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High temperature reactions of chloroform with methane

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ABSTRACT

Thesis title : High Temperature Reactions of Chloroform with Methane.

Siozopoulos Thomas, Master of Science in Chemical Engineering, 198~~6~~7

Thesis directed by : Dr Joseph Bozzelli, Professor
Dept. of Chemistry & Chemical Engineering.

The reactions of Chloroform with Methane were studied at atmospheric pressure in the temperature range of 550-800 deg C, and using three different reactor diameters.

The reaction was found to follow pseudo-first order kinetics in the presence of excess Methane and Argon, and the kinetic parameters were determined for each of the reactor sizes.

The resulting global Arrhenius expressions are:

For 0.4 cm ID $K_{exp} = 2.03 * 10^{8} \exp(-34000/RT)$
For 1.05 cm ID $K_{exp} = 9.86 * 10^{8} \exp(-37950/RT)$
For 1.6 cm ID $K_{exp} = 4.17 * 10^{8} \exp(-36760/RT)$

An increase in the surface to volume ratio of the reactor tube was found to accelerate the decomposition rate of Chloroform, but it did not effect the stable product distribution.

After decoupling the homogeneous gas phase rate constant and the wall rate constant, the first order reaction rate expressions were obtained as follows:

For gas phase : $K_b = 6 * 10^{10} \exp(-46700/RT)$
For the wall : $K_w = 8.8 * 10^{6} \exp(-33000/RT)$

The major stable reaction products, identified by Mass/Spec. analysis, were C_2H_2, CH_3Cl, C_2H_3Cl, $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4, C_2HCl_5, C_2Cl_6 and traces of CCl_4, $C_2H_2Cl_4$, $C_3H_2Cl_4$, C_4HCl_5 and C_4Cl_6.

The residence times used ranged from 0.5 sec to 3.2 sec. Complete destruction of all the chlorinated compounds occured at 800 deg C and residence time less than 0.5 sec.

A reaction mechanism was established, including all the elementary steps needed to lead to the observed product distribution.

It was proven that the initial reaction step is unimolecular decomposition of chloroform, taking place by an HCl molecule elimination and carbene formation, as the following scheme describes :

$$CHCl_3 \text{ ---> } :CCl_2 + HCl$$

HIGH TEMPERATURE REACTIONS OF CHLOROFORM WITH METHANE

by
Thomas Siozopoulos

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering
198~~6~~7

APPROVAL SHEET

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Major : Chemical Engineering

Minor : Computer Science

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I. INTRODUCTION

Industrial production processes for plastics, solvents, thermostable insulators, pesticides and other chemicals, result in a large amount of chlorinated organic waste such as chloroplastics, chlorocarbon solvents, polychlorinated benzenes and biphenyls (PCB), DDT and others.

The disposal of chlorinated organics has recently become a major environmental issue, especially since many chlorinated hydrocarbons previously considered as safe, have proven to be toxic and/or carcinogenic (22).

Many technologies are presently under development for conversion of toxic waste to nontoxic endproducts.

From non-thermal methods we mention carbon adsorption, chlorinolysis, Na-based dechlorination (The only commercially available method) (18), photolytic and microwave plasma destruction, activated sludge, trickling filters and various bacterial methods.

Biological treatment has been proven applicable, breaking down substances like PCB's and pentachlorophenol, but limited to water treatment with low pollutant concentrations and only some chlorocarbons.

Another, very short sighted, method of disposal could be by land filling. Strong opposition for this method is demonstrated nowadays because of the existing possibilities of a future toxic waste leak into the groundwater system (36).

High temperature incineration is presently considered as an effective, practical and economical approach for the disposal of toxic chlorinated wastes.

According to the US EPA regulations the toxic material should have a residence time of over 2 sec in the combustion zone at temperatures over at least 1200 deg C in the presence of excess oxygen.

The major drawback of this method is that, though complete destruction of the input chlorocarbon stream is reported, the formation of toxic byproducts, such as CL2 COCL2 and fragments of the parent species containing chlorine, is observed in the product stream. Discharge of these products in the environment is highly unacceptable.

The emmission of these toxic species has been suggested as due to the persistence of halogen carbon bond of the parent species or the formation of halogen carbon bond, in an oxygen rich combustion environment where there is no desirable and stable end adduct for the chlorine.

Instead of detoxifying halocarbons in an oxidizing atmosphere,with all the above problems and PIC 's (Products of incomplete combustion) a promising alternative is the use of a reducing atmosphere which may result in a desirable end product, HCL, for chlorine uptake.

S.C.Chuang (17) summarizes the advantages of using a hydrogen rich atmosphere in the following :

I. Hydrogen chloride formation is thermodynamically favorable since H-Cl bond (103 kcal/mol) and C-Cl bond (81 kcal/mol).
In addition to that HCl can be easily collected and neutralized.

II. Fuel would only be needed to heat the reagents (not as a reagent itself). The result would be reduction in fuel requirements.

III. With this method all the chlorine would be abstracted from the parent species, under proper conditions,and the ideal product would be the corresponding gaseous hydrocarbons, HCl and carbon.

The most important advantage of experiments using this method would be the resulting information related to kinetic parameters, product analysis and effects of reaction conditions on product distribution and selectivities.

This information would lead to a better understanding of the chemistry of these, so far unexplored, reducing reactions and also provide reference data for modeling combustion and thermal reactions of chlorinated waste.

II. PREVIOUS STUDIES

II1. THERMAL DECOMPOSITION OF CHCl3

The thermal decompositition of chloroform was studied by Lessig (1) in 1932 . He reported pressure irregularities with time and the formation of a "yellow crystalline material together with a tar".

In 1935 Verhoek (2) measured the pressure increase due to the pyrolysis of CHCl3 and identified only HCl as a product, but he suspected the presence of hexachloroethane.

There was neither product analysis results nor reaction mechanism proposed, in these studies.

In 1956 Semeluk and Bernstein et. al.(3,4) studied the pyrolysis of $CHCl_3$ bulk reaction and reported the products analysis and kinetic parameters they proposed as an initial step for the reaction mechanism, the separation of a chlorine atom from chloroform.

$CHCl_3$ ---> $.CHCl_2$ + .Cl

After products analysis, the major products reported were HCl and C_2Cl_4 and minor chlorinated hydrocarbons "probably present" such as CCl_4 , $C_2H_2Cl_2$, cis and trans dichloroethylene and C_2Cl_2.

An inhibition effect was also reported, caused by the HCl formation.

Addition of HCl in the reactants resulted in the following expression for the $CHCl_3$ decomposition.

$$-\frac{d(CHCl_3)}{dt} = \frac{k*(CHCl_3)}{[\ 1 + b*(HCl)\ ]^{0.5}}$$

Shilov and Sabirova (5) proposed that the initial step in the thermal decomposition of $CHCl_3$, is the breaking of Chloroform into HCl and dichlorocarbene.

$CHCl_3 \Longleftrightarrow :CCl_2 + HCl$

This also explains the inhibitory effect of HCl in pressure ranges of 1.18 to 35.9 mm Hg.

The above mechanism is supported over the one proposed by Semeluk et. al. by the results of another report by Murgulescu and Weismann (6) for a CH_4, $CHCl_3$ system.

Other studies include the one by Arbeiter & Lemoan (7) and of Vacherot and Parant (8) who studied the thermal decomposition of Chloroform over silica.

They claim that "reaction is very complex". It is possible that the radicals CCl_3, $CHCl_2$, CCl_2 are formed and proceed toward stable products.

A recent study by Herman, Magnota, Buss, and Lee, (9) examines the pulsed CO_2 laser multiple-photon dissociation of deuterated Chloroform ($CDCl_3$), in a molecular beam using 11μ radiation. The only observed dissociation channel was hydrogen chloride elimination (> 99.1 %) with no evidence of simple chlorine atom cleavage (< 0.9 %) .

Two other studies reported in the literature were concerned with the estimation of the activation energy of the initial step in chloroform thermal decomposition (Hydrogen chloride elimination).

Benson and Spokes (10) obtained a lower limit of 53 kcal/mol in a low pressure pyrolysis reactor.

Scug et. al. (11) measured the appearance of C_2Cl_4 by ultraviolet absorption after a shock tube pulse giving a 54.5 kcal/mol activation energy at 1200 K .

All reports agree on a unimolecular decomposition as the initial step.

II2. THERMAL DECOMPOSITION OF CHLOROFORM W' H2 OR CH4

The reaction of CHCl3 with atomic hydrogen was studied by Clark and Tedder (18) in a flow system . They proposed a decomposition by the carbene route at low temperatures.

In a more general study Louw et.al. (12,13) and Manion et.al. (14) have reported that conversion of chlorocarbons like, dichloroethylene, dichloroethane, tetrachloroethylene, chlorobenzene, dichlorobenzene and polychlorobiphenyls in a hydrogen atmosphere resulted in hydrogen chloride and the corresponding hydrocarbons where chlorine in hydrocarbons was replaced by hydrogen .

Many relevant studies were done in the research laboratories at NJIT . For all of them kinetic parameters and product distributions have been reported.

Chuang (17) studied the reactions of hydrogen with chloroform and 1,1,2 trichloroethane . The reaction produced mainly methane, acetylene, ethylene, hydrogen chloride and carbon for temperatures above 850 °C, demonstrating the complete abduction of chlorine atoms by hydrogen atoms, in favor of HCl formation. Two papers were published from this work (20,22).

Mahmood (18) studied also reactions of chloroform and trichloroethylene with hydrogen and he reported an activation energy of 35.3 kcal/mol for the gas phase (bulk) reaction, and 43.4 kcal/mol for the wall reaction.

Hwang (21) studied the reactions of chloroform w' water vapor and observed C2Cl4 as a major product and CCl4, C2HCl3 and C2H2Cl2 as minor products at temperatures below 700 °C . Above 1000 deg C all chlorinated products were essentially converted to carbon, CO, CO_2, and HCL with some traces of C_2H_2.
One paper was published from this work (20).
Catalytic reactions of chloroform w' hydrogen over various catalysts have been investigated by Yang (19).

Murgulescu and Weissmann (6) have studied the influence of methane on the thermal decomposition of chloroform.
They deduced that HCl and dichlorocarbene formation was the dominant route, because the observed products apparently resulted from the competitive formation and subsequent decomposition of pentachloroethane and 1,1 dichloroethane, as the following scheme describes :

Initially unimolecular decomposition

$CHCl_3 \Longleftrightarrow :CCl_2 + HCl$

followed by two parallel reactions

$:CCl_2 + CH_4 \longrightarrow CHCl_2-CH_3$

$:CCl_2 + CHCl_3 \longrightarrow CHCL_2-CCl_3$

to yield pentachloroethane and 1,1 dichloroethane.

This mechanism was tested by passing the decomposed products through a toluene stream .

If a chlorine atom was present in the system due to the alternate initiation step : $CHCl_3 \Longleftrightarrow .CHCl_2 + .Cl$

then a hydrogen atom would be detached from toluene and HCl and benzyl radical would be formed. The benzyl radical would dimerize next to yield dibenzyl according to the following scheme:

$$.Cl + C_6H_5{-}CH_3 \longrightarrow .C_6H_5{-}CH_2 + HCl$$

$$2\ .C_6H_5{-}CH_2 \longrightarrow C_6H_5{-}CH_2{-}CH_2{-}C_6H_5$$

Since dibenzyl is only produced in traces, the theory for initiation step of Semeluk and Bernstein (4) does not have any profound basis.

Another related study is the chlorine catalyzed polymerization of methane and pyrolysis of the resulting methylchloride, studied by Benson and Weissmann (15).

This study demonstrates the formation of C_2 hydrocarbons at temperatures above 980 °C, like C_2H_4 and C_2H_2, but does not result to a mechanism of $CHCl_3$ decomposition.

III. THEORY

III1. UNIMOLECULAR AND PSEUDO FIRST ORDER REACTIONS

The reactions of chlorinated hydrocarbons with hydrogen or methane are likely to be initiated by a unimolecular decomposition of the chlorinated species as this study and previous studies (16-22) demonstrate.

A unimolecular decomposition is generally described by the following scheme:

$$A \longrightarrow \text{Products} \qquad \text{(a)}$$

A question of importance in unimolecular decompositions is how a single molecule becomes sufficiently energetic by itself to cause it to react. The theory of Lindemann (23) later developed by Hinshelwood (24) explains this by postulating that actually bimolecular collisions generate extraenergetic molecules which then decompose:

$$A + M \underset{2}{\overset{1}{\longleftrightarrow}} A^* + M \qquad \text{(b)}$$

$$A^* \xrightarrow{3} Q + \dots \text{(slow)} \qquad \text{(c)}$$

Here M stands for the third body which could be a reactant, a product, or an added nonreactive gas molecule.

A* stands for the energized molecule.

Then the rate of product formation observed is :

$$\frac{dC_Q}{dt} = k_3 C_{A*} \qquad \text{(d)}$$

The concentration of A* is found from the kinetics :

$$\frac{dC_{A*}}{dt} = k_1 C_A C_M - k_2 C_{A*} C_M - k_3 C_{A*} \quad (e)$$

To solve this differential equation in conjunction with a similar one for species A would be very difficult, and recourse is usually made to the "steady state approximation". This assumes that $dC_{A*}/dt = 0$, or that the right-hand side of Eq.(e) is in a pseudo equilibrium or stationary state .

With this approximation Eq.(e) is easily solved:

$$C_{A*} = \frac{k_1 C_A C_M}{k_3 + k_2 C_M}$$

Then $$\frac{dC_Q}{dt} = \frac{k_1 k_3 C_A C_M}{k_3 + k_2 C_M} \quad (f)$$

In our system where M is present in large excess (Methane and argon have a 10:1 concentration ratio to chloroform) its concentration C_M remains practically unchanged by the formation of the energized radical adduct. The rate of energization can be assumed to be in equilibrium with the rate of collisional deactivation .

The unimolecular decomposition of the radical adduct to products becomes the rate limiting process and a pseudo-first order behavior is observed where $dC_Q / dt = k\, C_A$.

Since C_M is approximately constant, k can be defined as :

$$k = \frac{k_1 \; k_3 \; C_M}{k_3 + k_2 \; C_M}$$

Here k is the observed first order global rate constant and its limiting values are :

I. For high concentrations (pressure) $k_2 C_M \gg k_3$ since reaction (c) is presumably slow, and so,

$$\frac{dC_Q}{dt} = \frac{k_1 k_3}{k_2} C_A \quad \text{and} \quad k = \frac{k_1 k_3}{k_2}$$

which is a first order reaction rate.

II. Conversely as the total pressure of the system is decreased, a point is reached where the collisional activation process becomes rate limiting. At pressures below this so called transition pressure the reaction follows second order kinetics.

