ABSTRACT

This is an experimental study on thermolytic reactions of chloroform with excess water vapor where kinetic parameters are determined and complete product analysis made at atmospheric pressure over a temperature range from 550to 1050 °C. In this study, water vapor was introduced as a reactant to convert chlorine in chlorocarbons to stable HCl which is an easily neutralized end-product and thereby completely destroy chloroform. Substantial amounts of thermodynamically stable species: HCl, CO, CO_2, C(s) etc. were observed as products.

The reaction was studied in a 46cm tubular flow reactor mounted in a furnace that had three independently temperature-controlled heating zones and was capable of operating temperatures to 1200 °C with a constant temperature (+/- 5 °C) profile, over its central (80%) region. Complete end-product analysis was performed by flame ionization/ thermal conductivity gas chromatography (FID/TCD GC) and GC/Mass Spectrometer.

The major products below 700 °C are hydrogen chloride, tetrachloroethylene and carbon tetrachloride, with vinyl chloride, dichloroethylene, trichloroethylene as minor products.Complete destruction of the parant chloroform took place at temperature around 750 °C and residence time of 0.5 sec. . All the chlorocarbon products were destroyed at temperature above 1000 $^{\circ}$C. Kinetic parameters are determined as a function of reagent residence time, temperature, concentration and reactor diameter. The results show that the wall reaction contributes to the overall conversion at the higher temperatures (kw/kb= 0.25 ~ 0.5) and the wall reaction has a higher activation energy than the bulk reaction. The vapor phase activation energy of 28.4 kcal/mol is in fair agreement with unimolecular decomposition data in the literature, indicating that the initial step in this study consists primarily of chloroform decomposition via unimolecular reaction.

CONVERSION AND KINETICS IN THE REACTION OF CHLOROFORM WITH WATER VAPOR AT HIGH TEMPERATURES

by

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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
~~1984~~
1985

APPROVAL SHEET

Title of Thesis: Reaction of Chloroform with Water Vapor at High Temperature

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ACKNOWLEDGEMENT

I would like to express my appreciation to Dr. Joseph Bozzelli, who was more than just my thesis advisor; he was also my mentor and friend. I shall always respect and admire him, and I shall always cherish the fulfilling learning experience I have had during my work with him.

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I. INTRODUCTION

A. Overview : Detoxification of Chlorinated Organics in Oxygen

In line with the increase in usage demands for plastics, solvents and other chemicals and with the consequent growth in industry, the disposal of chemicals considered hazardous or toxic has recently become a major environmental as well as political issue. Some of these are chlorinated chemical species as chloro-plastics, PCB´s, DDT, chlorocarbon solvents and other chlorinated chemicals. These species may undergo partial oxidation or reduction during incineration to produce more dangerous toxic or carcingenic species such as phosgene or dioxin. Certainly the emission of these unwanted combustion products is not desirable nor beneficial to the environment.

High temperature incineration in a reactor is presently considered a practical first generation technology for chemical detoxification where the US EPA requires the materials have a 2-second residence time at a temperature of 1200 °C in the presence of excess oxygen (1). This technique may destroy all the initial species, but the chlorine products usually found in this combustion system also include partially composed and oxidized fragments of the initial chlorinated reactants such as phosgene (an extremely toxic species), chlorinated aldehydes, chlorobenzenes etc. Higher molecular weight species such as chlorinated dibenzofurans and dioxins are also found (usually trace quantities) as products from these combustion systems. The relatively low content of hydrogen-containing species in the reactor or inlet mixtures combined with excess oxygen often precludes the stoichiometric formation of HCl in incineration and may be the cause of these unwanted species.

Several novel methods for degradation of chlorinated species include those of Roberts and Sawyer (2) who have employed dimethyl sulfoxide and dimethylformamide solutions of super oxide ion to convert CCl_4 to solutions of carbonates and chlorides. A second method was utilized by Hertzler, et. al. (3), who oxidized selected chlorocarbon species in a microwave plasma vapor phase tubular flow reactor. These reactions of Hertzler et. al., unfortunately, required low pressure and therefore low feed through rates. Arnold, et. al. (4) characterized the emission spectra from flames produced in the reaction of atomic oxygen with halomethanes in initial attempts to study spectroscopy, which would lead to kinetics research on these systems and found evidence of C_2 species. Lee et.al. (5) have studied thermal oxidation pyrolysis of organic compounds including vinyl chloride in a narrow reactor and did not consider wall reactions,however. Greenberg and

Whitaker (6), Yosium et. al. (7) and Dustin (8) have studied the catalytic oxidation of halocarbon species using complex molten salt reactors. Again these studies are still at the research and pilot scale level, and their potential to treat large amount of hazardous compounds is still unknown.

B. Detoxification of Chlorinated Waste with Hydrogen or Water Vapor.

The incineration of chlorocarbons in an O_2-rich environment does not provide a thermodynamically favorable sink for the chlorine atom (a stable and desirable end adduct), it might be better to utilize a combination oxidation/reduction atmosphere of hydrogen or water vapor where the thermodynamically favorable sink for Cl atom HCl results, which could then be quantitatively neutralized or collected.

In a previous study by S.C. Chuang (9) there were three important advantages observed when hydrogen or water vapor was used instead of an oxidizing atmosphere:

1. It is more thermodynamically favorable to form HCl since the H-Cl bond is 103 kcal/mole and the C-Cl bond is 81 kcal/mole . The HCl, could easily be scrubbed with caustic, in addition.
2. The process of hydrogen or water vapor reduction of toxic chlorinated carbons is efficient and economical , because fuel (energy input) would only be used to heat the reagents (eg. water and solvent) not as a reagent itself.

3. Most importantly, these reactions provide much-needed kinetic parameters and reaction-product information important to understanding the chemistry of these hitherto largely unexplored reducing reactions.

The favored thermodynamics of these reactions, (halocarbons with hydrogen or water),are verified by the large equilibrium constants (Kp´s) list in Appendix I.

The high temperature thermal reactions of chlorocarbon with hydrogen or water vapor have only scarcely been studied with little or no stoichiometric or stable end product results available. Arnold et. al. (10) have reported on flame production and characterized the emission spectra from reactions of atomic hydrogen with halocarbon in a low pressure flow reator. Some of the elementary reactions were mentioned in their study such as:

$$H + CHCl_3 \longrightarrow HCl + CHCl_2$$

$$H + CH_3Cl \longrightarrow HCl + CH_3$$

$$H + CH_2Cl_2 \longrightarrow HCl + CH_2Cl$$

$$H + CCl_4 \longrightarrow HCl + CCl_3$$

$$H + HCl \longrightarrow H_2 + Cl$$

Vance et. al. (11) and Costes et. al. (12) both reported on reaction of hydrogen atoms with carbon tetrachloride postulating the initial mechanism as:

$$H + CCl_4 \longrightarrow HCl + CCl_3$$

with an activation energy around 34.5 kcal/mole. Vance also found a comparison of HCl formed with the number of hydrogen atoms entering indicates that complete conversion of atomic hydrogen into HCl at 150-200 °C, and a pressure of approximately 0.8 mm and a CCl_4:H ratio of about 10:1.

Gaisnovich et. al. (13) have studied the vapor-phase hydrolysis of carbon tetrachloride in the temperature range of 350 to 550 °C by high temperature infrared spectroscopy. Before Gaisnovich, the hydrolysis of carbon tetrachloride by water in the condensed phase below 100 °C had been studied by Fells et. al. (14) and M.E. Hill (15), and it was established that the hydrolysis takes place with the formation of only CO_2 and HCl by a reaction of first order with respect to CCl_4. The above authors consider that in the stage limiting the reaction rate the CCl_4 molecule decomposes with the formation of the intermediate CCl_3OH, which decomposes rapidly to phosgene and then to CO_2 and HCl. The Gaisinovich and Ketov study, however, showed that the vapor phase reaction proceeded at an appreciate rate above only 300 °C and obeys an equation of second order with respect to CCl_4. Phosgene was detected in the hydrolysis products and the activation energy calculated was 12.02 kcal/mole, with only a global mechanism proposed.

$$CCl_4 + H_2O \text{ ----> } COCl_2 + HCl$$

$$COCl_2 + H_2O \text{ ----> } CO_2 + HCl.$$

Gaisinovich and Ketov also found that above 450 °C, the hydrolysis of CCl_4 was also accompanied by thermal decomposition according to the proposed overall equation

$$2CCl_4 \;\text{----->}\; C_2Cl_4 + Cl_2 + Cl_2$$

In 1932, the thermodecomposition of chloroform ($CHCl_3$) was studied by Lessig (16). He reported that the pressure increase with time was very irregular and observed the formation of a "yellow crystalline material together with a tar". In 1935, Verhoek (17) measured the pressure increase due to the pyrolysis of chloroform at 452 and 512 ^{o}C. He identified only hydrogen chloride as a product, but suspected the presence of hexachloroethane. In these studies the overall products analysis and reaction mechanism has not been clearly reported.

Again in 1954 and 1956, the pyrolysis of gaseous chloroform were studied by Semeluk et. al. (18) in which the products analysis was reported in part II (1956) (19). In products analysis, hydrogen chloride and tetrachloroethylene were found as the major products and a variety of other chlorinated hydrocarbons have been identified using infrared techniques where carbon tetrachloride, 1,1-dichloroethylene, cis and trans-dichloroethylene and dichloroacetylene were classed "probably present", and Asym-tetrachloroethane, 1,1,1-trichloroethane, 1,2-dichloroethane were classed "probably absent".

The reaction mechanism proposed was:

$$
\begin{aligned}
CHCl_3 &\longrightarrow CHCl_2 + Cl \\
Cl + CHCl_3 &\longrightarrow HCl + CCl_3 \\
Cl + CCl_3 &\longrightarrow CCl_4 \\
CCl_3 &\longrightarrow CCl_2 + Cl \\
CCl_2 + CHCl_3 &\longrightarrow C_2Cl_4 + HCl
\end{aligned}
$$

In Semuluk study, due occassional overlapping absorption bands, it was not possible to prove the presence or absence of some compounds by infrared spectra alone, and carbon tetrachloride was not positively determined by the infrared method unless mass spectral analysis was also used. In addition, Semeluk et. al.(19) indicated that the over-all reaction is evidently very complex and a complete quantitative treatment appears unlikely.

C. Present Work on Detoxification of Chloroform with Water Vapor.

Noting that the use of hydrogen introduced either as H, H_2, or as H_2O offers a viable means of detoxification through halogen removal as hydrogen chloride, it was felt that a thorough investigation into the kinetics and mechanism of the reactions of hydrogen introduced with chlorocarbons should be undertaken. H_2O vapor is also often co-injected into incineration for more efficient combustion of these species but there is no known or published mechanism for this improvement (20).

Chloroform was chosen as the reactant because it is a reasonable model compound to start with and there is a lack of data involving this compound in reactions with water vapor. In addition, vapor phase hydrolysis has been little studied, and it is of practical importance for the future in detoxifying hazardous waste effectively and economically.

A tubular reactor combined with gas chromatography and GC/Mass Spectrometer for analysis of the stable end products permitted significant kinetic results to be obtained. In this study a great deal of effort was required to maintain constant temperature within +/- 5 ^{o}C along the reactor by using three continuous and independently controlled sections for determination of the overall destruction (Global) kinetics.

II. THEORY

A. Homongeneous Gas Phase Reaction Theory

1. Introduction

The reactions of chlorinated hydrocarbons with water vapor can be studied in a homogeneous gas phase reactor, because they occur at high temperatures and where significant concentration (pressures) of both species readily exist. In addition, great progress has been made in recent years in the elucidation of elementary reactions from the overall (global) chemical process. Thus, we intended to deal primarily with overall reactions that follow a series of simple mechanistic schemes, since it is from the study of these types of reactions that an understanding of the more intimate details of kinetic processes may emerge.

2. General Consideration on Apparatus

Since the reactions of chlorinated hydrocarbon with water vapor like most gas-phase reactions of stable species occur at elevated temperature, some method must be devised for maintaining the reaction vessel at a uniform and constant temperature.

The consistancy of temperature is important, since the rate of a reaction increase significantly for small rises in temperatures, as it occurs in the exponent of a rate constant. Uniformity is also of importance,since if appreciable temperature gradient exist in the reaction vessel the rate data will be of dubious validity due to this large temperature dependency. This temperature uniformity can not be achieved by using a single zone furnace, therefore, a multizone furnace with each zone controlled separately by a temperature controller was employed to keep temperature consistent and uniform (+/-5 ^{o}C) along the tubular reactor.

For the measurement of temperature, a thermocouple (22) and a microprocessor controlled temperature indicator with a multipoint switch were used, so that any given thermocouple can be brought into circuit as desired, is also integral in reading an accurate steady state temperature, as it is internally referenced.

In order to test the homogeneity of the reactions studied, the surface-to-volume(S/V) ratio of the reaction vessel should be altered (23). A small variation in S/V can be made by changing the tube diameter; in our case of a cylindrical tubular reactor $S/V = 2/r$ where S is the surface area, V is the volume and r is the radius of cylindical vessel. Three different diameters of quartz tube : 0.5, 1.05 and 1.6 cm ID, have been used in this study. These give S/V ratios of 5.0, 1.9 and 1.25/cm and show a factor of 4 variation. The reaction time may be calculated from a knowledge of total vapor (reagent) flow rate and the volume of reaction vessel. If there is no change in the number of molecules (or moles) in the reaction, then the reaction time or contact time , is the ratio of reactor volume to rate of flow at entrance to the vessel , measured at the temperature and pressure of the reaction (23). [volume/(volume/sec.)]equals seconds.

3. **Investigation of The Stoichiometry of a Reaction.**

It is often necessary to understand the chemistry involved before modelling calculations are performed on a given reaction. Three questions arise here:

(a) What is the main reaction involved?

(b) Are there any side-reactions?

(c) Do the products themselves react under the conditions of investigation?

Detailed study of these questions for the reaction of chloroform with water vapor will be discussed in the results and discussion section.

Where the reaction products are stable under the given conditions, it will suffice to allow the reaction to proceed to completion, and then carry out a complete analysis of the products. In general, two common analytical techniques that have been applied to this kind of kinetic investigation are mass spctrometry(24) and vapor-phase chromatography (25), which have the advantage of being more generally accessible. These two tecniques were therefore used together (26) in this study and provided a very useful means of studying the reaction products of chloroform with water vapor.

4. Measurement of rate of reaction

Having established the stoichiometry of a reaction from product analysis, measurements of rate may be made by either following the disappearance of one or more of the reactants or the appearance of one or more of the products or a combination of both. In the reaction of chloroform with water vapor, loss of chloroform was employed to monitor the primary kinetics with reaction products also recorded.

B. Unimolecular Reaction Theory

The reactions of chlorinated hydrocarbons with hydrogen or water vapor were observed to be unimolecular as a first step with first order reaction kinetics by S.C. Chuang (9), similar to the gas-phase thermal decomposition of hydrocarbons (27). The decomposition of methyl chloride and ethyl chloride have also been considered to exihibit unimolecular reactions by Robinson and Holbrook (28).

The manner in which collisions can be responsible for activation and yet the overall rate proportional to the first power of the concentration was considered by Lindemann in 1921 (29) and subsequently developed by Hinshelwood(30). Since a collision involves at least two molecules, it would appear that a unimolecular reaction must be one taking place without collision, perhaps as a spontaneous disruption or transformation of the reacting molecule. Frost and Pearson (31) have shown that a unimolecular reaction would be expected to be first order and that the rate constant can be interpreted as a probability of reaction per unit time. They also indicated that the temperature is of great importance and the rate constant follows an exponential Arrhenius expression when first-order chemical reactions are considered to be unimolecular.

