-01   -4.482E+01
    600.00   -5.846E+01   -5.727E+01   -2.725E+01   1.484E-01   -4.211E+01
    800.00   -5.883E+01   -5.724E+01   -2.778E+01   1.509E-01   -3.660E+01
   1000.00   -5.917E+01   -5.719E+01   -2.817E+01   1.556E-01   -3.101E+01
   1200.00   -5.949E+01   -5.711E+01   -2.846E+01   1.612E-01   -2.534E+01
   1500.00   -5.995E+01   -5.697E+01   -2.880E+01   1.700E-01   -1.675E+01
   2000.00   -6.066E+01   -5.669E+01   -2.921E+01   1.844E-01   -2.246E+00
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                    THERMODYNAMIC ANALYSIS for REACTION
                    Rx           2 CF2CL     = C2F4CL2
                    Hf (Kcal/mol) -132.000    -219.000
                    S (cal/mol K)  136.600      86.000

dHr (kcal/mol)    (298K) =      -87.00    dHr avg (298., 1500. K) =      -85.97
dU (dE) (kcal/mol) (")   =      -86.41    dUr avg (298., 1500. K) =      -84.78
dSr (cal/mol K)   ( " )  =      -50.60    dSr avg (298., 1500. K) =      -48.80
dGr  (kcal/mol)   ( " )  =      -71.91    dGr avg (298., 1500. K) =      -42.10
         Af/Ar    ( " )  =   5.798E-07   Af/Ar avg (298., 1500. K ) = 4.330E-06

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -8.700E+01   -8.640E+01   -5.059E+01   5.870E-07   -7.182E+01
    400.00   -8.675E+01   -8.596E+01   -4.988E+01   1.115E-06   -6.680E+01
    500.00   -8.643E+01   -8.544E+01   -4.918E+01   1.991E-06   -6.184E+01
    600.00   -8.607E+01   -8.488E+01   -4.852E+01   3.322E-06   -5.696E+01
    800.00   -8.531E+01   -8.372E+01   -4.743E+01   7.661E-06   -4.737E+01
   1000.00   -8.458E+01   -8.259E+01   -4.661E+01   1.448E-05   -3.797E+01
   1200.00   -8.388E+01   -8.150E+01   -4.598E+01   2.391E-05   -2.871E+01
   1500.00   -8.287E+01   -7.989E+01   -4.523E+01   4.361E-05   -1.504E+01
   2000.00   -8.125E+01   -7.727E+01   -4.429E+01   9.317E-05    7.330E+00
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                           THERMODYNAMIC ANALYSIS for REACTION
                         Rx            2 CF2CL    = C2F4        + CL2
                         Hf (Kcal/mol) -132.000    -157.400      0.000
                         S (cal/mol K)  136.600      71.800     53.300

dHr (kcal/mol)    (298K) =       -25.40     dHr avg (298., 1500. K) =       -25.23
dU (dE) (kcal/mol) (")   =       -25.40     dUr avg (298., 1500. K) =       -25.23
dSr (cal/mol K)   ( " )  =       -11.50     dSr avg (298., 1500. K) =       -11.17
dGr  (kcal/mol)   ( " )  =       -21.97     dGr avg (298., 1500. K) =       -15.19
          Af/Ar   ( " )  =    3.065E-03    Af/Ar avg (298., 1500. K ) = 3.622E-03

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   -2.540E+01   -2.540E+01   -1.149E+01   3.076E-03   -2.195E+01
   400.00   -2.531E+01   -2.531E+01   -1.124E+01   3.500E-03   -2.082E+01
   500.00   -2.525E+01   -2.525E+01   -1.111E+01   3.730E-03   -1.970E+01
   600.00   -2.521E+01   -2.521E+01   -1.103E+01   3.879E-03   -1.859E+01
   800.00   -2.512E+01   -2.512E+01   -1.090E+01   4.136E-03   -1.640E+01
  1000.00   -2.499E+01   -2.499E+01   -1.076E+01   4.446E-03   -1.423E+01
  1200.00   -2.482E+01   -2.482E+01   -1.061E+01   4.809E-03   -1.209E+01
  1500.00   -2.453E+01   -2.453E+01   -1.039E+01   5.368E-03   -8.946E+00
  2000.00   -2.397E+01   -2.397E+01   -1.007E+01   6.297E-03   -3.834E+00
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                           THERMODYNAMIC ANALYSIS for REACTION
                         Rx            2 CF2CL    = C2F4CL      + CL
                         Hf (Kcal/mol) -132.000    -167.000     28.900
                         S (cal/mol K)  136.600      79.900     39.500

dHr (kcal/mol)    (298K) =        -6.10     dHr avg (298., 1500. K) =        -5.26
dU (dE) (kcal/mol) (")   =        -6.10     dUr avg (298., 1500. K) =        -5.26
dSr (cal/mol K)   ( " )  =       -17.20     dSr avg (298., 1500. K) =       -15.71
dGr  (kcal/mol)   ( " )  =        -0.97     dGr avg (298., 1500. K) =         8.86
          Af/Ar   ( " )  =    1.740E-04    Af/Ar avg (298., 1500. K ) = 3.679E-04

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   -6.096E+00   -6.096E+00   -1.719E+01   1.751E-04   -9.400E-01
   400.00   -5.875E+00   -5.875E+00   -1.655E+01   2.409E-04    7.469E-01
   500.00   -5.609E+00   -5.609E+00   -1.596E+01   3.245E-04    2.372E+00
   600.00   -5.319E+00   -5.319E+00   -1.543E+01   4.233E-04    3.942E+00
   800.00   -4.718E+00   -4.718E+00   -1.457E+01   6.538E-04    6.938E+00
  1000.00   -4.135E+00   -4.135E+00   -1.392E+01   9.072E-04    9.784E+00
  1200.00   -3.583E+00   -3.583E+00   -1.342E+01   1.169E-03    1.252E+01
  1500.00   -2.787E+00   -2.787E+00   -1.282E+01   1.575E-03    1.645E+01
  2000.00   -1.509E+00   -1.509E+00   -1.209E+01   2.282E-03    2.266E+01
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                          THERMODYNAMIC ANALYSIS for REACTION
                       Rx            CF2S        + H2          = CH2F2
                       Hf (Kcal/mol)  -39.400      0.000     -108.000
                       S (cal/mol K)   57.500     31.200       59.000

dHr (kcal/mol)    (298K) =       -68.60     dHr avg (298., 1500. K) =       -69.54
dU (dE) (kcal/mol) (")   =       -68.01     dUr avg (298., 1500. K) =       -68.35
dSr (cal/mol K)   ( " )  =       -29.70     dSr avg (298., 1500. K) =       -31.69
dGr  (kcal/mol)   ( " )  =       -59.74     dGr avg (298., 1500. K) =       -41.05
        Af/Ar     ( " )  =    2.145E-02    Af/Ar avg (298., 1500. K ) = 2.379E-02

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   -6.861E+01   -6.801E+01   -2.974E+01   2.119E-02   -5.969E+01
   400.00   -6.915E+01   -6.835E+01   -3.129E+01   1.293E-02   -5.663E+01
   500.00   -6.959E+01   -6.859E+01   -3.227E+01   9.858E-03   -5.345E+01
   600.00   -6.993E+01   -6.874E+01   -3.290E+01   8.604E-03   -5.019E+01
   800.00   -7.037E+01   -6.878E+01   -3.355E+01   8.307E-03   -4.353E+01
  1000.00   -7.052E+01   -6.854E+01   -3.372E+01   9.498E-03   -3.680E+01
  1200.00   -7.047E+01   -6.808E+01   -3.367E+01   1.170E-02   -3.006E+01
  1500.00   -7.021E+01   -6.723E+01   -3.348E+01   1.606E-02   -1.999E+01
  2000.00   -6.971E+01   -6.573E+01   -3.319E+01   2.479E-02   -3.318E+00
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                          THERMODYNAMIC ANALYSIS for REACTION
                   Rx            CF2S       + H2          = CHF2        + H
                   Hf (Kcal/mol)  -39.400     0.000      -57.100      52.100
                   S (cal/mol K)   57.500    31.200       61.700      27.300

dHr (kcal/mol)    (298K) =        34.40     dHr avg (298., 1500. K) =        34.47
dU (dE) (kcal/mol) (")   =        34.40     dUr avg (298., 1500. K) =        34.47
dSr (cal/mol K)   ( " )  =         0.30     dSr avg (298., 1500. K) =         0.33
dGr  (kcal/mol)   ( " )  =        34.31     dGr avg (298., 1500. K) =        34.18
        Af/Ar     ( " )  =    1.163E+00    Af/Ar avg (298., 1500. K ) = 1.178E+00

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    3.440E+01    3.440E+01    2.944E-01   1.160E+00    3.431E+01
   400.00    3.433E+01    3.433E+01    9.543E-02   1.049E+00    3.429E+01
   500.00    3.430E+01    3.430E+01    3.417E-02   1.017E+00    3.429E+01
   600.00    3.431E+01    3.431E+01    5.388E-02   1.027E+00    3.428E+01
   800.00    3.444E+01    3.444E+01    2.281E-01   1.122E+00    3.426E+01
  1000.00    3.468E+01    3.468E+01    4.910E-01   1.280E+00    3.419E+01
  1200.00    3.500E+01    3.500E+01    7.831E-01   1.483E+00    3.406E+01
  1500.00    3.548E+01    3.548E+01    1.143E+00   1.778E+00    3.377E+01
  2000.00    3.609E+01    3.609E+01    1.498E+00   2.125E+00    3.310E+01
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                         THERMODYNAMIC ANALYSIS for REACTION
                    Rx          CF2S       + H2        = CHFS       + HF
                    Hf (Kcal/mol)  -39.400     0.000     26.000     -65.300
                    S (cal/mol K)   57.500    31.200     53.300      41.500

dHr (kcal/mol)    (298K) =        0.10     dHr avg (298., 1500. K) =       -0.39
dU (dE) (kcal/mol) (")   =        0.10     dUr avg (298., 1500. K) =       -0.39
dSr (cal/mol K)  ( " )   =        6.10     dSr avg (298., 1500. K) =        5.23
dGr  (kcal/mol)  ( " )   =       -1.72     dGr avg (298., 1500. K) =       -5.09
          Af/Ar  ( " )   =   2.154E+01    Af/Ar avg (298., 1500. K ) = 1.391E+01

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    9.811E-02    9.811E-02    6.094E+00    2.147E+01   -1.730E+00
   400.00   -2.606E-02   -2.606E-02    5.739E+00    1.796E+01   -2.322E+00
   500.00   -1.826E-01   -1.826E-01    5.391E+00    1.508E+01   -2.878E+00
   600.00   -3.569E-01   -3.569E-01    5.073E+00    1.285E+01   -3.401E+00
   800.00   -7.151E-01   -7.151E-01    4.558E+00    9.913E+00   -4.361E+00
  1000.00   -1.037E+00   -1.037E+00    4.197E+00    8.268E+00   -5.235E+00
  1200.00   -1.297E+00   -1.297E+00    3.959E+00    7.335E+00   -6.049E+00
  1500.00   -1.664E+00   -1.664E+00    3.687E+00    6.395E+00   -7.195E+00
  2000.00   -2.330E+00   -2.330E+00    3.304E+00    5.274E+00   -8.938E+00
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                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx          CFCL       + H2        = CH2FCL
                       Hf (Kcal/mol)   -5.000     0.000     -62.600
                       S (cal/mol K)   65.500    31.200      63.200

dHr (kcal/mol)    (298K) =      -57.60     dHr avg (298., 1500. K) =      -58.36
dU (dE) (kcal/mol) (")   =      -57.01     dUr avg (298., 1500. K) =      -57.17
dSr (cal/mol K)  ( " )   =      -33.50     dSr avg (298., 1500. K) =      -35.19
dGr  (kcal/mol)  ( " )   =      -47.61     dGr avg (298., 1500. K) =      -26.72
          Af/Ar  ( " )   =   3.168E-03    Af/Ar avg (298., 1500. K ) = 4.089E-03

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   -5.761E+01   -5.701E+01   -3.354E+01    3.130E-03   -4.755E+01
   400.00   -5.812E+01   -5.733E+01   -3.502E+01    1.974E-03   -4.412E+01
   500.00   -5.851E+01   -5.752E+01   -3.589E+01    1.597E-03   -4.057E+01
   600.00   -5.879E+01   -5.759E+01   -3.639E+01    1.485E-03   -3.695E+01
   800.00   -5.908E+01   -5.749E+01   -3.682E+01    1.597E-03   -2.962E+01
  1000.00   -5.911E+01   -5.712E+01   -3.686E+01    1.958E-03   -2.225E+01
  1200.00   -5.896E+01   -5.658E+01   -3.673E+01    2.511E-03   -1.488E+01
  1500.00   -5.853E+01   -5.555E+01   -3.641E+01    3.679E-03   -3.912E+00
  2000.00   -5.766E+01   -5.368E+01   -3.591E+01    6.314E-03    1.417E+01
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                          THERMODYNAMIC ANALYSIS for REACTION
                  Rx            CFCL        + H2          = CH2F        + CL
                 Hf (Kcal/mol)   -5.000      0.000       -8.000      28.900
                 S (cal/mol K)   65.500     31.200       55.300      39.500

dHr (kcal/mol)    (298K) =        25.90     dHr avg (298., 1500. K) =       25.40
dU (dE) (kcal/mol) (")  =        25.90     dUr avg (298., 1500. K) =       25.40
dSr (cal/mol K)   ( " )  =        -1.90     dSr avg (298., 1500. K) =       -2.97
dGr  (kcal/mol)   ( " )  =        26.47     dGr avg (298., 1500. K) =       28.07
         Af/Ar    ( " )  =   3.843E-01    Af/Ar avg (298., 1500. K ) = 2.248E-01

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    2.589E+01    2.589E+01   -1.920E+00   3.806E-01   2.647E+01
   400.00    2.560E+01    2.560E+01   -2.768E+00   2.483E-01   2.671E+01
   500.00    2.536E+01    2.536E+01   -3.312E+00   1.889E-01   2.701E+01
   600.00    2.517E+01    2.517E+01   -3.658E+00   1.587E-01   2.736E+01
   800.00    2.495E+01    2.495E+01   -3.984E+00   1.346E-01   2.813E+01
  1000.00    2.491E+01    2.491E+01   -4.029E+00   1.316E-01   2.894E+01
  1200.00    2.501E+01    2.501E+01   -3.938E+00   1.378E-01   2.974E+01
  1500.00    2.533E+01    2.533E+01   -3.704E+00   1.550E-01   3.088E+01
  2000.00    2.595E+01    2.595E+01   -3.345E+00   1.857E-01   3.264E+01
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                          THERMODYNAMIC ANALYSIS for REACTION
                  Rx           CFCL         + H2          = CHFS        + HCL
                 Hf (Kcal/mol)   -5.000      0.000       26.000     -22.000
                 S (cal/mol K)   65.500     31.200       53.300      44.600

dHr (kcal/mol)    (298K) =         9.00     dHr avg (298., 1500. K) =        8.47
dU (dE) (kcal/mol) (")  =         9.00     dUr avg (298., 1500. K) =        8.47
dSr (cal/mol K)   ( " )  =         1.20     dSr avg (298., 1500. K) =        0.19
dGr  (kcal/mol)   ( " )  =         8.64     dGr avg (298., 1500. K) =        8.30
         Af/Ar    ( " )  =    1.829E+00   Af/Ar avg (298., 1500. K ) = 1.101E+00

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    8.996E+00    8.996E+00    1.187E+00   1.817E+00   8.640E+00
   400.00    8.789E+00    8.789E+00    5.920E-01   1.347E+00   8.553E+00
   500.00    8.591E+00    8.591E+00    1.497E-01   1.078E+00   8.517E+00
   600.00    8.406E+00    8.406E+00   -1.893E-01   9.091E-01   8.519E+00
   800.00    8.081E+00    8.081E+00   -6.590E-01   7.177E-01   8.608E+00
  1000.00    7.825E+00    7.825E+00   -9.453E-01   6.214E-01   8.771E+00
  1200.00    7.640E+00    7.640E+00   -1.115E+00   5.705E-01   8.978E+00
  1500.00    7.479E+00    7.479E+00   -1.237E+00   5.367E-01   9.334E+00
  2000.00    7.305E+00    7.305E+00   -1.338E+00   5.101E-01   9.980E+00
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                          THERMODYNAMIC ANALYSIS for REACTION
                       Rx            CHFS        + H2          = CH3F
                      Hf (Kcal/mol)   26.000      0.000     -55.900
                      S (cal/mol K)   53.300     31.200      53.300

dHr (kcal/mol)    (298K) =      -81.90    dHr avg (298., 1500. K) =      -82.90
dU (dE) (kcal/mol) (")   =      -81.31    dUr avg (298., 1500. K) =      -81.71
dSr (cal/mol K)  ( " )   =      -31.20    dSr avg (298., 1500. K) =      -33.30
dGr  (kcal/mol)  ( " )   =      -72.60    dGr avg (298., 1500. K) =      -52.96
       Af/Ar     ( " )   =   1.008E-02   Af/Ar avg (298., 1500. K ) = 1.055E-02

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00  -8.191E+01   -8.132E+01   -3.124E+01   9.951E-03   -7.254E+01
   400.00  -8.247E+01   -8.168E+01   -3.287E+01   5.850E-03   -6.933E+01
   500.00  -8.294E+01   -8.194E+01   -3.390E+01   4.340E-03   -6.599E+01
   600.00  -8.330E+01   -8.211E+01   -3.457E+01   3.717E-03   -6.256E+01
   800.00  -8.377E+01   -8.218E+01   -3.526E+01   3.504E-03   -5.557E+01
  1000.00  -8.396E+01   -8.197E+01   -3.547E+01   3.944E-03   -4.849E+01
  1200.00  -8.393E+01   -8.155E+01   -3.545E+01   4.782E-03   -4.139E+01
  1500.00  -8.366E+01   -8.068E+01   -3.525E+01   6.599E-03   -3.079E+01
  2000.00  -8.290E+01   -7.892E+01   -3.482E+01   1.096E-02   -1.327E+01
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                          THERMODYNAMIC ANALYSIS for REACTION
                 Rx            CHFS        + H2         = CH3        + F
                Hf (Kcal/mol)   26.000      0.000       34.800      18.900
                S (cal/mol K)   53.300     31.200       46.300      37.900

dHr (kcal/mol)    (298K) =       27.70    dHr avg (298., 1500. K) =       27.64
dU (dE) (kcal/mol) (")   =       27.70    dUr avg (298., 1500. K) =       27.64
dSr (cal/mol K)  ( " )   =       -0.30    dSr avg (298., 1500. K) =       -0.46
dGr  (kcal/mol)  ( " )   =       27.79    dGr avg (298., 1500. K) =       28.05
       Af/Ar     ( " )   =   8.599E-01   Af/Ar avg (298., 1500. K ) = 7.923E-01

   T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00   2.770E+01    2.770E+01   -3.041E-01   8.581E-01    2.779E+01
   400.00   2.764E+01    2.764E+01   -4.768E-01   7.867E-01    2.783E+01
   500.00   2.759E+01    2.759E+01   -5.807E-01   7.466E-01    2.788E+01
   600.00   2.756E+01    2.756E+01   -6.367E-01   7.258E-01    2.794E+01
   800.00   2.755E+01    2.755E+01   -6.512E-01   7.206E-01    2.807E+01
  1000.00   2.762E+01    2.762E+01   -5.829E-01   7.458E-01    2.820E+01
  1200.00   2.774E+01    2.774E+01   -4.684E-01   7.900E-01    2.830E+01
  1500.00   2.802E+01    2.802E+01   -2.605E-01   8.771E-01    2.841E+01
  2000.00   2.863E+01    2.863E+01    8.499E-02   1.044E+00    2.846E+01
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                        THERMODYNAMIC ANALYSIS for REACTION
                 Rx             CHFS        + H2          = CH2F        + H
                Hf (Kcal/mol)   26.000       0.000        -8.000      52.100
                S (cal/mol K)   53.300      31.200        55.300      27.300

dHr (kcal/mol)    (298K) =        18.10    dHr avg (298., 1500. K) =        18.03
dU (dE) (kcal/mol) (")  =         18.10    dUr avg (298., 1500. K) =        18.03
dSr (cal/mol K)   ( " )  =        -1.90    dSr avg (298., 1500. K) =        -2.15
dGr  (kcal/mol)   ( " )  =        18.67    dGr avg (298., 1500. K) =        19.97
          Af/Ar   ( " )  =    3.843E-01   Af/Ar avg (298., 1500. K ) = 3.387E-01

   T (K)  dH(Kcal/mol)   dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    1.810E+01     1.810E+01    -1.910E+00   3.825E-01   1.867E+01
   400.00    1.797E+01     1.797E+01    -2.289E+00   3.160E-01   1.888E+01
   500.00    1.788E+01     1.788E+01    -2.478E+00   2.873E-01   1.912E+01
   600.00    1.784E+01     1.784E+01    -2.550E+00   2.771E-01   1.937E+01
   800.00    1.789E+01     1.789E+01    -2.489E+00   2.858E-01   1.988E+01
  1000.00    1.807E+01     1.807E+01    -2.294E+00   3.152E-01   2.036E+01
  1200.00    1.833E+01     1.833E+01    -2.056E+00   3.553E-01   2.080E+01
  1500.00    1.879E+01     1.879E+01    -1.714E+00   4.221E-01   2.136E+01
  2000.00    1.960E+01     1.960E+01    -1.246E+00   5.342E-01   2.209E+01
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                        THERMODYNAMIC ANALYSIS for REACTION
                 Rx             CHFS        + H2          = CH2S        + HF
                Hf (Kcal/mol)   26.000       0.000       101.400     -65.300
                S (cal/mol K)   53.300      31.200        44.100      41.500

dHr (kcal/mol)    (298K) =        10.10    dHr avg (298., 1500. K) =        10.03
dU (dE) (kcal/mol) (")  =         10.10    dUr avg (298., 1500. K) =        10.03
dSr (cal/mol K)   ( " )  =         1.10    dSr avg (298., 1500. K) =         1.00
dGr  (kcal/mol)   ( " )  =         9.77    dGr avg (298., 1500. K) =         9.13
          Af/Ar   ( " )  =    1.740E+00   Af/Ar avg (298., 1500. K ) = 1.655E+00