As a result of $k_2 C_M \ll k_3$, $\frac{dC_Q}{dt} = k_1 C_M C_A$ and $k = k_1 C_M$

This is known as the falloff region since the observed rate constant decreases as the pressure or third body concentration is decreased.

Thus, this theory indicates that simple decompositions that are first order at high pressures should change to second order at low pressures. Many years of experimentation have shown this to be the case. Better quantitative agreement with the data is provided by more elaborate but similar theories-see Laidler (25) or Benson (26).

For an exhaustive discussion of unimolecular reaction theory see Robinson and Holbrook (28) or Forst (29).

III2. TUBULAR FLOW REACTOR THEORY AND RELATED ASSUMPTIONS

Kinetic measurements like the ones of the present study, are routinely done in a tubular flow reactor system,which consists of a flow tube within a furnace.

An effort is made to maintain conditions that maximize radial diffusion and minimize pressure drop,axial diffusion and wall reaction, or in other words conditions that justify the plug flow assumption.

Plug flow is a simplified and idealized picture of the motion of a fluid, whereby all the fluid elements move with a uniform velocity along parallel streamlines (27).

Generally in tubular flow reactors radial mixing is due to molecular diffusion and axial mixing due to fluid velocity gradients (18). The Reynolds numbers (N_{re}) for this study are consistently below 10000, which means the laminar flow regime.

For different range of Reynolds numbers in the laminar flow regime the following mechanisms of dispersion may be assumed to take place in the tubular reactor (34,35).

1) For Reynolds numbers in the upper range of laminar flow, molecular diffusion effects in dispersion are negligible compared to the contribution of the velocity profile.

2) In the midrange of Reynolds numbers, both radial and axial diffusion effects are significant in comparison with the contribution of the velocity profile.

3) In the low range, the velocity profile has a smaller effect than molecular diffusion, which is the case in the present study.

As a result for the present study axial diffusion is assumed to be negligible.

A more rigorous analysis more applicable for our system is found in the paper by Poirier and Carr (31). They utilize both radial diffusion and laminar velocity profile to estimate the radial diffusion effects and the proximity to ideal plug flow assumption. They solved numerically the continuity equations for first order reactions considering radial diffusion and they propose that for D/kR >= 0.5 (R is the reactor radius) plug flow approximation is satisfactory. For the present study D/kR values were above 0.5 and indicate that a plug flow assumption is valid.

The best proof for the validity of the plug flow assumption is provided by the comparison of the kinetic values found by plug flow analysis,with values obtained by applying the numerical solution of the continuity equation for first order kinetics with laminar flow, radial dispersion and both bulk and wall reactions (16).

The conservation equation which is numerically solved,is according to Bird, Stewart and Lightfoot (32)

$$-v(r)\frac{C}{z} + D\left\{\frac{{}^{2}C}{r^{2}} + \frac{1}{r}\,\frac{C}{r} + \frac{{}^{2}C}{z^{2}}\right\} = kC$$

Where r is the reactor radius, v(r) the radial velocity distribution, z distance along the reactor axis, D the diffusion coefficient, k the reaction rate constant and C the concentration of the reacting species (function of z and r).

This analysis though rigorous and computer time consuming, is valuable in determining kb and kw (bulk and wall reaction rate constants) and proving the validity of plug flow assumption (PFR). Deviations under similar conditions were within 10 % of PFR assum.(16)

The PFR assumption made the analysis of experimental data simpler, avoiding complications as an effect of non-ideality.

III3. METHODS FOR KINETIC ANALYSIS WALL AND BULK RATE CONSTANTS

Assuming the ideal plug flow model as valid, we can deduce that all the fluid elements have the same residence time within the reactor, and that there is not any axial diffusion or radial concentration gradient.

The equation describing the conversion of reactants to products is:

$$t = \frac{V}{v_0} = C_{A0} \frac{dX_A}{-r_A} \qquad (a) \qquad (30)$$

Where t is the space time or residence time for a specific run, estimated by dividing the reactor volume (V) with the volumetric flow rate of the gas at the reactor temperature (v_0).

C_{A0} is the initial reactant concentration (inlet chloroform concentration for our case), X_A is the conversion of the reactant which can be expressed as $X_A = (1 - C_A/C_{A0})$, and finally r_A is the reaction rate for reactant A (Chloroform) which follows pseudo first order kinetics due to the large excess of one of the reagents.

As a result $r_A = -k_{exp} C_A$ and equation (a) yields :

$$-\ln (C_A/C_{A0}) = k_{exp}\, t \qquad (b)$$

C_A is the reactant concentration at the reactor exit and k_{exp} the observed experimental global rate constant.

It is obvious from equation (a) that one can manipulate the residence time by varying the reactants flow rate and for constant inlet conditions plot $-\ln (C_A/C_{A0})$ vs t for a specific temperature, obtaining in this way the global reaction rate constant k_{exp} from the slope of the plotted line.

Using equation (b) to estimate k_{exp} at different reactor temperatures, the temperature dependence of k_{exp} can be determined using the Arrhenius law :

$$\ln(k_{exp}) = \ln_A - E_A/RT \qquad (c)$$

Where A is the Arrhenius pre-exponential factor, E_A is the activation energy, R is the universal gas constant and T is the reactor temperature in degrees Kelvin.

As demonstrated in many previous studies (16-22) the decomposition of chlorinated hydrocarbons is also a function of the reactor diameter . The observed conversion and k_{exp} is the result of two parallel reactions, one homogeneous occurring in the bulk of the gas and one heterogeneous occurring on the reactor wall surface.

As a result the contribution of the wall reaction as opposed to the bulk phase reaction, is a function of the ratio of wall surface to reactor volume, S/V . This is equal to 2/R where R is the reactor tube radius.

For plug flow conditions and first order kinetics, Kaufman (33) has derived the following relationship relating k_{exp} and 2/R .

$$k_{exp} = k_b + (2/R)\ k_w$$

Where k_b stands for the bulk phase reaction rate constant and k_w for the wall reaction rate constant.

Using reactors of different radius or surface to volume ratios, and keeping other reaction conditions the same,one can decouple these two reactions and estimate k_b and k_w by plotting k_{exp} vs 2/R.

The derived values for each temperature can then be used to evaluate activation energies and frequency factors for the wall and bulk phase reactions using the Arrhenius equation.

IV. EXPERIMENTAL METHODS

IV1. GENERAL DESCRIPTION

The reactions of Chloroform with Methane have been studied using the reactor system depicted in Figure #1.

The high temperature tubular flow reactor was operated isothermally in the range 550 deg C - 950 deg C, and at constant pressure of 1 atm.

Methane gas diluted with Argon was passed through a two stage saturation bubbler half filled with Chloroform, and sitting in an ice bath at 0 deg C. The flow of the two gases was controlled by calibrated rotameters, and glass beads within the bubbler dispersed the gas into foam providing sufficient contact time for saturation to occur independently of the flow rate used.

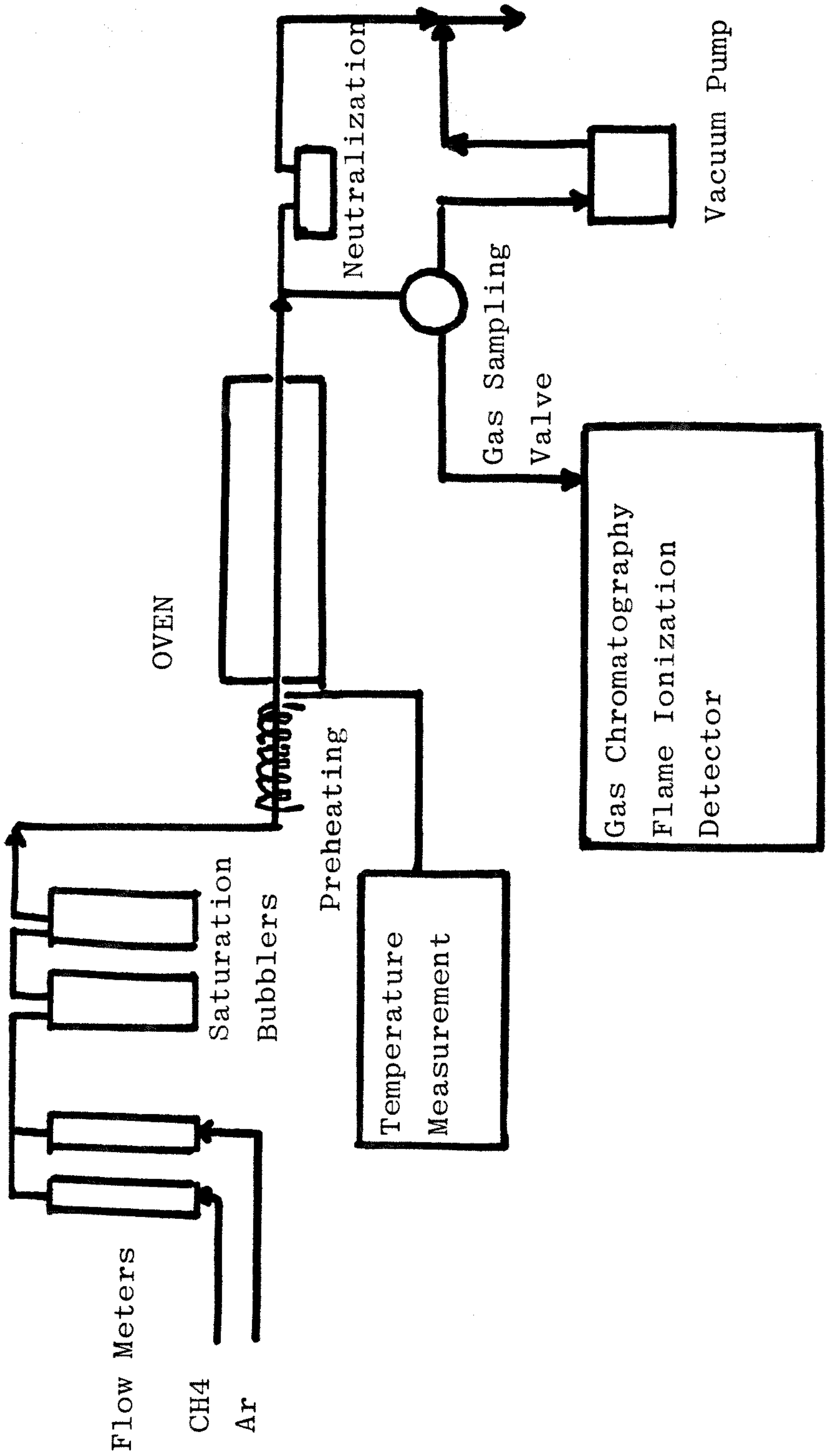
The saturated with Chloroform vapor, gas mixture was preheated to 130 deg C - 150 deg C before entering the reactor tube .

Three quartz reactor tubes were utilized in this study of either 0.4, 1.05, or 1.6 cm ID. The reactor tube in use was housed in a three zone Mellen clamshell electric furnace. Two zones of 3 in each and 100 volts operating voltage, were interconnected by a middle zone of 9 in and 180 volts op.v. providing a total length of 15 in.

The voltage provided to the heating zones was controlled by voltage transformers (variacs) . The furnace itself was insulated and enclosed in a LINDBERG HEVI-DUTY furnace enclosure.

By proper use of switching valves the gas mixture could bypass the reactor tube, and be fed directly through a separate heated transfer line, to the GC sampler. This made possible the evaluation of the initial concentration of chloroform for each run.

FIGURE #1



EXPERIMENTAL SYSTEM

The reactor outlet gases were passed through heated transfer lines to the GC sampler and the exhaust. Two glass wool filters a large before the exhast valve and a smaller before the GC sampling valve ensured the removal of any carbon particles from the gas mixture, preventing contamination of the GC sampling system.

About one tenth of the total outlet flow rate was routed through the GC sampler, with the help of a vacuum pump and proper adjustment of a needle valve controlling the vacuum line.

The rest of the outlet flow after filtration, was passed through a sodium-bicarbonate flask to neutralize the HCl, and then released to the atmosphere via a laboratory hood.

IV2. TEMPERATURE MEASUREMENT AND CONTROL

The three zone furnace equipped with three independent Burling Instr. Company, temperature controllers, made it possible to maintain nearly isothermal conditions within the reactor tube.

Three chromel-alumel thermocouples (type K) housed in a second quartz tube inside the furnace, provided continous feedback of temperature to the controllers. An inert gas flow was maintained in the tube to simulate better the reactor conditions, provide more realistic measurements, and eliminate radiation errors (36).

An additional type K thermocouple connected with an Omega model 650 temperature indicator,was used to monitor the actual temperatures moving it along the reactor axis . Readings were taken every 1 inch, while an inert gas flow was maintained to reduce the radiation error,the objective being a steady state for each point.