The manner in which the molecules become activated was long a mystery, since activation by collision was first ruled out because it was thought that the reaction would have to be bimolecular and second-order in that event rather than unimolecular and first-order. However, the Lindemann-Hinshelwood theory shows that a mechanism can be set up to account for the observed results (32).

The main concepts of the theory can be stated briefly following the stoichiometric reaction A+M --> products as follows:

(1) Activation by collision

$$A + M \longrightarrow A' + M \qquad k_1$$

where A´ is an activated molecule, that is, one with sufficient energy for reaction. The symbol M can be used to designate any molecule which may be a reactant, a product, or an added non-reactive gas molecule, and k_1 is the rate constant for the bimolecular reaction.

(2) Deactivation by collision

$$A' + M \longrightarrow A + M \qquad k_2$$

This is the reverse of the activation process and is expected to occur at the first collision of A´ after it has been formed,if it is has not already reacted in the meantime. $k_2 >> k_1$ since the activation process is limited by the energy requirement.

(3) Spontaneous reaction

$$A' \dashrightarrow \text{products} \qquad k_3$$

This is a "true" unimolecular process in the same sense as is radioactive disintegration. k_3 is a first order rate constant. Assuming that the efficiency of the various molecules in causing activation or deactivation is not very different, the steady state approximation on A' and the above mechanism leads to:

$$- d[A]/dt = k_1\ k_3\ [M][A]/\ (k_2\ [M] + K_3).$$

If [M] is approximately constant during a run, the above expression is that of a psuedo first-order reaction.

Define k' as $\qquad k' = k_3\ k_1[M]/(k_2[M] + k_3)$

so that $\qquad -d\ [A]/dt = k'[A]$

where k' is the observed first-order rate constant. It also has limiting value for high and low pressure. At high pressure:

$$k_2\ [M] >> k_3, \text{ and } \quad k' = k_3\ k_1/k_2$$

therefore $\qquad -d[A]/dt = k'\ [A]$

the reaction being of the first order. On the other hand if the pressure is low: $k_2\ [M] >> k_3$ and $\quad k' = k_1\ [M]$

$$-d[A]/dt = k_1\ [A]\ [M]$$

and the reaction is of the second order overall.

Since non-chemically reactive gases (inert gases) may also contribute to the activation process, the rates of unimolecular reactions in the intermediate or low pressure regions should be capable of restoration to the high-pressure values by the addition of an inert gas. From studies of this effect, the relative efficiencies for activation and deactivation of different added gases may be determined. The above two criteria namely, the fall in the first order rate coefficient as the pressure is lowered and its restoration to the high-pressure value in the presence of sufficient inert gas - constitute an important vertification of the unimolecular character of a first-order gas reaction (28).

C. Chemical Reactor Theory and Kinetics

Flow reactors are commonly used for the study of fast gas- phase reactions and the conditions are normally employed which give minimum viscous pressure drop, axial diffusion, wall reaction and maximum radial diffusion. Such conditions are discussed in some detail by Kaufman (33). Poirier and Carr (34) have indicated that the experimental conditions of gas-phase reactions most frequently used are such that laminar flow occurs and the resulting parabolic velocity profile gives rise to a distribution of residence time for the reactive species in which those traveling near the wall remain in the reactor longer and experience larger degree of reaction than those traveling nearer the center of the reactor. To simplify these complicated flow conditions, Poirer et.al. (34) suggested that this difficulty might be circumvented by operating at sufficiently low pressure and concentration such that radial diffusion (dispersion) becomes extremely rapid, flattening out the radial profile. One can assume, to a close approximation, that the radial concentration profile is flat and the concentration of reactive species is therefore independent of radial distance and reaction time is equal to axial distance divided by average velocity (ideal plug flow conditions). In addition, Denbigh (35) has made the plug flow assumption as being an idealized state of flow such that:

"(1) Over any cross-section normal to the fluid motion - the mass flow rate and the fluid properties (pressure, temperature and composition) are uniform and;

(2) There is negligible diffusion relative to bulk flow."

From the above discussion and the study of the axial dispersion model which has been well explained by S.C. Chuang (9), the gas-phase reactions of chlorinated hydrocarbons with hydrogen or water vapor in tubular flow reactors at high temperature were studied and considered as cases of plug flow with wall reactions and negligible axial diffusion. Such a flow condition is theoretically a steady-state flow: one in which the varied compositions at any point along the reactor length remain unchanged with time,when inlet flows and compositionsare constant (36). It can be shown that we are within 10% of ideal plug flow conditions due to the elevated temperatures at 1 Atm P.

Assuming plug flow conditions then, the equation describing the compositions is (36):

$$t = \frac{V}{v_O} = C_{AO} \int \frac{dX_A}{-r_A} \qquad [1]$$

for the reaction A + M ---> products, where t is the space time in the reactor, space time references inlet conditions, V is the volume of reactor, v_O is the velocity of the reactant flow. C_{AO} is the inlet concentration of reactant

A, the halocarbon (chloroform) in this case, X_A is the conversion of reactant A defined as:

$$X_A = 1 - C_A/C_{AO} \qquad [2]$$

where C_A is the concentration of A in the reactor at the point of consideration and r_A is the rate of reaction with respect to A. The rate is defined as:

$$-r_A = dC_A/dt \qquad [3]$$

For the primary reaction $CHCl_3 + H_2$ ---->products, the rate may be expressed as:

$$dC_A/dt = -kC_A C_B \qquad [4]$$

where A is the chloroform and B is the reagent, water. The determination of k, the rate constant of the reaction, was one of the main objectives of this study.

In this study a "large excess" of one reagent (water) is used, and the assumption is made that the concentration of this excess reactant remains constant throughout the reaction. Sicilio and Peterson (37) have studied the rates of second-order reactions and find they are frequently represented by pseudo first-order kinetics when a "large excess" of one reactant is used. When the ratio of reactant concentration is very large, usually greater than 5 , a second-order reaction may be adequately represented by pseudo first-order kinetics due to the fact that the concentration of the excess reactant remains essentialy constant. The ratio of reactant concentration (H_2O : $CHCl_3$) in this study is usually greater than 10 and is sufficiently valid for the above first-order assumption. Therefore, equation(4) becomes:

$$dC_A/dt = - k' C_A \qquad [5]$$

where k' is called apparent rate constant, and $k' = k C_B$. For an irrevisible first-order reaction, the relationships between concentration, rate constant and space time in the reactor are (36):

$$-\ln \frac{C_A}{C_{AO}} = k't \qquad [6]$$

$$\text{or} \quad -\ln (1-X_A) = k't \qquad [7]$$

In addition to the above discussions including unimolecular reaction theory, the gas phase reaction of chlorinated hydrocarbons with water vapor can be shown to follow pseudo first-order kinetics experimentally. An additional method devised by Wilkinson (38) can also be utilized as an aid in determining the order of a reaction:

$$\text{Here} \quad -dC_A/dt = k'' C_A^{n} \qquad [8]$$

$$[1/(n-1)](1/C_A^{n-1} - 1/C_{AO}^{n-1}) = k''t \qquad [9]$$

$$\text{or} \quad (1-X)^{1-n} = 1 + (n-1) k'''t \qquad [10]$$

where $k''' = k'' C_{AO}^{n-1}$, n is the order of a simple reaction and $k'' = k'$ for first-order.

In equation [10], if $(1-X)^{1-n}$ is expanded by the binomial theorem and terms higher than the second degree in X are discarded it can be put in the form:

$$t/X = 1/k''' + nt/2 \qquad [11]$$

$$\text{and} \quad t/X = 1/k' + t/2 \quad (n=1) \qquad [12]$$

If t/X is plotted against t for equation [11] (or [12]), it is a straight line with slope of n/2 (or 1/2 for a first order reaction) and intercept $1/k'''$ (or $1/k'$). Over the range up to X = 0.4, the lines for actual data in this study will be shown to be remarkably straight with order of the reaction to the nearest half integer. After the order is obtained, the intercept will yield k (or k′) which can be used to obtain an apparent or overall rate constant.

From a physical kinetic point of view, the overall reaction rate constant k′ is made up of a function of the bulk rate constant k_b and a function of the wall rate constant k_w : $k' = f(k_b) + f(k_w)$. Analytical results for first-order kinetics in flow tube reactor with wall reactions were studied by Ogen (39) for cases of Poiseuille flow, with first-order gas-phase and wall reactions, and with negligible axial diffusion. A convenient method was outlined in his study for correcting observed rate constants for the combined effects of wall reactions and small radial concentration gradients which is similar to the results obtained earlier by Kaufman(33). While we are presently doing detailed analysis of this type of system (wall + homogeneous, including laminar flow and radial diffusion) using an exact continuity equation, a straight forward analysis is given by Kaufman (33) where $k'=k_b + (2/r)\ k_w$. The specified activation energy are also determined.

III. EXPERIMENTAL

A. Inlet and Reactor System

The reactions of water vapor with chloroform were studied in tubular reactor between 550 and 1050 °C at atmospheric pressure, with operation in the plug flow regime. A schematic of the experimental apparatus is shown in Fig. 1. One multizone furnace and three quartz reactor tubes were utilized in this study, with average flow velocities ranging from 0.2 to 3.0 m/sec (see Appendix II).

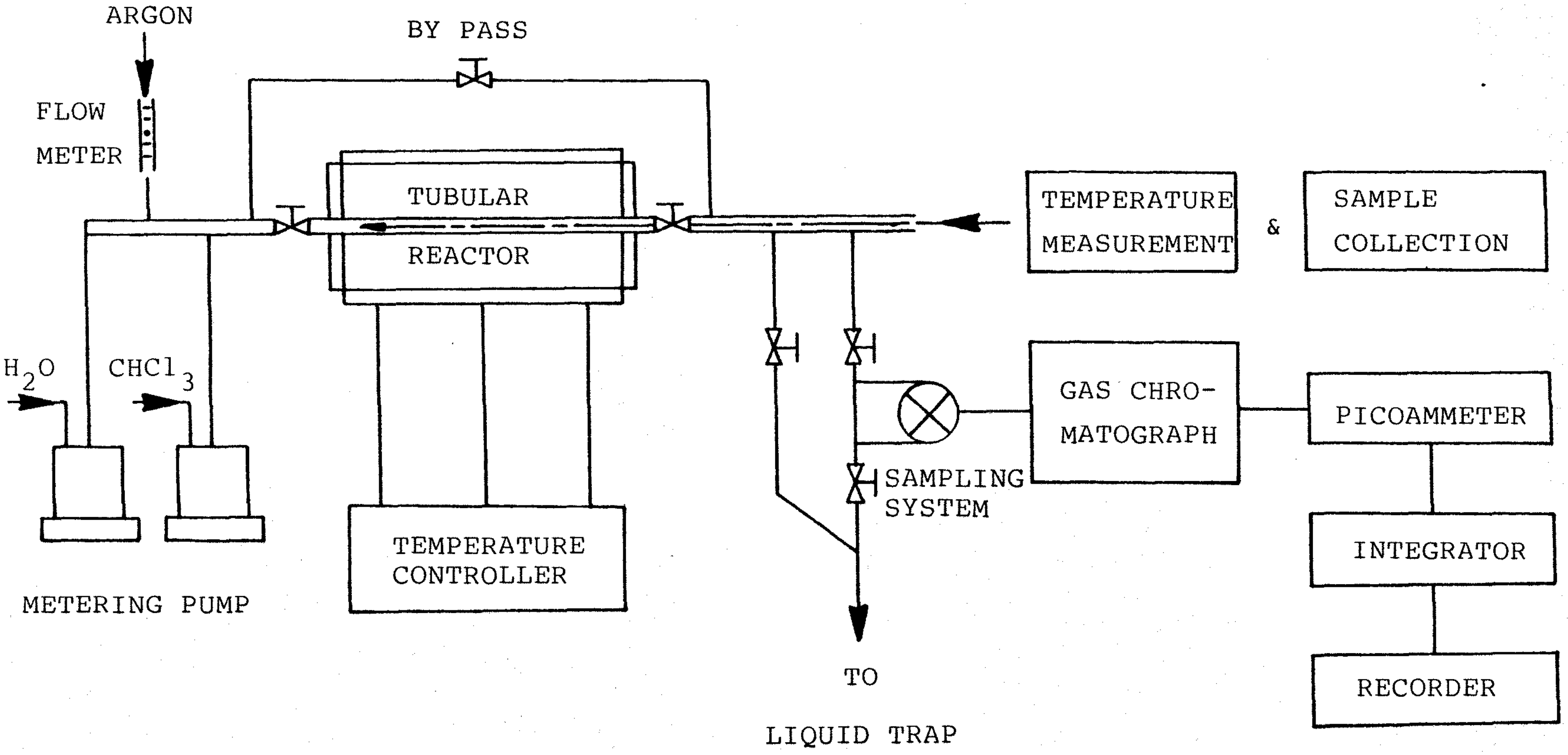
The reagent inlet metering and delivery systems are designed to permit input of gas or vapor to the reactor flow tube at total (combined) pressure around 1 atm. Liquid reagents (water and chloroform) were inlet to the reactor using a syringe pump, Orion Research Inc. Model 341A and Harvard Apparatus Co. Model No 600-000, which could be adjusted to the desired ratios: water to chloroform of 1:1 to 100:1.

Argon was inlet to the reactor through calibrated rotameter and served as carrier gas before the entrance of chloroform and water. All of the inlet reagents (Argon with Chloroform and water) were preheated (100 ~ 150 °C and vaporized immediately on inlet by heating tape.

The reactor system consists of quartz tube, multizone furnace and temperature controller. Three different size quartz tubes have been used in this study. They are 0.4,

Figure 1.

EXPERIMENTAL APPARATUS



1.05 and 1.6 cm ID. The multizone (three zone) furnace, 5 cm OD and 46 cm length was used for the reactor oven, which was capable of operating to above 1100 ^{o}C. The furnace elements were made by Mellen Company Inc. New Hampshire, Model No´s 12-135 (7.5 cm in length x 3.1 cm diameter for each end zone) and 12-151 (30 cm length for the center zone). Each furnace zone was controlled, by a Burling Instrument Company temperature controller with TC input. Higher amounts of heat were input to the end heaters per unit length, to overcome heat losses. To quickly obtain an indication of the temperature profile along the reactor, three Chromel-Alumel thermocouples are situated at three fixed stations (5, 20, 25 cm) along the reactor, between the reactor and furnace as illustrated in Fig.2.

The temperature control system consist of.

1. A controller module which provides adjustments for establishing the furnace temperature set point, the proportional band and reset action.