   T (K)  dH(Kcal/mol)   dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
   300.00    1.010E+01     1.010E+01     1.101E+00   1.741E+00   9.770E+00
   400.00    1.011E+01     1.011E+01     1.123E+00   1.760E+00   9.658E+00
   500.00    1.009E+01     1.009E+01     1.095E+00   1.735E+00   9.547E+00
   600.00    1.007E+01     1.007E+01     1.047E+00   1.694E+00   9.440E+00
   800.00    9.997E+00     9.997E+00     9.458E-01   1.610E+00   9.241E+00
  1000.00    9.925E+00     9.925E+00     8.647E-01   1.545E+00   9.060E+00
  1200.00    9.865E+00     9.865E+00     8.103E-01   1.504E+00   8.893E+00
  1500.00    9.809E+00     9.809E+00     7.676E-01   1.472E+00   8.657E+00
  2000.00    9.781E+00     9.781E+00     7.505E-01   1.459E+00   8.280E+00
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                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx            CF2CL2      = CFCL2      + F
                     Hf (Kcal/mol) -114.100     -17.500     18.900
                     S (cal/mol K)   72.000      69.900     37.900

dHr (kcal/mol)    (298K) =      115.50    dHr avg (298., 1500. K) =       115.60
dU (dE) (kcal/mol) (")   =      114.91    dUr avg (298., 1500. K) =       114.41
dSr (cal/mol K)  ( " )   =       35.80    dSr avg (298., 1500. K) =        36.10
dGr  (kcal/mol)  ( " )   =      104.83    dGr avg (298., 1500. K) =        83.14
         Af/Ar   ( " )   =   1.004E+03   Af/Ar avg (298., 1500. K ) = 3.880E+02

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00    1.155E+02    1.149E+02    3.581E+01    1.004E+03    1.048E+02
   400.00    1.156E+02    1.149E+02    3.623E+01    9.284E+02    1.012E+02
   500.00    1.157E+02    1.147E+02    3.641E+01    8.122E+02    9.752E+01
   600.00    1.158E+02    1.146E+02    3.647E+01    6.981E+02    9.388E+01
   800.00    1.157E+02    1.142E+02    3.644E+01    5.177E+02    8.659E+01
  1000.00    1.157E+02    1.137E+02    3.636E+01    3.977E+02    7.930E+01
  1200.00    1.156E+02    1.132E+02    3.628E+01    3.170E+02    7.204E+01
  1500.00    1.154E+02    1.124E+02    3.615E+01    2.376E+02    6.118E+01
  2000.00    1.151E+02    1.111E+02    3.595E+01    1.618E+02    4.315E+01
```

```
                         THERMODYNAMIC ANALYSIS for REACTION
                       Rx            CLF         = CL         + F
                     Hf (Kcal/mol)  -12.000      28.900     18.900
                     S (cal/mol K)   52.000      39.500     37.900

dHr (kcal/mol)    (298K) =       59.80    dHr avg (298., 1500. K) =        60.43
dU (dE) (kcal/mol) (")   =       59.21    dUr avg (298., 1500. K) =        59.24
dSr (cal/mol K)  ( " )   =       25.40    dSr avg (298., 1500. K) =        26.62
dGr  (kcal/mol)  ( " )   =       52.23    dGr avg (298., 1500. K) =        36.50
         Af/Ar   ( " )   =   5.356E+00   Af/Ar avg (298., 1500. K ) = 3.276E+00

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)    dG(Kcal/mol)
   300.00    5.981E+01    5.921E+01    2.542E+01    5.368E+00    5.218E+01
   400.00    6.006E+01    5.927E+01    2.616E+01    5.861E+00    4.960E+01
   500.00    6.030E+01    5.930E+01    2.669E+01    6.097E+00    4.695E+01
   600.00    6.051E+01    5.932E+01    2.707E+01    6.182E+00    4.427E+01
   800.00    6.089E+01    5.930E+01    2.763E+01    6.124E+00    3.879E+01
  1000.00    6.124E+01    5.925E+01    2.801E+01    5.942E+00    3.323E+01
  1200.00    6.156E+01    5.917E+01    2.830E+01    5.731E+00    2.759E+01
  1500.00    6.200E+01    5.902E+01    2.863E+01    5.418E+00    1.905E+01
  2000.00    6.270E+01    5.872E+01    2.903E+01    4.973E+00    4.628E+00
```

```
                          THERMODYNAMIC ANALYSIS for REACTION
                     Rx           H2         + F          = HF         + H
                      (Kcal/mol)    0.000      18.900      -65.300      52.100
                    S (cal/mol K)  31.200      37.900       41.500      27.300

dHr (kcal/mol)    (298K) =      -32.10     dHr avg (298., 1500. K) =      -32.19
dU (dE) (kcal/mol) (")  =      -32.10     dUr avg (298., 1500. K) =      -32.19
dSr (cal/mol K)   ( " )  =       -0.30     dSr avg (298., 1500. K) =       -0.46
dGr  (kcal/mol)   ( " )  =      -32.01     dGr avg (298., 1500. K) =      -31.77
         Af/Ar    ( " )  =   8.599E-01    Af/Ar avg (298., 1500. K ) = 7.922E-01