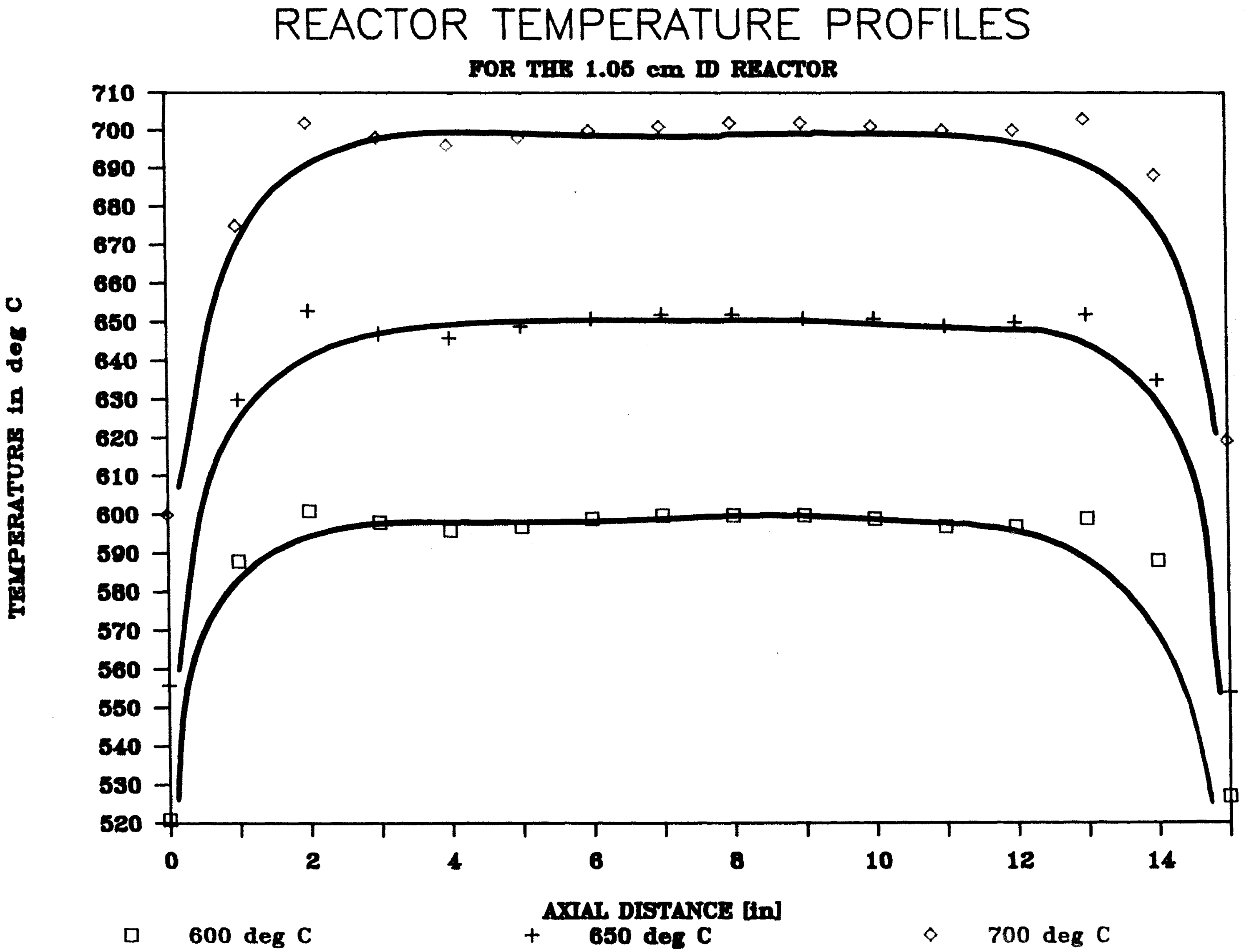

REACTOR TEMPERATURE PROFILES
FOR THE 1.05 cm ID REACTOR
TEMPERATURE in deg C
710
700
690
680
670
660
650
640
630
620
610
600
590
580
570
560
550
540
530
520
0
2
4
6
8
10
12
14
AXIAL DISTANCE [in]
□ 600 deg C
+ 650 deg C
◇ 700 deg C

FIGURE #2

As Figure #2 demonstrates, this system helped to obtain isothermal temperature profiles within ± 5 deg C over 85 % of the total furnace length.

Sensor degradation after a period of exposure to high temperatures made it necessary to periodically verify the thermocouple calibration, in order to avoid measurement errors.

IV3. DATA COLLECTION AND ANALYSIS WITH GAS CHROMATOGRAPHY

A Varian 3700 model gas chromatograph was used for the quantitative analysis of the reaction products, using a flame ionization detector (FID).

For separation of the products, a 10 ft long, 1/8 in OD, stainless steel tube packed with Porapak Q 50-80 mesh, was used. Argon carrier gas was supplied to the column inlet at a pressure of 60 psig, and 32 cc/min.

The sampling and injection system consisted of a fixed volume sample loop (1.5 ml) together with a six port Valco model gas sampling valve, all maintained at 150 deg C and 1 atm.

The packed column was maintained at 150 deg C . After an injection the oven temperature was raised to 220 deg C at a rate of 10 deg C / min and held at 220 deg C until completion of the analysis.

The flame ionization detector was maintained at 270 deg C and was fed with Ar make-up gas at a rate of 30 ml/min, Hydrogen at 35 ml/min and Air at 300 ml/min respectively. The signal amplification range was set to 10^{-9} amps/mv. Integration was performed with a 4270 integrator/plotter using an attenuation of 256 and a chart speed of 1 in/min.

A representative chromatogram is shown in Figure #3, together with retention times and peak identification.

Calibration of the flame ionization detector to obtain appropriate molar response factor was done by injecting a known quantity of the relevant compound such as CH_3Cl, C_2H_5Cl, $CHCl_3$ etc. and measuring the corresponding response area. The response factors for C1 chlorocarbons are close to one, while the value for the C2 compounds is twice as much. This is in general agreement with the principle of flame ionization detectors which are known as carbon counters. The relative response factors can thus be considered as corresponding to the number of carbon atoms in the molecule.

TABLE I

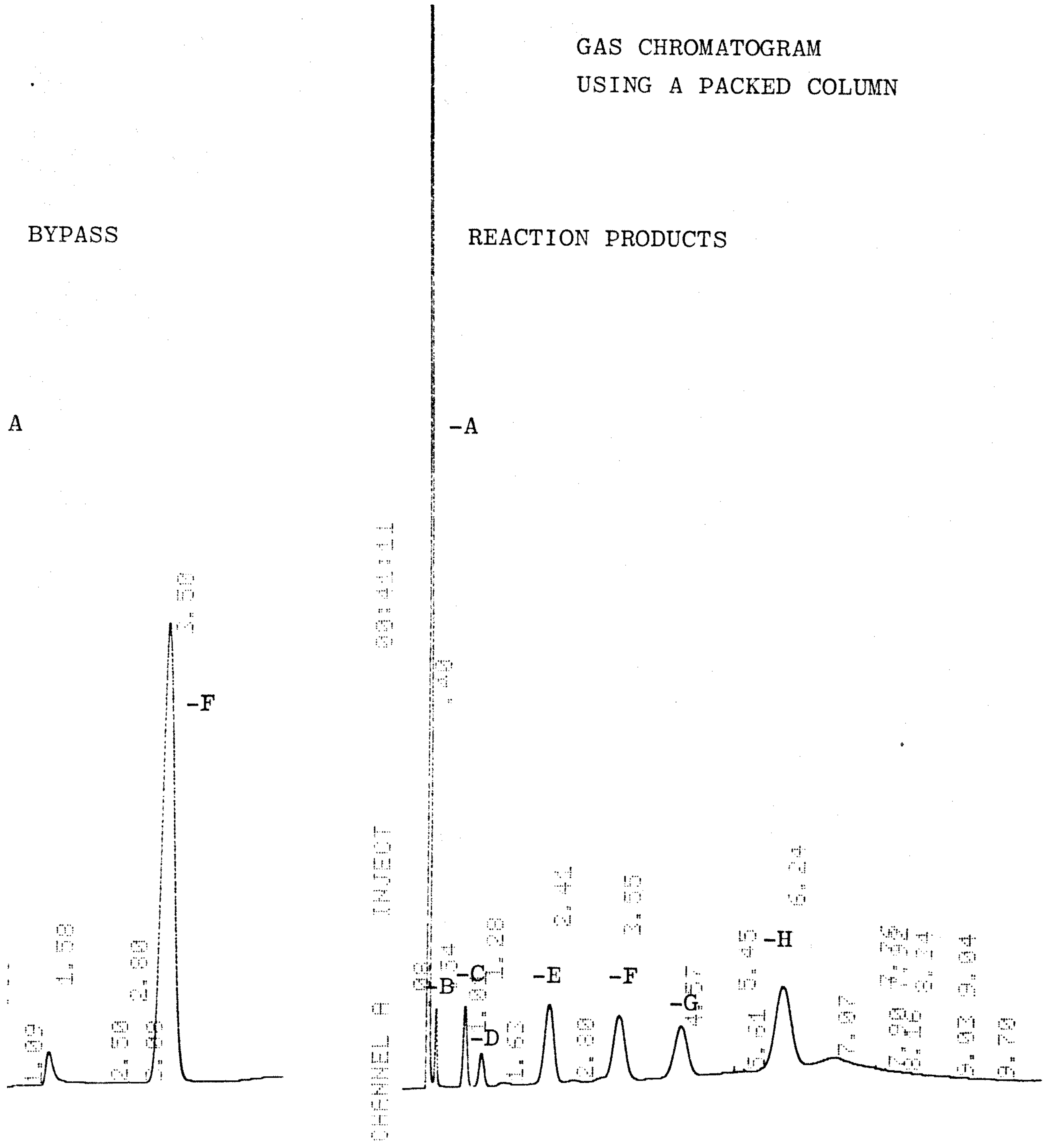
response FACTORS FOR THE OBSERVED PRODUCTS

COMPOUND	response FACTOR Based on C6H6	RELATIVE response FACTOR (RRF) Based on CHCl3
C_6H_6	1	
CH_4	6	
C_2H_2	3	0.375
CH_3Cl	6.5	0.816
C_2H_3Cl	3.05	0.383
$C_2H_2Cl_2$	3.1	0.39
$CHCl_3$	7.96	1
C_2HCl_3	3.13	0.398
C_2Cl_4	2.78	0.35

Corrected area = measured area from chromatogram * RRF

FIGURE #3

GAS CHROMATOGRAM
USING A PACKED COLUMN



A- CH4
B- C2H2
C- CH3C1
D- C2H3C1
E- C2H2C12
F- CHC13
G- C2HC13
H- C2C14

IV4. ANALYSIS OF HCL

The HCl quantitative analysis,was performed at 630 C, 650 C and 665 deg C, at a residence time of about 0.8 sec,using the 1.05 cm ID reactor tube. More data were collected for a single temperature at 650 deg C and residence times of 0.3,0.75 and 1 sec.

For the purposes of this analysis the reactor outlet gases were passed through a two stage bubbler before transfer to the exhaust system. Each of the two stages contained 20 ml NaOH solution of 0.01 N. The time required by the first stage to reach the phenolophthalein end point was recorded. After this point, the bubbling was stopped, the solutions from the two stages were combined and the resulting solution was titrated to its end point by standardized HCl solution. The rate of HCl production by the reaction was then easily calculated.

Knowing the chlorine molar flowrate entering the reactor as chloroform, and having done a quantitative analysis of the reaction products, we were able to make an estimate of the chlorine which escaped the GC analysis in the form of HCl and write a realistic material balance.

Despite the rigorous analysis methods applied,some chlorine still remained unaccounted for, a fact due to certain heavy chlorocarbons which were observed in the mass spectrometric analysis but were absent from our chromatograms. They must have been absorbed by the column material did not elute at the temperature range used for the oven and the specific packed column.

A solution would be the use of a General purpose stationary phase capillary column, which has a far greater potential for these, high molecular weight, products separation (retains them less strongly).

IV5. QUALITATIVE ANALYSIS OF REACTION PRODUCTS BY MASS SPECTROMETRY

The analysis of the reactor outlet gases was performed on a Kratos model MS25 Double Focussing Magnetic Sector Mass Spectrometer equipped with a Carlos Erba GC . This GC was equipped with a 50 m long 0.2 mm ID fused silica capillary column coated with a methyl silicone stationary phase (OV101).

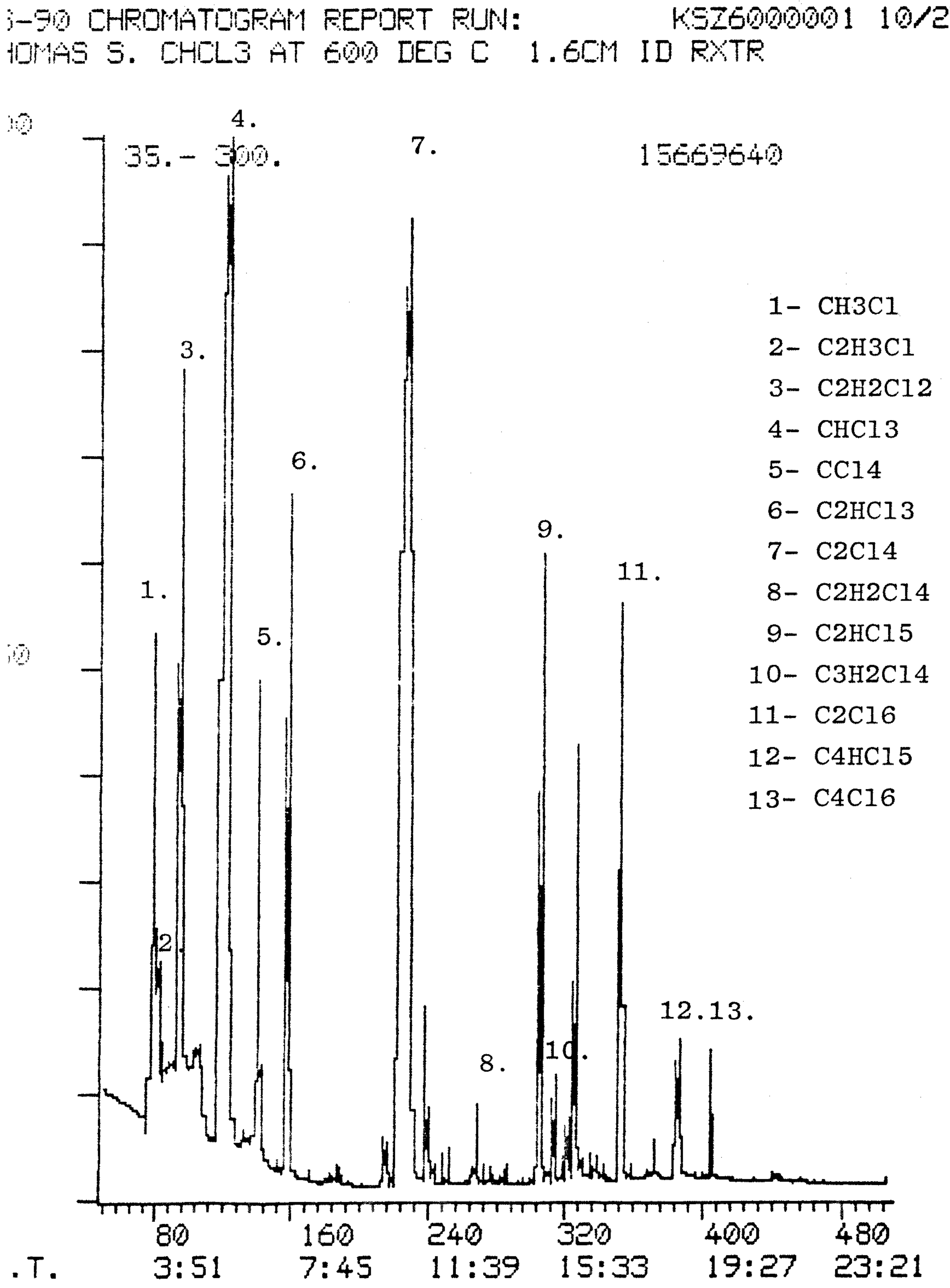
Evacuated 25 ml stainless steel cylinders were used for collection of gas samples at the reactor exit.

Injection of the samples into the GC/MS was made possible with the use of a six port gas sampling valve. The sample was cryogenically focused inside the GC oven by using liquid nitrogen.

A sample chromatogram from the Mass Spectrometer analysis is shown in Figure #4.