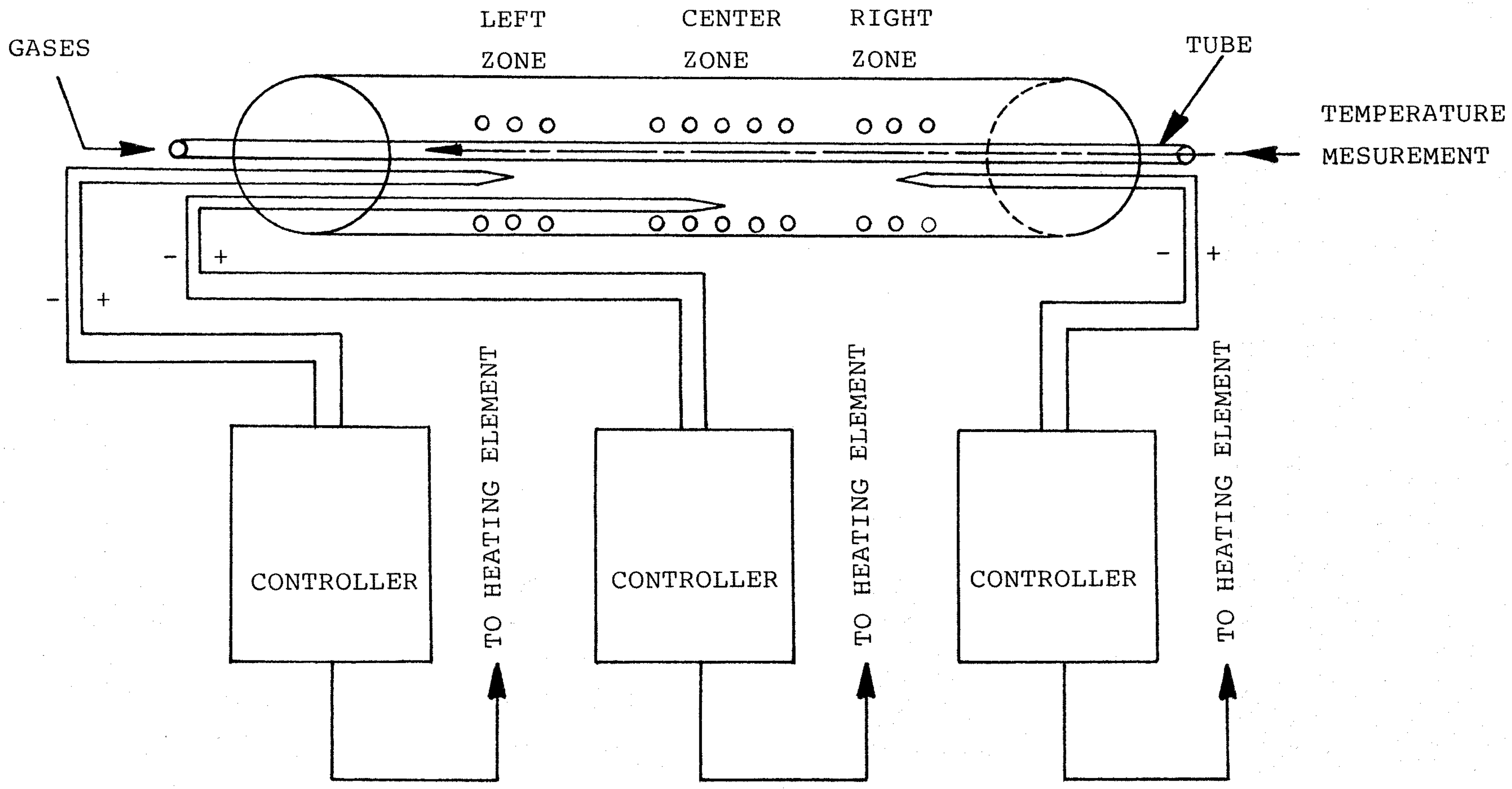
2. A variac for each controler to limit the voltage which the controller was sending to its specified furnace element.

3. The thermocouples which sense the temperature of the respective zones; and

4. The furnace elements being controlled.

The output of the sensor is compared to the set point level. The difference between set point and sensor output is monitored by a difference amplifier which drives a switching circuit and energizes the relay thus powering the load.

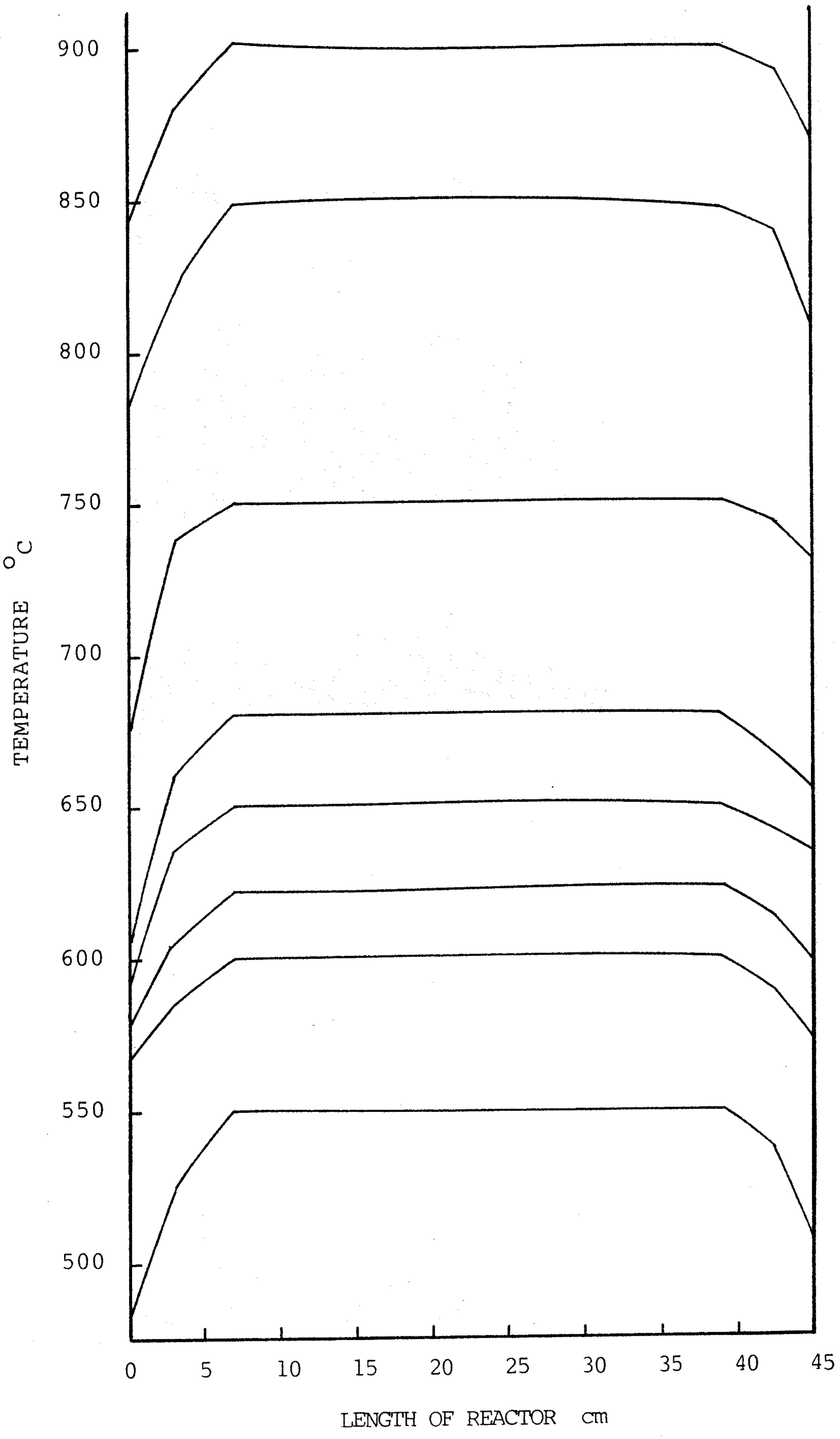
Figure 2. MULTI-ZONE FURNACE



The exact longitudinal temperature profile of the reactor was measured before each individual run with a Chromel-Alumel thermocouple which moved along the length of the reactor interior while gases were flowing. The temperature was read directly from Omega Microprocessor Controlled Temperature Indicator, Model 650, where therocouple linearization, cold junction compensation, gain and offset error correction are automatically performed via firmware internal to the microprocessor. For each temperature measurement (within the reactor tube), it took 30 seconds to one minute to reach steady state. As can be seen from the temperature profile (Fig. 3) , a significant fraction (between 80 and 90%) of the 46cm reactor is at constant temperature within +/- 5 ^{o}C as required for meaningful kinetic measurments.

1/4" Teflon tubing, fittings and valves were utilized in the flow system which were made by Galtak Corporation, in order to increase the flexibility of mounting, cleaning and ease of operation in addition to preventing corrosion from hydrogen chloride. The valves fitted in the line at the furnace inlet and outlet are as close to the furnace as possible, considering the temperatures involved. They served to isolate reactor and by-pass flow system completely, so that no product diffusion from the reactor occured when the inlet reagents passed through the by-pass.

Figure 3. TEMPERATURE PROFILES



The by-pass was used to measure the pure reactant concentration. The reactor exit and by-pass was maintained at approximate 100 to 150 °C by a heating jacket to prevent any of the reactant or reaction products from condensing.

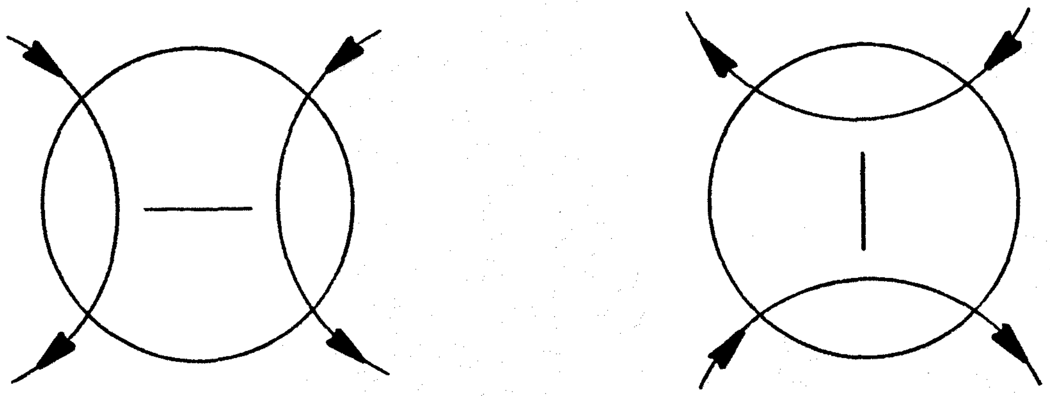
B. Gas Chromatography and Analysis.

The reactor effluent is quantitatively analyzed with an on-line Varian Aerograph series 1400 gas chromatograph modified for flame ionization detection (FID). The sample is collected for this analysis by drawing reactor effluent through a 1/4" ID Teflon tube loop with a heated Teflon lined 4 port sampling valve Conant Controls Inc. (Boston, Mass.).

A Schematic showing operation of this sample collection is shown in Fig. 4. Fast-action plug valves with only 1/4 turn from full open to full close were used to isolate the sampling valve as and to minimize dead volume within the sampling system. Sample collection and injection are always performed for a constant known fixed time, usually 20 seconds, in order to get accurate and consistent results.

The analytical GC column was 2 meter in length , 3.1 mm OD stainless tube with 10% SE 52 on chromasorb P. It is normally operated isothermally at 75 °C. All flows to the GC were measured by calibrated flow meters: 30 cc/min. for hydrogen, 250-300 cc/min for air, and 30 cc/min for nitrogen. The FID was maintained about 150 °C in a separate

Figure 4. GAS CHROMATOGRAPH SAMPLING SYSTEM



SAMPLE BEING COLLECTED

SAMPLE BEING INJECTED

heating assembly. Batteries provided the 270 volt potential across the FID electrodes outside the flame.

The FID response is highest to aliphatic hydrocarbons and chlorinated organics but it has little or no response to air, water, CO, CO_2 and fixed gases. Moderate temperature changes do not greatly affect the performance of the FID. The detector is operated above 150 ^{o}C to prevent condensation of water , and is always operated above the highest column temperature to prevent condensation of column effluent.

The FID (on-line GC) is only capable of analyzing aliphatic hydrocarbons and chlorinated organics so a second detector, thermal conductivity (TCD), with a 100/120 sphercarb, 1.5m x 3mm column and nitrogen as carried gas was added to the GC in order to detect CO, CO_2, CH_4 abd HCl. These species were inlet to the GC by batch syringe injection from a septum sampling port on the end of the reactor outlet line.

A Hewlett-Parkard Model 3370A integrator and Beckman multi-volt recorder were used in conjunction with GC. Amplification of the ionization current was achieved by the picoammeter, and output to the recorder. This output signal was also sent to the 3370A integrator and/or a Franklin ACE 100 computer with chromatochart from Interactive Microwave Inc. (state college, Penna) for accurately quantitative integration.

Additional product identification was achieved by collecting a sample of the reactor products with a 10 cc syringe directly from the reactor effluent as shown in Fig 1. and storage in a glass pyrex 20cc tube with rubber cap (batch sampling),used for collection, and analysis by a mass spectometer. A varian MAT 44 GC/mass spectometer was used for this purpose.

Kinetic runs utilizing the gas chromatograph analysis started only after the reaction had stabilized, the oven of chromatograph reached their thermal equilibrim, and a steady base-line was attained on the GC recorder (FID). An experimental run established the product distribution under study at five to seven different space velocities for the reactants, from the lowest to the highest argon flows with a constant input flow rate of water and chloroform at each given temperature run. In addition, a chart which showed argon flow rate with respect to integrator response (peak area) of chloroform, from by-pass run was made as a calibration at each ratio between chloroform and water for use in determining the conversion (see Appendix II).

IV. RESULTS AND DISCUSSION

A. Products Analysis

The reaction of chloroform with water vapor was studied in 0.4, 1.05, 1.6 cm ID, 46 cm long tubular reactors and with four ratios of reagents ($CHCl_3$:H_2O) as shown in the Table below:

Table 1.

Case	Reactor Diameter (cm)	$CHCl_3$:H_2O
I	0.4	1:14.7
II	0.4	1:7.1
III	1.05	1:16.2
IV	1.60	1:16.8

Argon served as carrier gas and as an aid to vaporize chloroform and water through the reactor. The conversion of chloroform, based on initial concentration, for reactions in the temperature range 550 to 900 ^{o}C and at different reactor diameter is shown in Fig. 5. The destruction of chloroform clearly increases with increasing temperature and residence time, and over 99% destruction of chloroform was observed at temperatures above 750 ^{o}C.

In Fig. 5 , for the same reactor diameter (0.4 cm ID) and a factor of two decrease in chloroform to water ratio, the conversion of chloroform for case I is as much as three time that for case II in the temperature range 550 to 650 ^{o}C. Case II and case IV also have over 95% conversion of chloroform above 750 ^{o}C.

Figure 6 to 9 show the decomposition of chloroform versus residence time for varous temperatures and reagent concentration ratios in the different reactors. The results show that the decomposition of chloroform decreases slightly with increasing reactor diameter in the same range of reaction times, since the larger reactor needs the longer residence time to obtain the same conversion as that of the smaller reactor. The primary products observed in the temperature range 600 to 850 ^{o}C and residence time between 0.4 and 0.5 seconds for case I ($CHCl_3$:H_2O = 1: 14.7) are shown in Fig.10.

The product distributions for chlorocarbon as a function of residence time and reaction temperatures of 601, 623, 649 and 680 ^{o}C are shown in Fig. 11 through 14. These diagrams illustrate that the major products below 700 ^{o}C are tetrachloroethylene, and carbon tetrachloride, vinyl chloride , dichloroethylene and trichloroethylene, were minor products. These diagrams also show that tetrachloroethylene and carbon tetrachloride formation increase with residence time at the temperature below 680 ^{o}C but decrease with residence time at the temperature above 680 ^oC, and Vinyl chloride, dichloroethylene and trichloroethylene formation increase with residence time below 650 ^oC but decrease with residence time at the temperature above 650 ^oC.