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)   (Af/Ar)   dG(Kcal/mol)
    300.00   -3.210E+01   -3.210E+01   -3.015E-01   8.592E-01   -3.201E+01
    400.00   -3.213E+01   -3.213E+01   -3.752E-01   8.279E-01   -3.198E+01
    500.00   -3.216E+01   -3.216E+01   -4.400E-01   8.014E-01   -3.194E+01
    600.00   -3.219E+01   -3.219E+01   -4.964E-01   7.789E-01   -3.189E+01
    800.00   -3.225E+01   -3.225E+01   -5.883E-01   7.437E-01   -3.178E+01
   1000.00   -3.231E+01   -3.231E+01   -6.588E-01   7.178E-01   -3.165E+01
   1200.00   -3.237E+01   -3.237E+01   -7.145E-01   6.980E-01   -3.152E+01
   1500.00   -3.246E+01   -3.246E+01   -7.803E-01   6.752E-01   -3.129E+01
   2000.00   -3.260E+01   -3.260E+01   -8.598E-01   6.488E-01   -3.088E+01
```

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CHAPTER 1
INTRODUCTION

Methanol has played an important role in industry and environmental fields. It is of "widespread interest as an additive and an alternative to conventional transportation fuels"(1) because of potential reductions in pollutant emissions. Specifically, methanol is indicated to aid in reduction of unburned hydrocarbons, which enhance ozone production and photo-chemical smog formation. Methanol is easily produced from petroleum and non-petroleum resources such as coal, wood etc. It is also an "important intermediate species formed in the combustion of the high-octane-number fuel additive MTBE".(1)

The oxidation and pyrolysis of gas phase methanol has been studied widely over the past half century by several different methods: diffusion flame, shock-tube and static or flow reactors. Study on pyrolysis and oxidation of methanol by diffusion flames was reported by Smith and Gordon(2) in 1956. They used a quartz probe sampling technique to extract stable species from the flame regions. The samples were analyzed with a consolidated analytical mass spectrometer. The temperature measured in the flames varied from about 200 C at the wick to about 1400 C at the tip and edge of the flame. From the analysis of these products, they indicated that "the mechanism of burning involves a pyrolysis of the alcohol followed by an oxidation of the pyrolysis products. The pyrolysis of methanol was free radical induced by the small percentage of O_2 which diffuses in near the base of the burner, and H or OH radicals which come from the reaction of O_2 an H_2".

Even earlier studies were reported by Fletcher(3) in 1934 and Someno(4) in 1942. Fletcher studied the pyrolysis of methanol in a static system at pressure less than atmospheric and temperatures between 626-730C. He proposed that the pyrolysis occurs in two stages; the first stage gives formaldehyde and hydrogen, and the formaldehyde is pyrolyzed in the second stage to CO and H_2.

Someno(4) studied the thermal decomposition and slow combustion of monohydric alcohols. He worked in quartz vessels at sub-Atmospheric pressure and temperatures up to 650 C. Identification of products was made spectrographically (IR and visible spectroscopy). Ketones, aldehydes, ketenes and unsaturated hydrocarbons were found in the products. Formaldehyde was found only in the products from the slow oxidation.

A shock-tube study of the ignition of methanol with oxygen was made by Cooke and co-workers(5). The experiment was performed in stoichiometric mixtures of methanol and oxygen diluted with 95% argon at shock generated temperatures from 1300-1600 C, pressure range 200-300 Torr. They found methanol was less reactive than ethanol. In the high temperature conditions, the following reactions were reported to evolve:

$CH_3OH = CH_3 + OH$

$CH_3OH = CH_2OH + H$

with fission of the O-H bond less likely to occur.

Bowman(6) also studied the high temperature oxidation of methanol behind reflected shock waves in temperature range 1272-1907 C. The reaction of methanol-oxygen mixtures, dilute in argon, was initiated by reflected shock waves in a shock tube. The concentrations of O, OH, H_2O and CO were measured using various spectroscopic techniques. He said: "Following shock-heating, oxidation appears to proceed through two distinct phases: an induction period, in which the concentrations of radical species and water increase rapidly with little change in temperature; followed by exothermic reaction with the concentration of radical species and water slowly approaching equilibrium values". He proposed a small reaction mechanism and indicated that the significant reactions include "thermal decomposition of methanol, attack of radicals O, OH and H on methanol and thermal decomposition of the important radical intermediate CH_2OH".

Aronowitz et al(7) reported methanol oxidation results ($CH_3OH/O_2/N_2$) in an adiabatic, turbulent flow reactor, having plug flow characteristics that allowed for chemical sampling with high spatial resolution. Experiments were performed at atmospheric pressure, in the temperature and equivalence ratio ranges of 680-880 C and

0.03-3.16 respectively. He found "major products included CO, CO_2 and H_2O with small amounts of H_2 and CH_2O. Trace quantities of hydrocarbon products were observed at the more fuel rich equivalence ratios". He specifically emphasized the importance of HO_2 chemistry to the oxidation of methanol in this temperature region and atmospheric pressure which Westbrook et al(8) had previously indicated that hydroperoxyl radicals can be important in high temperature chemistry.