FIGURE #4

GAS CHROMATOGRAM USING A
CAPILLARY COLUMN



V. RESULTS AND DISCUSSION

V1. REACTION OF $CHCl_3$ WITH CH_4 IN AN INERT ATMOSPHERE

The reaction of $CHCl_3$ with CH_4 in the presence of excess argon gas, has been studied at 1 atm pressure, high temperatures and three different reactor diameters.

The different prevailing experimental conditions are listed below:

REACTOR LENGTH	:	38.1 cm
REACTOR DIAMETERS	:	0.4, 1.05, 1.6 cm
TEMPERATURES	:	552, 600, 650, 706, 750, 800 deg C
RANGE OF RESIDENCE TIMES	:	0.15 - 1.3 sec, for the 0.4 cm ID
	:	0.40 - 2.8 sec, for the 1.05 cm ID
	:	0.50 - 3.2 sec, for the 1.6 cm ID

The most appropriate temperature range for collection of kinetic data was between 600 and 665 deg C,where conversions varied from 20 % to 80 % depending on the residence time. Below 580 deg C the conversion was insignificant, while above 680 deg C it was almost complete and inappropriate for kinetic studies.

The expected decrease of the chloroform normalized concentration $[CHCl_3]/[CHCl_3]_o$, with increasing residence time at different temperatures is demonstrated by Figure #5.

Since in our system CH_4 and Ar are in large excess compared to chloroform (1:12) the pseudo first order model can be applied for the $CHCl_3$ kinetics. Figure #6 shows the linear relationship between $-\ln(C/Co)$ and residence time, for several different temperatures of the 1.05 ID reactor.

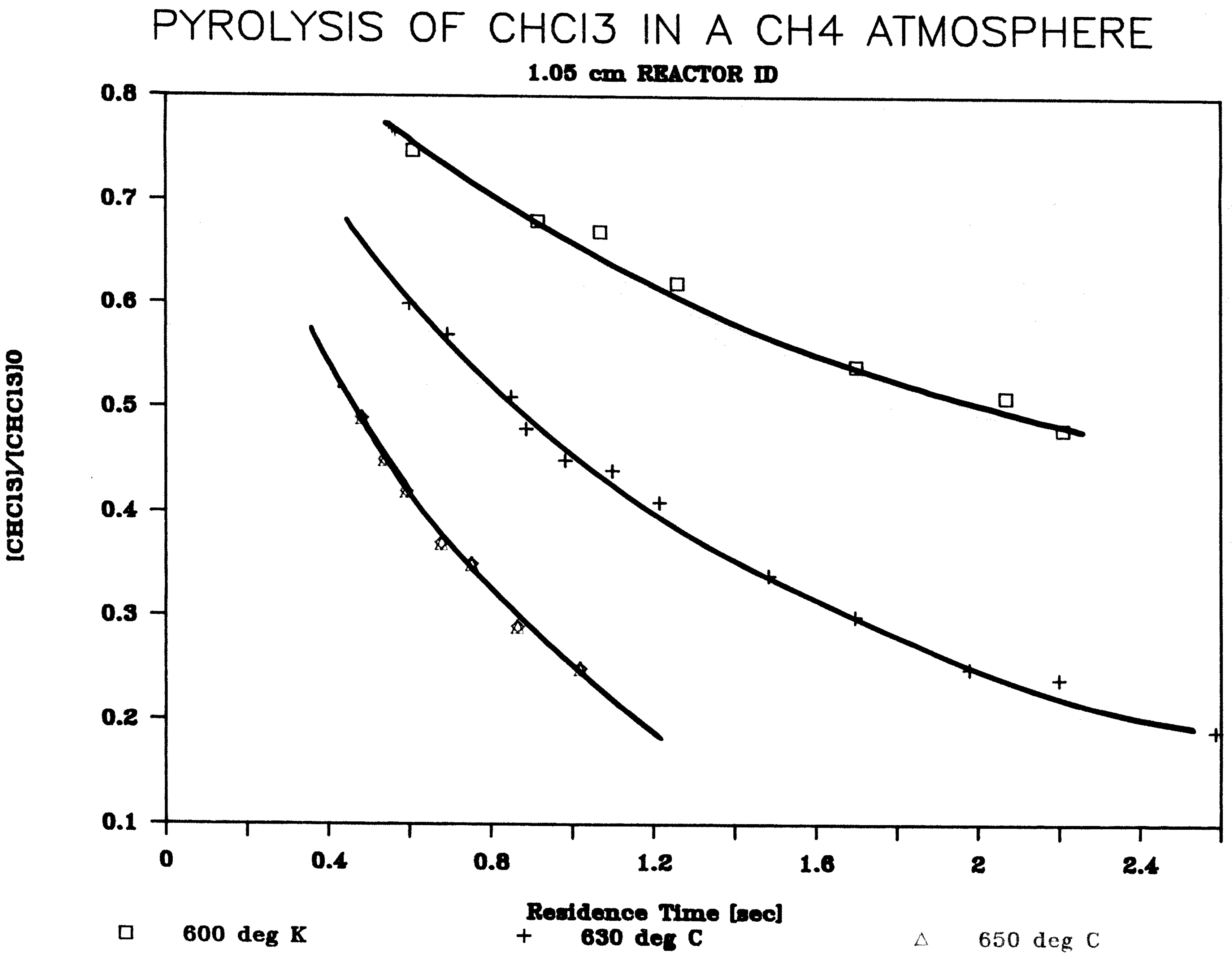

PYROLYSIS OF CHCl3 IN A CH4 ATMOSPHERE
1.05 cm REACTOR ID
[CHCl3]/[CHCl3]0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.4
0.8
1.2
1.6
2
2.4
Residence Time [sec]
□ 600 deg K
+ 630 deg C
△ 650 deg C

FIGURE #5

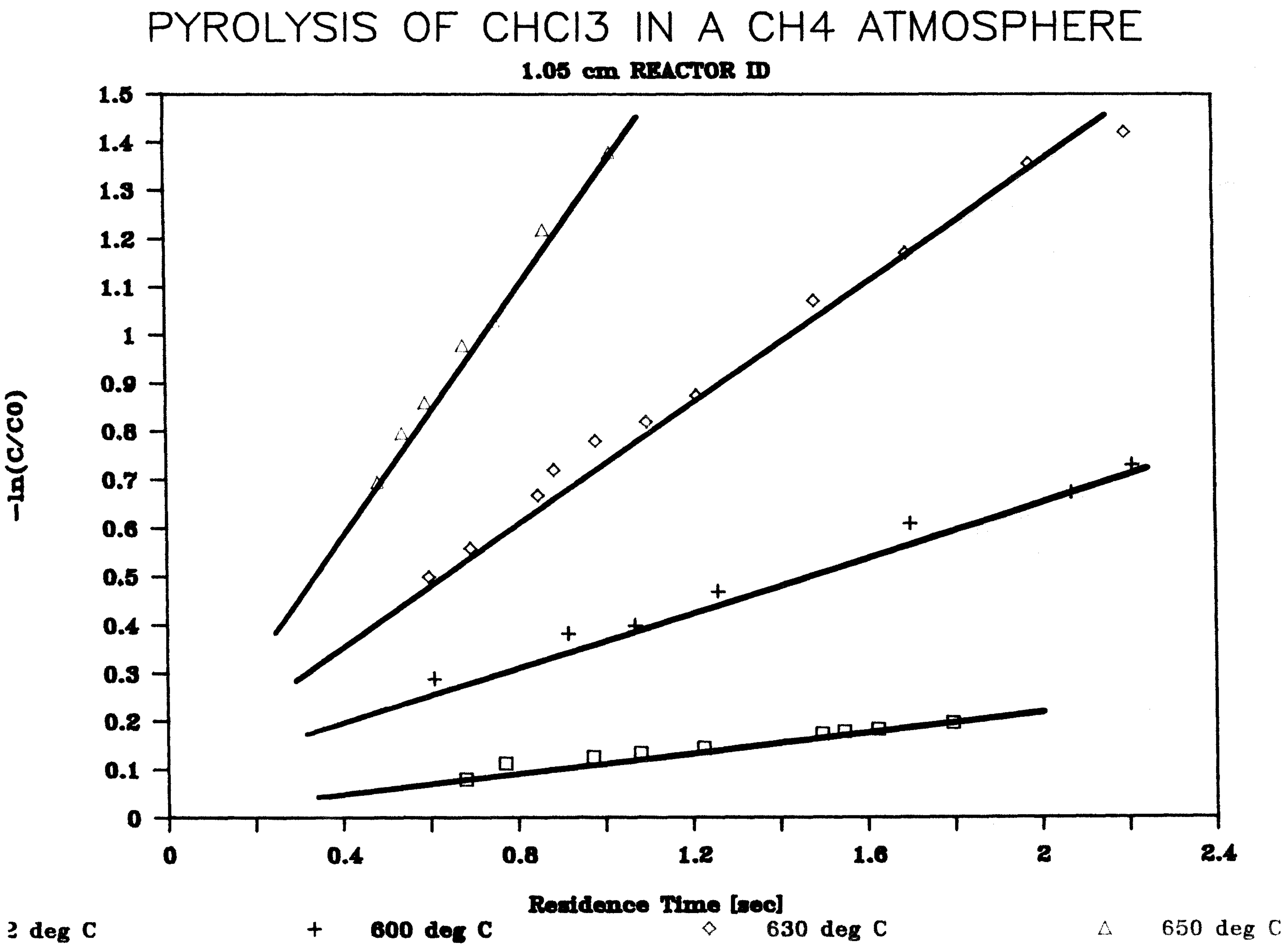

PYROLYSIS OF CHCl3 IN A CH4 ATMOSPHERE
1.05 cm REACTOR ID
-ln(C/C0)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
Residence Time [sec]
2 deg C
+ 600 deg C
◇ 630 deg C
△ 650 deg C

FIGURE #6

The observed global rate constant for each temperature is estimated from the slope of the corresponding line in the graph.

A deviation from the first order model was observed at high temperatures and low residence times. Obviously this is due to the high flow velocity which distorts the isothermality of our temperature profile or doesn't allow enough contact time for saturation in the bubbler.

The temperature dependency of the global reaction rate constant Kexp is expressed by the Arrhenius Law :

$$\ln (Kexp) = \ln (Ao) + (-E/RT)$$

where Ao is the frequency factor, a measure of the percentage of successful collisions, and E is the activation energy (energy barrier for reaction to occur). Plotting ln (Kexp) vs 1/T we can estimate the activation energy E from the slope and the pre exponential factor from the intercept.

The conducted experiments for the three different reactor diameters resulted to the following equations :

REACTOR ID	ARRHENIUS EXPRESSION
0.4	$Kexp = 2.03 * 10^8 \exp(-34000/RT)$
1.05	$Kexp = 9.86 * 10^8 \exp(-37950/RT)$
1.6	$Kexp = 4.17 * 10^8 \exp(-36760/RT)$

The difference between the reaction rate constants, is due to the contribution of a wall reaction which becomes significant at large surface to volume ratios (small ID reactor) . This subject is discussed in the following section together with the appropriate methods to obtain kinetic data for the gas phase only, omitting the wall effect.

The decomposition rate for this kind of reactions was shown to be affected by the surface to volume ratio of the reactor (S/V), by several previous studies as well as the present one.

The observed experimental rate constants are the combined effect of a reaction on the wall surface and a simultaneous reaction in the bulk gas phase.

Our results for the 0.4 cm ID reactor (large S/V area) compared with the 1.05 cm ID, show an increased reaction rate for the larger surface to volume ratio, reactor . This points to the fact that at large S/V values or in small diameter laboratory reactor tubes, the wall surface heterogeneous reaction contributes significantly to the overall reaction rate and accelerates it.

Since wall reactions are considered unimportant in an industrial scale pyrolysis unit, a method is needed to decouple the wall and bulk phase reaction rate constants .

Kaufman 's equation : $Kexp = Kb + (2/R) * Kw$ was used, assuming the ideal plug flow model .

A series of experiments varying the S/V ratio and holding all other reaction conditions the same, made it possible to plot 2/R vs Kexp for three different temperatures, Figure #9.
The resulting lines will have a slope of Kw and an intercept of Kb.

The Arrhenius behavior of Kb and Kw was easily determined from the values obtained for three different temperatures : 600, 630, 650 C.

The resulting expressions are listed below together with Table II for the values of the global rate constants and the Kb, Kw values for different temperatures and reactor ID 's.
Related Figures are #6 - #10

TABLE II

RATE CONSTANTS FOR CHCl3 + CH4 in excess Ar gas

	Global Rate Constants [1/sec]			Bulk Kb [1/sec]	Wall Kw [cm/sec]
Diam.	0.4	1.05	1.6		
Temp. deg C					
600	0.577	0.273	0.254	0.12	0.044
630	1.124	0.576	0.48	0.25	0.086
650	1.95	1.19	0.9	0.61	0.134
E cal/mol	34000	37950	36760	46700	33000