Again, experimental data for the primary products observed in the temperature range 550 to 900 ^oC for case III ($CHCl_3$: H_2O = 1: 16.2) are shown in Fig. 15 at residence time between 1.6 and 1.7 seconds. The product distributions as function of residence time for the reaction temperature of 602, 623 and 650 ^oC are shown in Fig 16 through 18. These diagrams show that the primary product concentration increase with residence time at the temperature below 650 ^oC and are nearly completely destroyed (over 99.99 %) except vinyl chloride (99.83%) at the temperature of 900 ^oC.

From a chemical point of view, it is important to investigate the material balance for each atomic species, to ensure that none of the products has escaped detection. In this study, three regions in the flow system have been applied to analyze product distribution qualitatively and quantitatively. They are the solid graphitic carbon remaining in the reactor tube, the liquids condensing in the trap and the gases passing through to on-line GC chromatograph.

The total condensed liquids contain mostly H_2O and HCl, and account for 90 to 95 % of the liquid feed stream. The remainder is accounted for by the gas products and solid graphitic carbon. The presence of significant quantities of HCl was confirmed qualitatively by GC/Mass Spectrometry and the pH meter. A substantial amount of hydrogen chloride has been found in GC/Mass Spectrometry analysis and no molecular chloride has been detected. This shows that the chlorine from reacted chlorinated hydrocarbons has been completely converted to hydrogen chloride. The pH values for the condensed liquid stream was around 0.7 to 1.0 and the molarity (M) obtained from titration by 6M NaOH with phenolphthalein as indicator was around 3.0 to 4.0 M, for a 250 ml volume of gas at atmospheric temperature and pressure. Thus, for $CHCl_3$, greater than 85% of the feed Cl in the parent is removed as HCl.

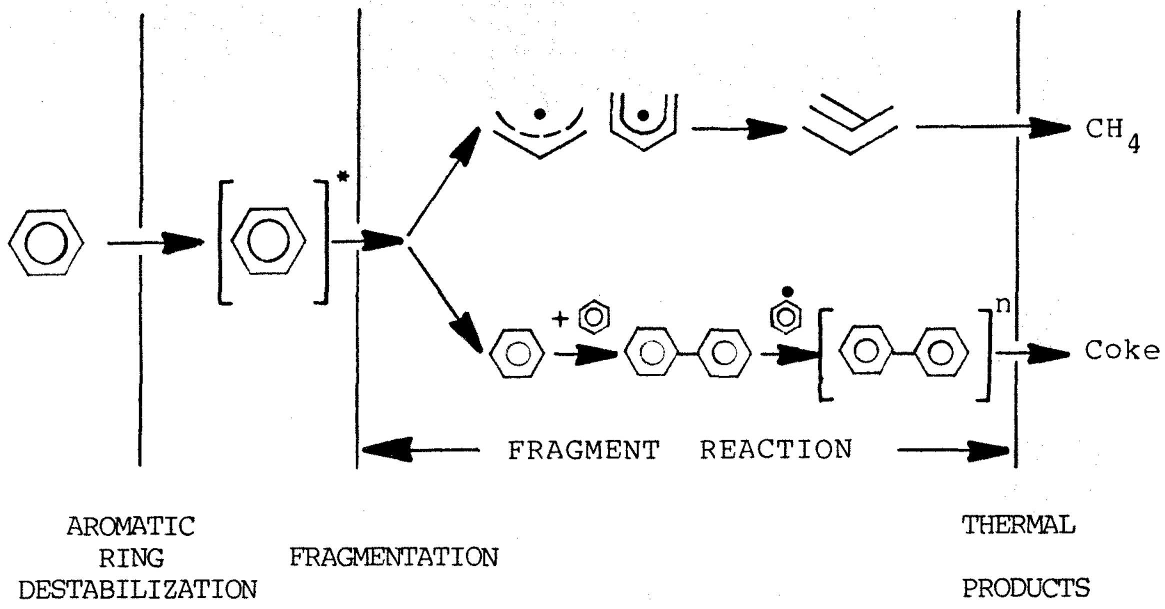
While all of the chlorocarbons products formed decrease with temperature above 700 ^{o}C, the GC/TCD analysis showed that the amounts of CO, CO_2, H_2, CH_4 and H_2O gradually increased with increasing temperature, with HCl, C(s) also observed. All chlorocarbons were nearly completely destroyed (over 99.99%) at 1050 ^{o}C with products showing a substantial amount of CO, CO_2, H_2, CH_4, C_2H_2, H_2O, HCl and C(s). Complete destruction of the parent reagent chloroform took place at temperature around 750 ^{o}C for case I and III, and 850 ^{o}C for case II and IV.

Since the graphitic carbon (coke) appeared as flakes on the walls of the reactor tube, it is likely that the wall acted as a site for what amounted to a "hydrogen elimination" or "polymerization" of carbon species in this study. This coking phenomena has been well studied by Y.T. Shah et. al. (40) and by G.F. Froment et.al. (41,42). In the initial period of the run the rate of coke formation appears to be rather rapid and after some time the rate of coking decreases and the amount of coke is more or less constant with little or no measureable increase. The higher coking rate at the earlier time is probably due to the surface effects of the reactor tube walls. After a certain amount of time the surface becomes covered with a coke layer and this surface effect presumably diminishes. The coke formed during the later period is most probably thermal coke, i.e., formed as a result of homogeneous reaction rather than that formed on the surface. It was also observed that the coke formed was much fluffier and the liquid condensate had a darker color at temperatures higher than 850 °C for 0.4 cm ID reactor and 900 °C for 1.05 cm ID reactor. This observation indicates that at higher temperature, a large amount of coke may be carried away by the flowing stream.

No qualitative or quantitative analysis on the kinetics of coke deposition in the treatment of chlorocarbons is available in the literature to the best of our knowledge. However, the principal emphasis of this work is not to determine a mechanism of coke formation but to investigate reactions that efficiencly convert toxic and or hazardous chlorocarbons into HCl and either cabon oxides or useful hydrocarbons. Carbon (solid) is however, found in some experiments of this research and a few previous studies can be used as references in describing the mechanistic pathways to this coke formation. G.F. Froment in one study on olefin production (43) indicated that heavy products condensed on the tubes, gradually lost hydrogen and finally yielded a carbonaceous material, in studies on thermal cracking for olefin production. Gay et. al. (44) proposed the following radical mechanism for the coke formation in shock tube pyrolysis of acetylene:

$$C_2H_2 \rightarrow C_4H_3 \rightarrow C_4H_2 \rightarrow C_6H_2 \rightarrow C_8H_2 \longrightarrow \text{coke}$$

Yatish T. Shah et. al.(40) have indicated that coke which is mainly composed of high-molecular weight hydrocarbons of aromatic nature probably decomposes by itself as well as further reacts with other products, at temperatures similar to ours. Virk et.al. (45) have reported the following pathways that coke and methane can be formed by benzene decomposition during pyrolysis.



Note that this is in fair agreement with our findings since both benzene light hydrocarbons and methane were found in our system.

One possible mechanism of coke formation in our systen can be postulated from recent literature on sooting in flames by Stephen J. Harris et. al. (46). The proposed pathway to coke formation as it applies to our system includes the the following steps:

(1) Unimolecular Decomposition

$CHCl_3$ ----> $CHCl_2$ + Cl
and/or
$CHCl_3$ ----> CCl_2 + HCl

(2) Chain Branching

$Cl + CHCl_3 \text{ ----> } HCl + CCl_3$

$Cl + H_2O \text{ ----> } HCl + CCl_3$

(3) HCl Elimination

$C_2H_2Cl_4 \text{ ----> } C_2HCl_3 + HCl$

$C_2HCl_3 \text{ ----> } C_2Cl_2 + HCl$

(4) Abstraction Reactions

$H + C_2Cl_2 \text{ ----> } C_2Cl + HCl$

$Cl + C_2Cl_2 \text{ ----> } C_2Cl + Cl_2$

(5) Continuation and Molecular Weight Growth (MWG)

$CHCl_2 + CHCl_3 \text{ ----> } CHC_2Cl_4 + Cl$

$CCl_2 + CHCl_3 \text{ ----> } C_2HCl_5$

$C_2Cl + C_2Cl2 \text{ ----> } C_4Cl_2 + Cl$

$C_4Cl_2 + C_2Cl \text{ ----> } C_6Cl_2 + Cl$

....

.... ----> Carbon (solid graphite)

Figure 5.

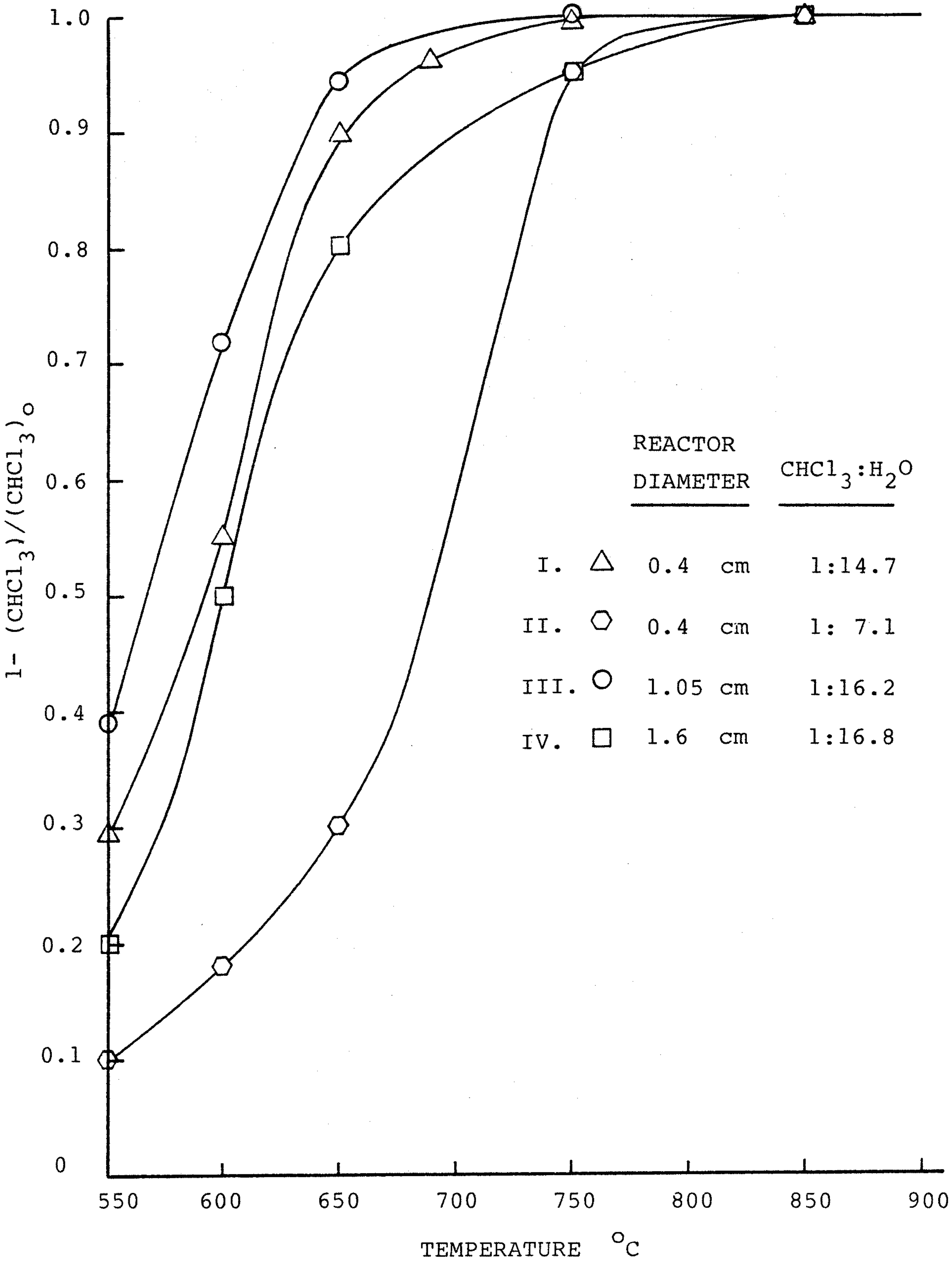
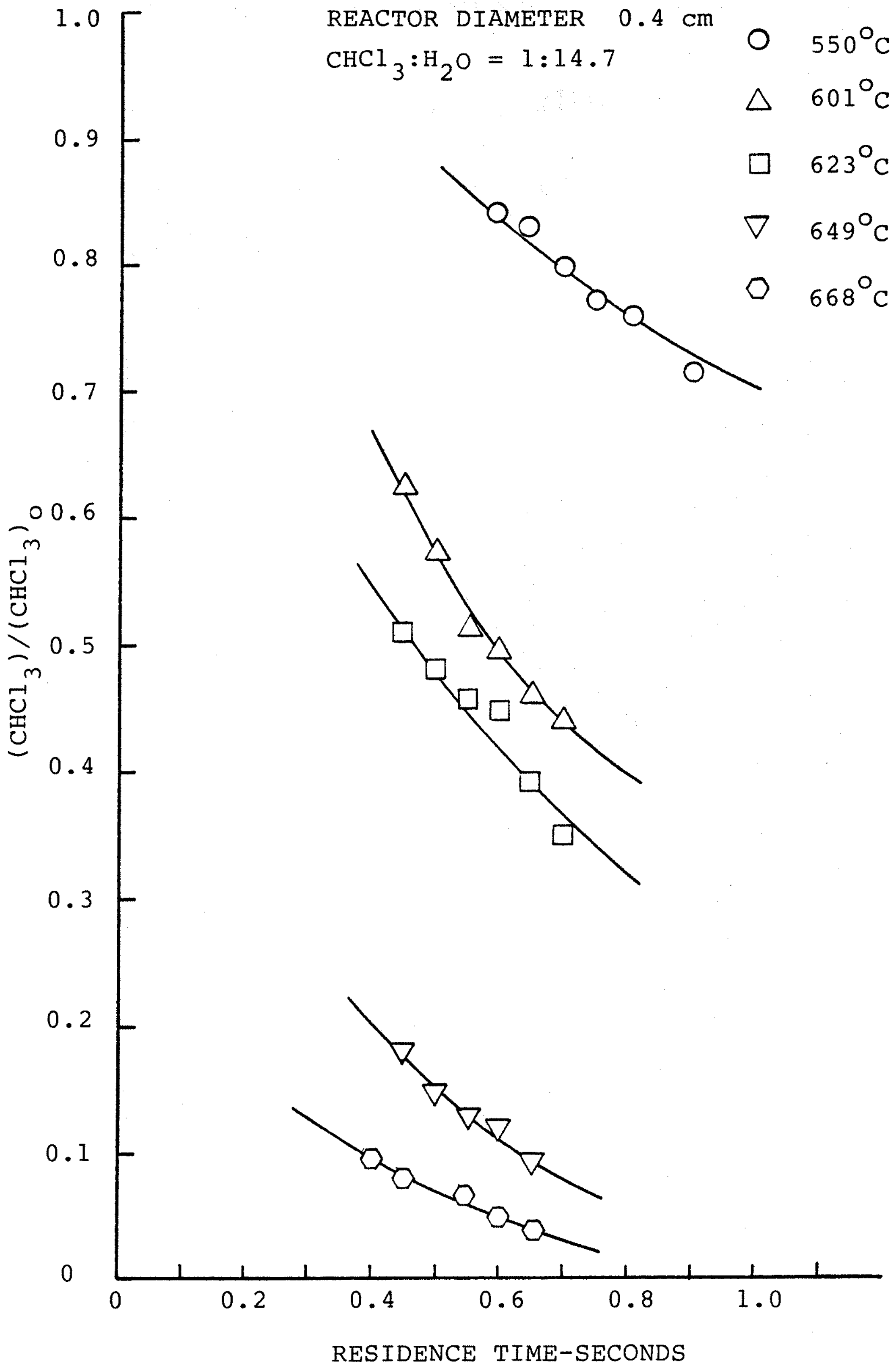

1- (CHCl$_3$)/(CHCl$_3$)$_o$
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
550
600
650
700
750
800
850
900
TEMPERATURE °C
REACTOR DIAMETER
CHCl$_3$:H$_2$O
I. △ 0.4 cm 1:14.7
II. ⬡ 0.4 cm 1: 7.1
III. ○ 1.05 cm 1:16.2
IV. □ 1.6 cm 1:16.8

Figure 6.



REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O = 1:14.7$
○ 550°C
△ 601°C
□ 623°C
▽ 649°C
⬡ 668°C
$(CHCl_3)/(CHCl_3)_o$
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

Figure 7.

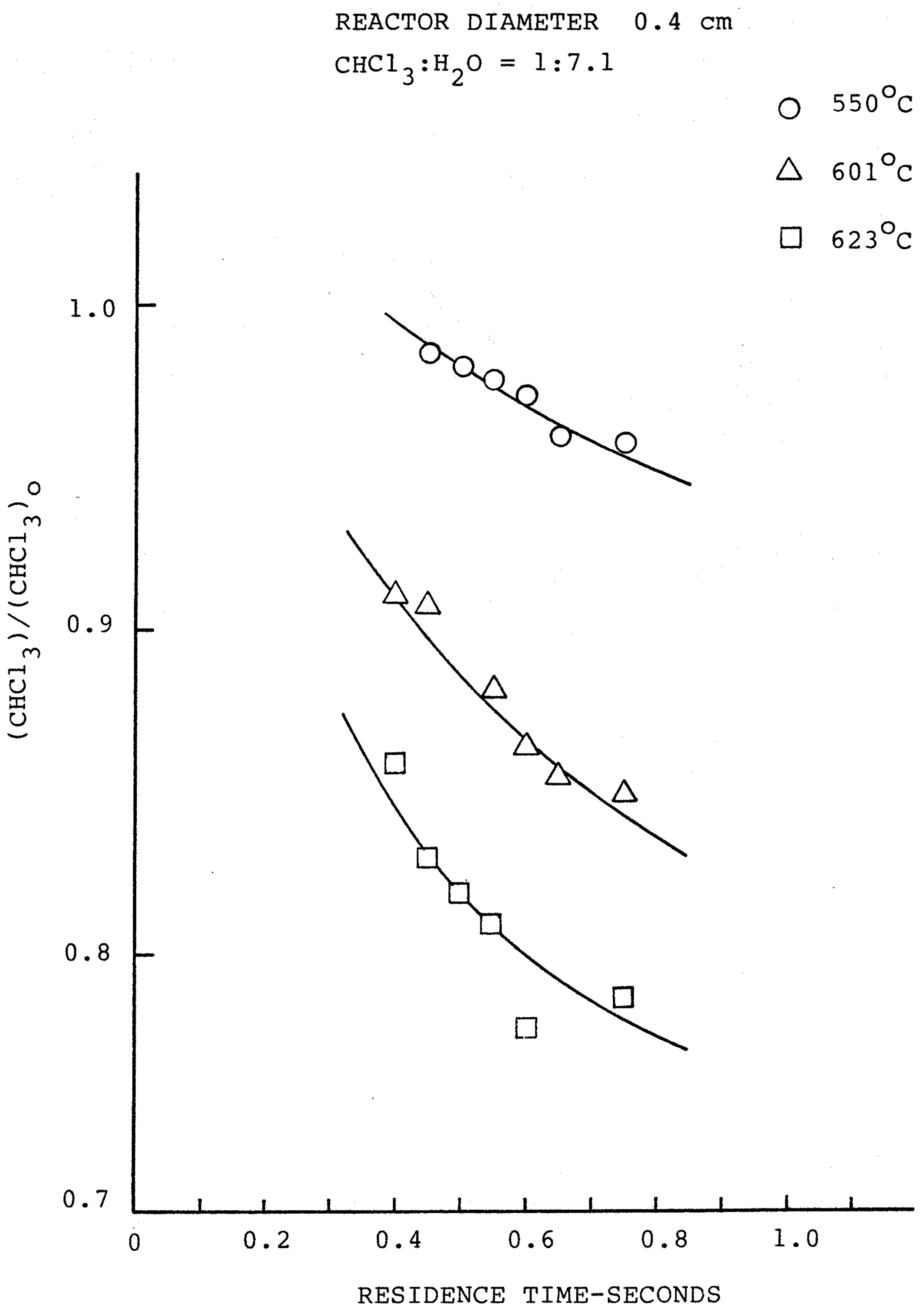

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:7.1
○ 550°C
△ 601°C
☐ 623°C
$(CHCl_3)/(CHCl_3)_o$
1.0
0.9
0.8
0.7
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

Figure 8.

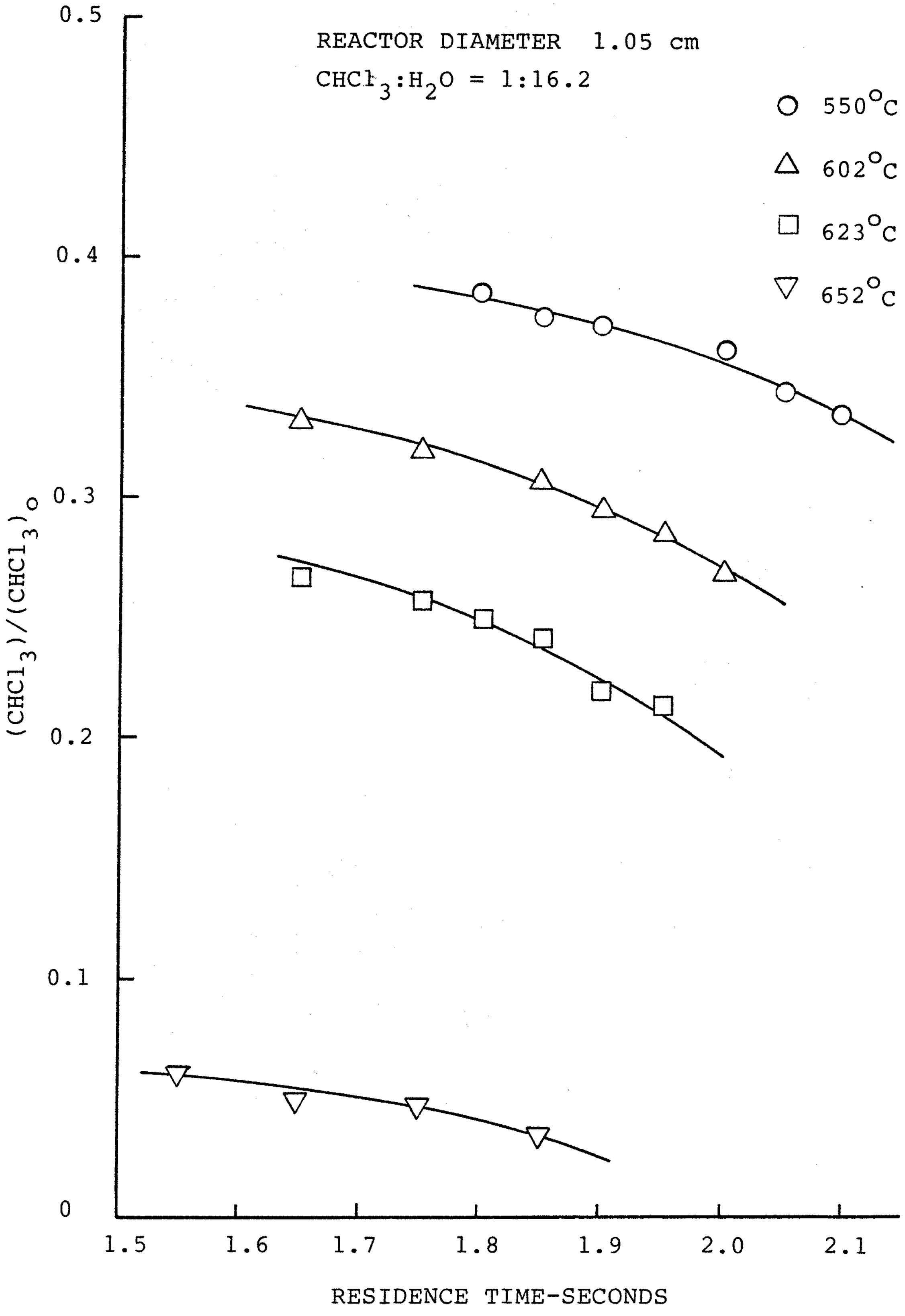
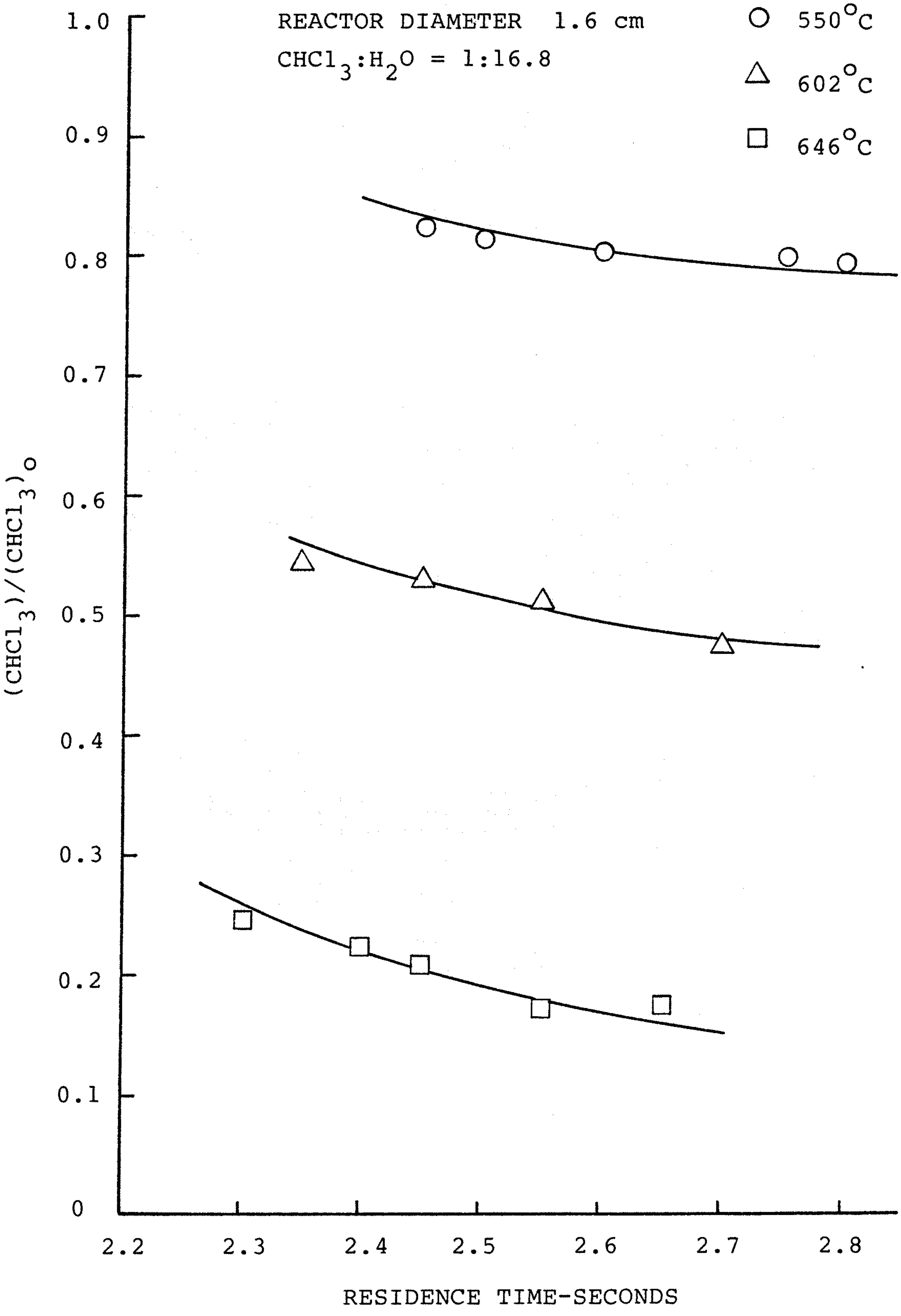

REACTOR DIAMETER 1.05 cm
$CHCl_3:H_2O = 1:16.2$
○ 550°C
△ 602°C
□ 623°C
▽ 652°C
$(CHCl_3)/(CHCl_3)_o$
0.5
0.4
0.3
0.2
0.1
0
1.5
1.6
1.7
1.8
1.9
2.0
2.1
RESIDENCE TIME-SECONDS

Figure 9.



REACTOR DIAMETER 1.6 cm
$CHCl_3:H_2O$ = 1:16.8
○ 550°C
△ 602°C
☐ 646°C
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$(CHCl_3)/(CHCl_3)_o$
2.2
2.3
2.4
2.5
2.6
2.7
2.8
RESIDENCE TIME-SECONDS

Figure 10.