A study of methanol combustion in laminar flames was made by Vandooren and Van Tiggelen (9) in 1981. A detailed mechanism and rate constants of elementary steps for lean methanol flames burning at 40 Torr were investigated by using molecular beam sampling coupled with mass spectrometric analysis. They reported that "about 70% of the fuel molecules were consumed by reaction with hydroxyl radical and 30% by reaction with hydrogen atom". The main initial product was CH_2OH which reacts further, principally with the molecular oxygen. "The occurrence of electronically excited CH_2O was detected and attributed to highly exothermic reactions between CH_2OH and O, H or OH radicals". They indicated that the formaldehyde conversion occurred via reactions with radicals, mainly OH, or by unimolecular (low pressure limit) decomposition process.

Important elementary reactions of CH_2OH with molecular and atomic oxygen in the methanol oxidation system was studied by Grotheer et al(10) using direct discharge flow reactor in the temperature range between 25-400 C at pressure around 1 mbar. Radical profiles were monitored by a low energy-electron impact ionization mass spectrometer. The rate coefficient was measured for the CH_2OH + O reaction. They found that "the $CH_2OH + O_2$ reaction exhibits a strong non-Arrhenius behavior".

Recent studies on methanol oxidation and pyrolysis are also reported by Norton and Dryer(1,11,12). In 1989, they performed the methanol oxidation experiment using a turbulent flow reactor at equivalence ratios of 0.6-1.6 and initial temperatures of 752-817C at atmospheric pressure. They found "at intermediate extents of reaction, a marked deceleration in chemical reaction rate was observed to effect a `plateau' in the energy release and species concentration profiles". They communicated that "experimental observations on the intermediate-temperature flow reactor oxidation of methanol, combined with their updated modeling, yield an improved view of some important details of methanol chemistry under flow reactor conditions". These new insights "concern the importance of HO_2 radicals during all stages of fuel decay, the causes of a chemical deceleration before the CO peak under fuel-rich conditions, and the origin of small amounts of CH_4 and early CO_2". They indicate that "the existing and widely-used mechanism(13) for methanol oxidation is in error" and should be updated.

Norton and Dryer presented a kinetic mechanism(11) for methanol pyrolysis which matched multiple sets of experimental data from static, flow, and shock tube reactors, covering temperatures of 700 to 1720 C and pressures of 0.3 to 1 atmosphere. They indicated "the model results were highly sensitive to the rates of unimolecular fuel decomposition and of various chain termination reactions that remove CH_2OH and H radicals, as well as to experimental temperature uncertainties. The fuel decomposition reaction $CH_3OH = CH_2OH + H$, which had previously been included only in mechanisms for high temperature conditions, was found to have a significant effect at low temperatures as well, through radical combination..., The reaction:

$CH_3O + CO = CH_3 + CO_2$

rather than:

$CH_3OH + H = CH_3 + H_2O$,

was found to be the dominant source of CH_3 at low temperatures. The reverse of $CH_3 + OH = CH_2OH + H$ was important to CH_3 production at high temperatures".

One of the principle problems with the Norton-Dryer mechanism is that it does not consider pressure effects of the important unimolecular and bimolecular reactions. For example, the pressure dependence of the decomposition steps below are not fully included or analyzed for the different systems:

$CH_3OH \text{ --> } CH_3 + OH$

CH_3OH --> $CH_2OH + H$

and more importantly the correct path way analysis for

$CH_2OH + O_2$->[$.OOCH_2OH$]# -> $.OCH_2OH + O$

-> [HOOC.HOH]# -> $HCO_2 + OH$

-> [$HOOCH_2O.$]# -> $CH_2O + HO_2$

-> $CH_2OH + O_2$ (Reverse - No Rxn)

-> $.OOCH_2OH$ (Stabilization)

as well as reactions of $CH_2O + O_2$ to form [CH_3OOO]# and its further reactions.

An example is that the Norton-Dryer Mechanism does nothing to properly incorporate the negative temperature dependence, pressure effects and correct reaction pathways that account for the observations by Grotheer.

These pressure dependent reactions are very important in formation of CO and CO_2. It is specifically important to evaluate properly the CO_2 formation path from HCO_2 formation in the reaction of $CH_2OH + O_2$ shown above. This reaction proceeds through a chemically activated intermediate, which can be stabilized, dissociate back to reactants (no reaction) or react via isomerization to either HOOC.HOH or $HOOCH_2O$. isomers; both of which will immediately dissociate to lower energy products as shown above.

Further items missing from the present mechanisms include pathways for formation of higher molecular weight products, such as the formation of methyl ethers, which we observe and report for the first time in this study.

This study presents experimental data on the decomposition of methanol in several different reaction environments - fuel lean to fuel rich at temperatures between 600 and 850 C. Methane fuel is also added in several of the systems studied in order to provide experimental data on the use of methanol as an additive in motor vehicle fuels. This data will be a basis, along with that in the literature, on the validation of a model, for methanol oxidation and pyrolysis that can be used for evaluation and simulation of methanol combustion under atmospheric conditions as well as in compression engines or turbines, where pressures are very different from atmospheric.

CHAPTER 2
EXPERIMENTAL METHOD

2.1 Experimental Apparatus

A diagram of the experimental apparatus is shown in Figure 2.1. The oxidation and pyrolysis of methanol with methane/oxygen was analyzed by varying the temperature, residence time and reactant ratios. The temperature range of 500 to 850 C and residence time range of 0.3 to 2.0 seconds were studied in three reaction ratios in a high temperature tubular flow reactor which operated isothermally at 1 atm pressure in this study.