$$Kb = 6 * 10^{10} \exp(-46700/RT)$$

$$Kw = 8.8 * 10^{6} \exp(-33000/RT)$$

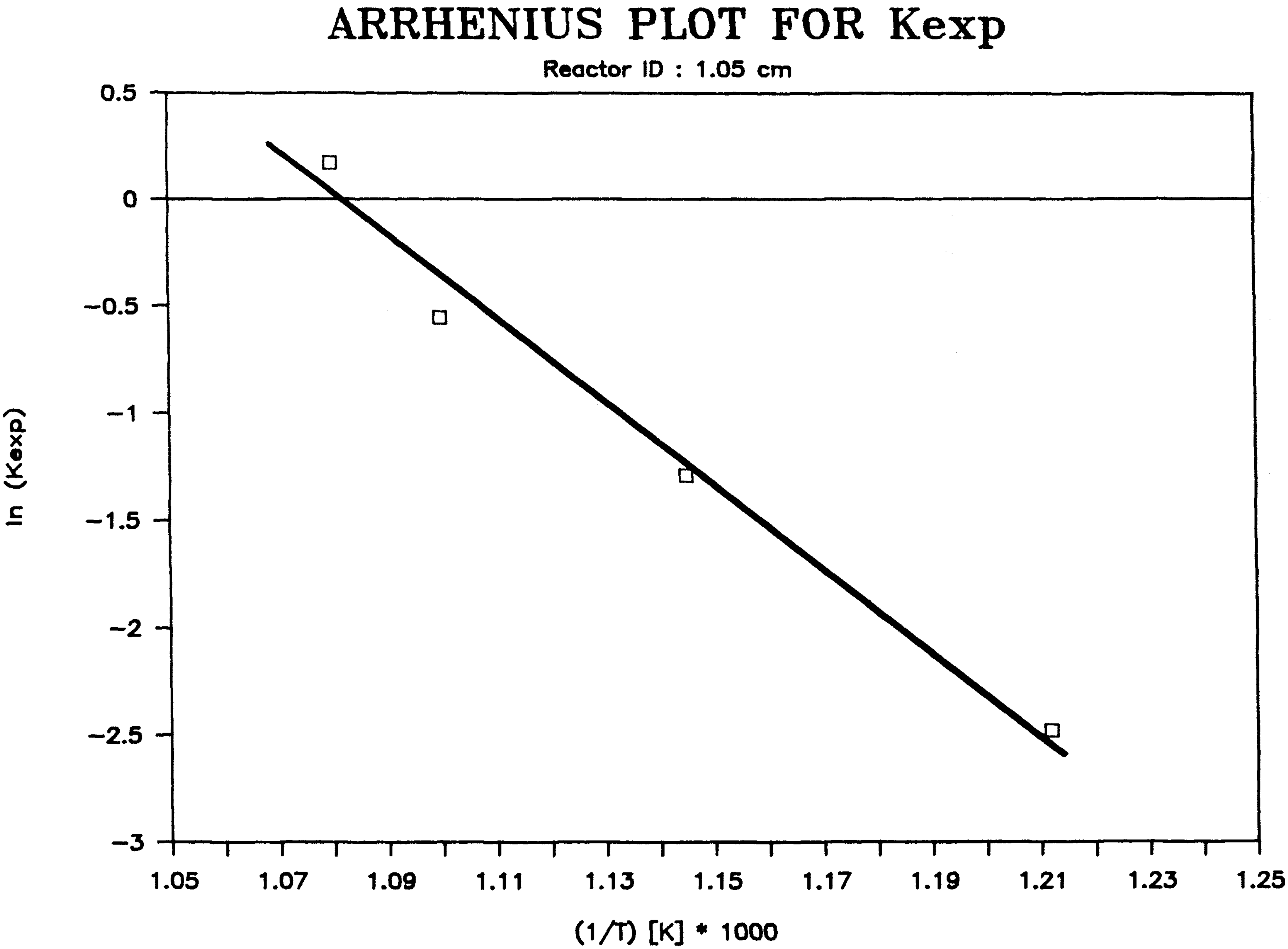
These results are in fair agreement with the work of Shilov and Sabirova (5) reporting :

$$K1 = 2.6 * 10^{11} \exp(-47000/RT)$$

and with Murgulescu and Weissmann (6) reporting :

$$K1 = 2.89 * 10^{11} \exp(-47500/RT)$$

for the gas phase reaction.



ARRHENIUS PLOT FOR Kexp

Reactor ID : 1.05 cm

FIGURE #7

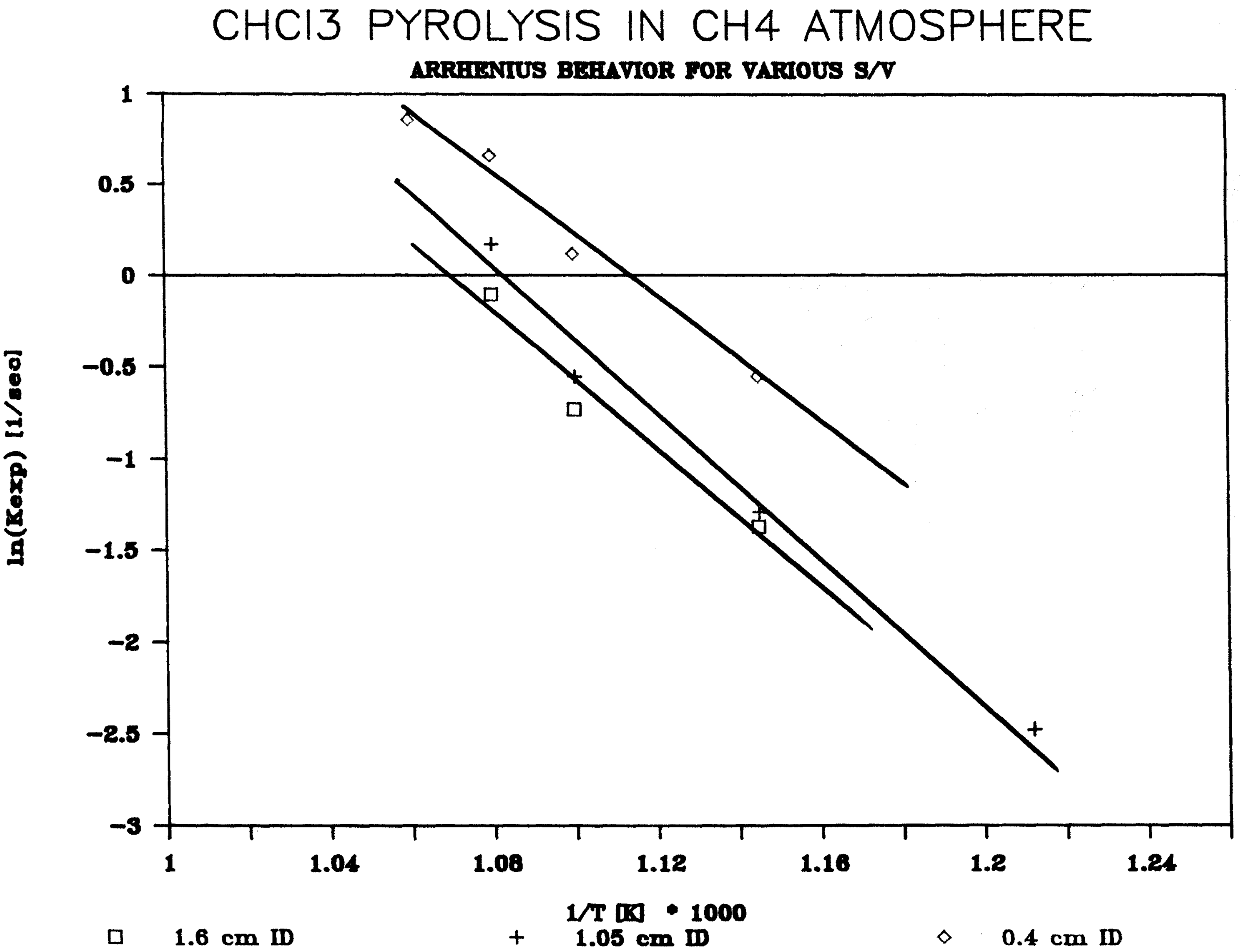
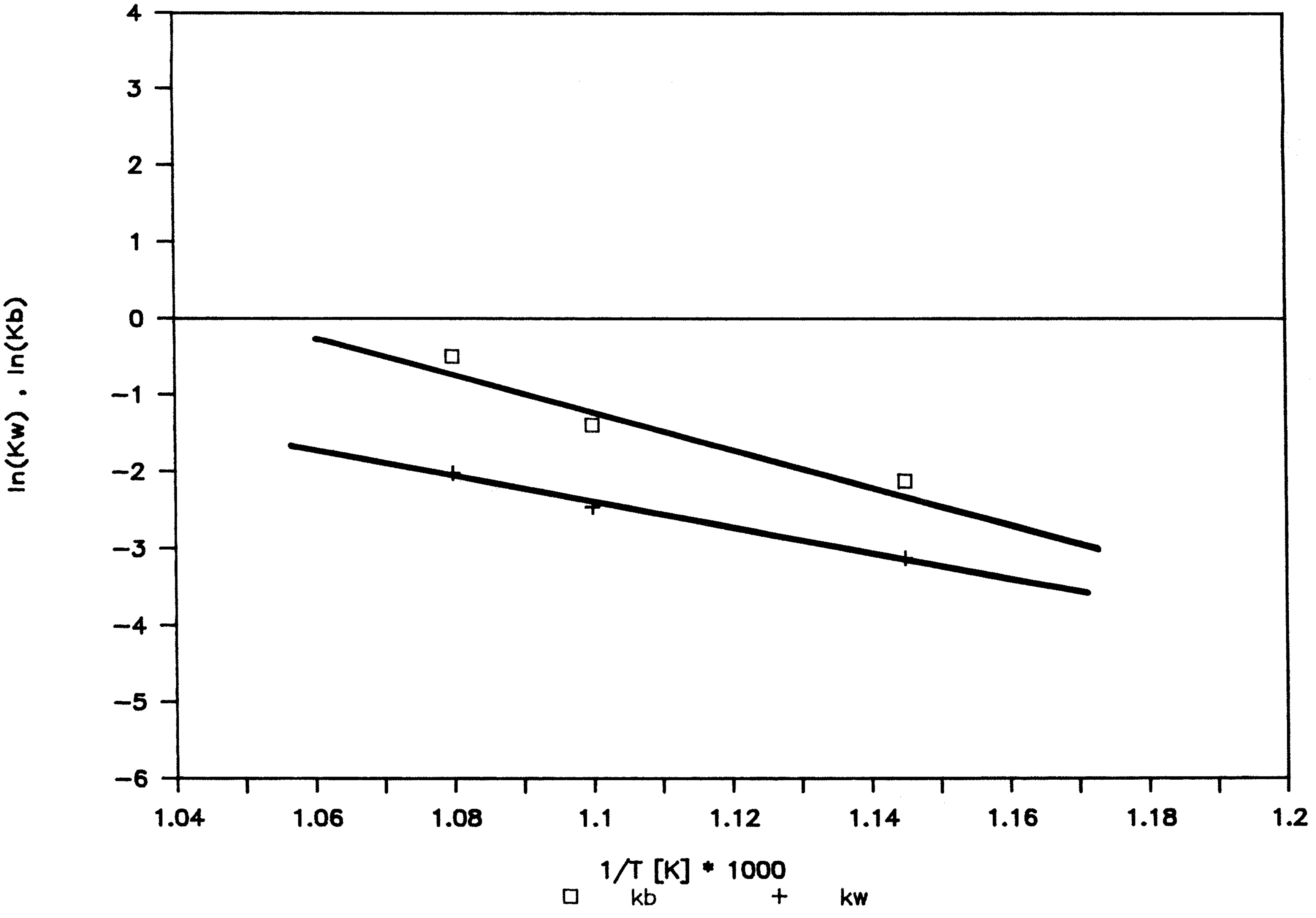

CHCl3 PYROLYSIS IN CH4 ATMOSPHERE
ARRHENIUS BEHAVIOR FOR VARIOUS S/V
ln(Kexp) [1/sec]
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
1
1.04
1.08
1.12
1.16
1.2
1.24
1/T [K] * 1000
□ 1.6 cm ID
+ 1.05 cm ID
◇ 0.4 cm ID

FIGURE #8



CHCl3 PYROLYSIS IN CH4 ATMOSPHERE

ARRHENIOUS PLOT FOR Kb , Kw

FIGURE #9

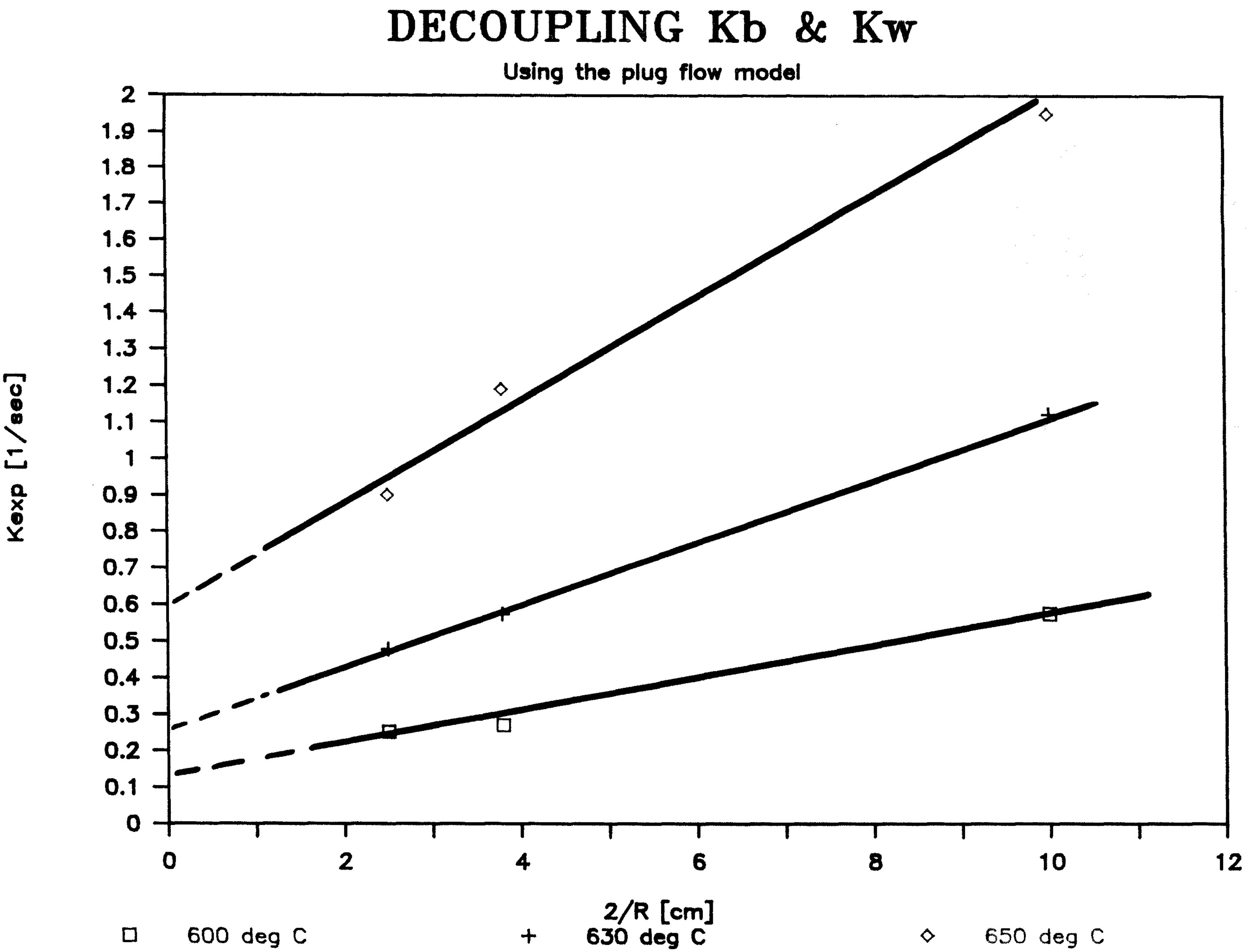

DECOUPLING Kb & Kw
Using the plug flow model
Kexp [1/sec]
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
12
2/R [cm]
□ 600 deg C
+ 630 deg C
◇ 650 deg C

FIGURE #10

V2. PRODUCT DISTRIBUTION FOR CHLOROFORM REACTION WITH CH4

Repeated analysis of the reactor outlet gases by Mass Spectrometry, identified a large number of stable products.