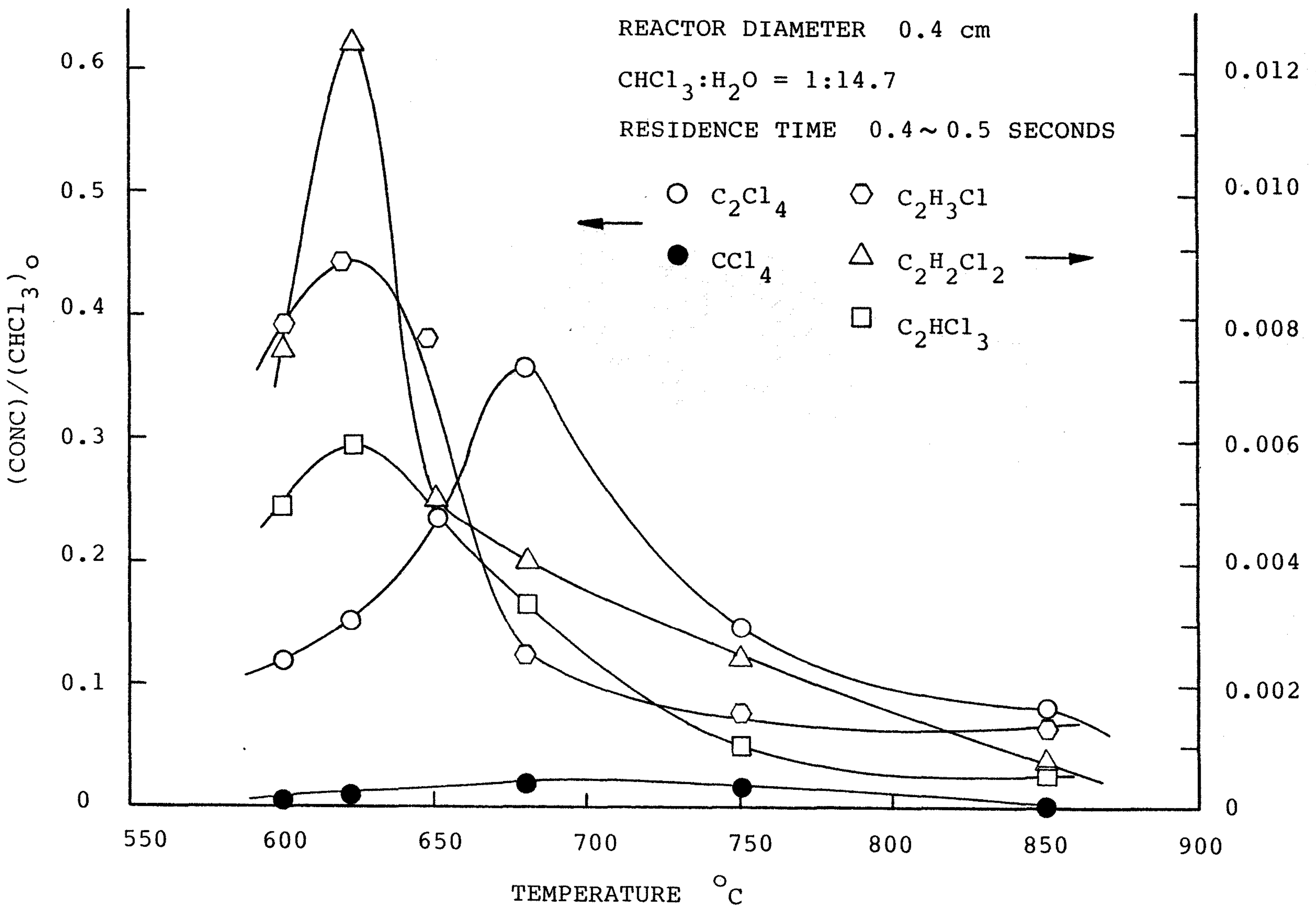

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
RESIDENCE TIME 0.4 ~ 0.5 SECONDS
○ C_2Cl_4
● CCl_4
⬡ C_2H_3Cl
△ $C_2H_2Cl_2$
□ C_2HCl_3
(CONC)/$(CHCl_3)_o$
0
0.1
0.2
0.3
0.4
0.5
0.6
0
0.002
0.004
0.006
0.008
0.010
0.012
550
600
650
700
750
800
850
900
TEMPERATURE °C

Figure 11.

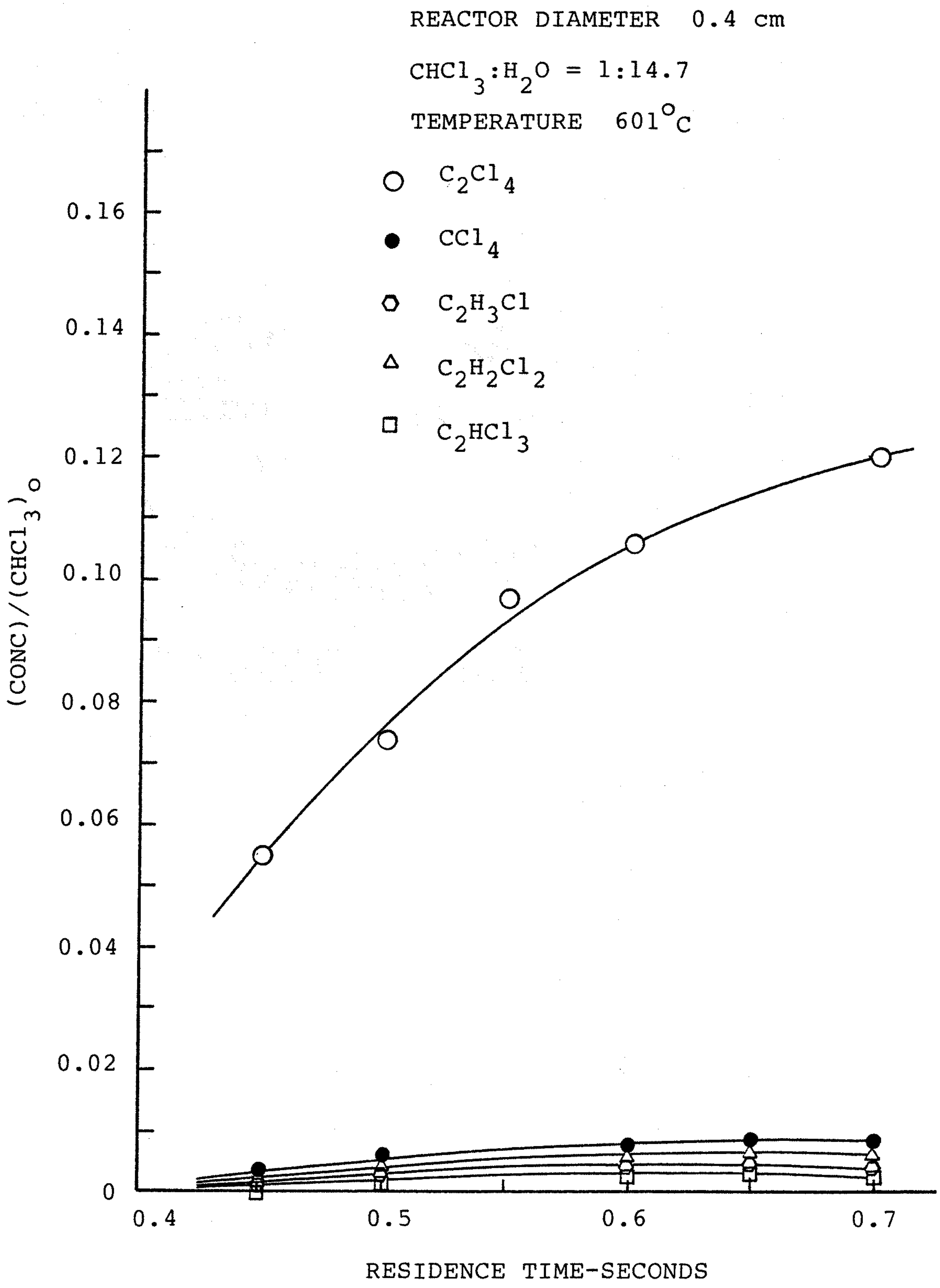

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 601°C
○ C_2Cl_4
● CCl_4
⬡ C_2H_3Cl
△ $C_2H_2Cl_2$
□ C_2HCl_3
$(CONC)/(CHCl_3)_o$
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0.4
0.5
0.6
0.7
RESIDENCE TIME-SECONDS

Figure 12.

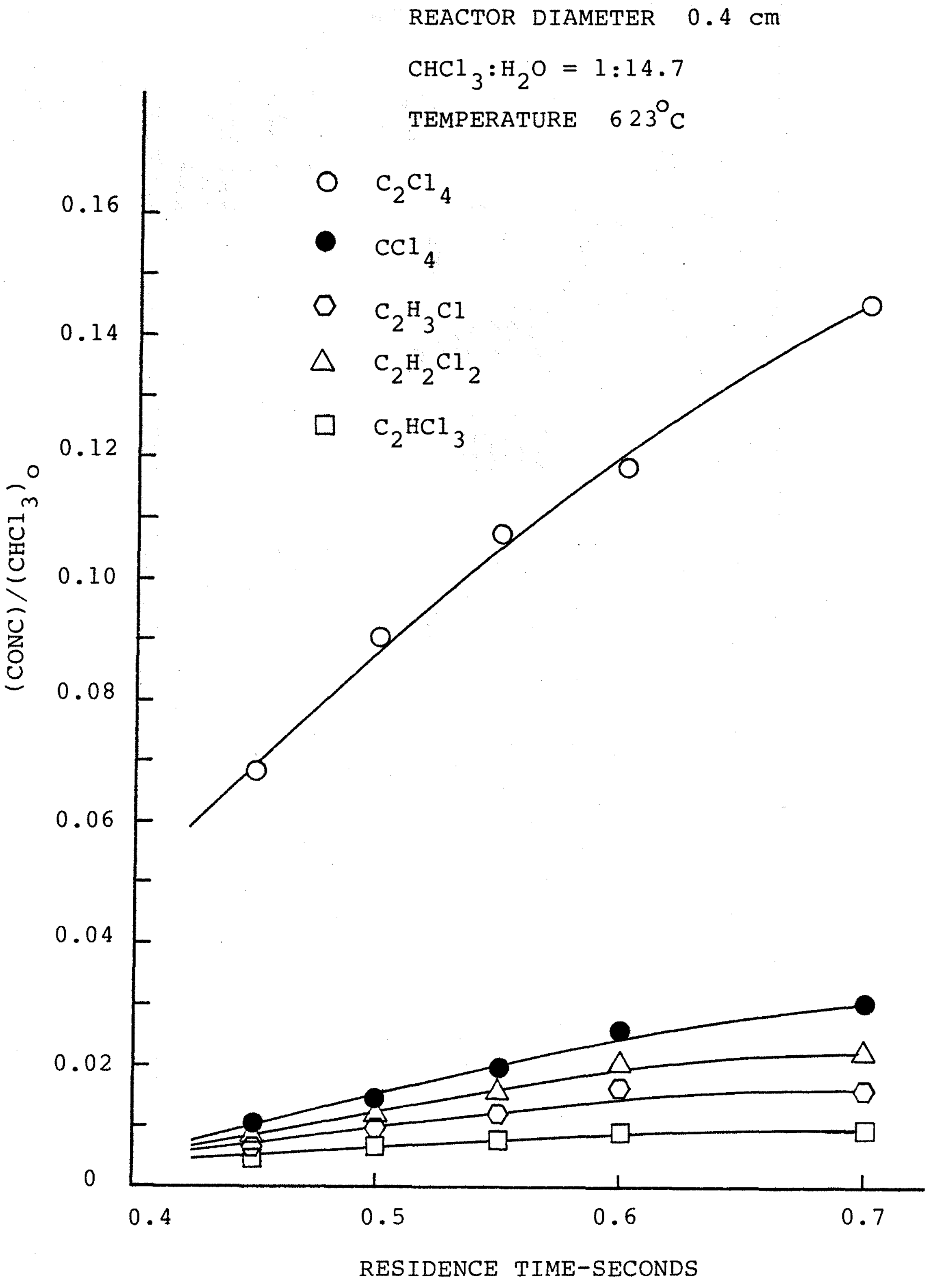

REACTOR DIAMETER 0.4 cm
$CHCl_3$:H_2O = 1:14.7
TEMPERATURE 623°C
○ C_2Cl_4
● CCl_4
⬡ C_2H_3Cl
△ $C_2H_2Cl_2$
□ C_2HCl_3
$(CONC)/(CHCl_3)_o$
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0.4
0.5
0.6
0.7
RESIDENCE TIME-SECONDS

Figure 13.

REACTOR DIAMETER 0.4 cm

$CHCl_3:H_2O$ = 1:14.7 TEMPERATURE 649°C

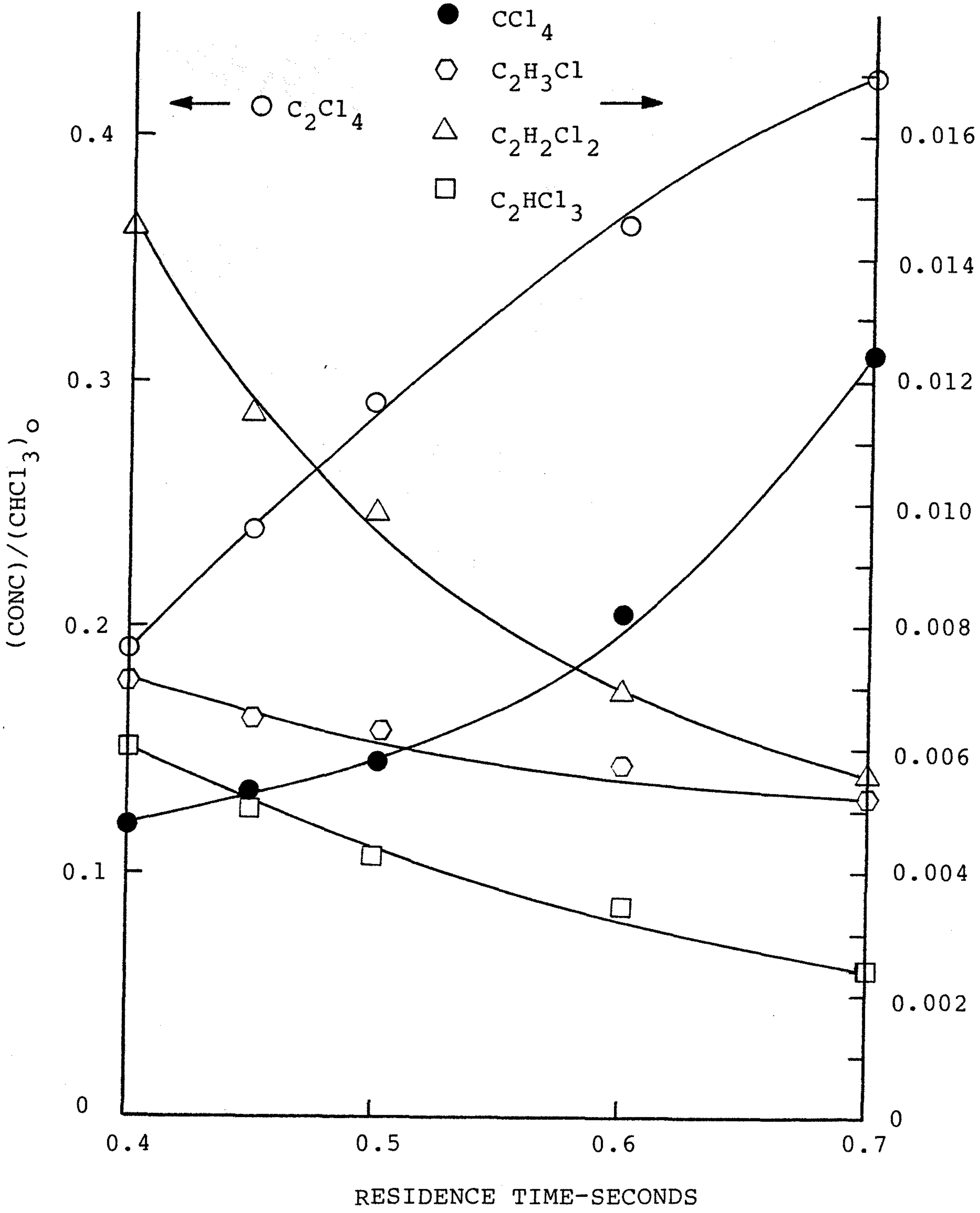


Figure 14.