The carrier gas (Ar) was passed through a saturation bubbler set which contained the liquid methanol held at OC using an ice bath. A second argon flow stream (after the bubbler) was used as make-up gas in order to achieve the desired mole fraction between reagents. Methane and oxygen were then added to the CH_3OH/Ar flow as required. Before entering the reactor, the feed mixture could be transferred directly from the bubbler to the GC sampling valve via a by-pass line. This was necessary to determine the GC peak area that corresponded to the input initial concentration of the reagents without going through the high temperature reactor. The mixtures were preheated to about 100 C to improve the reactor temperature control. A small fraction of the reactor effluent gas passed through a heated line to the GC sampler and exhaust. All gas lines to the analytical equipment were held at about 100 C to limit condensation.

A quartz tube of 10.5 mm ID was chosen as the reactor for minimal effect of reactor wall and good control of the temperature profile and residence time. Three reactant ratio sets which represent the stoichiometric, fuel rich and fuel lean conditions were studied.

I. $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 3.5 : 94.5$ $\phi = 1.0$

II. $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 2 : 96$ $\phi = 1.75$

III. $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 5 : 93$ $\phi = 0.7$

2.2 Temperature Control and Measurement

A quartz reactor tube of 10.5mm i.d. was housed within a three zone electric tube furnace (Lindberg electric tube furnace) of 46 cm length equipped with three independent temperature controllers (Omega Engineering, Inc.) in order to adjust the operation condition nearly isothermally (± 5 C). The actual temperature profile of the tubular reactor was obtained using type K thermocouple probe moved coaxially within the reactor. The temperature measurements were performed with a steady flow rate of Argon gas through the reactor tube. The temperature profiles with tight temperature control obtained as shown in Figure 2.2 were isothermal to within ± 5 C for 39 cm for all temperature ranges of this study. Figure 2.3 shows isothermal temperature profiles at several temperatures.

2.3 Quantitative Analysis of Reaction Products

A Varian 3700 on-line gas chromatograph with flame ionization detector was used to determine the concentration of the reaction products. The line between reactor exit and GC were heated to 100 C to limit condensation. The channel A of the GC used a 1.8 meter long by 1/8" O.D. stainless steel tube packed with 1% Alltech AT-1000 on Graphpac GB as the column to analyze heavy molecular compounds. Channel B used 1.8 meter long by 1/8" O.D. stainless steel column packed with Porapak T 80/100 mesh to light molecular compounds: methane, formaldehyde, carbon monoxide, and carbon dioxide.

A six port gas sample valve with 1.0 ml volume sample loop was maintained at 170 C and 1 atm pressure. Chromatogram peak integration was performed with a Varian 4270 integrator/plotter. Table 2.1 shows the retention time of compound and peak identification.

A catalytic convertor which contained 5% ruthenium on alumina catalyst was placed between column B effluent and the FID of channel B. CO and CO_2 separated by column B was then reacted with H_2 in the convertor which was maintained at 330 C to form CH_4 that can be detected by FID B.

Calibration of the flame ionization detector to obtain appropriate molar response factors was done by injecting a known quantity of the relevant compound such as CH_4, CO, CO_2, etc., then measuring the corresponding response area. The relative response factor was determined for compounds shown in Table 2.2. The sensitivity of flame ionization detector corresponds to the number of carbons. We find that the response factors for all C_1 compounds is similar, and the response factor of C_2 compounds are nearly twice the response of the C_1 compounds.

2.4 Qualitative Analysis of Reaction Products

We employed GC/MS (Hewlett Packard 5988) with a 50 m length, 0.22 mm ID methyl-silicone capillary column to check the GC identification. Evacuated 25 ml stainless steel sampling cylinders were used to collect the reactor effluent gas. Injection of the samples into the GC/MS made use of a six port gas sampling valve.

2.5 Detailed Reaction Model Interpretation and Integration by CHEMKIN program

CHEMKIN is a package of FORTRAN programs which are designed to facilitate a chemist's interaction with the computer in modeling chemical kinetics. The CHEMKIN package(14) is composed of four important species :

(i) The INTERPRETER is a program which first reads the user's symbolic description of the reaction mechanism.

(ii) The Thermodynamic Data Base has exactly the same format as that used by the NASA complex chemical equilibrium code by Gordon and McBride(15).

(iii) The Linking File is ready by an initialization subroutine which is called from the user code, which contains all the current information on the element, species, and reaction mechanism.

(iv) The Gas-Phase Subroutine Library, which are called to return information on the elements, species, reactions, equation of state, thermodynamic properties, chemical reduction rates, sensitivity parameters, derivatives of chemical production rates, and derivatives of thermodynamic properties. Generally the input to these routines will be the state variables of the gas--pressure or density, temperature, and the species composition. All routine can be called with the species composition defined as mass fractions, mole fractions, or molar concentration.

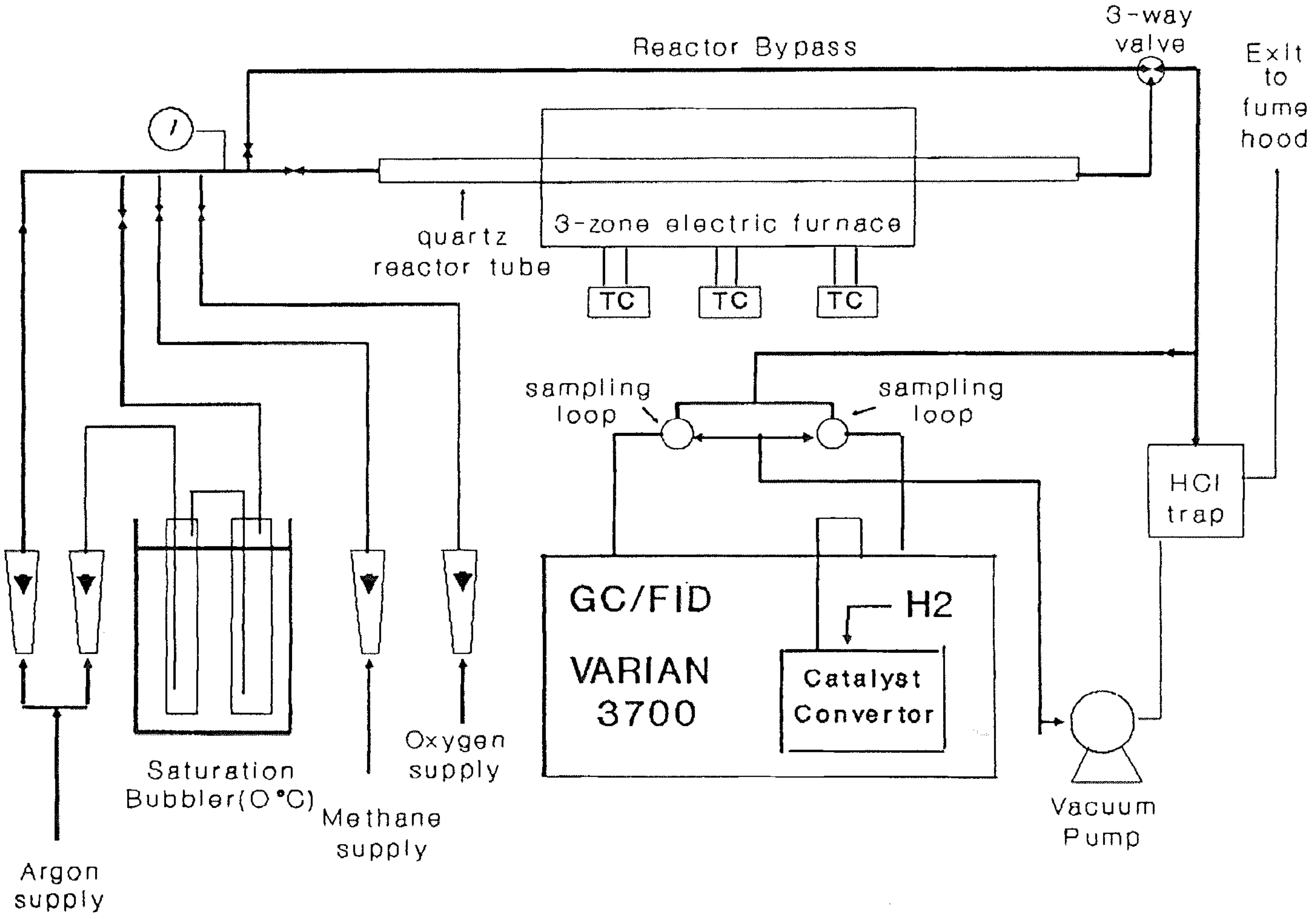


Figure 2.1 Experimental System

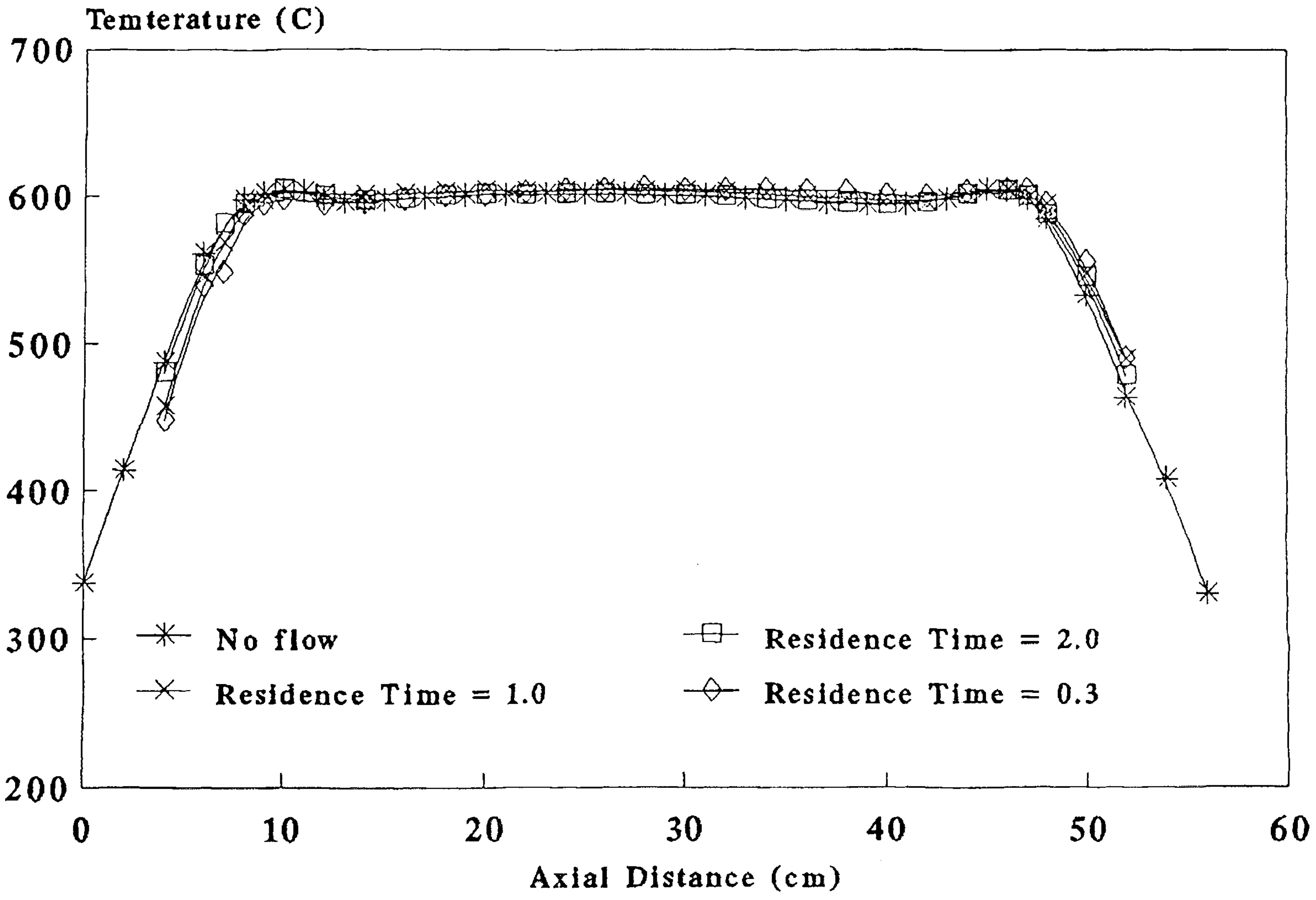


Fig 2.2 Reactor Temperature Profiles with Tight Control

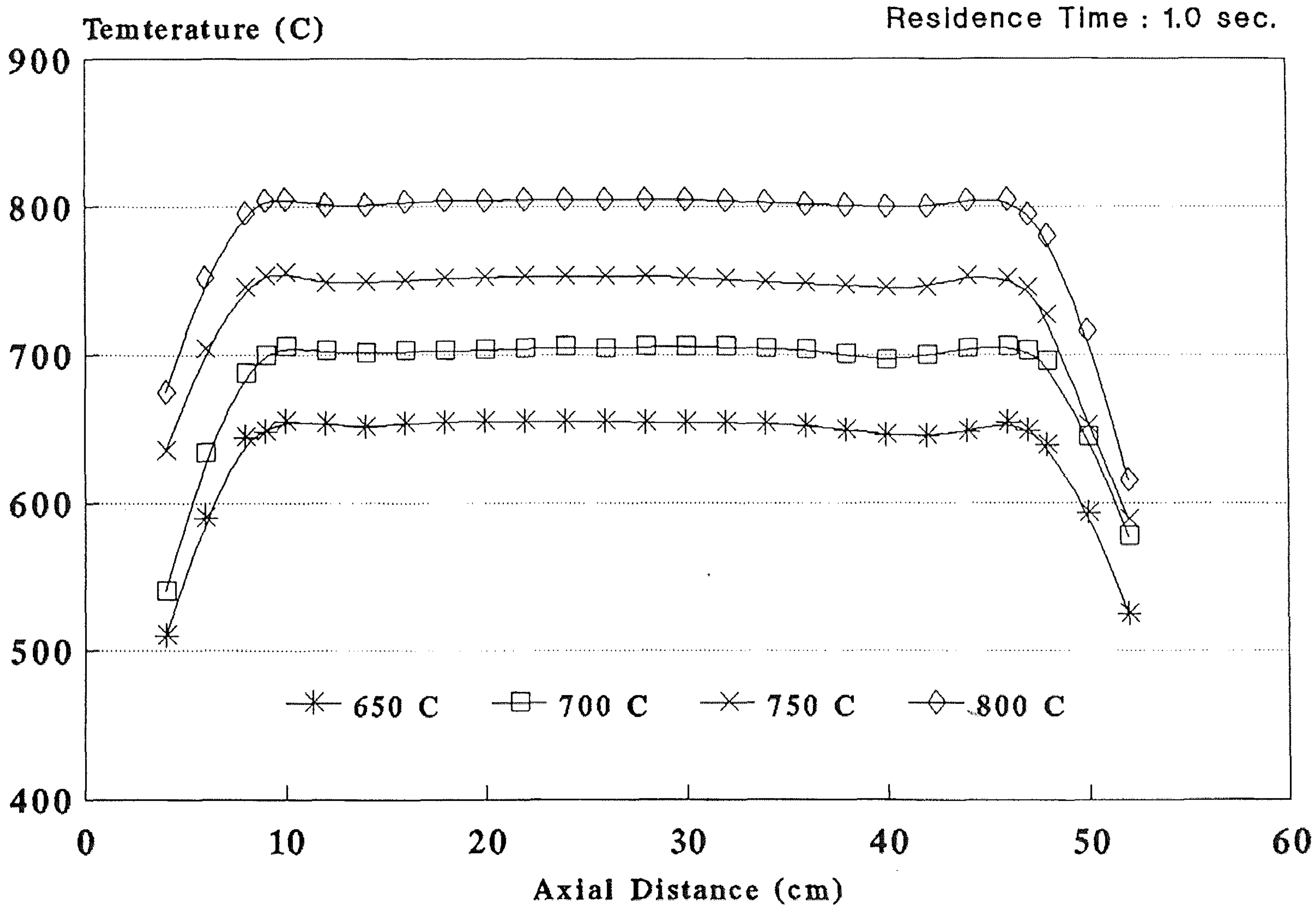


Fig 2.3 Reactor Temperature Profiles with Tight Control