The conditions prevailing during the sample collection were 650 deg C and 80 % conversion of $CHCl_3$,or 630 deg C and 70 % conversion.

Identified major products were C_2H_2, CH_3Cl, C_2H_3Cl, $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4, C_2HCl_4 C_2Cl_6 and traces of CCl_4, $C_2H_2Cl_4$, $C_3H_2Cl_4$, C_4HCl_5 and C_4Cl_6.

The product distribution as a function of residence time is shown for different temperatures in Figures #11 - #16 .

Major products observed are $C_2H_2Cl_2$, C_2HCl_3 and C_2Cl_4.

The concentration of C_2H_2, CH_3Cl and C_2H_3Cl was also monitored and shown to be kept at low levels (0.01 < [conc]/[CHCl3]o < 0.02)

The relationship between CH_4 concentration and C_2H_2, C_2H_3Cl product formation is demonstrated by increasing the CH_4 to $CHCl_3$ inlet gas mixture ratio to 5/1.

The acetylene and vinylchloride production increases due to increased pyrolysis of CH_4, and after attack of the CH_3-H bond by $:CCl_2$ radicals, produced from $CHCl_3$ decomposition .

The following reaction scheme describes the situation :

$$\text{(a)}\quad :CCl_2 + CH_4 \longrightarrow CH_3\text{-}CHCl_2$$

$$CH_3\text{-}CHCl_2 \longrightarrow CH_2{=}CHCl + HCl$$

This and the complete absence of chlorine molecules are strong evidence that the initial unimolecular decomposition of chloroform is taking place by an HCl molecule abstraction and carbene formation,as the following scheme describes :

$$CHCl_3 \longrightarrow :CCl_2 + HCl$$

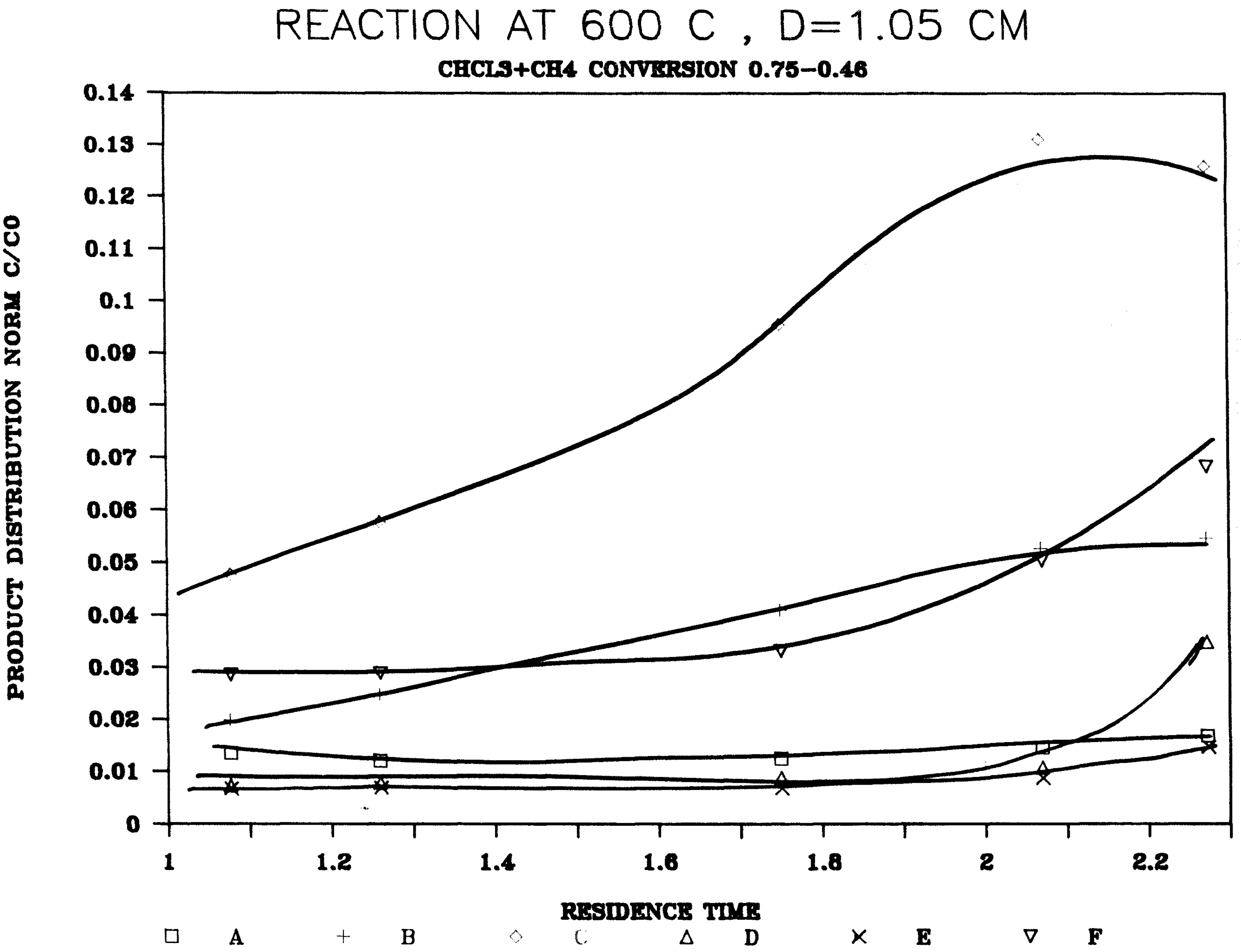

REACTION AT 600 C , D=1.05 CM
CHCL3+CH4 CONVERSION 0.75-0.46
PRODUCT DISTRIBUTION NORM C/C0
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
1.2
1.4
1.6
1.8
2
2.2
RESIDENCE TIME
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #11

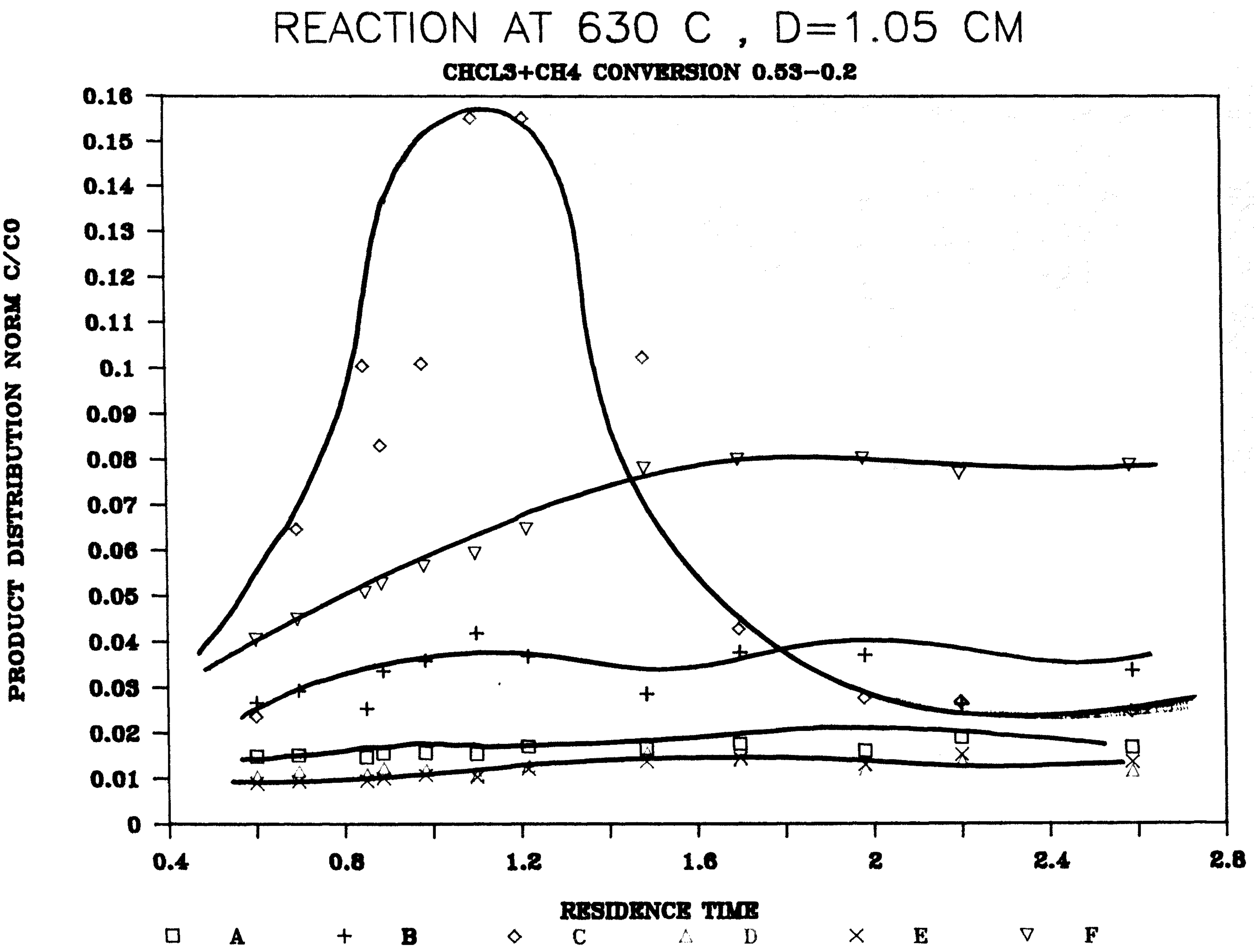

REACTION AT 630 C , D=1.05 CM
CHCL3+CH4 CONVERSION 0.53-0.2
PRODUCT DISTRIBUTION NORM C/CO
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.4
0.8
1.2
1.6
2
2.4
2.8
RESIDENCE TIME
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #12

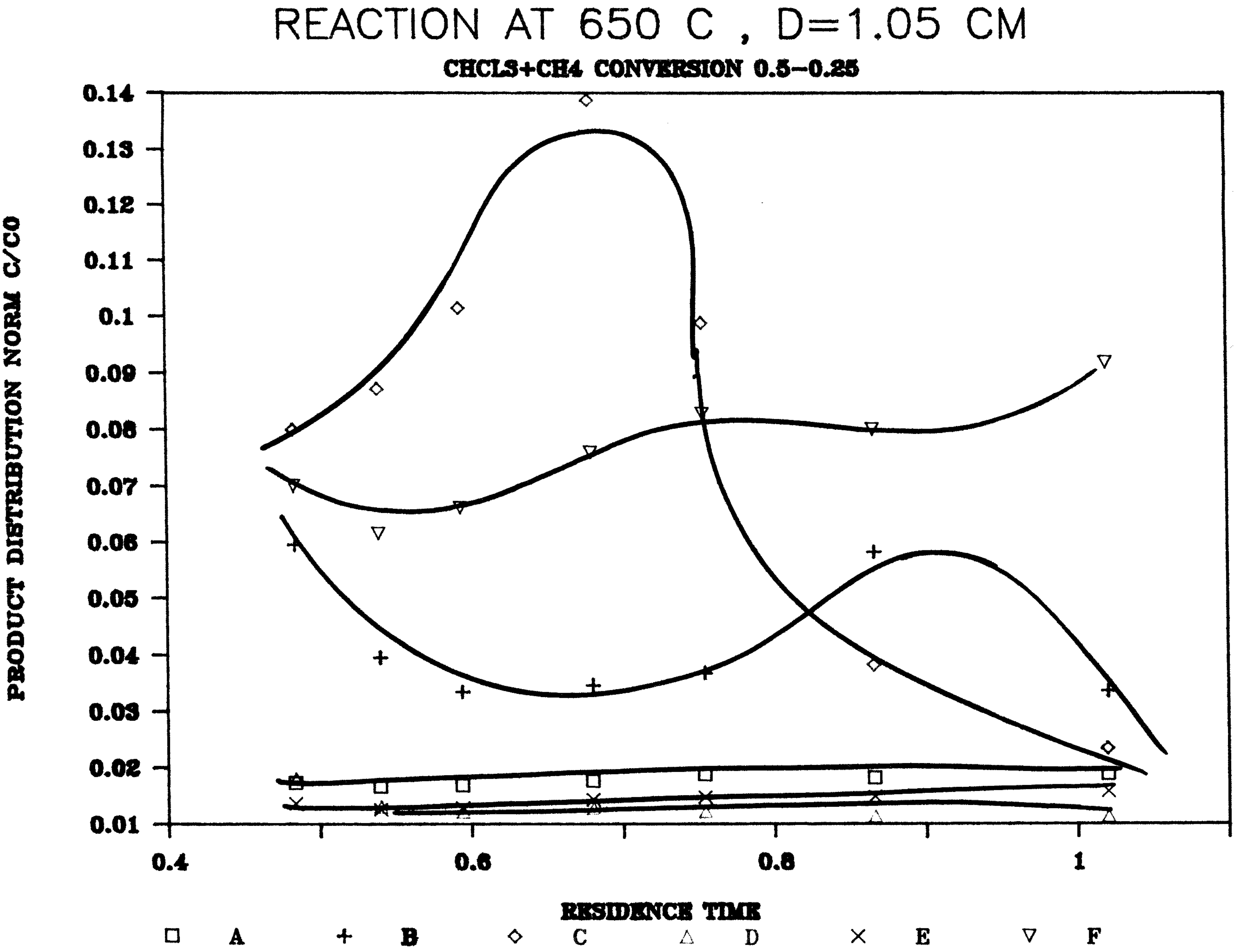

REACTION AT 650 C , D=1.05 CM
CHCL3+CH4 CONVERSION 0.5–0.25
PRODUCT DISTRIBUTION NORM C/C0
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.4
0.6
0.8
1
RESIDENCE TIME
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #13