REACTOR DIAMETER 0.4 cm

$CHCl_3:H_2O = 1:14.7$ TEMPERATURE 680°C

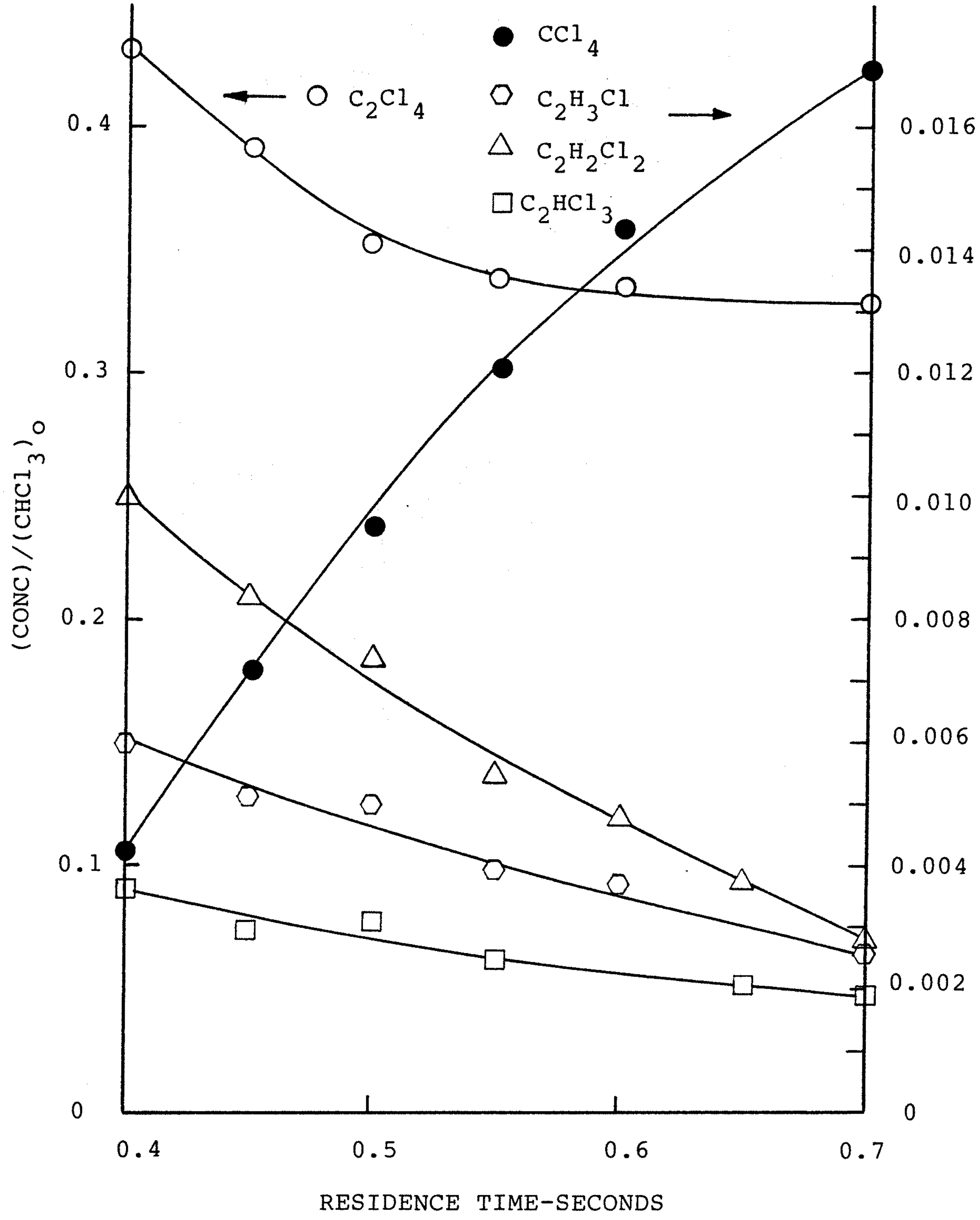
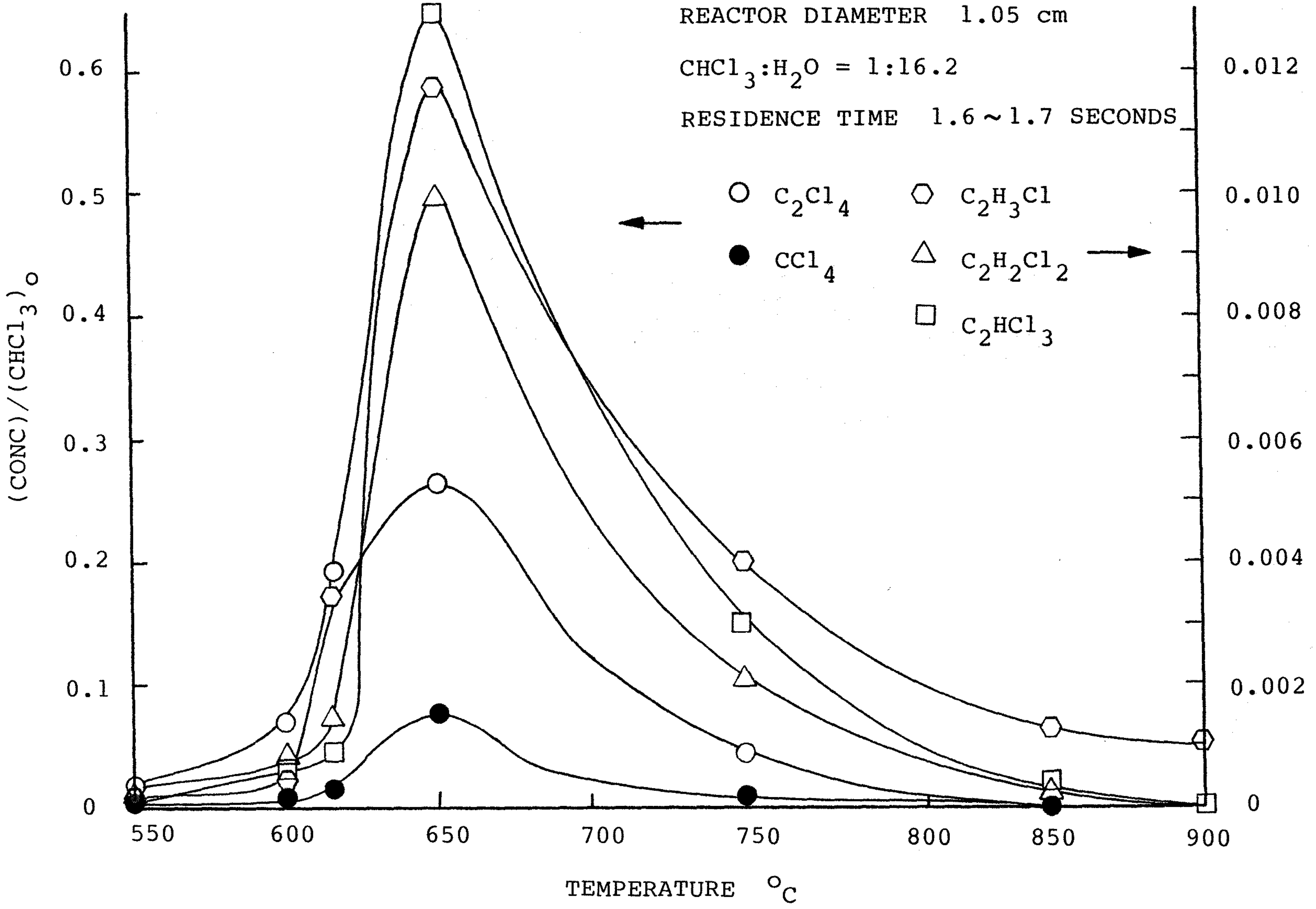


Figure 15.



REACTOR DIAMETER 1.05 cm

$CHCl_3:H_2O$ = 1:16.2

RESIDENCE TIME 1.6 ~ 1.7 SECONDS

Figure 16.

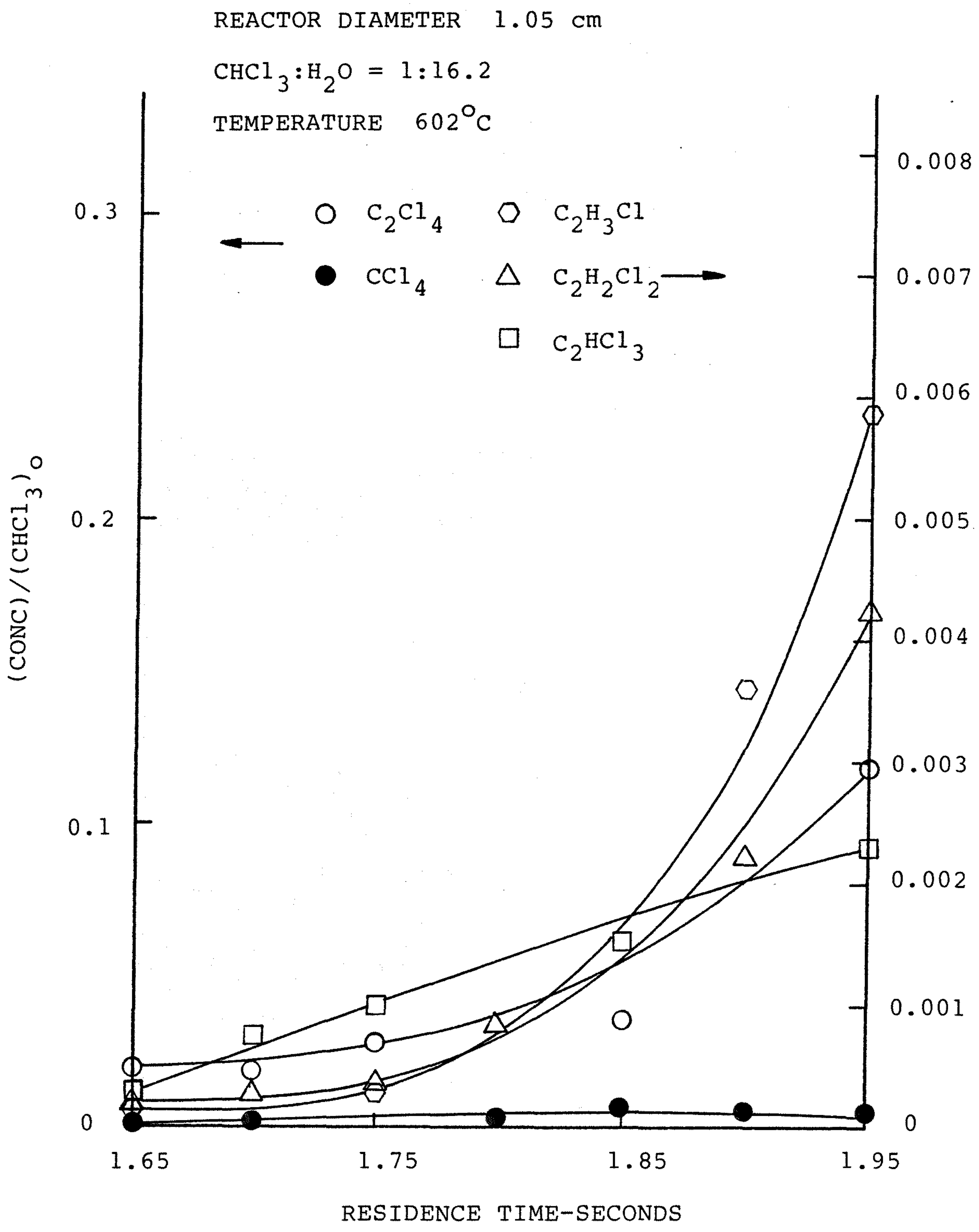

REACTOR DIAMETER 1.05 cm
$CHCl_3:H_2O$ = 1:16.2
TEMPERATURE 602°C
○ C_2Cl_4
● CCl_4
⬡ C_2H_3Cl
△ $C_2H_2Cl_2$
□ C_2HCl_3
(CONC)/(CHCl3)o
0.3
0.2
0.1
0
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
1.65
1.75
1.85
1.95
RESIDENCE TIME-SECONDS

Figure 17.

REACTOR DIAMETER 1.05 cm

$CHCl_3:H_2O$ = 1:16.2 TEMPERATURE 623°C

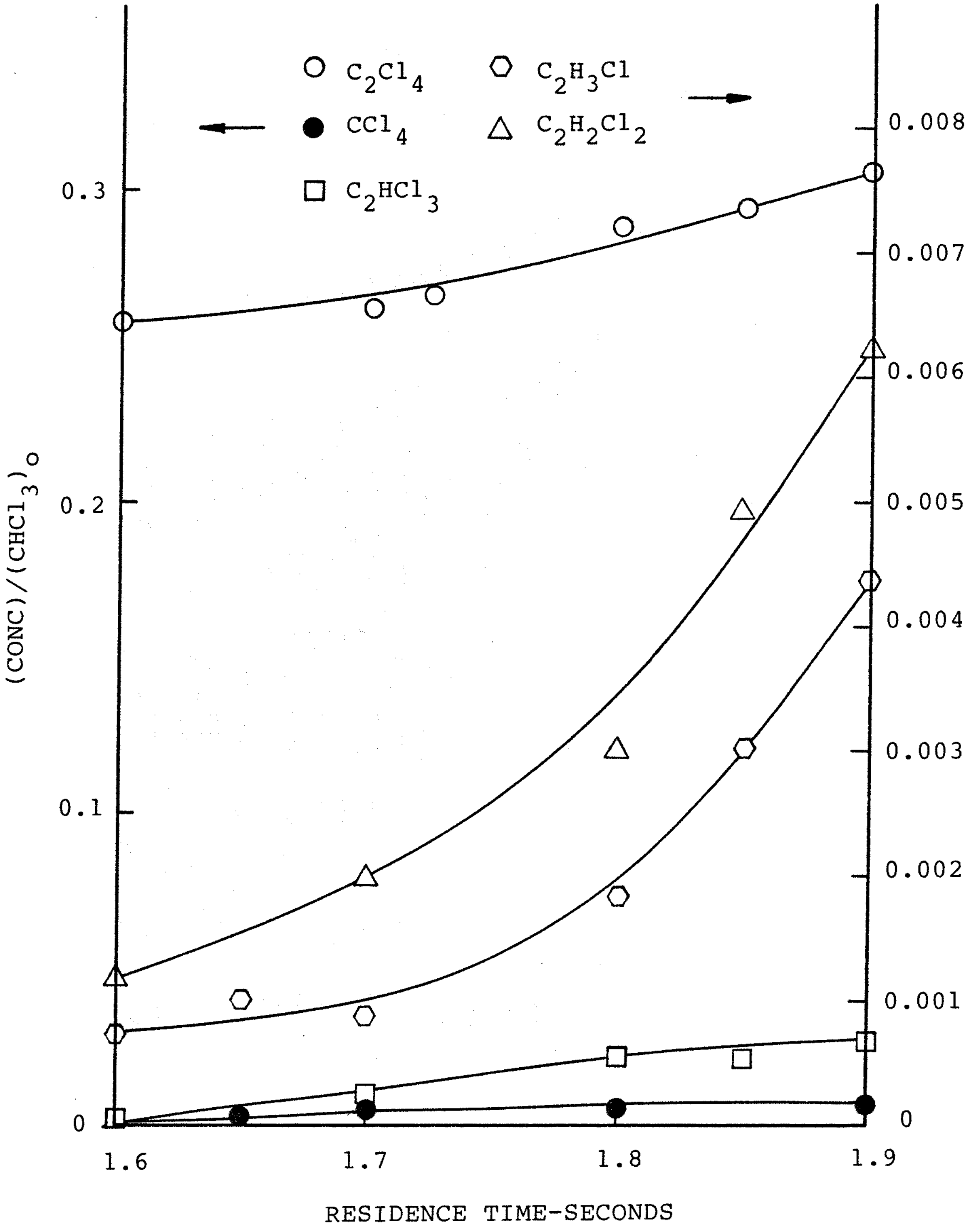
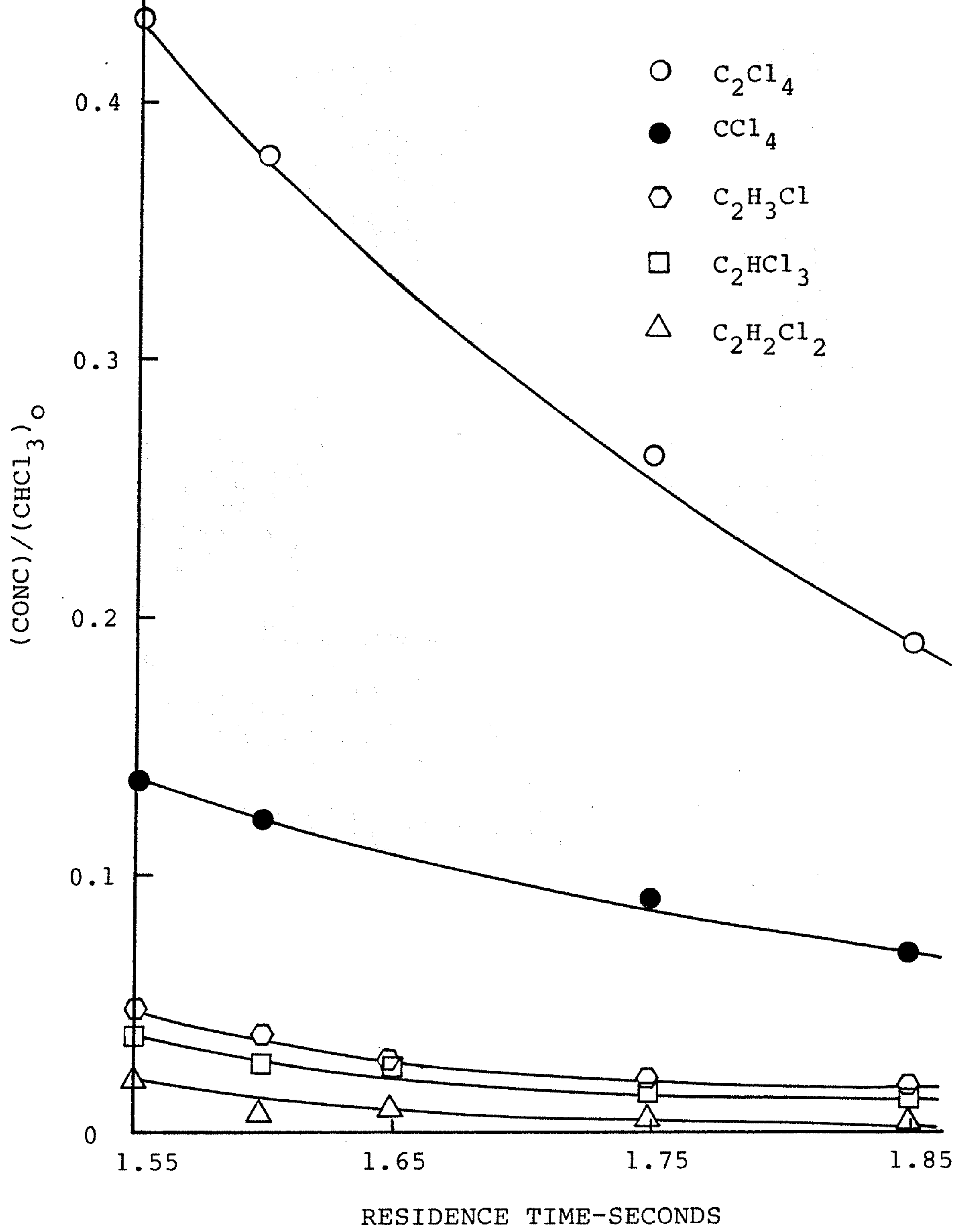