Table 2.1 Average Retention Time

Porapak T

Compound	Average Retention Time (min)
CO	0.60
CH_4	0.90
CO_2	3.30
C_2H_4	3.80
C_2H_6	4.40
CH_2O	11.40
CH_3OCH_3	14.20
CH_3OH	15.80
$CH_3OCH_2OCH_3$	21.60

Alltech 1000

Compound	Average Retention Time (min)
CH_4	1.50
C_2H_4	2.50
C_2H_6	3.00
CH_3OH	5.90

Table 2.2 Relative Response Factor (RRF)

Porapak T

Compound	Relative Response Factor (RRF)
CO	0.72
CH_4	1.00
CO_2	0.05
C_2H_4	1.82
C_2H_6	1.87
CH_2O	0.95
CH_3OCH_3	1.90
CH_3OH	0.95
$CH_3OCH_2OCH_3$	2.85

Alltech 1000

Rentention Time	Relative Response Factor (RRF)
CH_4	1.00
C_2H_4	2.02
C_2H_6	2.06
CH_3OH	0.55

Corrected Area = Measured Area / RRF

CHAPTER 3
RESULT AND DISCUSSION

3.1 Reaction of Methanol in $CH_4/O_2/Ar$ Atmosphere

Experimental results on decay of methanol and methane are shown in Figures 3.1-3.6, which plot the normalized concentration (C/Co) as a function of reaction time and temperature in the three reaction environments. Figure 3.7 and 3.8 show methanol and methane decay as a function of temperature at 1.0 second reaction time in the three different reactants ratios.

The methanol consistently decreases with increasing reaction time for all temperature studied and different reaction environments. For a constant residence time, methanol exhibits a lower concentration with the increasing temperature in all reaction environments. Methane also consistently decreases in concentration for increases in temperature at constant time or increase in time at constant temperature. Longer reaction time or higher temperatures are, however, needed in the methane case relative to the methanol. Methanol decays more rapidly than the methane in three different reaction environments at relative low temperature. At high temperature and sufficient oxygen level(except the fuel rich), methanol and methane have the similar high decomposition rates.

The decomposition rate for methanol and methane both increase, with increasing O_2 levels from fuel rich, stoichiometric to fuel lean.

Methanol starts to decompose at 500 C at residence time of 1.0 second and 95% is converted at 750 C in all three reaction environments. Methane starts to react at about 650 C at residence time of 1.0 second and exhibits 95% conversion at 800 C at both stoichiometric and fuel lean conditions. The methane is, however, not completely converted at 850 C in the fuel rich environment.

3.2 Product Distribution and Material Balance

3.2.1 Product Distribution

Figure 3.19-3.24 illustrate the product distribution vs reaction time in the stoichiometric environment at different temperatures. Major products are CH_2O and CO at low temperature regime (initial of reaction), then CO and CO_2 at high temperature regime.

About 3% CH_3OCH_3, dimethyl ether, is detected in the temperature range 550-650C. A small amount of $CH_3OCH_2OCH_3$, formaldehyde dimethyl acetal (about 2%), is also found in the same temperature regime. Mass Spectrometry analysis has been used to verify and or identify the existence of $CH_3OCH_2OCH_3$. The Mass Spectrometry analysis are shown in Figure 3.39-3.40. The CH_3OCH_3 probably arises from combination of CH_3O + CH_3 radicals. Modeling results will be performed in future studies in this laboratory to validate the mechanism of dimethyl ether and formaldehyde dimethyl acetal formation. The appearance of $CH_3OCH_2OCH_3$ is accompanied by the observation of CH_2O. The acetal, CH_3-O-CH_2-O-CH_3 is likely formed by reaction of dimethyl ether with CH_3, OH, or CH_3O to form a radical:

$$CH_3\text{-}O\text{-}CH_3 \ + OH \ \text{-->} \ CH_3\text{-}O\text{-}CH_2. + H_2O$$

and then CH_3-O-CH_2. combines with a methoxy radical (CH_3O)

$$CH_3\text{-}O\text{-}CH_2. + CH_3O \ \text{-->} \ CH_3\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$$

A second mechanism of formation of these ether products are addition reactions of methoxy radicals (CH_3O) and/or methyl radicals (CH_3) with formaldehyde:

$$CH_3O + CH_2{=}O \ \text{<-->} \ CH_3\text{-}O\text{-}CH_2\text{-}O.$$

This followed by combination with a methyl radical will form the acetal:

$$CH_3\text{-}O\text{-}CH_2\text{-}O. + CH_3 \ \text{<-->} \ CH_3\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$$

These are important reactions that will readily occur in methanol systems. We report observations of these products for the first time in this study.

It is important to note that this is an initial experimental study and the reaction paths above are not complete. It is not appropriate to include all the possible abstraction, addition or combination reactions of the methyl, methoxy, alkoxy and aldehydic species in this system at this point of our study. These will be included however in our future reaction modeling studies so the model can be extended to conditions outside our experimental validation range.

When temperature increases above 650C, the CH_2O decreases, thus formaldehyde only exists for a short residence time. CO increases rapidly with the rapid conversion of methanol. The formation of CO_2 then arises when the large amount of CO produced starts to convert to CO_2. Above 750C, oxidation of CO occurs rapidly to the final product CO_2.

Minor products C_2H_4 and C_2H_6 are observed in high temperature range. The concentration of C_2H_4 and C_2H_6 are about 3% and 1% respectively. Methanol is completely decomposed at 750C and the total conversion of methane happens at 800C. Above 850C, only CO_2 exists in the reaction system.

The product distributions vs temperature in stoichiometric at different reaction times (0.3-2.0 sec) are shown in Figures 3.25-3.30. The CO exhibits high concentration at 750C and then rapidly decays to form CO_2 which is dominant product above 800 C. CH_2O only exists at low temperature range 500-700C with a concentration of about 20%. The minor products: CH_3OCH_3, $CH_3OCH_2OCH_3$, C_2H_4 and C_2H_6 seem to be grouped into two sections. CH_3OCH_3 and $CH_3OCH_2OCH_3$ appear below about 680C, where C_2H_4 and C_2H_6 are very low in concentration. Above 680C, C_2H_4 and C_2H_6 increase where CH_3OCH_3 and $CH_3OCH_2OCH_3$ disappear.