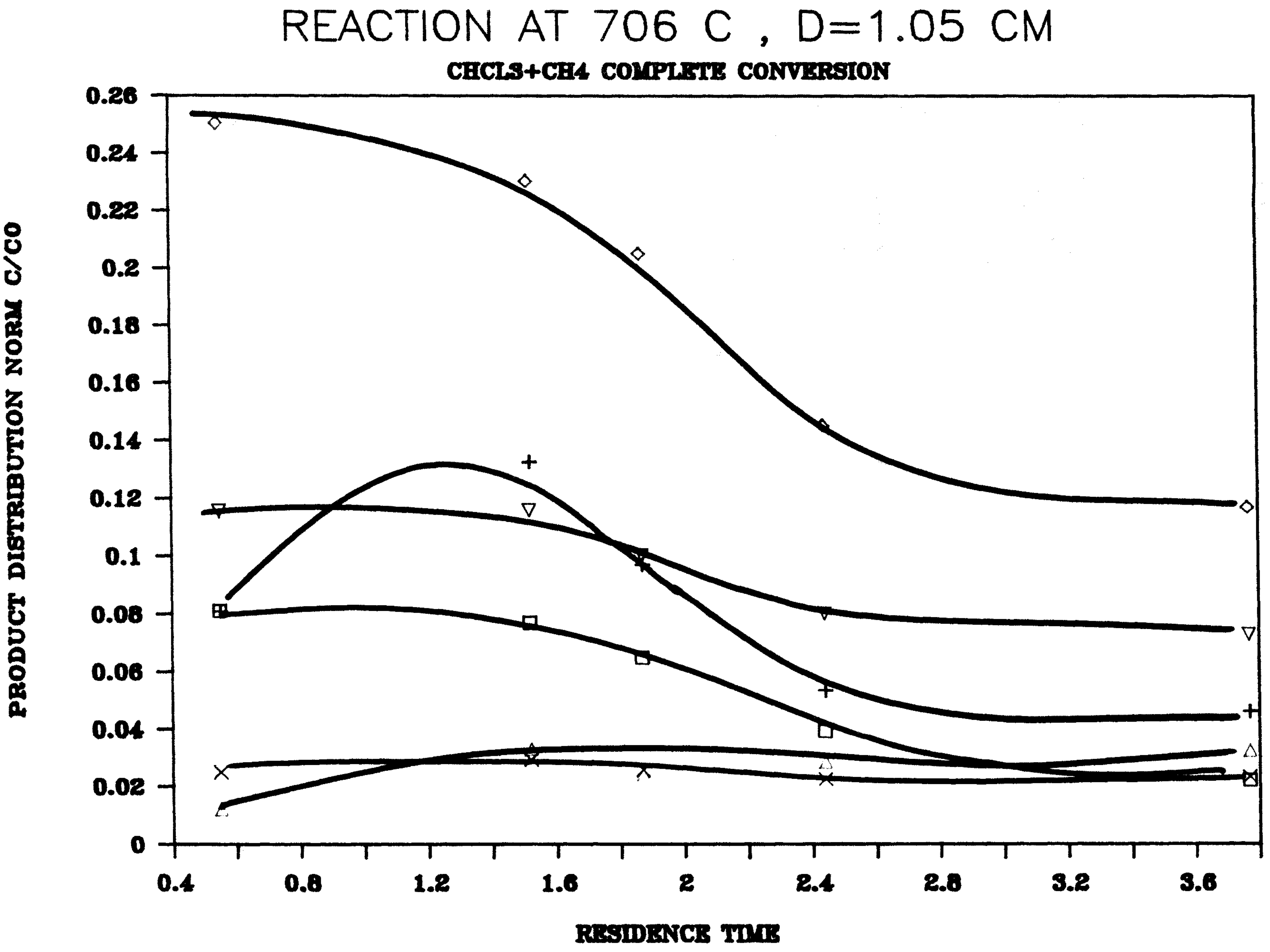

REACTION AT 706 C , D=1.05 CM
CHCL3+CH4 COMPLETE CONVERSION
PRODUCT DISTRIBUTION NORM C/CO
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
3.6
RESIDENCE TIME

FIGURE #14

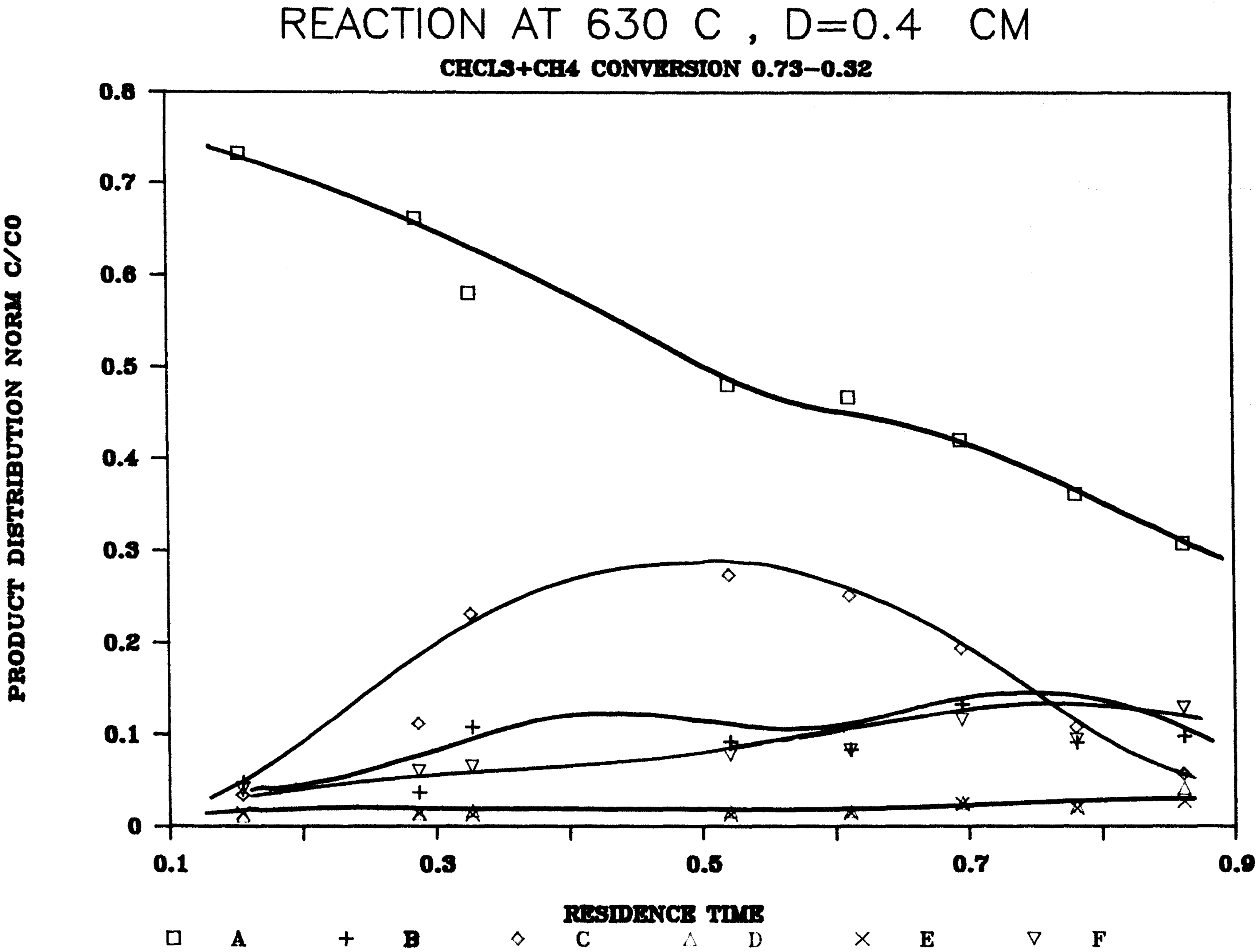

REACTION AT 630 C , D=0.4 CM
CHCL3+CH4 CONVERSION 0.73–0.32
PRODUCT DISTRIBUTION NORM C/C0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.3
0.5
0.7
0.9
RESIDENCE TIME
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #15

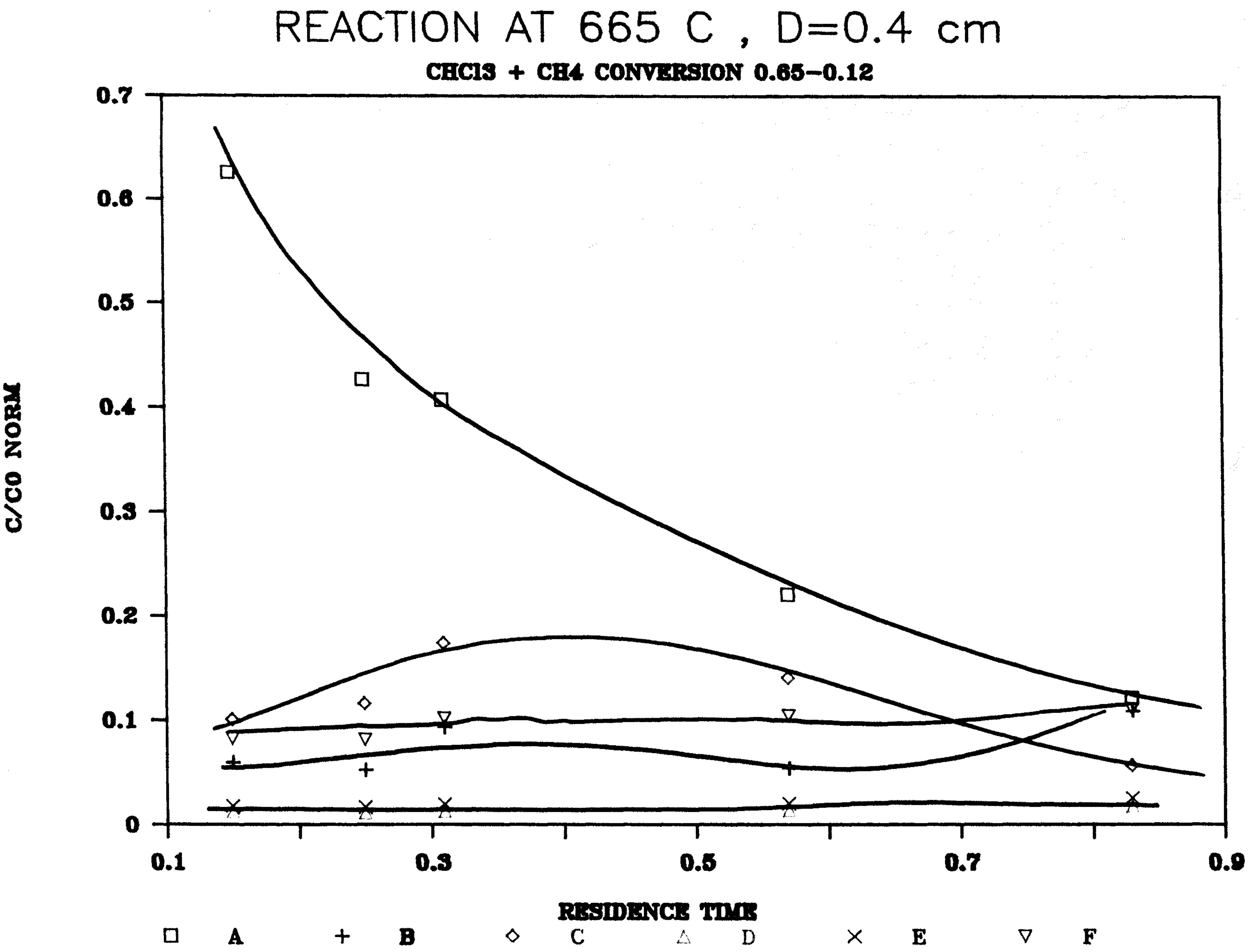

REACTION AT 665 C , D=0.4 cm
CHCl3 + CH4 CONVERSION 0.65-0.12
C/C0 NORM
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.3
0.5
0.7
0.9
RESIDENCE TIME
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #16

More evidence for this is provided by the fact that C_2Cl_4 and C_2HCl_5 are observed the first in larger concentrations than the second ,which is an unstable intermediate compound.

The presence of these two compounds is in agreement with the reaction scheme :

(b) $:CCl_2 + CHCl_3 \text{ ---> } (C_2HCl_5)^*$

$(C_2HCl_5)^* \text{ ---> } C_2Cl_4 + HCl$

Of course the scheme (b) is favored compared to scheme (a) because it is easier for the carbene to attack $CHCl_3$ since the CH_3-H bond is stronger . As a result the reaction rate for scheme (b) will be much more than for (a), and C_2Cl_4 will be in large excess compared to vinylchloride, which is the case demonstrated by our results.

As we can see from the Figures #11-#16 product formation is increasing with residence times for most products.

Reactions involving free radicals like $.CHCl_2$, $:CCl_2$, $.CH_3$, $.CCl_3$ $.C_2HCl_4$, .Cl, which are referred in detail in the proposed mechanism part of this work, are responsible for the presence of chlorinated C2, C3, and C4 hydrocarbons .

The C_2Cl_4 concentration is observed to pass through a maximum with increasing residence times (or reactant conversion) and then start dropping. This is obviously due to depletion of chloroform and subsequent pyrolysis of the C_2Cl_4 already formed, towards other products like $C_2H_2Cl_2$ etc, at higher residence times.

The temperature dependency of the product distribution is demonstrated in Figures #17, #18, for the 0.4 and 1.05 cm ID reactors and corresponding constant residence times of 0.7 and 1.2 sec respectively.

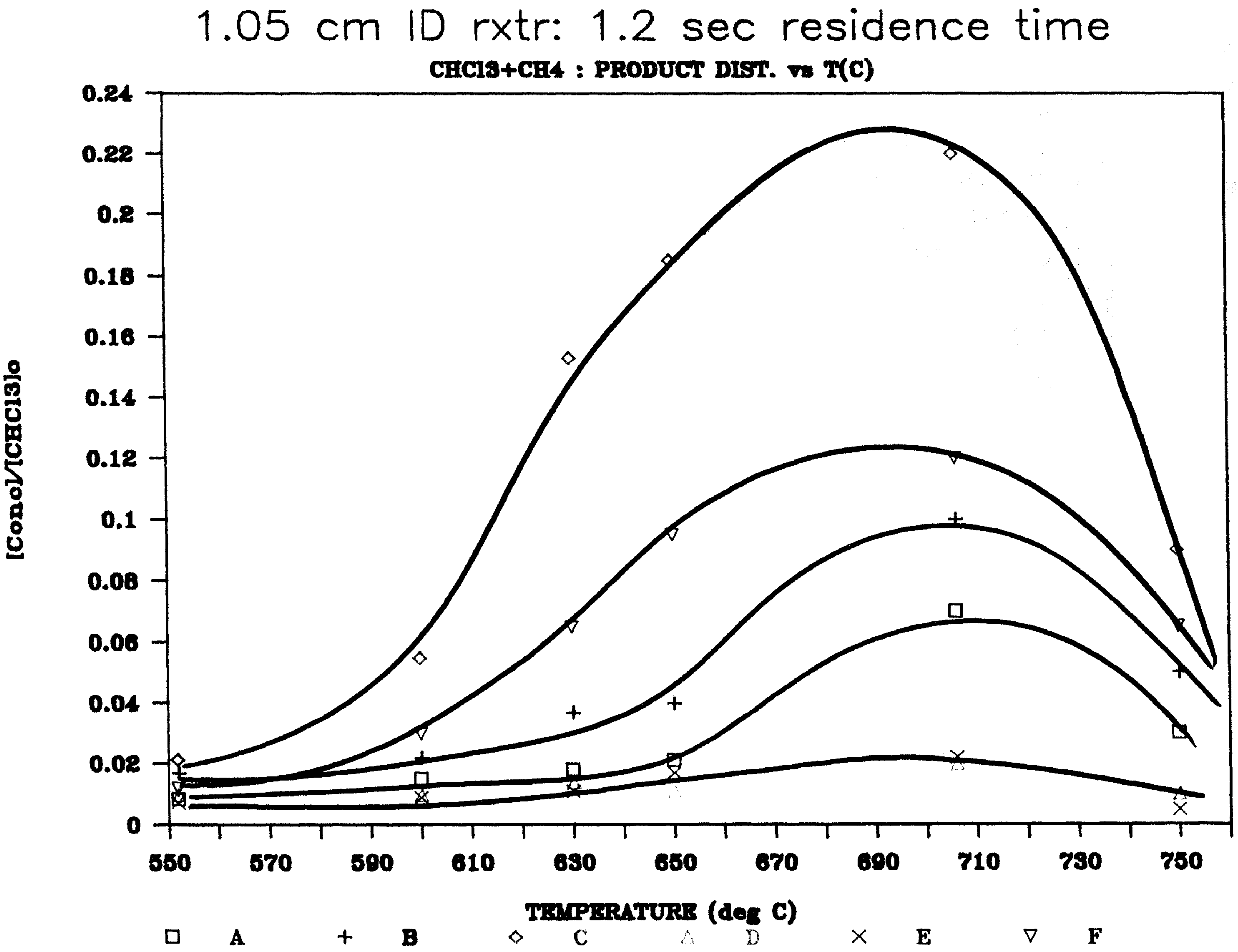

1.05 cm ID rxtr: 1.2 sec residence time
CHCl3+CH4 : PRODUCT DIST. vs T(C)
[Conc]/[CHCl3]o
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
550
570
590
610
630
650
670
690
710
730
750
TEMPERATURE (deg C)
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #17

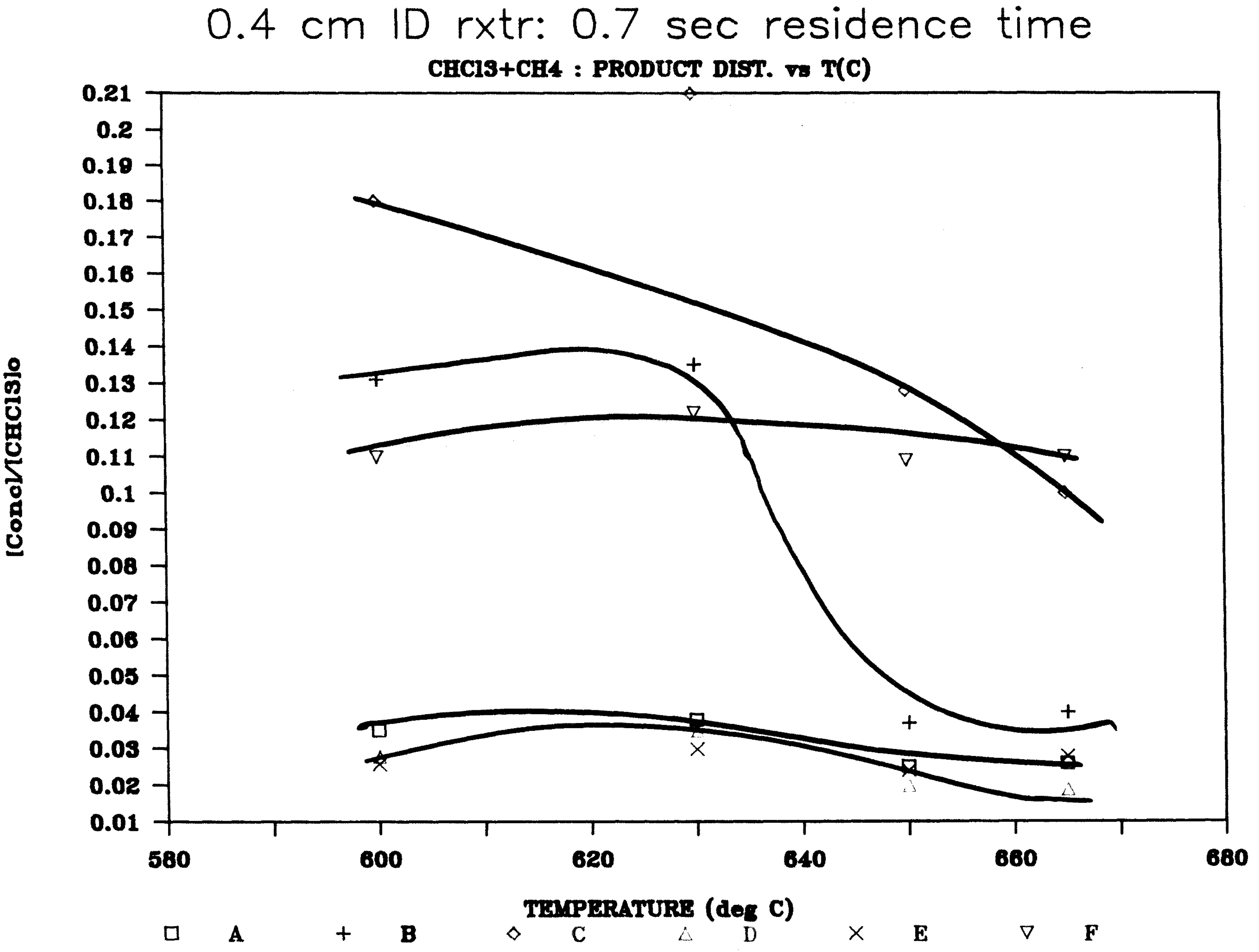

0.4 cm ID rxtr: 0.7 sec residence time
CHCl3+CH4 : PRODUCT DIST. vs T(C)
[Conc]/[CHCl3]o
0.21
0.2
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
580
600
620
640
660
680
TEMPERATURE (deg C)
□ A
+ B
◇ C
△ D
× E
▽ F

FIGURE #18

We notice that all the chlorocarbon concentrations increase with temperature until a maximum at 700 deg C approximately and then start dropping until they level off around 800 deg C.

This maximum is reached earlier for the 0.4 cm ID reactor since the reaction rate is larger due to increased S/V ratio, a fact demonstrated by the two graphs.

Less chlorinated substances demonstrate a more stable behavior with increased temperature than the heavily chlorinated . This was also observed by Chuang & Mahmood (17,18) an obvious result of the higher thermal stability of mono/dichlorocarbons.

All chlorinated compounds were found to be destroyed at a temperature of 800 deg C and a residence time less than 0.5 sec.

A material balance for 100 moles of carbon (Assuming 100 moles of chloroform entering the reactor) at different temperatures and for a constant residence time of 1.2 sec is shown in Table III.

The carbon being unaccounted for at high temperatures, is probably present into the heavy products not quantitated by our analysis and mostly due to carbon films formed on the reactor surface or withheld by the filters.

The material balance for 300 moles of chlorine (100 moles of chloroform) Table IV, shows that most of the chlorine is found in the identified products and the HCl whose production rate was measured for each temperature and the constant residence time of 1.2 sec.

This also leads to the conclusion that the unaccounted products (containing chlorine) were in fairly small concentrations, and that the chlorine is increasingly converted to HCl by elevating the temperature,an obvious conclusion from the experimental results of HCl analysis.

TABLE III

MATERIAL BALANCE FOR 100 MOLES OF CARBON FOR CHC13, CH4 SYSTEM

RESIDENCE TIME 1.2 SEC   REACTOR ID 1.05 CM

TEMP C -->	552	600	630	650	705
PRODUCT					
C_2H_2	0.85	1.5	1.8	2.1	7
CH_3CL	1	1	1.4	1.2	2
C_2H_3CL	0.75	0.9	1.1	1.7	2.2
$C_2H_2CL_2$	1.2	3	6.5	9.5	12
C_2HCl_3	1.7	2.2	3.7	4	10
C_2CL_4	2.15	5.5	15.3	18.5	22
$CHCl_3$	86	64	41	19	0.7
TOTAL C	93.65	78.1	70.8	56	55.2

TABLE IV

MATERIAL BALANCE FOR 300 MOLES OF CHLORINE FOR CHCl3, CH4 REACTION

RESIDENCE TIME 1.2 SEC   REACTOR ID 1.05 CM

TEMP C -->	552	600	630	650
PRODUCT				
CH_3CL	1	1	1.4	1.2
C_2H_3CL	0.32	0.45	0.55	.85
$C_2H_2CL_2$	1.2	3	6.5	9.5
C_2HCl_3	2.55	3.3	5.55	6
C_2CL_4	4.3	11	30.6	37
$CHCl_3$	258	192	123	57
HCl	---	54.32	97.89	166.66
TOTAL CL	267.37	265.07	265.49	278.11

V3. REACTION MECHANISM

One of the main goals in these studies is to establish a detailed reaction mechanism, describing all the elementary steps needed for the observed product formation.

The mechanism for this reaction system involves free radicals in chain reactions. These reactions consist of three essential steps:

1. Initiation or formation of the free radicals.
2. Propagation, by reaction of the free radicals with reactants.
3. Termination by reaction of free radicals to form stable products.

A chemical mechanism that may be the basis of the given overall observed kinetics and product distribution, is described below:

$$\text{CHCl3 ---> :CCl2 + HCl}$$

$$\text{:CCl2 + CH4 ---> (CHCl2CH3)*}$$

$$\text{(CHCl2CH3)* ---> HCl + }\underline{\text{C2H3Cl}}$$

$$\text{(CHCl2CH3)* ---> .CHClCH3 + .Cl}$$

$$\text{.CHClCH3 ---> }\underline{\text{C2H3Cl}}\text{ + .H}$$

$$\text{:CCl2 + Cl2 ---> (CCl4)*}$$

$$\begin{aligned}\text{(CCl4)* } &\text{---> }\underline{\text{CCl4}}\\ &\text{---> .Cl + .CCl3}\end{aligned}$$

$$\text{.CCl3 + CHCl3 ---> }\underline{\text{CCl4}}\text{ + .CHCl2}$$

$$\text{C2H3Cl + .H ---> HCl + .C2H3}$$

$$\text{.C2H3 ---> }\underline{\text{C2H2}}\text{ + .H}$$

$$\text{:CCl2 + CHCl3 ---> (C2HCl5)*}$$

$$\text{(C2HCl5)* ---> .Cl + .C2HCl4}$$

$$\text{.C2HCl4 ---> .Cl + }\underline{\text{C2HCl3}}$$

$$\text{.C2HCl4 + CH4 ---> }\underline{\text{C2H2Cl4}}\text{ + .CH3}$$

$\texttt{.CHCl2 + .CHCl2 ---> }\underline{\texttt{C2H2Cl4}}$

$\texttt{(C2HCl5)* ---> }\underline{\texttt{C2Cl4}}\texttt{ + HCl}$

$\texttt{(C2HCl5)* ---> .H + .C2Cl5}$

$\texttt{.Cl + C2Cl4 ---> .C2Cl5}$

$\texttt{.C2Cl5 + CHCl3 ---> }\underline{\texttt{C2Cl6}}\texttt{ + .CHCl2}$

$\texttt{.Cl + CH4 ---> .CH3 + HCl}$

$\texttt{.H + CH4 ---> .CH3 + H2}$

$\texttt{.CH3 + CHCl3 ---> }\underline{\texttt{CH3Cl}}\texttt{ + .CHCl2}$

$\texttt{C2Cl4 ---> .C2Cl3 + .Cl}$

$\texttt{.C2Cl3 + .C2Cl3 ---> }\underline{\texttt{C4Cl6}}$

$\texttt{C4Cl6 ---> .C4Cl5 + .Cl}$

$\texttt{.C4Cl5 + CH4 ---> }\underline{\texttt{C4HCl5}}$

$\texttt{.CH3 + .C2Cl5 ---> (C3H3Cl5)*}$

$\texttt{(C3H3Cl5)* ---> }\underline{\texttt{C3H2Cl4}}\texttt{ + HCl}$

$\texttt{(CHCl2CH3)* + .CH3 ---> C2H3Cl2 + CH4}$

$\texttt{(CHCl2CH3)* + .H ---> C2H3Cl2 + H2}$

$\texttt{(CHCl2CH3)* +.Cl ---> C2H3Cl2 + HCl}$

$\texttt{C2H3Cl2 ---> }\underline{\texttt{C2H2Cl2}}\texttt{ + .H}$

In the above scheme, the underlined compounds are reaction products identified with Mass/Spec analysis, the asterisc * indicates activated complex molecules and the period . denotes an unpaired electron for the radical.

VI. CONCLUSIONS

The thermal decomposition of Chloroform in the presence of excess Methane and Argon, was studied at atmospheric pressure in the temperature range of 550-800 deg C, and using three different reactor diameters.

The kinetic parameters and product distribution data were experimentally determined for each size reactor, resulting to the following expressions.

For 0.4 cm ID	$K_{exp} = 2.03 * 10^8 \exp(-34000/RT)$
For 1.05 cm ID	$K_{exp} = 9.86 * 10^8 \exp(-37950/RT)$
For 1.6 cm ID	$K_{exp} = 4.17 * 10^8 \exp(-36760/RT)$

Decoupling of the rate constants for reaction on the wall and in the bulk was accomplished with the plug flow model.

The temperature dependent expressions which were obtained for Kb and Kw are as follows :

For gas phase : $Kb = 6 * 10^{10} \exp(-46700/RT)$

For the wall : $Kw = 8.8 * 10^6 \exp(-33000/RT)$

Many chlorinated compounds were positively identified as stable reaction products. Complete destruction of all of them occured at 800 deg C and residence time less than 0.5, in favor of carbon, C_2H_2, C_2H_4 and HCl formation.

Carbon material balances show that CH_4 does not participate in a great extent in the reaction, for the range of temperatures in use.

It was proven that the initial reaction step is unimolecular decomposition of chloroform, taking place by an HCl molecule abstraction and carbene formation,as the following scheme describes :

$$CHCl_3 \text{ ---> } :CCl_2 + HCl$$

Products originating from Methane Reactions, like vinyl chloride, are generally in small concentrations, and are observed to increase by raising the $CH_4/CHCl_3$ ratio.

An important observation is that all chlorine from the chlorinated compounds is converted into hydrogen chloride at higher temperatures (above 800 deg C), which is easily collected and neutralized. Thus these types of reactions may be a good alternative to incineration of the chlorinated waste.

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