3.2.2 Main Products CH_2O, CO and CO_2

Distribution of main products: CH_2O, CO and CO_2 vs temperature or reaction time in the varied reaction environments are shown in Figure 3.33-3.38.

The concentration of CO increases faster under fuel lean conditions than stoichiometric and slower yet under fuel rich conditions when under initial reaction conditions. At stoichiometric conditions, higher temperature is needed for CO to reach its maximum concentration than under fuel lean conditions. Under fuel rich conditions, CO is the final product which does not convert to CO_2 due to the lack of oxygen.

CO_2 increases rapidly at 700C in fuel lean and at 750 C under stoichiometric conditions. CO_2 achieves it's maximum level at 850C for both fuel lean and stoichiometric conditions. In fuel rich-lowest oxygen environment, CO_2 is found at low concentration with little change from the increasing temperatures.

The intermediate product CH_2O exhibits almost same status in all three different reaction environments. It exists in the low temperature regime (500 to 700C) as the pyrolysis product of methanol and continually oxidizes to CO at higher temperature.

3.2.3 Material Balance

The material balance gives us important information about high molecular weight compounds and soot which are not quantitatively detected. The carbon material balances for the present study are listed in Table 3.1-3.3.

All three reaction systems show relatively good material balance over wide temperature below 750C and at 1.0 residence time. At higher temperature, especially in fuel lean, the material balance is low-apparent loss of carbon. This is probably due to the formation of relatively high levels of CO_2, which saturates our catalyst conversion reactor. This results in reduced conversion efficiency of the CO_2 levels to CH_4, which is detected by the FID. Future studies will need to correct this problem, or convert to a Thermo-Conductivity Detector for quantitative analysis of CO and CO_2. Since the efficiency of the catalyst conversion is not unlimited, only small levels of CO_2 can be converted to CH_4 which is detected by the FID.

3.3 Effects of Oxygen

In our study, we fix the percentage of methanol and methane at 1% respectively, and change the percentage of oxygen to meet the conditions of fuel rich, stoichiometric and fuel lean. All reaction environments are diluted in argon. Figures 3.7 and 3.8 show that there is limited effect on the decomposition of methanol by changes in oxygen for our temperature and pressure conditions. The methanol decreases a slightly faster in fuel lean than under stoichiometric and fuel rich conditions. Methane, when in fuel rich conditions, decreases much slower than under the stoichiometric or fuel rich cases. A trend of increasing rate of decomposition is observed from fuel rich to stoichiometric and then to fuel lean.

The same results can be found in the decomposition of methanol and methane vs reaction time, as shown in Figures 3.9-3.18.

The effect of oxygen is further illustrated in Figures 3.28, 3.31 and 3.32 which illustrate the product distribution vs temperature in fuel rich, stoichiometric and fuel lean conditions at residence time of 1.0 second. A trend is observed that CO occurs at lower temperature in the fuel lean case then in stoichiometric and fuel rich. CO also decreases faster in fuel lean with the increase of CO_2, then in stoichiometric. Under fuel rich conditions where the CO does not further convert to CO_2.

Relative concentrations of C_2H_4, C_2H_6 and $CH_3OCH_2OCH_3$ are observed to increased under fuel rich conditions and decrease in fuel lean. CH_3OCH_3 is just reverse, however, it decreases under fuel rich conditions and increases in fuel lean. In the fuel rich environment, trace acetylene, C_2H_2, (0.2%) is detected at high temperature - 850 C. This is because C_2H_2 is a relatively favorable product when lack of O_2 - pyrolysis conditions. In stoichiometric or fuel lean, the O_2 limits C_2H_2 production through very rapid reaction with the vinyl, C_2H_3 radical, which is the immediate precursor to acetylene in this reaction system. O_2 also limits C_2 (C_2H_6, C_2H_4) production, from combination of methyl radicals, by reaction with the methyl radicals.

Table 3.1 Material Balance for Carbon

Residence Time = 1.0 sec.

(CH_4 : CH_3OH : O_2 : Ar = 1 : 1 : 3.5 : 94.5)

Stoichiometric

	Temperature (C)						
Species	550	600	650	700	750	800	850
CH_4	1.0	1.0	0.961	0.835	0.161	0.008	0.006
CH_3OH	0.874	0.728	0.551	0.116	0.011	0.006	0.005
CO	0.004	0.020	0.360	0.779	1.872	0.770	0.047
CO_2	0.002	0.0	0.029	0.023	0.198	1.058	1.873
CH_2O	0.105	0.140	0.165	0.020	0.001	0.0	0.0
C_2H_4	0.0	0.0	0.0	0.004	0.018	0.0	0.0
C_2H_6	0.0	0.001	0.0	0.006	0.006	0.0	0.0
CH_3OCH_3	0.015	0.025	0.013	0.0	0.0	0.0	0.0
$C_3H_8O_2$	0.009	0.013	0.001	0.0	0.0	0.0	0.0
Total	2.009	1.927	2.08	1.783	2.267	1.842	1.931
C/Co (%)	100.5	96.4	104.0	89.2	113.4	92.1	96.6

Table 3.2 Material Balance for Carbon

Residence Time = 1.0 sec.

(CH_4 : CH_3OH : O_2 : Ar = 1 : 1 : 2 : 96)

Fuel Rich

	Temperature (C)						
Species	550	600	650	700	750	800	850
CH_4	1.0	1.0	0.979	0.864	0.699	0.616	0.142
CH_3OH	0.925	0.820	0.658	0.136	0.010	0.003	0.006
CO	0.003	0.013	0.347	0.680	1.610	1.409	1.664
CO_2	0.002	0.0	0.035	0.022	0.073	0.091	0.075
CH_2O	0.116	0.132	0.177	0.019	0.005	0.0	0.0
C_2H_4	0.0	0.0	0.0	0.003	0.012	0.031	0.024
C_2H_6	0.0	0.001	0.0	0.005	0.007	0.013	0.002
CH_3OCH_3	0.008	0.010	0.011	0.0	0.0	0.0	0.0
$C_3H_8O_2$	0.010	0.013	0.001	0.0	0.0	0.0	0.0
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.002
Total	2.064	1.989	2.208	1.729	2.416	2.163	1.915
C/Co (%)	103.2	99.5	110.4	86.5	120.8	108.2	95.8

Table 3.3 Material Balance for Carbon

Residence Time = 1.0 sec.

(CH_4 : CH_3OH : O_2 : Ar = 1 : 1 : 5 : 93)

Fuel Lean

	Temperature (C)						
Species	550	600	650	700	750	800	850
CH_4	1.0	1.0	0.958	0.783	0.006	0.010	0.003
CH_3OH	0.850	0.690	0.495	0.119	0.009	0.008	0.006
CO	0.004	0.094	0.394	0.821	0.017	0.0	0.0
CO_2	0.002	0.001	0.041	0.025	1.237	1.349	1.795
CH_2O	0.113	0.144	0.143	0.014	0.0	0.0	0.0
C_2H_4	0.0	0.0	0.0	0.006	0.0	0.0	0.0
C_2H_6	0.0	0.001	0.0	0.008	0.0	0.0	0.0
CH_3OCH_3	0.016	0.026	0.012	0.0	0.0	0.0	0.0
$C_3H_8O_2$	0.014	0.013	0.001	0.0	0.0	0.0	0.0
Total	1.999	1.969	2.044	1.776	1.269	1.367	1.804
C/Co (%)	99.9	98.5	102.2	88.8	63.5	68.4	90.2

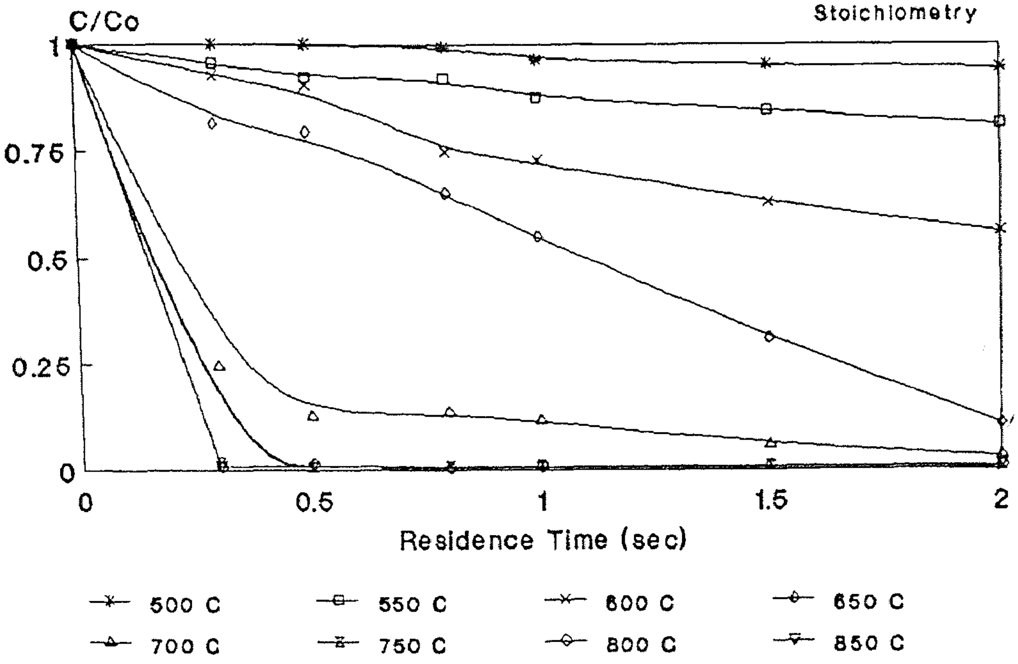


Figure 3.1 Decay of CH3OH vs Time

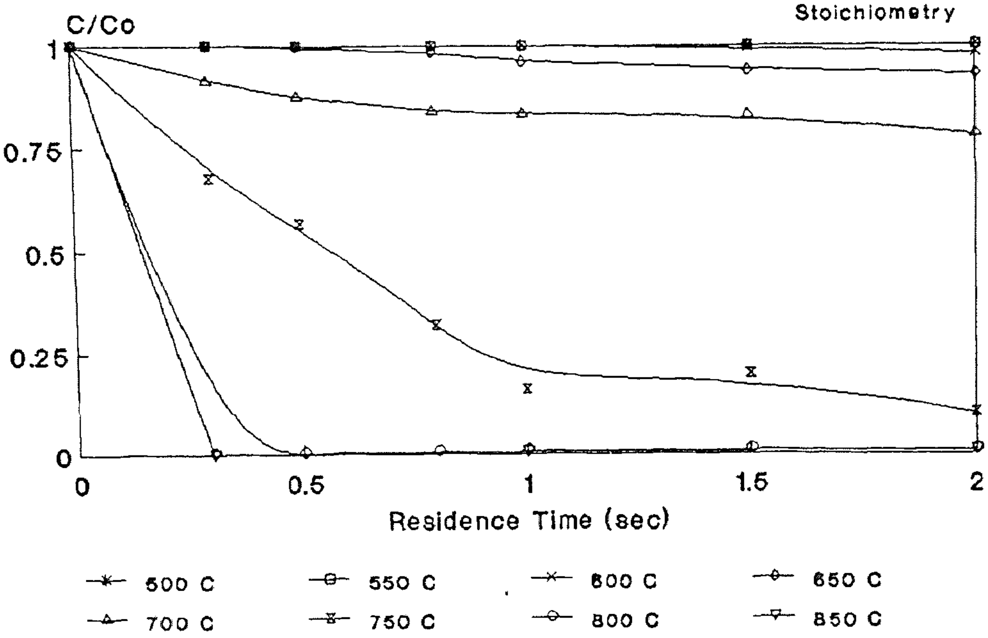


Figure 3.2 Decay of CH4 vs Time

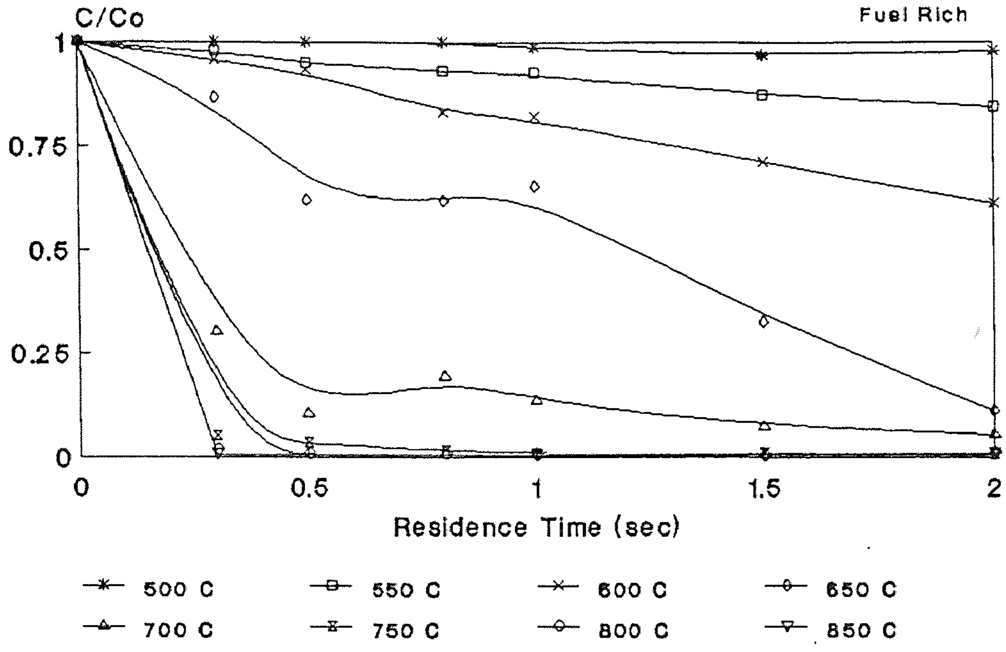


Figure 3.3 Decay of CH3OH vs Time

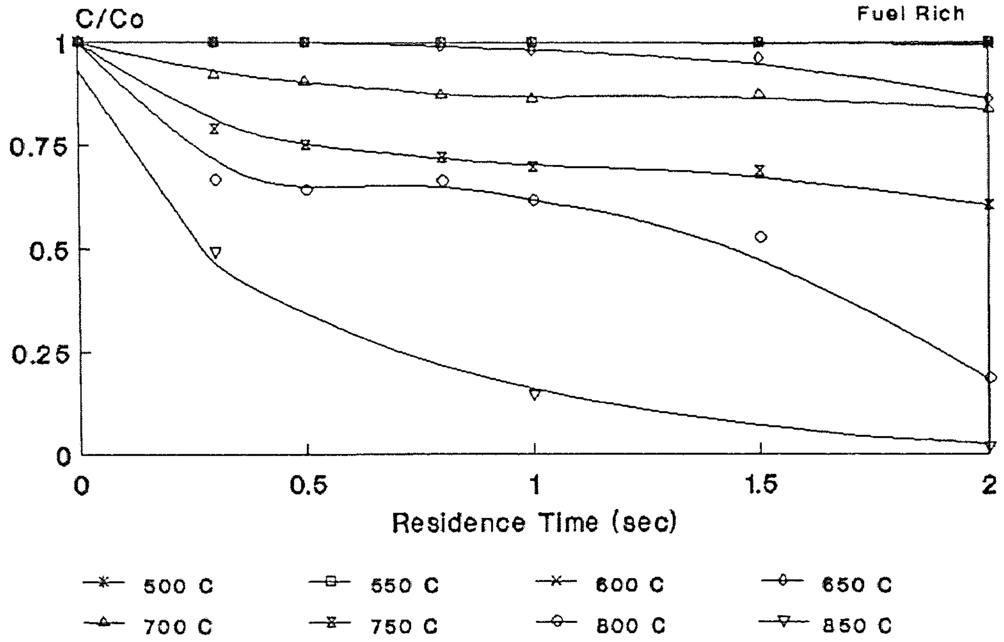
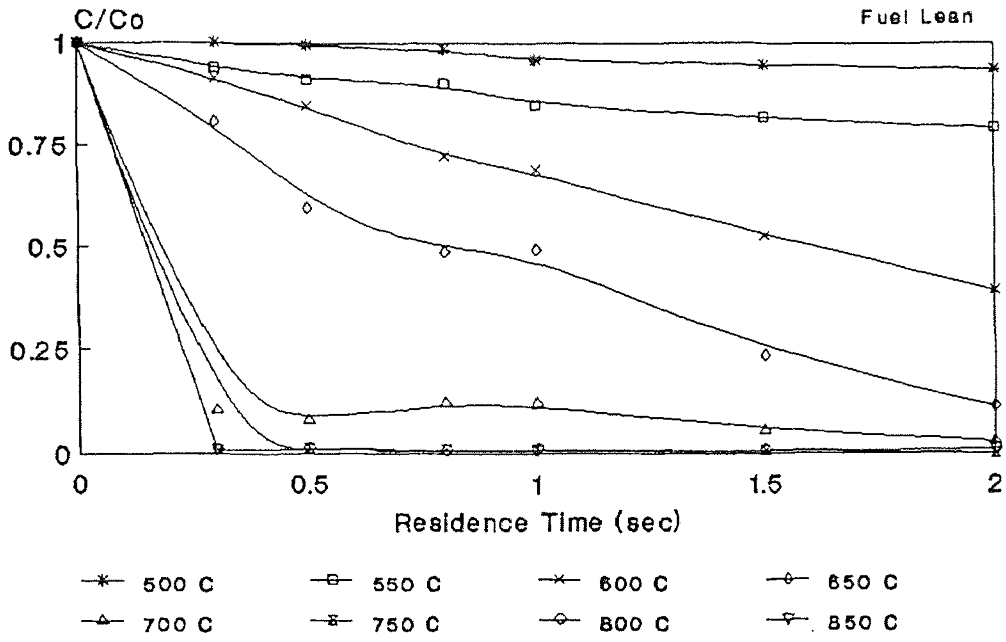


Figure 3.4 Decay of CH4 vs Time



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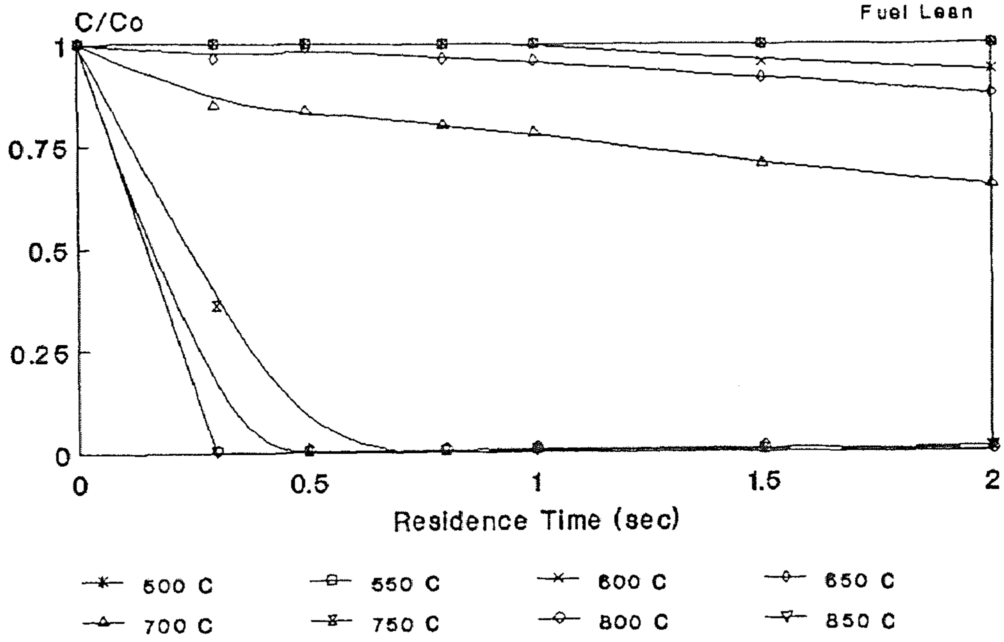
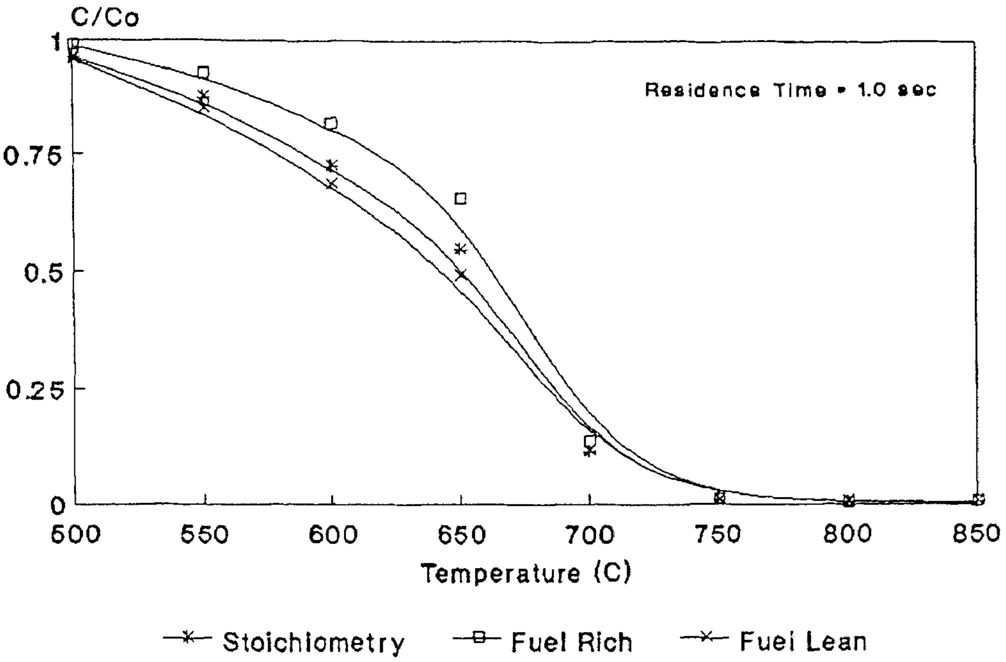


Figure 3.6 Decay of CH4 vs Time



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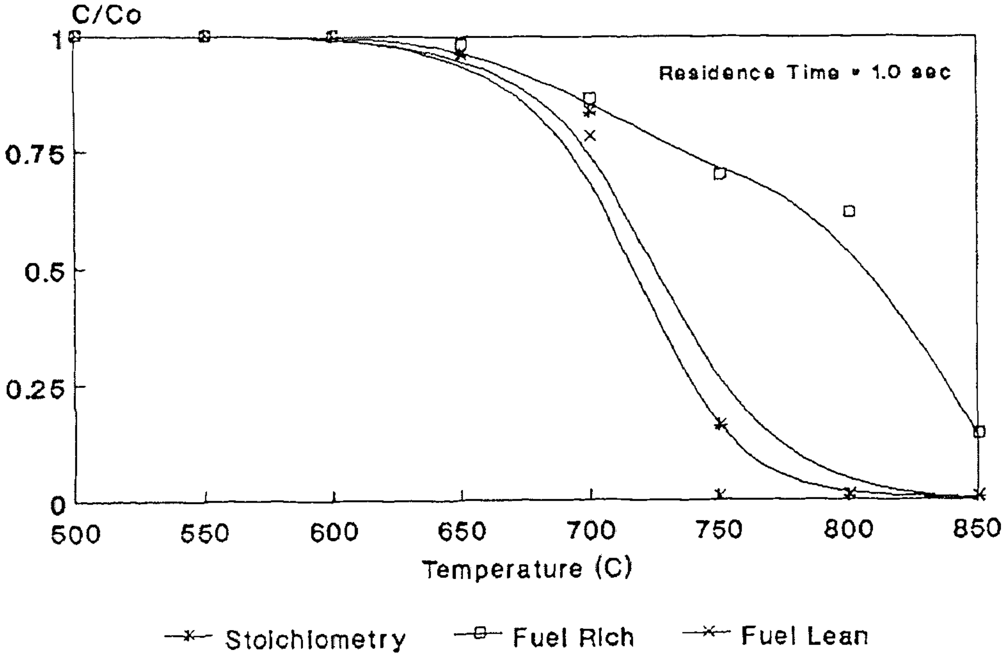


Figure 3.8 Decay of CH4 vs Temperature

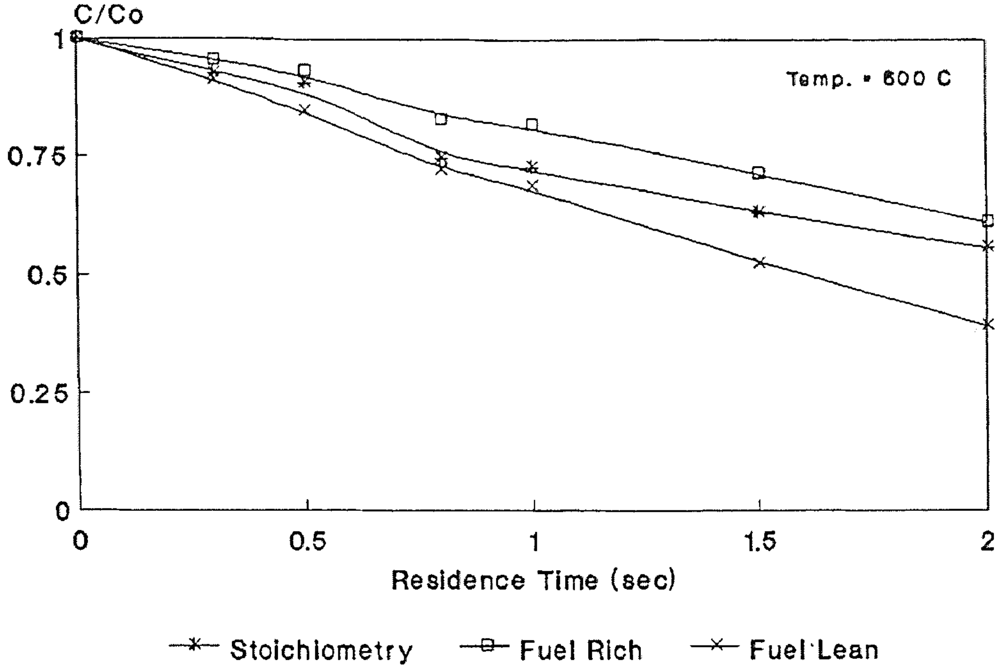


Figure 3.9 Decay of CH3OH vs Time

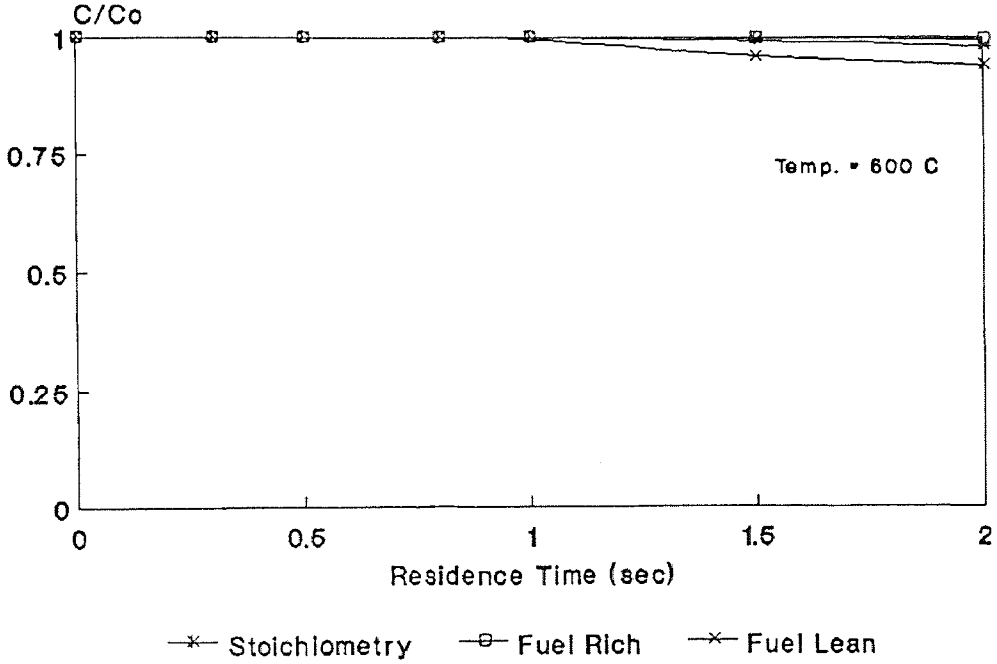


Figure 3.10 Decay of CH4 vs Time

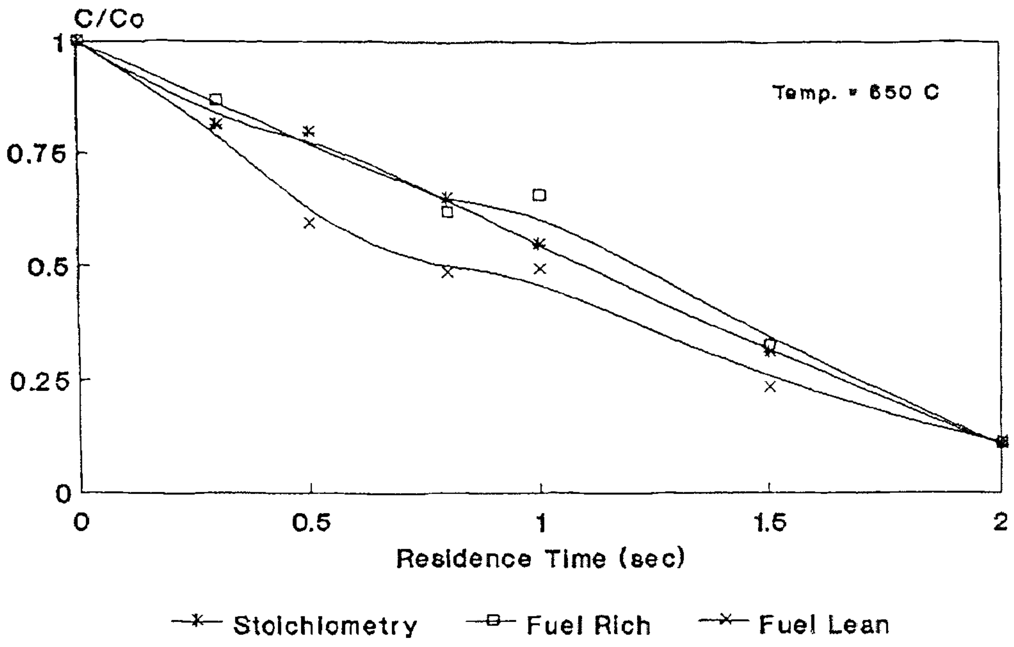


Figure 3.11 Decay of CH3OH vs Time

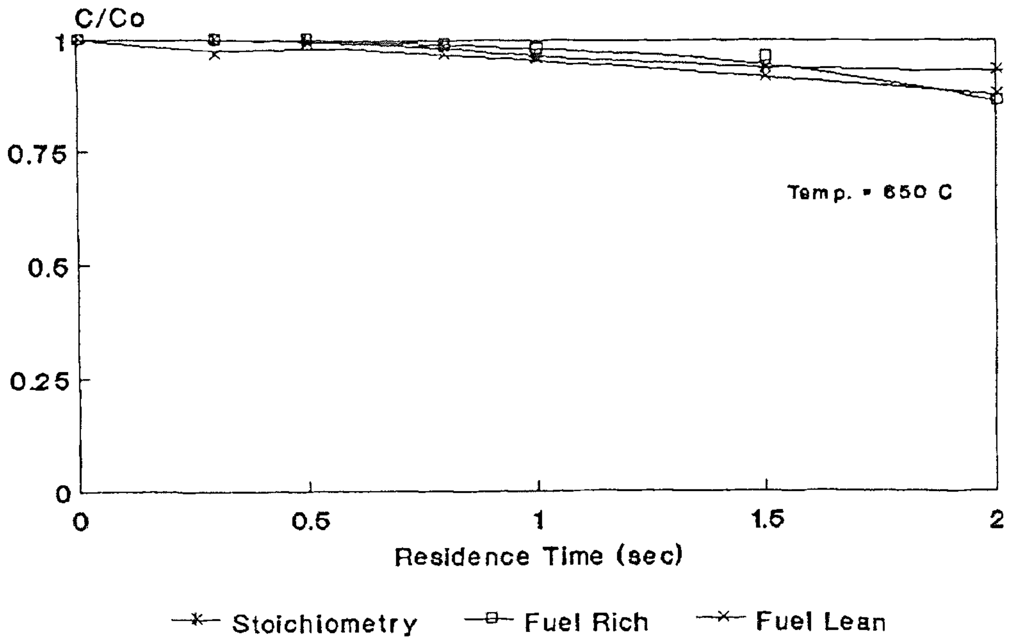


Figure 3.12 Decay of CH4 vs Time

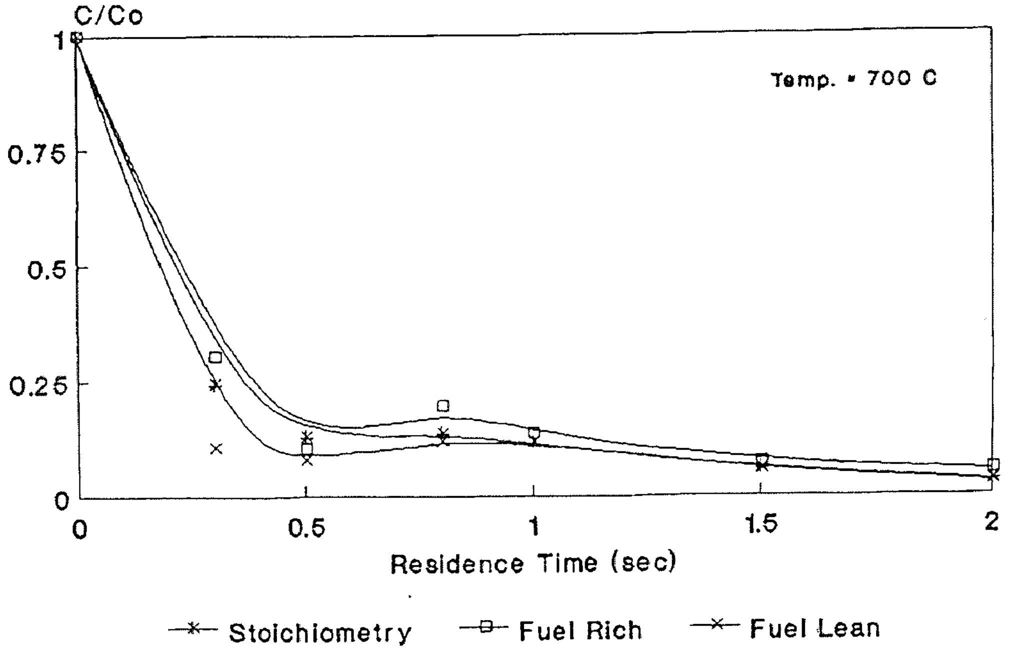


Figure 3.13 Decay of CH3OH vs Time

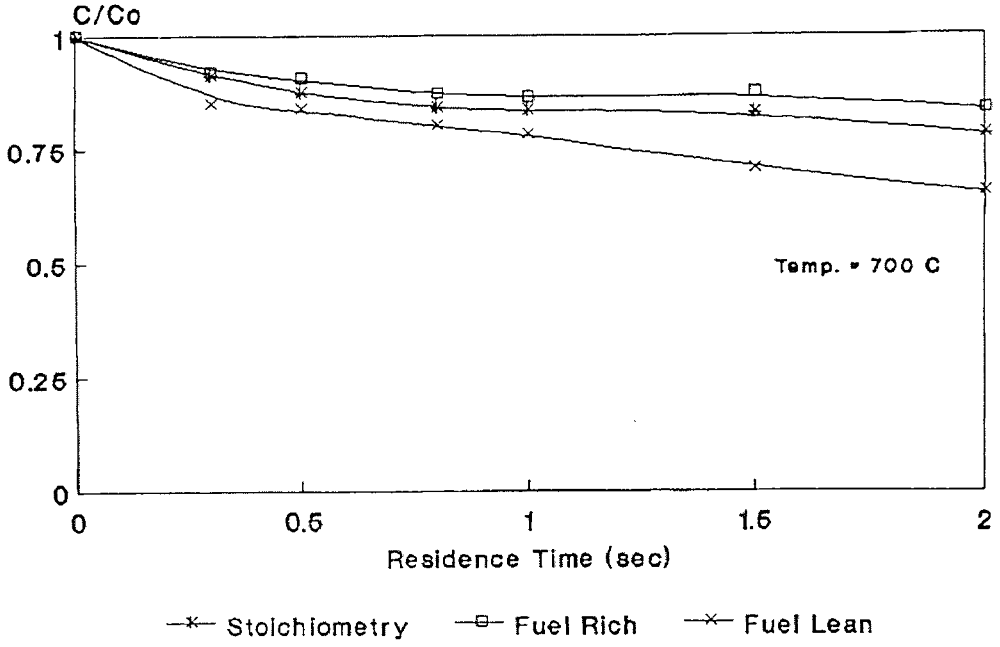


Figure 3.14 Decay of CH4 vs Time

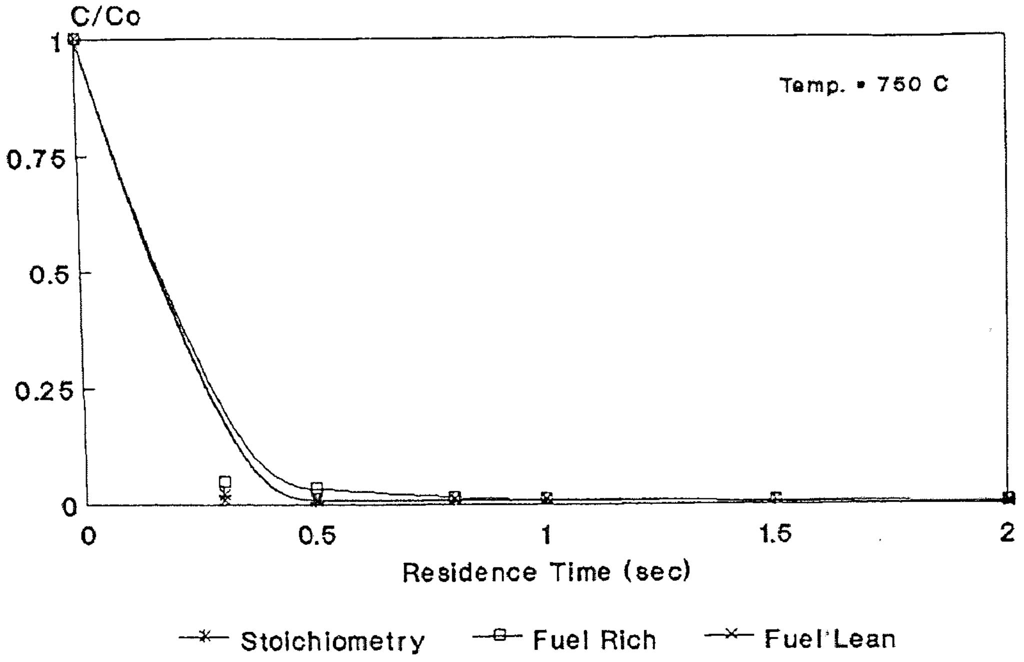
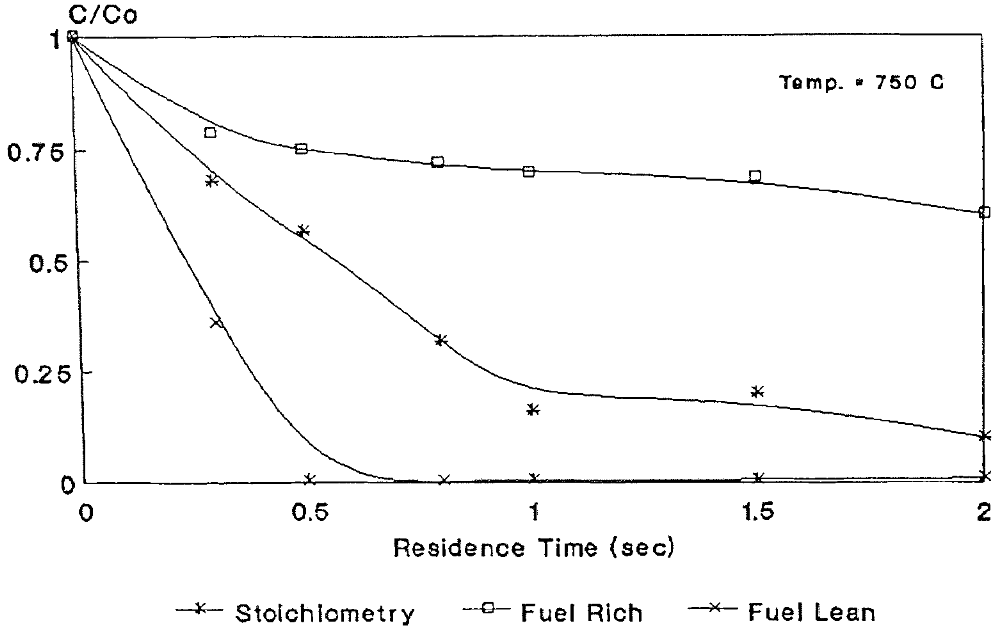


Figure 3.15 Decay of CH3OH vs Time



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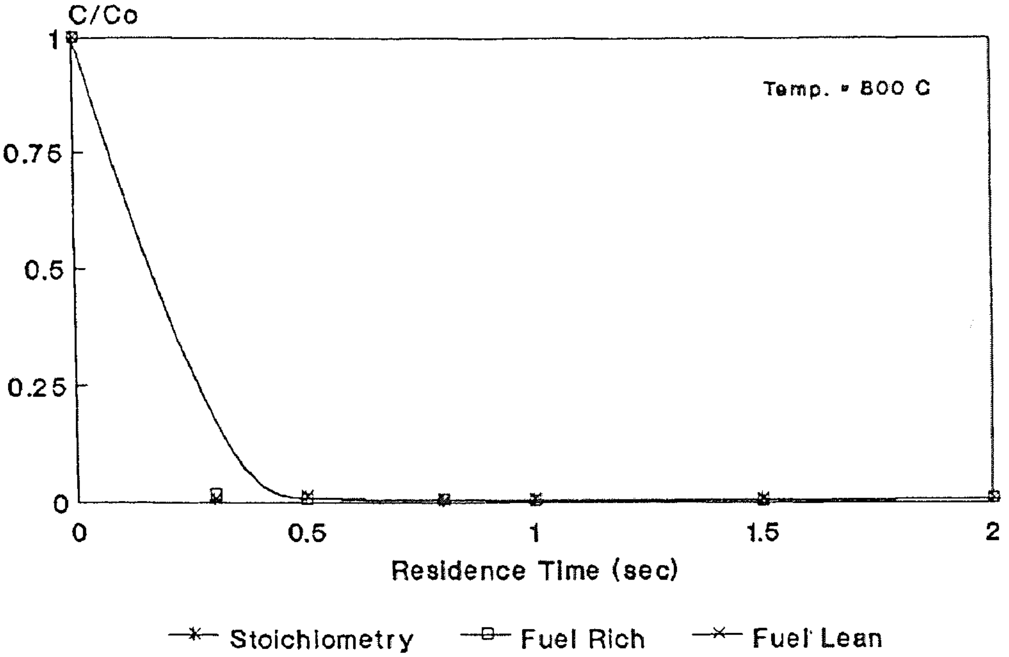


Figure 3.17 Decay of CH3OH vs Time

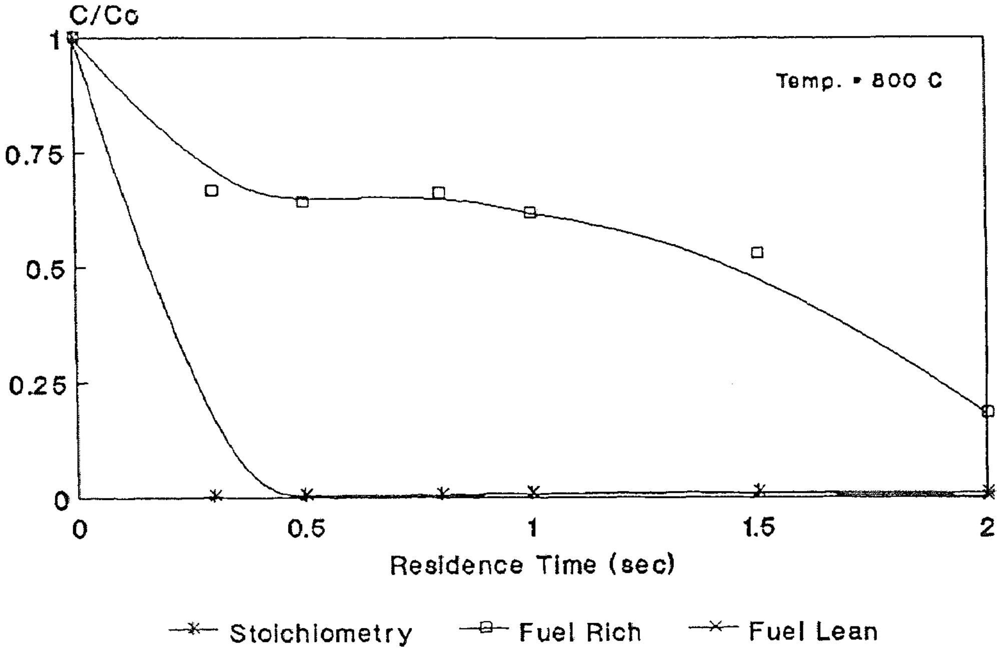
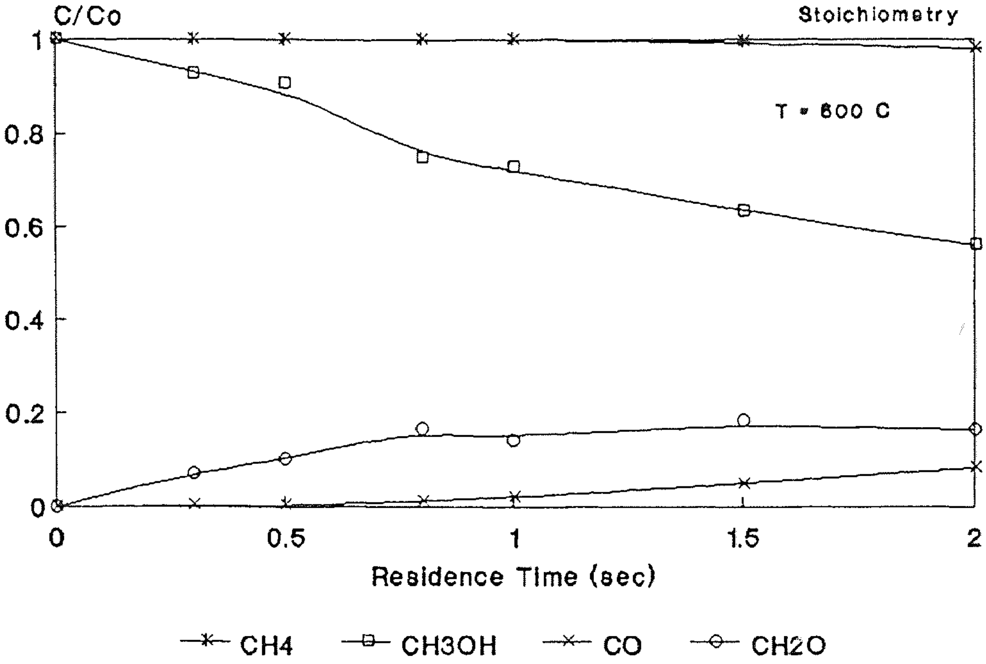


Figure 3.18 Decay of CH4 vs Time



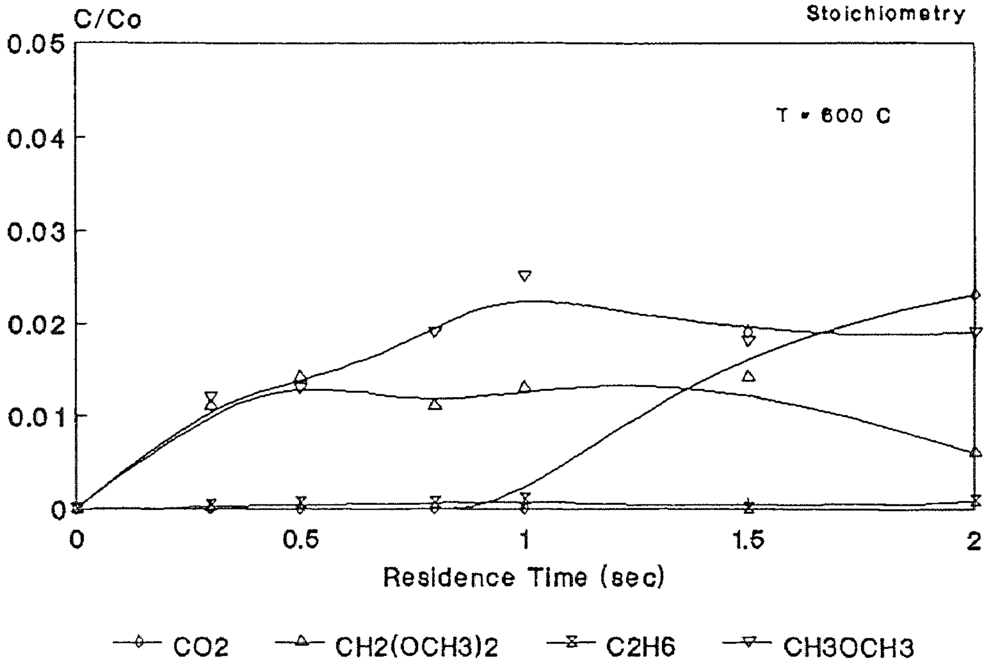
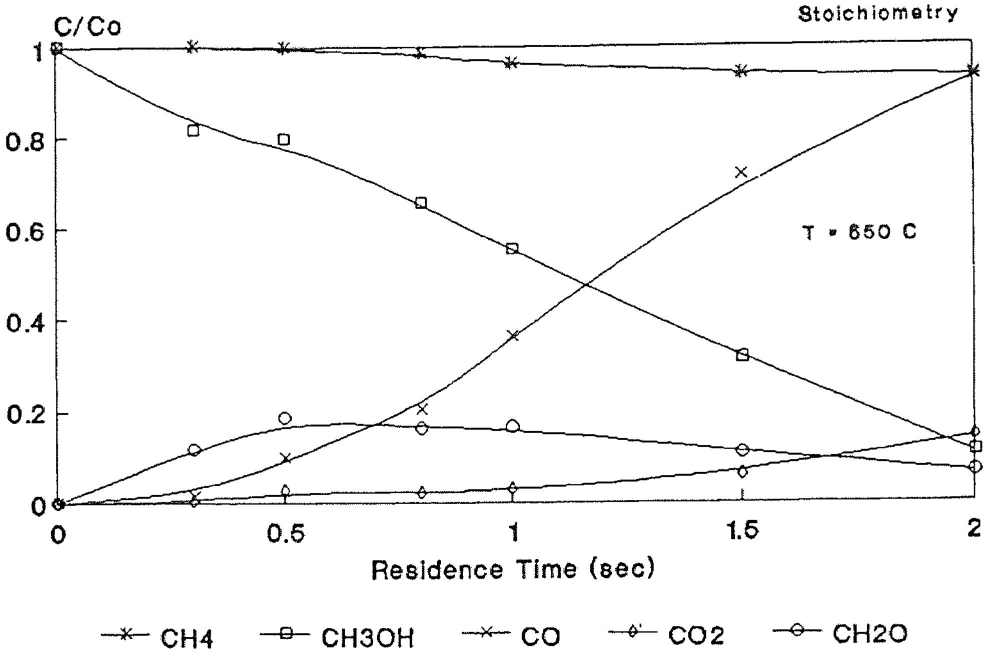


Figure 3.19 Product Distribution vs Time



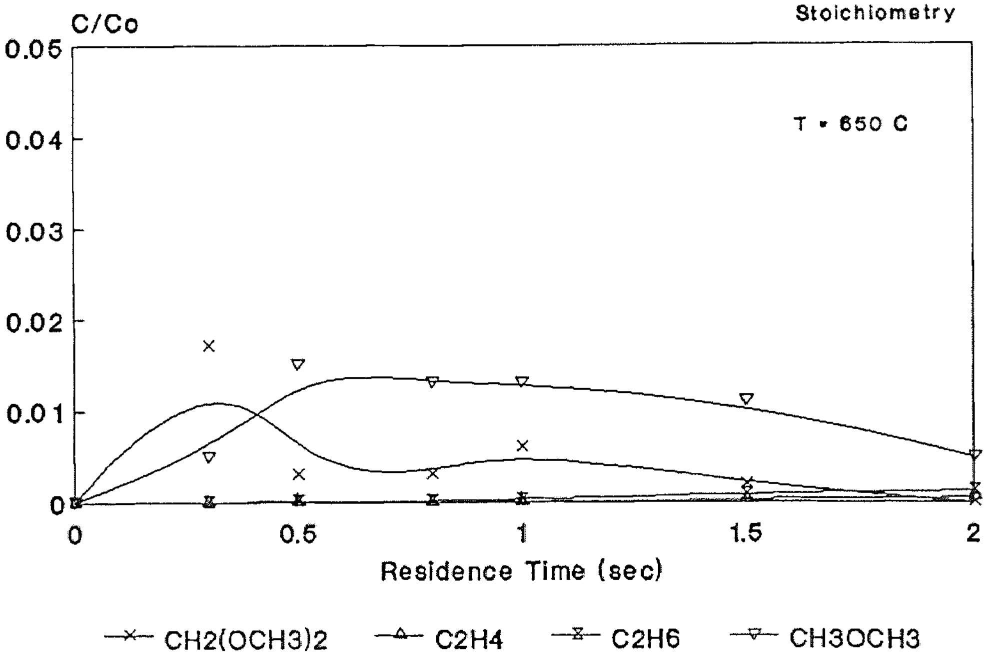
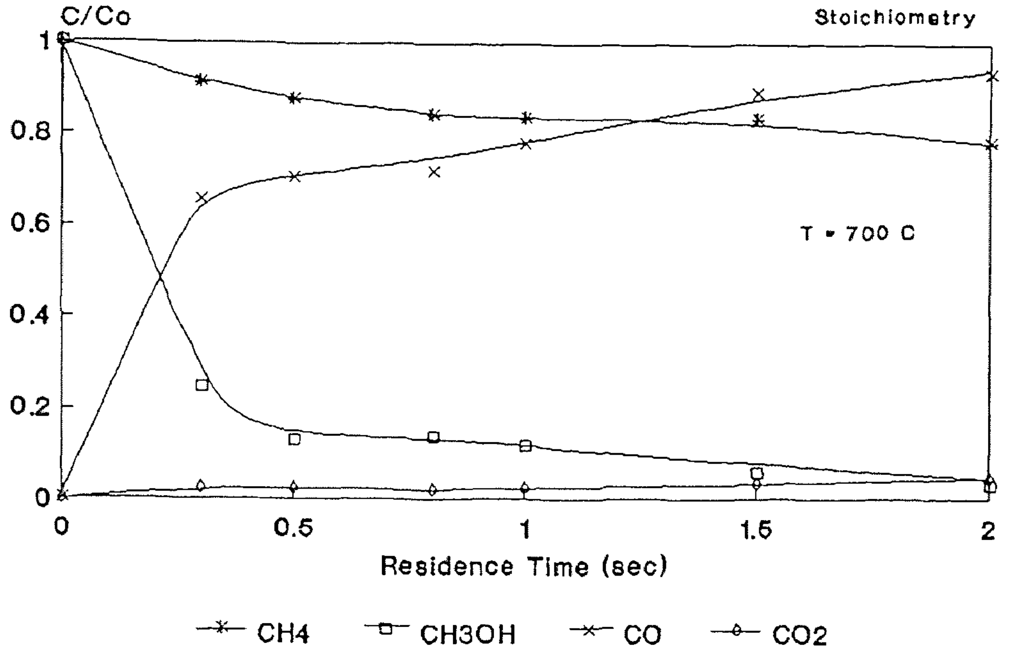


Figure 3.20 Product Distribution vs Time



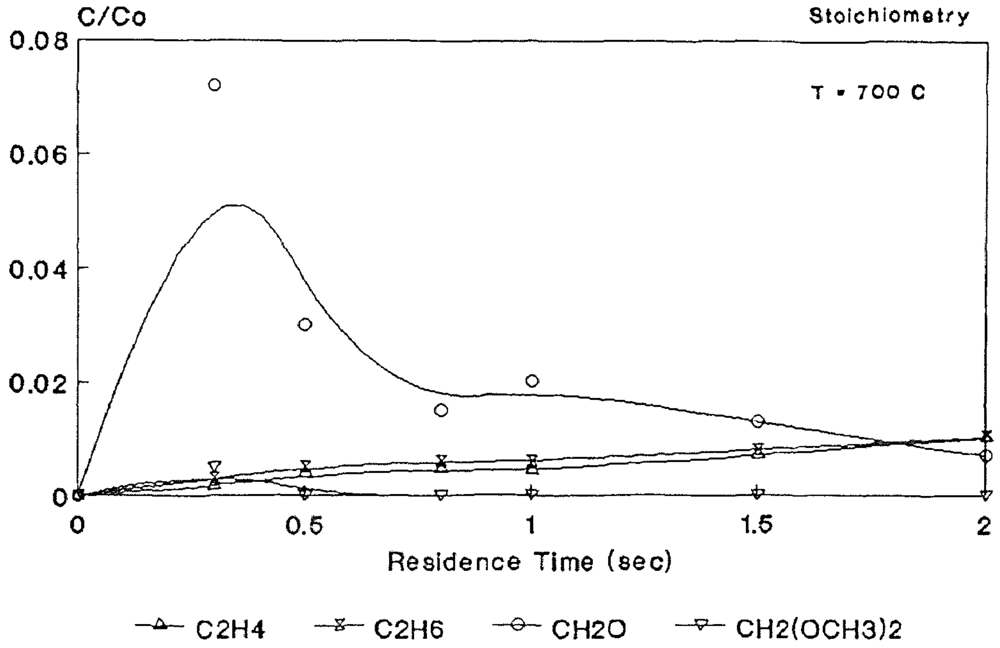
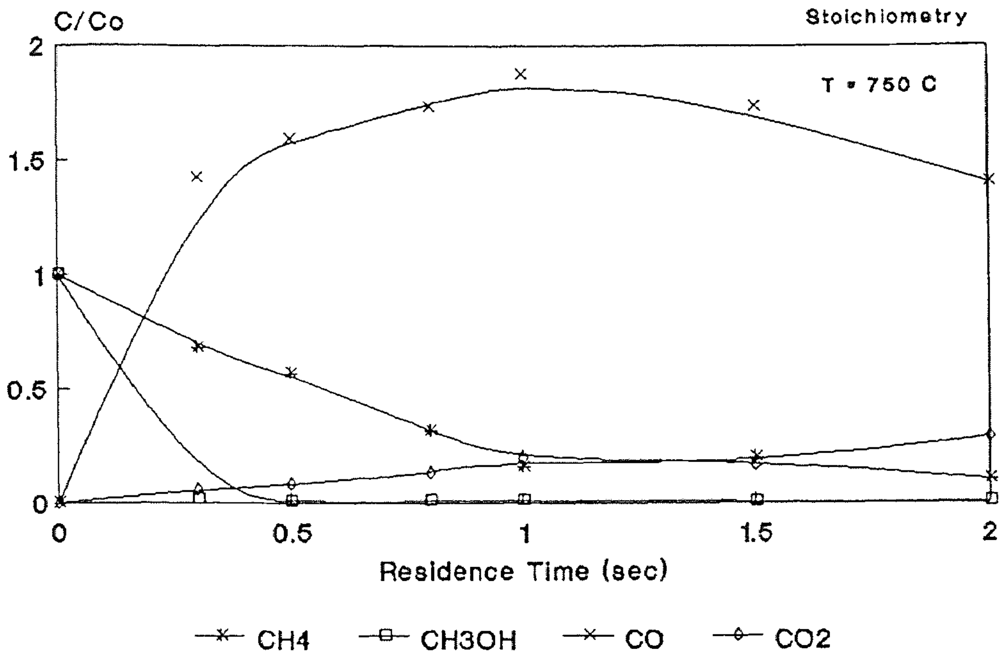


Figure 3.21 Product Distribution vs Time



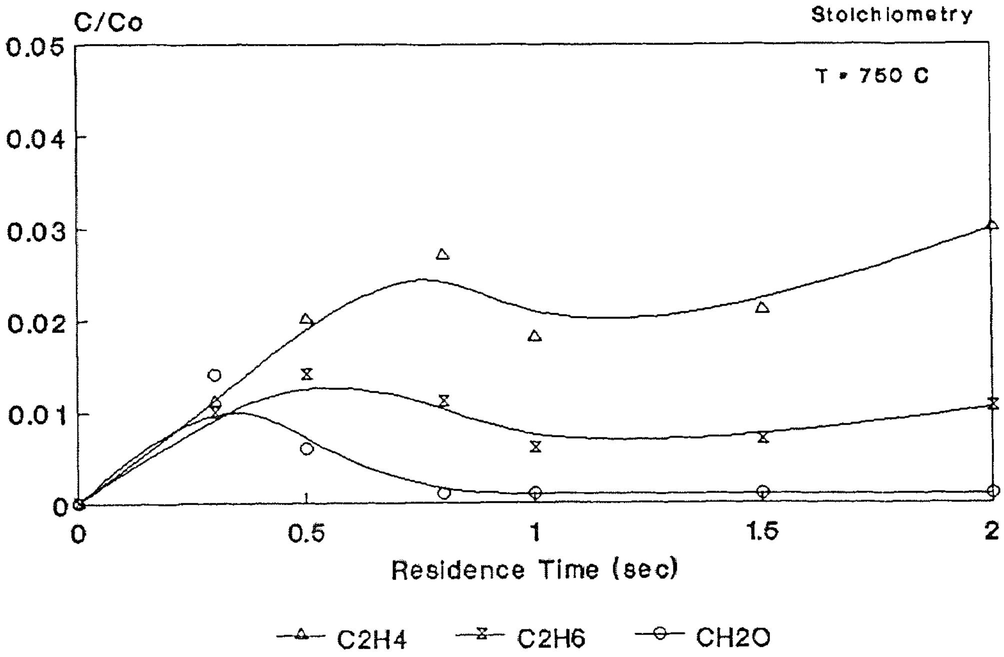


Figure 3.22 Product Distribution vs Time

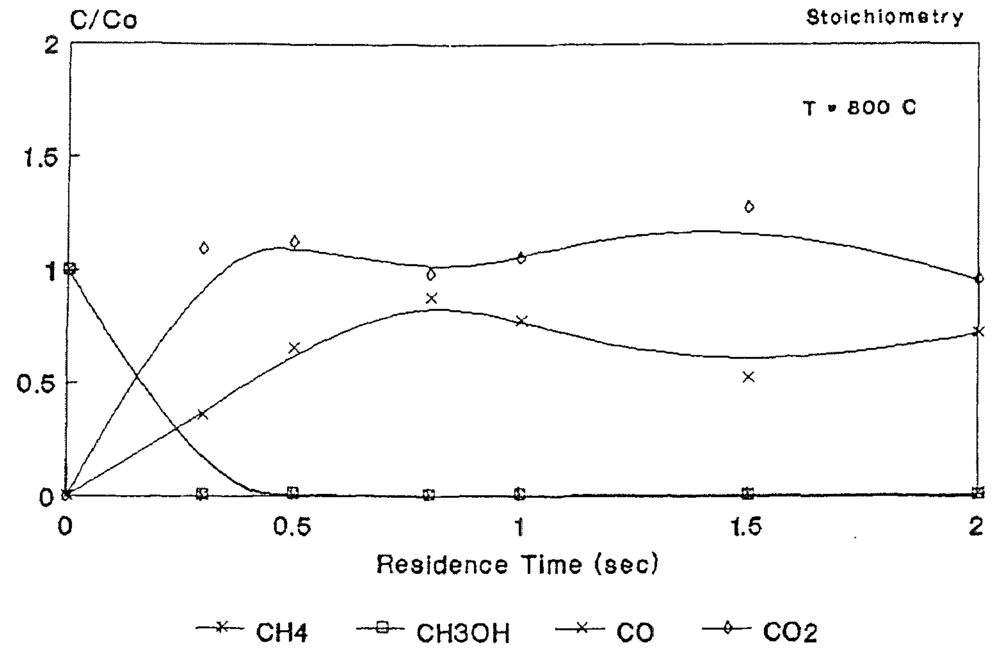
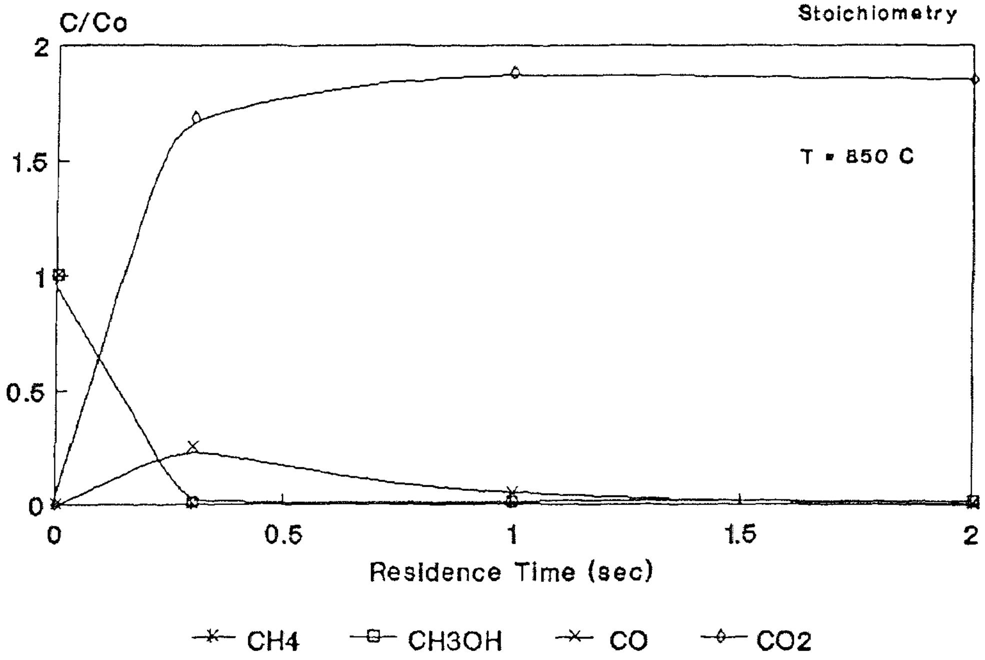


Figure 3.23 Product Distribution vs Time



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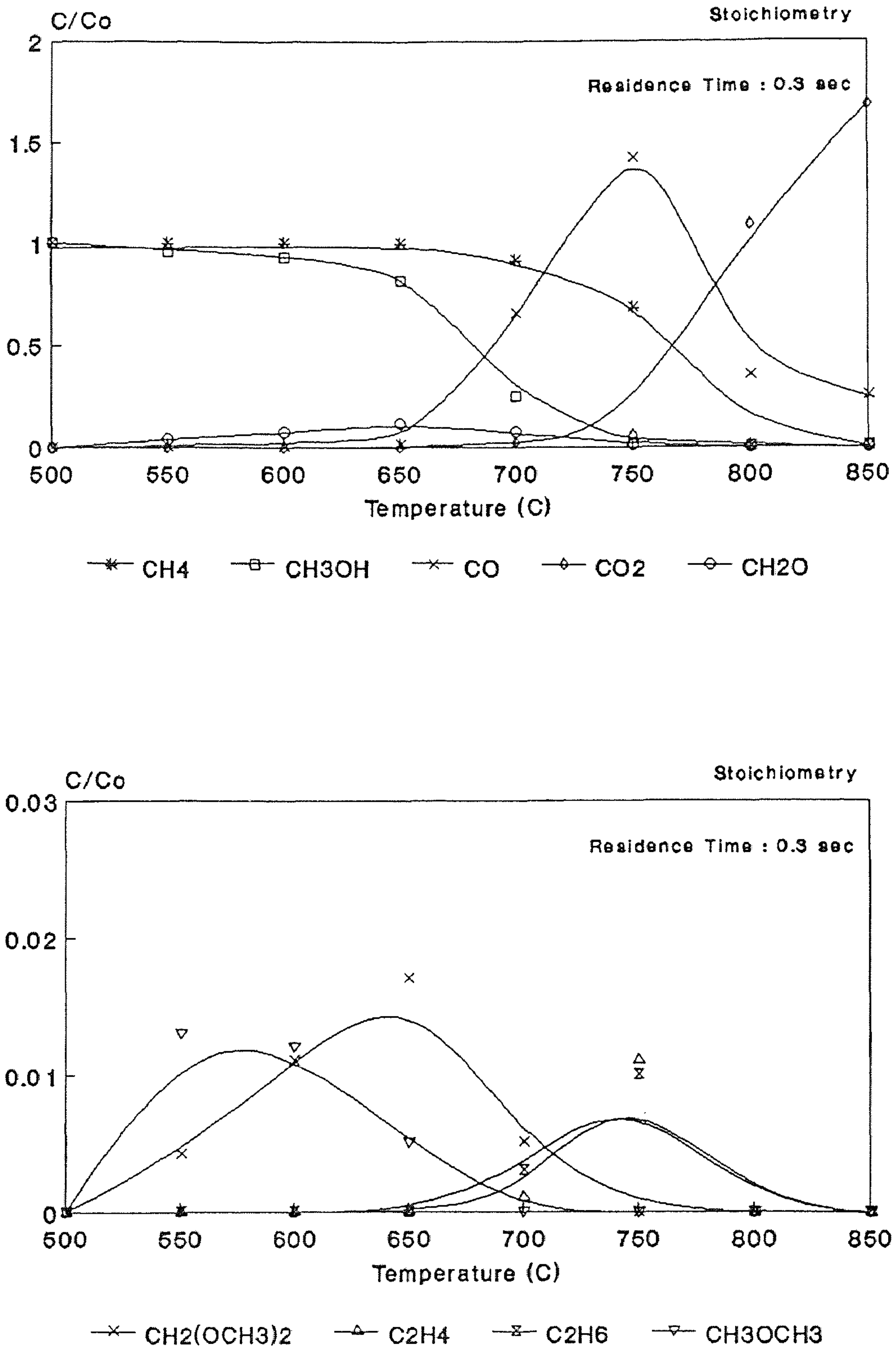
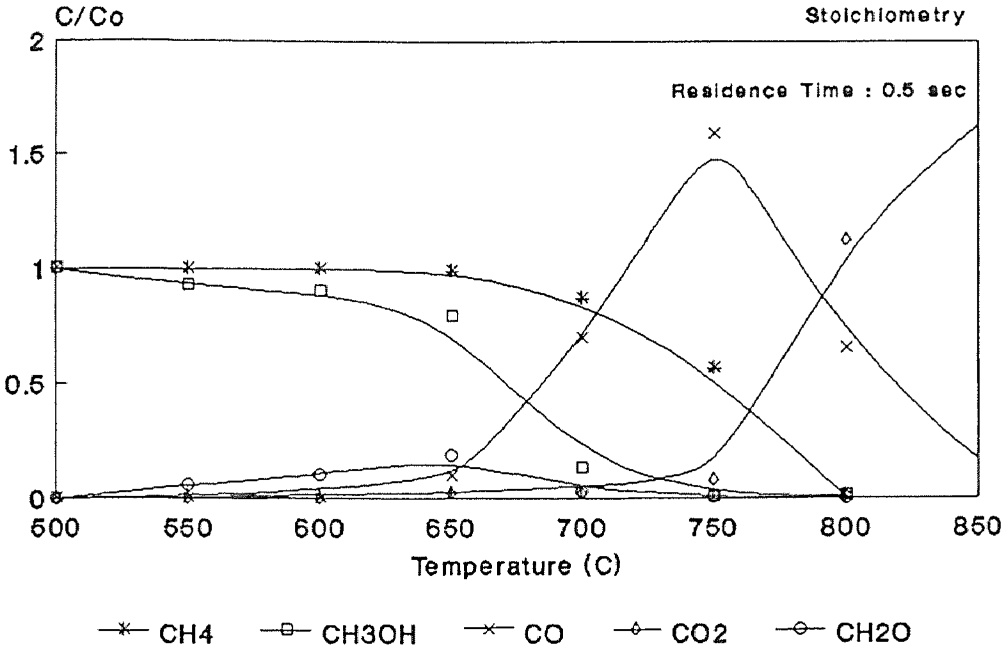


Figure 3.25 Product Distribution vs Temperature



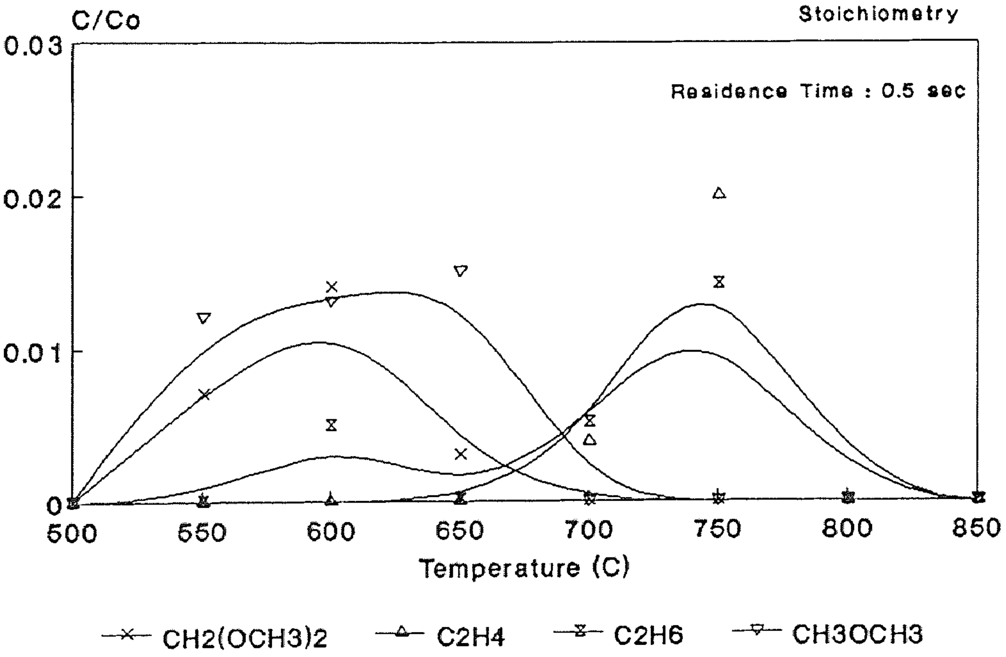
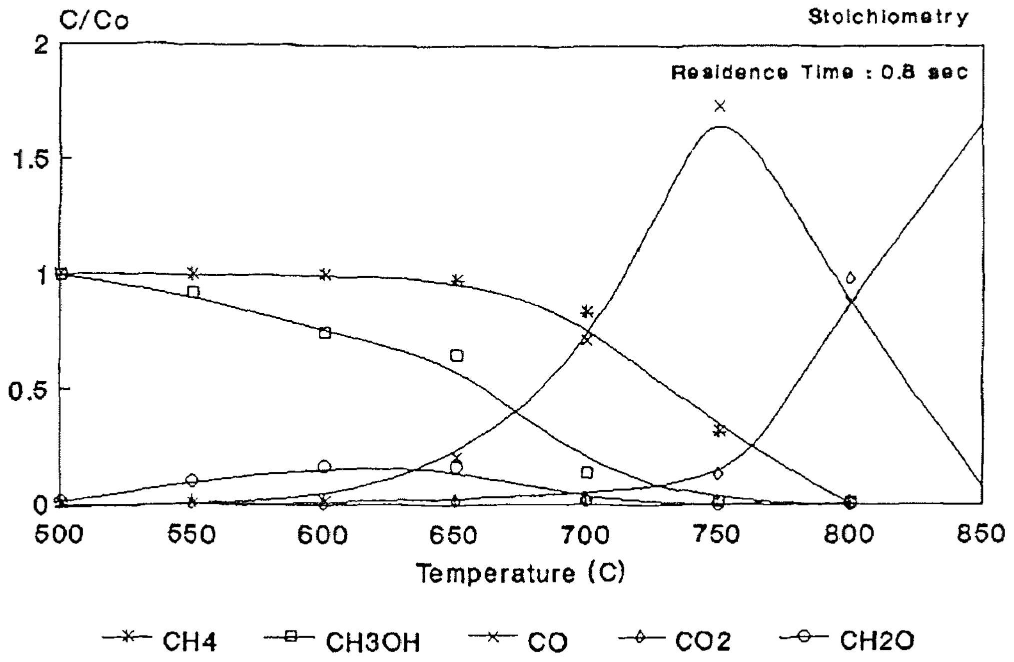


Figure 3.26 Product Distribution vs Temperature



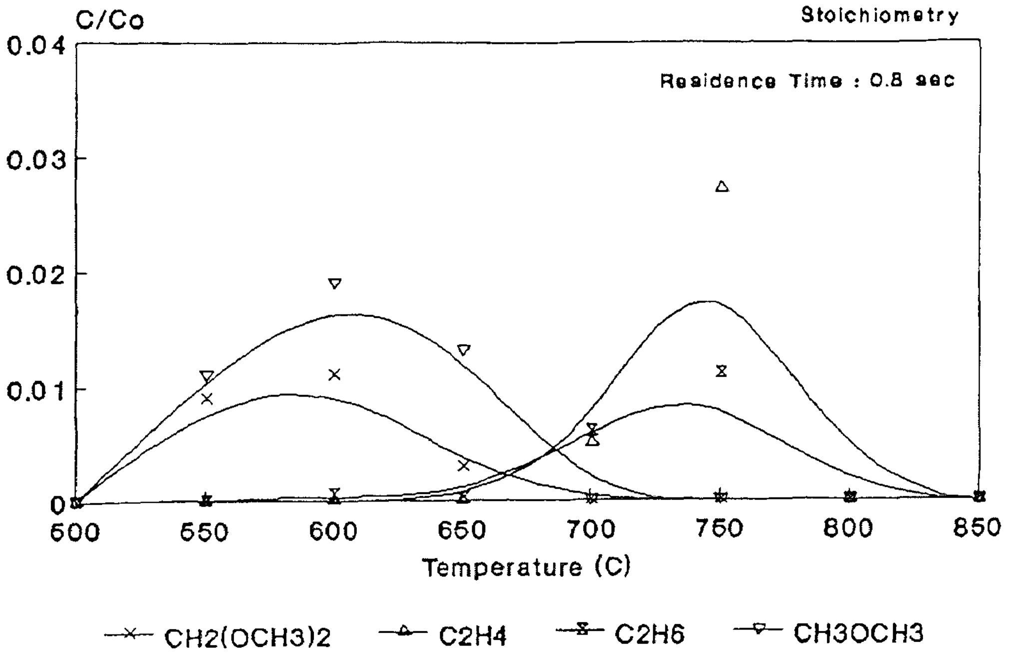


Figure 3.27 Product Distribution vs Temperature

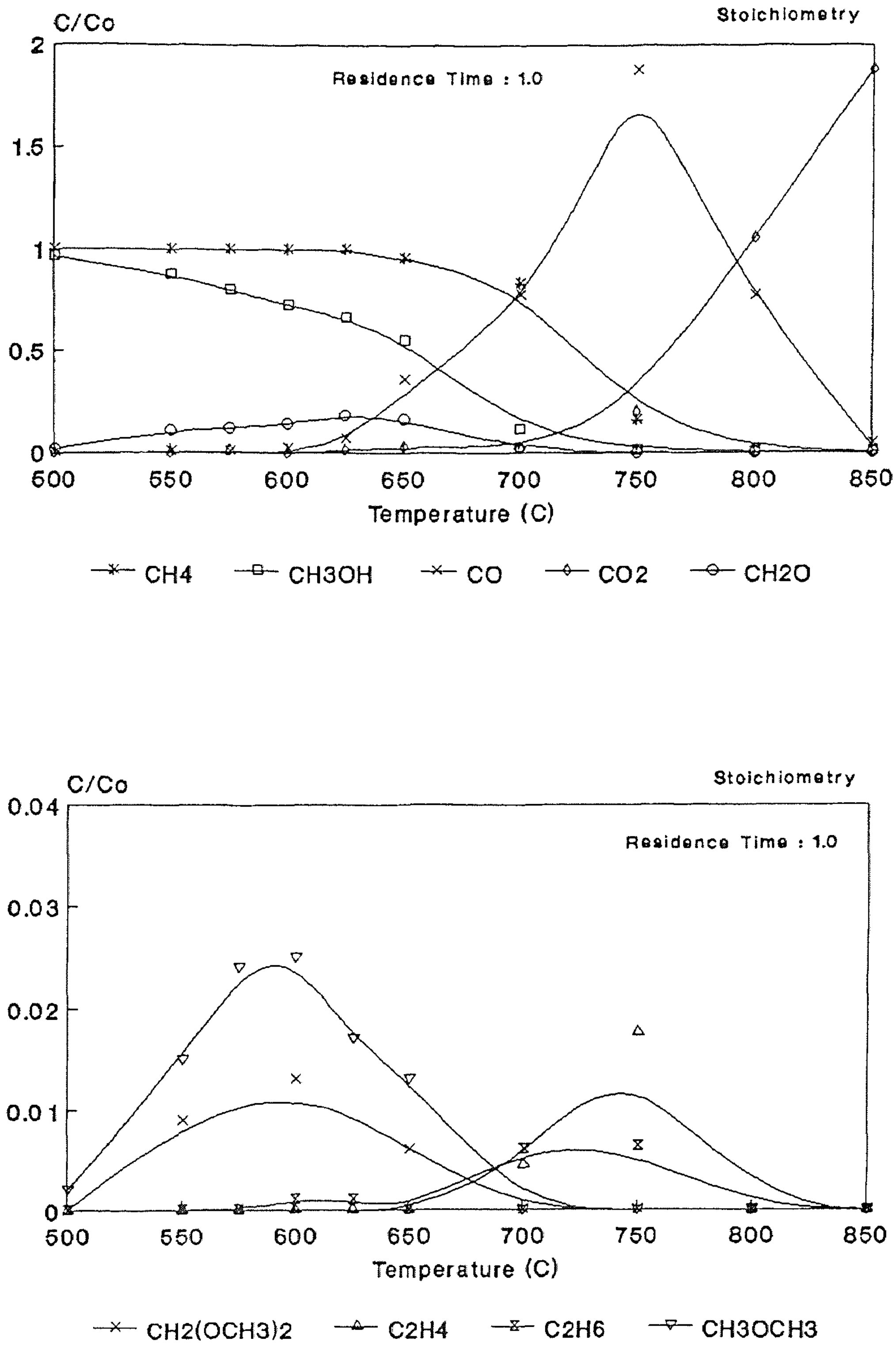


Figure 3.28 Product Distribution vs Temperature

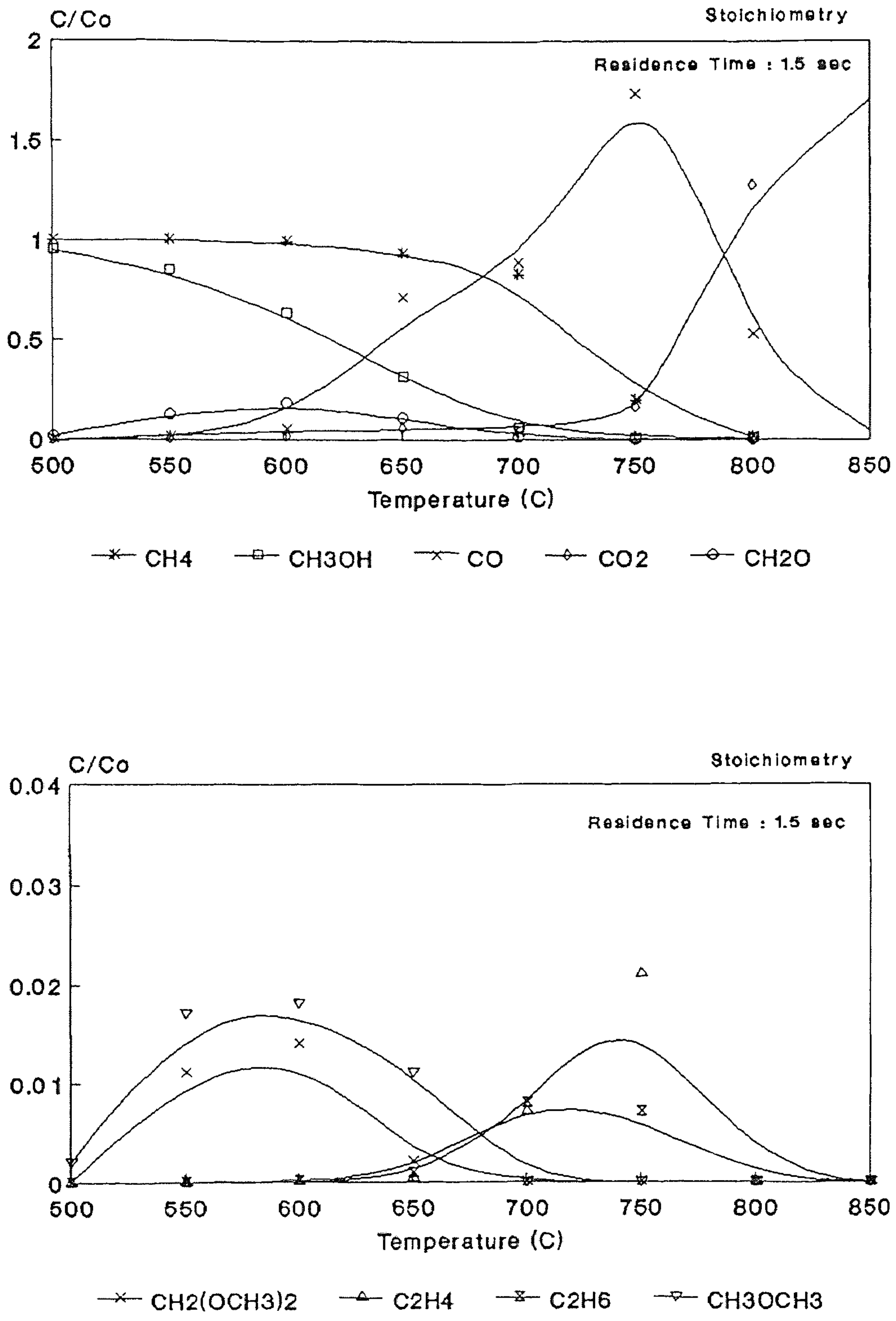


Figure 3.29 Product Distribution vs Temperature

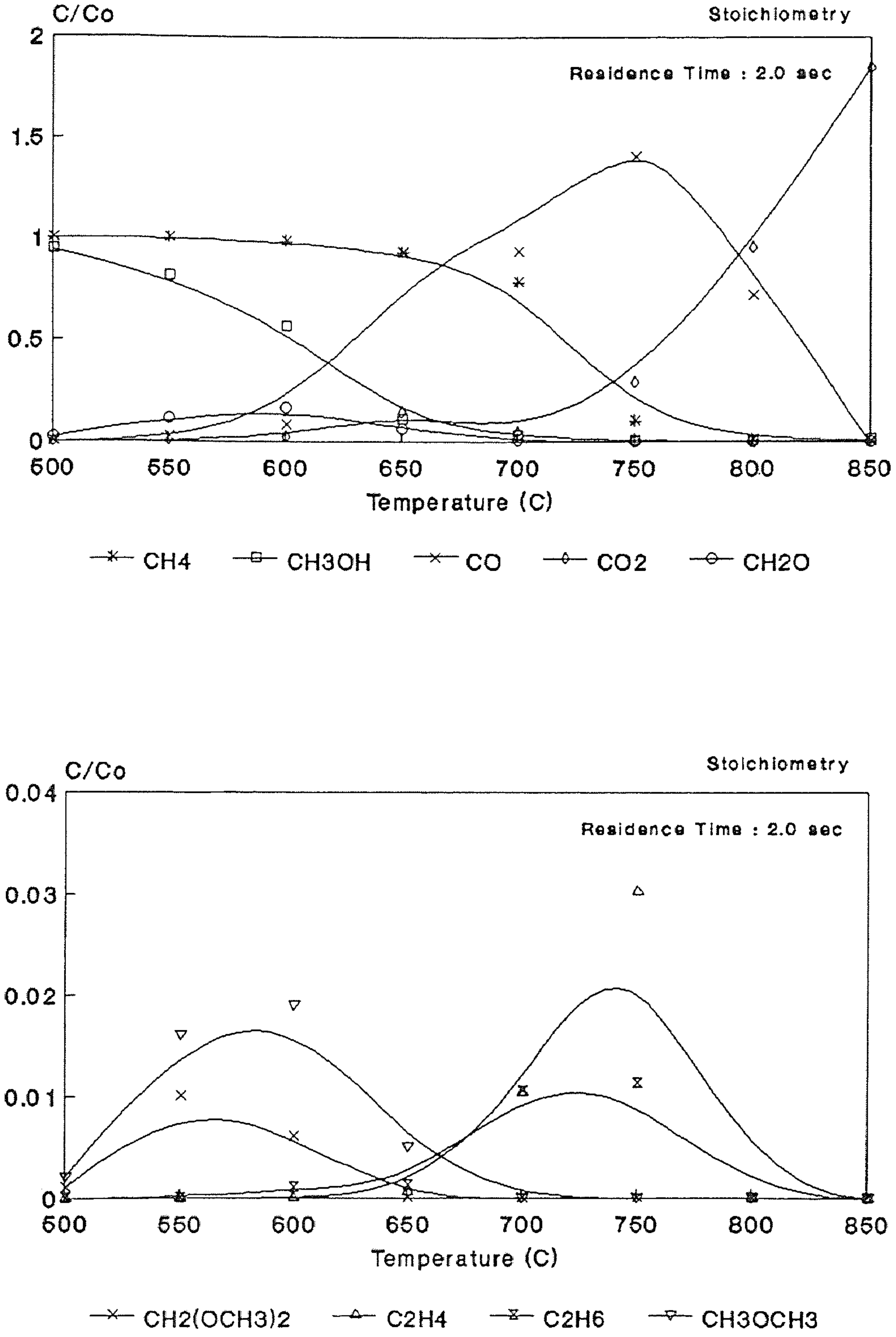
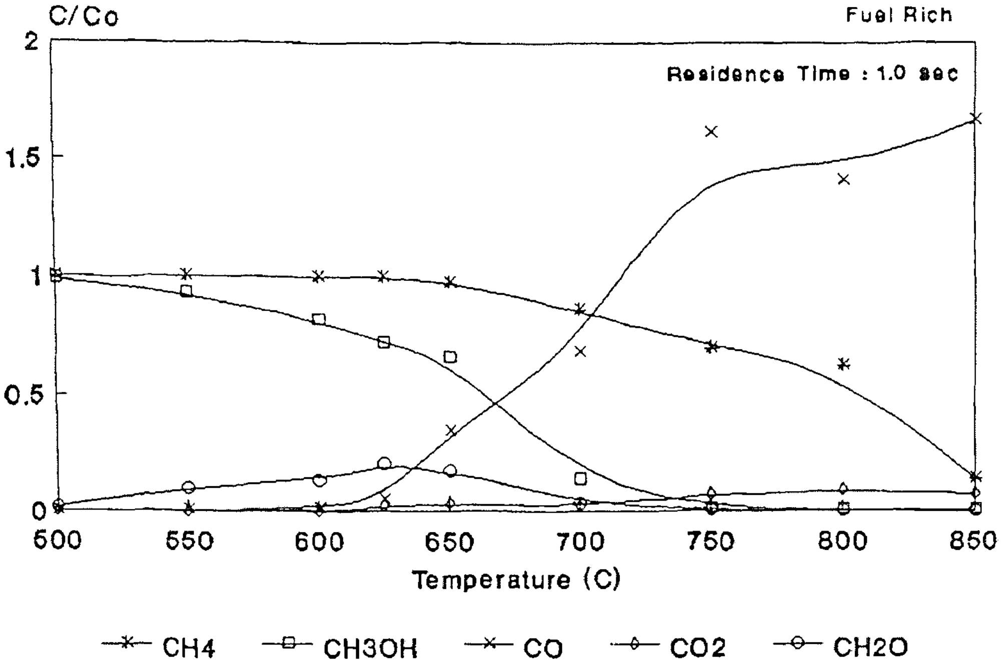


Figure 3.30 Product Distribution vs Temperature



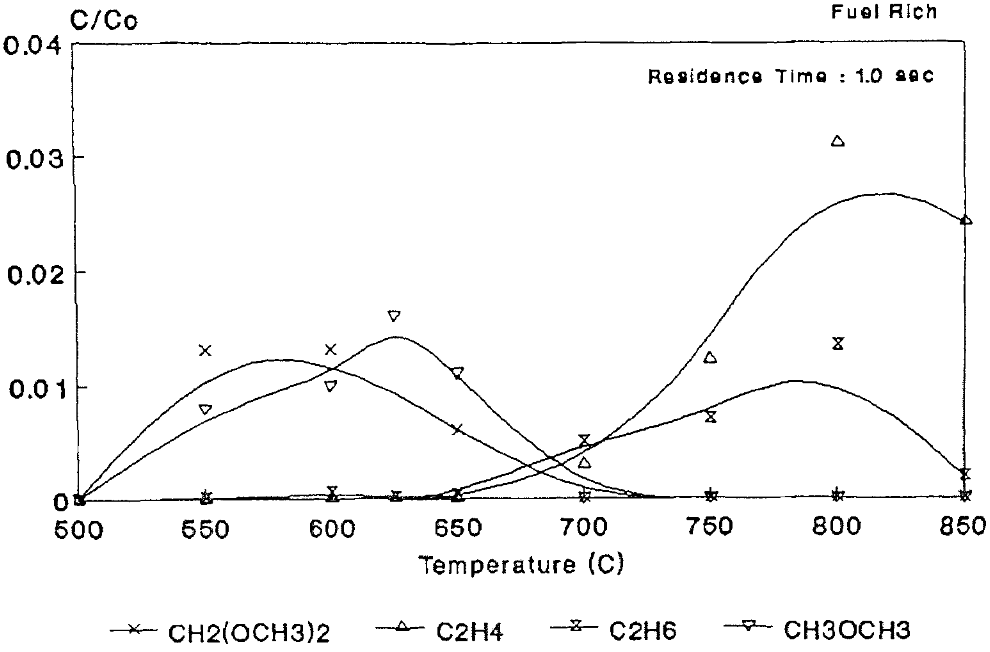


Figure 3.31 Product Distribution vs Temperature

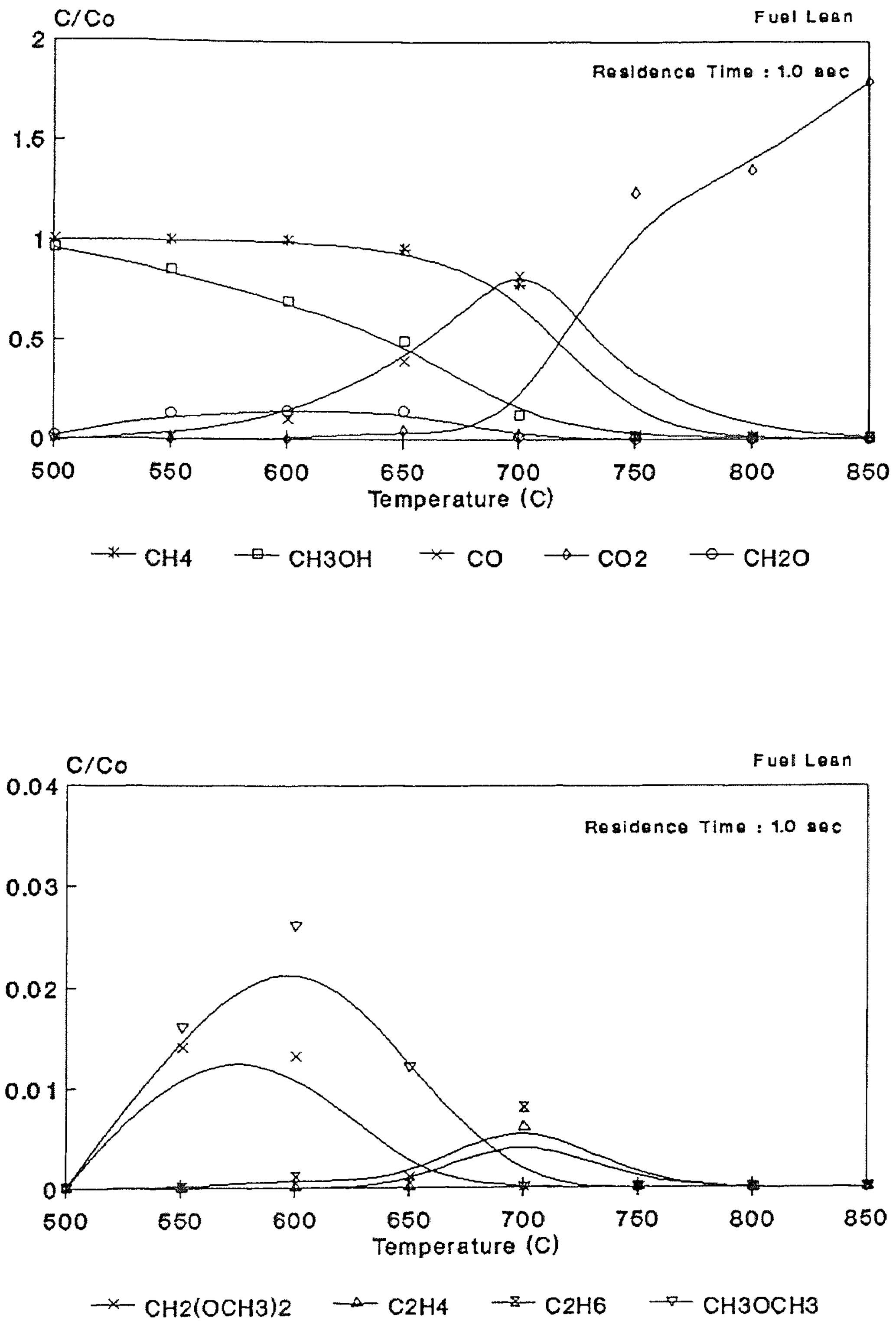


Figure 3.32 Product Distribution vs Temperature

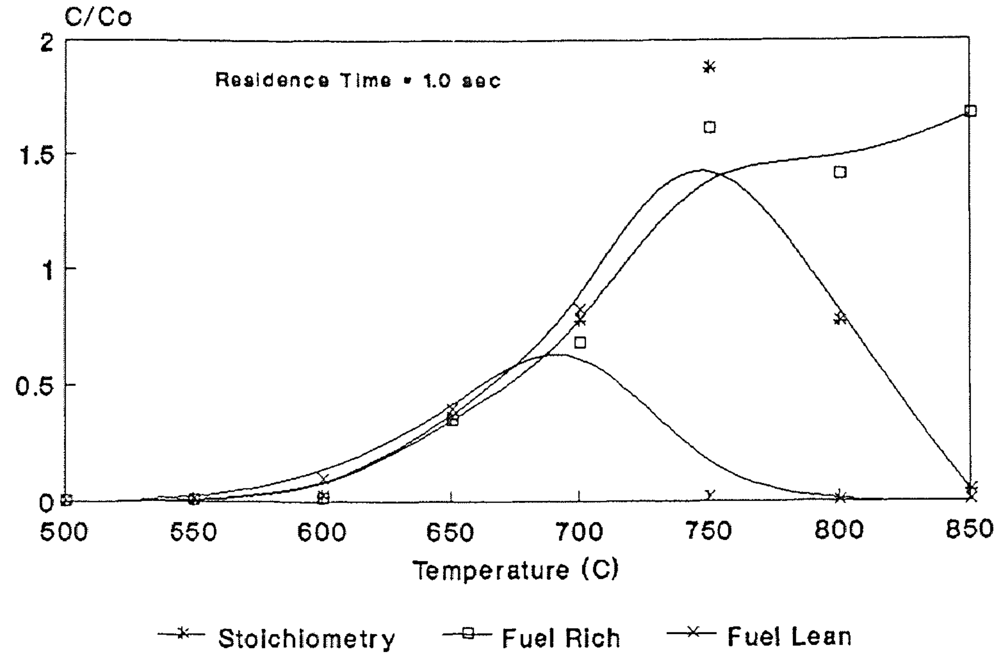


Figure 3.33 CO vs Temperature

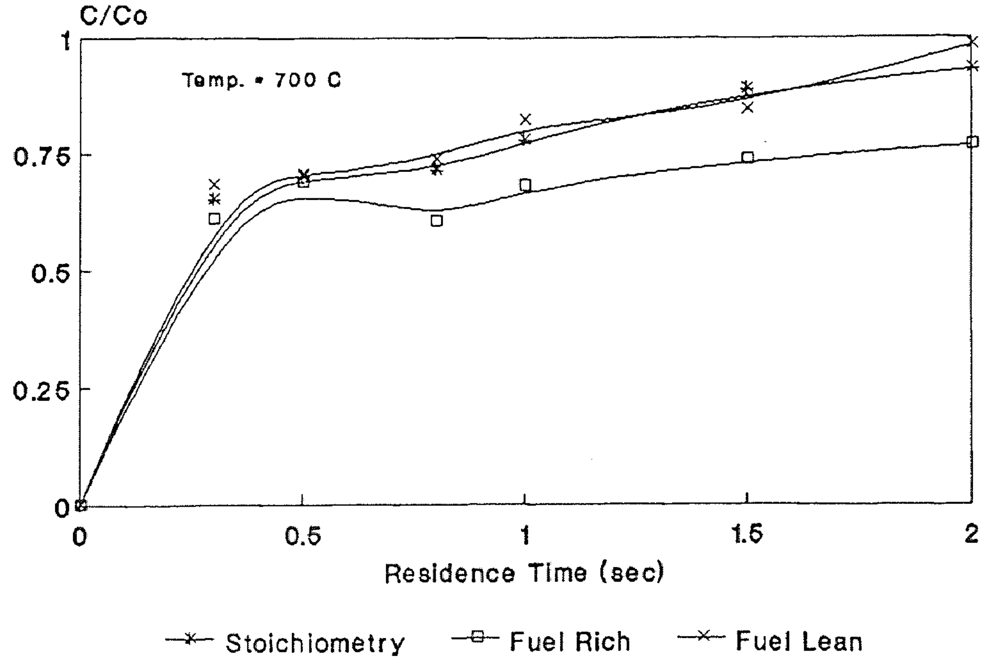


Figure 3.34 CO vs Time

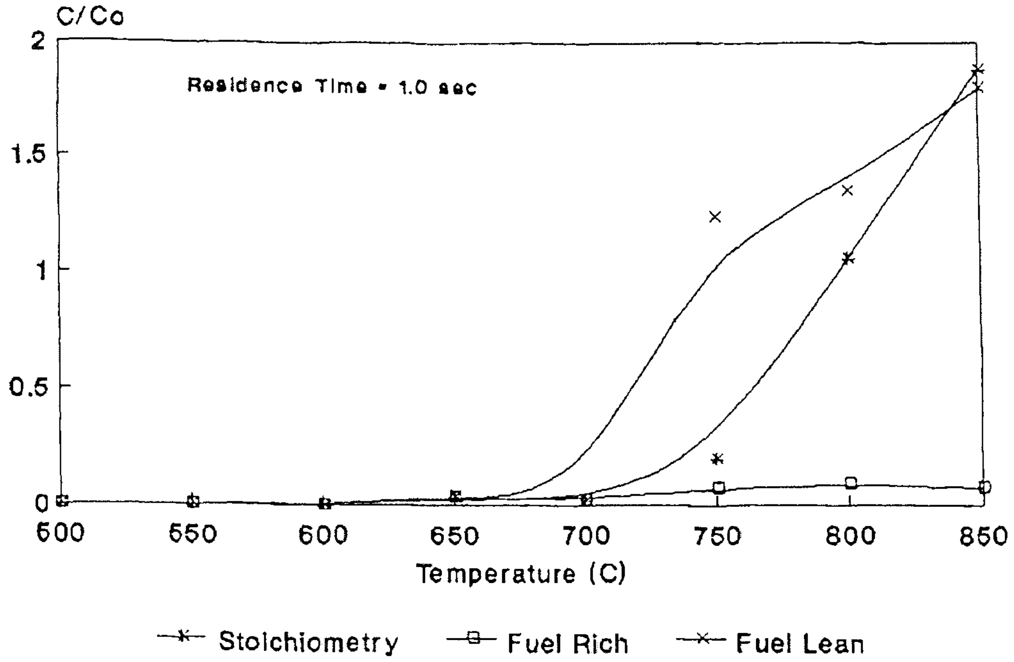


Figure 3.35 CO2 vs Temperature

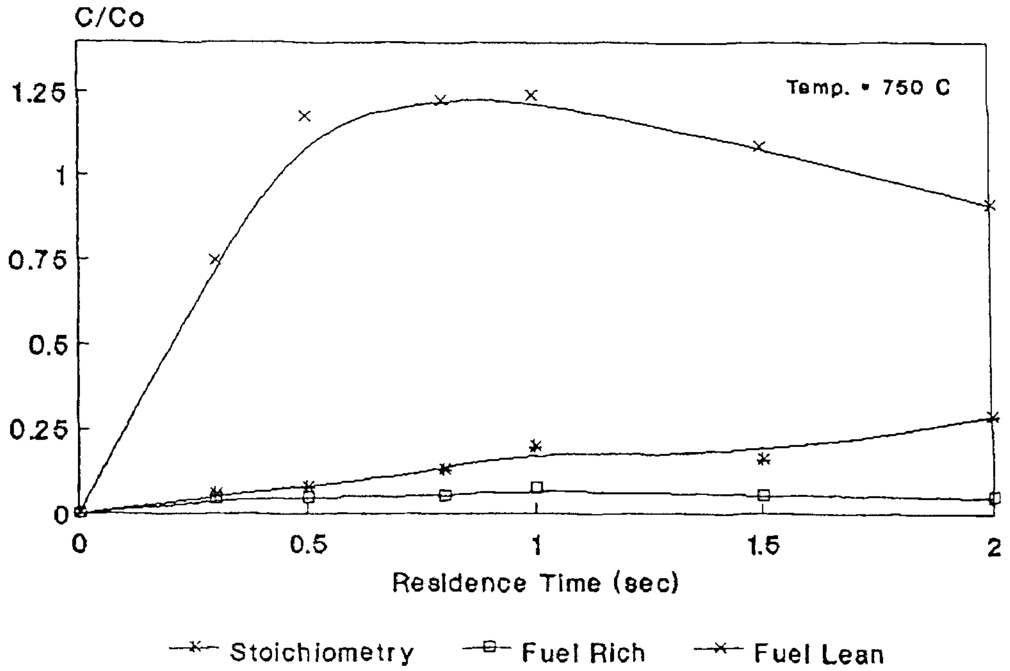


Figure 3.36 CO2 vs Time

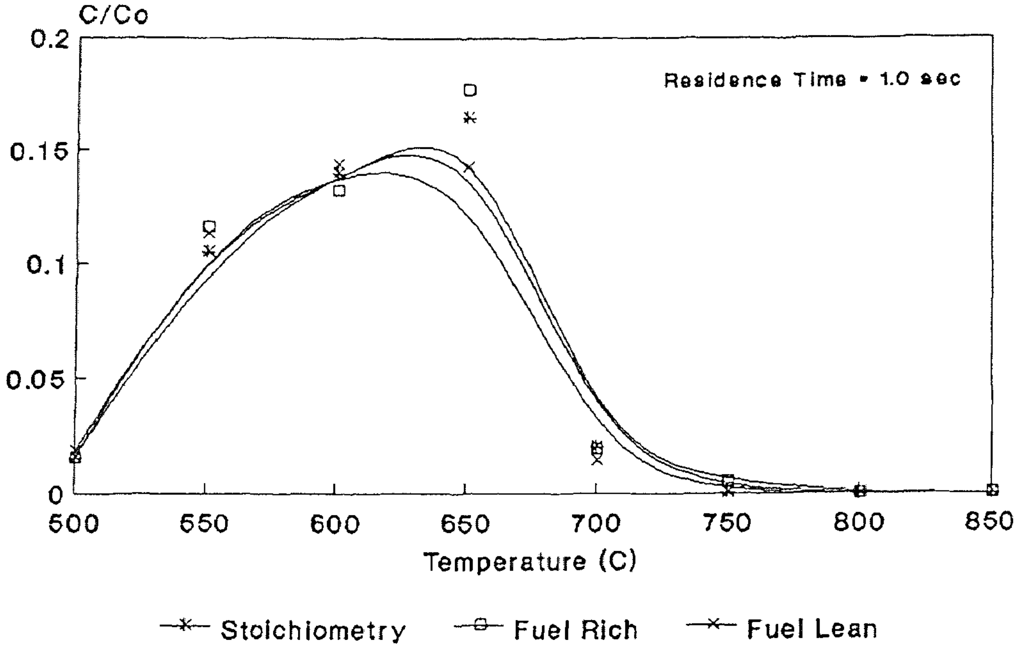


Figure 3.37 CH2O vs Temperature

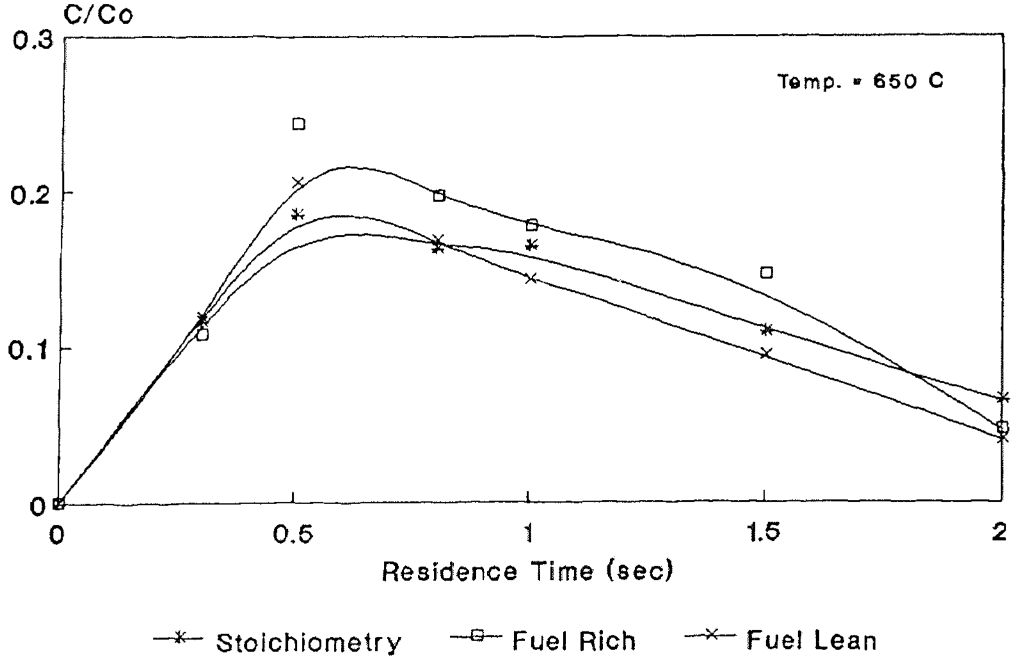


Figure 3.38 CH2O vs Time

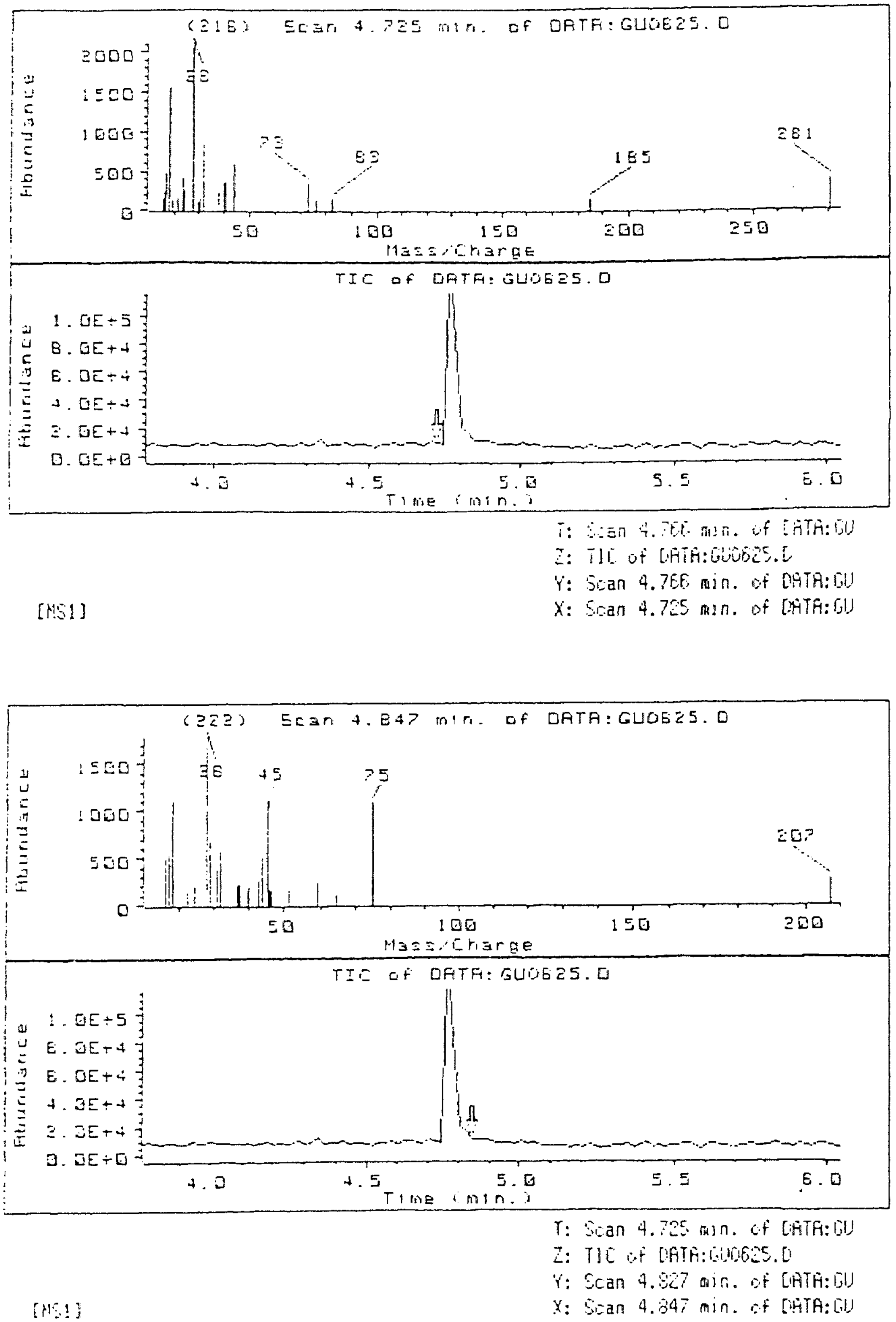


Figure 3.39 GC/MS Analysis

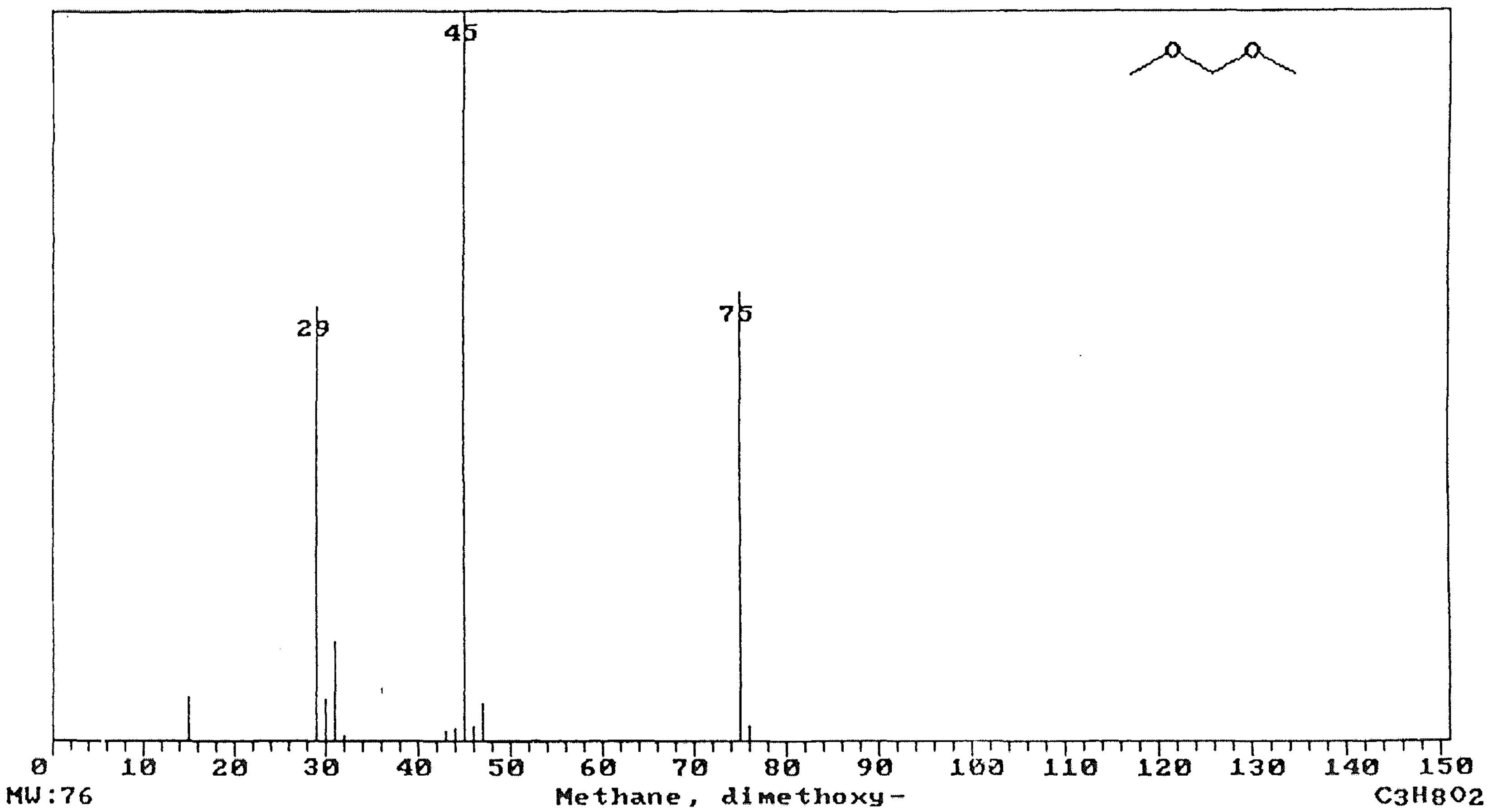


Figure 3.40 GC/MS Analysis

CHAPTER 4
CONCLUSION

Tubular flow reactor experiments on methanol oxidation are performed in the presence of methane fuel at varied fuel equivalence ratios, at 1 atmosphere pressure with residence times of 0.3 to 2.0 seconds and temperature range of 500-850 C. The equivalence ratios are:

(1) $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 2 : 96$ $\phi = 1.75$

(2) $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 3.5 : 94.5$ $\phi = 1.0$

(3) $CH_3OH : CH_4 : O_2 : Ar = 1 : 1 : 5 : 93$ $\phi = 0.7$

The extensive experimental data will be used as a basis for developing a detailed elementary reaction model for methanol/methane oxidation, i.e. validation of the model. Intermediate products: dimethyl ether (CH_3OCH_3) and formaldehyde dimethyl acetal($CH_3OCH_2OCH_3$), are observed in the low temperature regime (550-650C) and reported for the first time in this study. These products arise from the combination and addition reactions of CH_3O and CH_3 radicals with themselves and with CH_2O or CH_2OH radical.

These combination and addition reactions are important and readily occur in the methanol/methane system. It is a surprise that they have not been previously observed or anticipated. These observations reveal some new pathways in the methanol combustion process. The new reactions will be included in our reaction modeling studies so that the model can be extended to conditions outside our experimental validation range.

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