Figure 18.

REACTOR DIAMETER 1.05 cm

$CHCl_3:H_2O$ = 1:16.2 TEMPERATURE 650°C



B. Kinetic Analysis

The reaction of chloroform with excess water vapor has been studied in a pseudo first-order kinetic regime: both homogeneous unimolecular and heterogeneous. Plots of integrated rate equation parameters (36) are shown in Figures 19 through 21 for half order, first-order, and second order rate equations on chloroform decomposition using data from the 0.4 cm ID reactor. Plots representing the same conditions but by Wilkinson's method (38) are shown in Figures 22 through 24. The respective temperatures of 550 , 601 and 623 °C incorporate the optimun conversion range (for kinetic analysis) of $CHCl_3$ in the reactor. The data indicate that the reaction closely follows first-order decay with half order decay plots also showing reasonable fits by Wilkinson's method. The integrated rate equations alone or comparison of both integration and Wilkinson's methods (see Table 2) , show that only first-order decay plots fit the data. Data for the two other size reactors is quite similar where first order plots show the best fits.

Plots of $-\ln(1-X)$, where X is conversion of chloroform, versus residence time in seconds, are shown in Fig. 25 through 28 for case I to case IV, temperature range from 550 to 668 °C. The straight lines through to the origin give the values of overall rate constant k' as the slope, and indicate a first-order integrated rate equation fits the data well.

Table 2.

TEMPERATURE	REACTION ORDER	k´	
		INTEGRATED RATE METHOD	WILKINSON METHOD
550 °C	1/2 order	0.4389	0.3035
	1st order	0.3290	0.3225
	2nd order	0.0248	0.3749
601 °C	1/2 order	1.3661	0.9613
	1st order	1.1540	1.1163
	2nd order	0.2938	1.6614
623 °C	1/2 order	1.7250	1.1416
	1st order	1.4450	1.3640
	2nd order	0.3590	2.2590

Plots of ln (k′) versus 1/T, where k′ is the overall rate constant for the reaction as determined from the previous plots, and T is temperature in degrees Kelvin are shown in Fig. 29 through 32. The data shows relatively good straight line fits and indicate that the overall reaction for our two mode system (wall + Homogeneous) may be represented by a single rate constant with activation energies as determined. Individual wall and bulk rate constants are determined in the following.

As mentioned in the theory section, two types of reactions may be occurring in the reactor, one on the wall or inside surface of the reactor and one in the bulk vapor phase. Thus, a more accurate and mathematically correct analysis of the rate constants and activation energies is required. Figures 33 to 36 are plots of k′ versus 2/r for the determination of k_w and k_b values using linear regression analysis according to the expression given by Kaufman (33) where $k' = k_b + (2/r)\,k_w$, at the four average temperatures of 550, 601, 623 and 650 ^{o}C. The results obtained from these graphs are shown in Table 3 for the $CHCl_3$ to H_2O ratio of 1:16 with respect to three reactors of 0.4, 1.05 and 1.60 cm ID. It is apparent that the wall rate constant contributes significantly to the overall rate constant. The activation energies for the bulk and wall reactions are also shown in Figures 37 and 38 (or see Table 3) by plotting ln k_b versus 1/T and ln k_w versus 1/T,

Table 3.

TEMPERATURE	k´			k_b	k_w
	0.4 cm ID	1.05 cm ID	1.6 cm ID		
550 °C	0.329	0.246	0.106	0.093	0.025
601 °C	1.005	0.654	0.229	0.172	0.086
623 °C	1.445	1.073	0.485	0.421	0.107
650 °C	2.800	1.791	0.850	0.565	0.230
E / R	11.855	14.950	15.906	14.200	16.080

and show that the wall reaction has a higher activation energy than the bulk reaction. Above 700 °C however, the wall reaction becomes larger than reaction in the vapor phase. This indicates that below 700 °C the wall acts to stabilize the reaction, while at temperature above the cross over point the wall reaction accelerates the reaction. This is dramatically in figures.

The activation energy values in Table 3 are in fair agreement with unimolecular decomposition data in the literature and the primary observed products for this chloroform/water vapor reaction in the 600 to 650 °C temperature range are very similar to that of pure unimolecular reaction. These indicate that the initial step in the reaction consists primarily of chloroform decomposition via unimolecular reaction and further reaction with parent $CHCl_3$.

C. Mechanism Analysis

The following is a summary mechanism which explains the major products and kinetics observed in order to substantiate this study more fully. It is not meant to be exhaustive but it is felt that it accurately describes the global reactions in this work. The first step in the proposed mechanisn as mentioned in the theory and results section is homogeneous unimolecular decomposition of the parent chloroform into either:

$$CHCl_3 \longrightarrow \begin{array}{c} CHCl_2 + Cl \\ \text{or} \\ CCl_2 + HCl \end{array}$$

Subsequent Reactions Include:

Initial Chain Branching Reactions

$CHCl_2 + H_2O \longleftrightarrow CH_2Cl_2 + OH$

$CCl_2 + H_2O \longleftrightarrow CHCl_2 + OH$

$CHCl_2 + OH \longleftrightarrow CH_2Cl_2 + O$

$CCl_2 + OH \longleftrightarrow CHCl_2 + O$

$CHCl_3 + OH \longleftrightarrow CCl_3 + H_2O$

$CHCl_3 + OH \longleftrightarrow CCl_3 + HCl$

$OH + OH \longleftrightarrow H_2O + O$

$Cl + H_2O \longleftrightarrow HCl + OH$

$O + OH \longrightarrow O_2 + H$

$H + H_2O \longleftrightarrow H_2 + OH$

$H_2 + Cl \longleftrightarrow HCl + H$

$H_2 + CCl_2 \longleftrightarrow CCl_2H + H$

$H_2 + CCl_2H \longleftrightarrow CCl_2H_2 + H$

Formation of Specific Compounds

C_2Cl_4 formation:

$CHCl_3 + CCl_2 \longleftrightarrow C_2Cl_4 + HCl$

$CCl_2 + CCl_2 \longleftrightarrow C_2Cl_4$

$CCl_3 + CCl_3 \longleftrightarrow C_2Cl_4 + Cl_2$

$CHCl_3 + CHCl_2 \longleftrightarrow C_2H_2Cl_4 + Cl$

$CHCl_3 + CHCl_2 \longleftrightarrow C_2HCl_5 + H$

C_2HCl_3 formation:

$CHCl_2 + CHCl_2 \longleftrightarrow C_2H_2Cl_4 \longrightarrow C_2HCl_3 + HCl$

$CHCl_3 + CCl_2 \longleftrightarrow C_2HCl_3 + Cl$

$C_2H_2Cl_2$ formation

$CHCl + CHCl \longleftrightarrow C_2H_2Cl_2$

CCl_4 formation

$CCl_3 + HCl \longleftrightarrow CCl_4 + H$

$CCl_3 + Cl \longleftrightarrow CCl_4$

C_2H_2 formation

$C_2H_3Cl \longleftrightarrow C_2H_2 + HCl$

CO formation

$CHCl + OH \longrightarrow CO + H + Cl$

$CCl_2 + OH \longrightarrow CO + HCl + Cl$

CO_2 formation:

$HCO + OH \longrightarrow CO_2 + 2H$

$CO + O \longrightarrow CO_2$

CH_4 formation:

$CH_2Cl + H_2O \longleftrightarrow CH_3Cl + OH$

$CH_2Cl + OH \longleftrightarrow CH_3Cl + O$

$CH_3Cl \longleftrightarrow CH_3 + Cl$

$CH_3 + H_2O \longleftrightarrow CH_4 + OH$

At high temperatures, reactions similar to those in coal gasification will form CH_4, CO, CO_2 as well as H_2. Therefore, subsequently reactions of these species will also occur in our system.

D. Additional Kinetics Discussion

It is noted that C_{AO} is not constant, but is varied in each run. If C_{AO} were constant, the 2nd oder plots in Fig. 19, 20 and 21 would show a positive slope. A better way to plot the 2nd order data is a graph of $C_{AO}^2(V/F_{AO})$ versus $X/(1-X)$, where V/F_{AO} is constant through a given series of runs. These graphs are shown in Fig. 19′, 20′ and 21′ and show definite curvature for temperatures 601 and 623 ^oC. This further supports the conclusion that the data follow 1st order kinetics overall.

Figure 19.

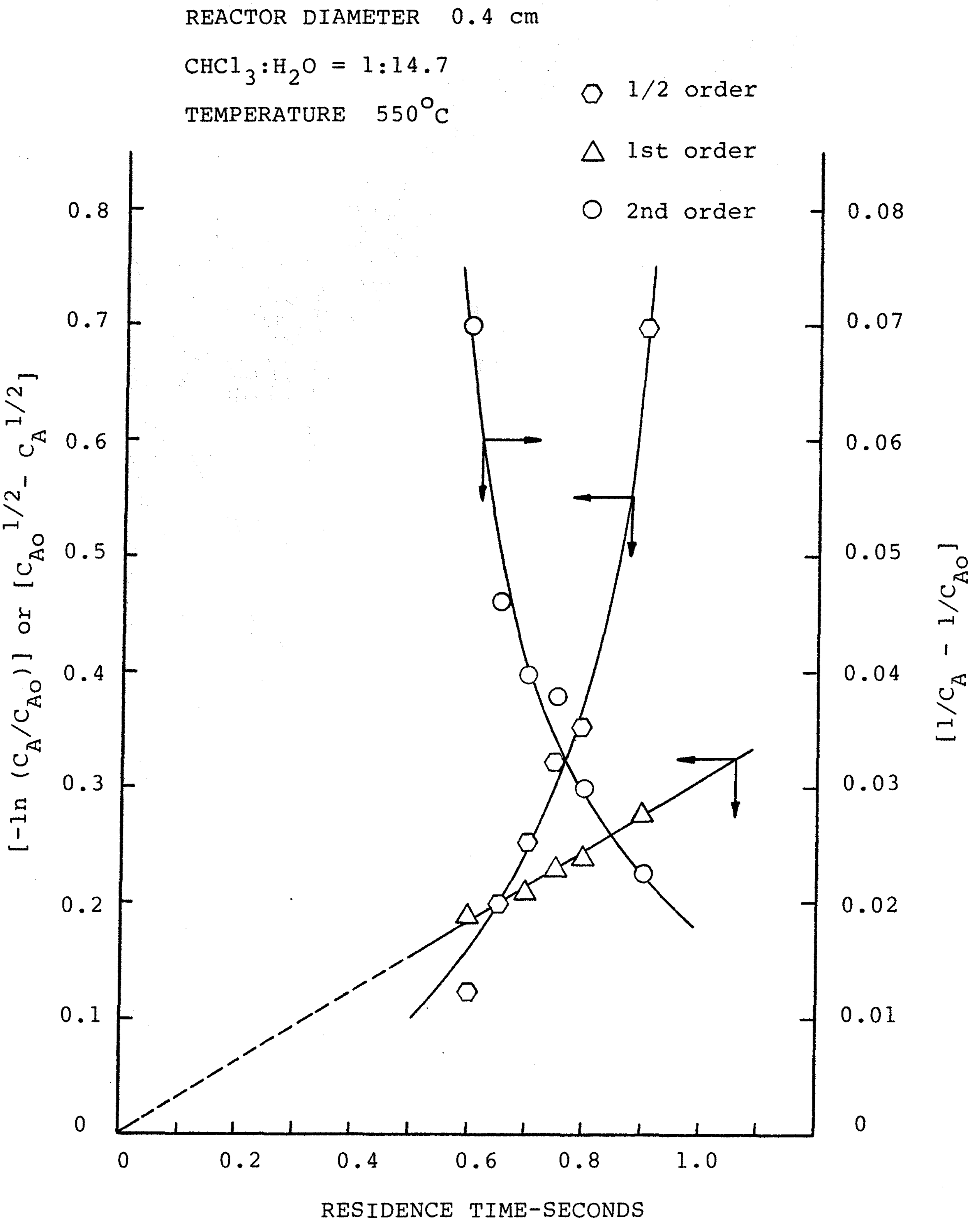
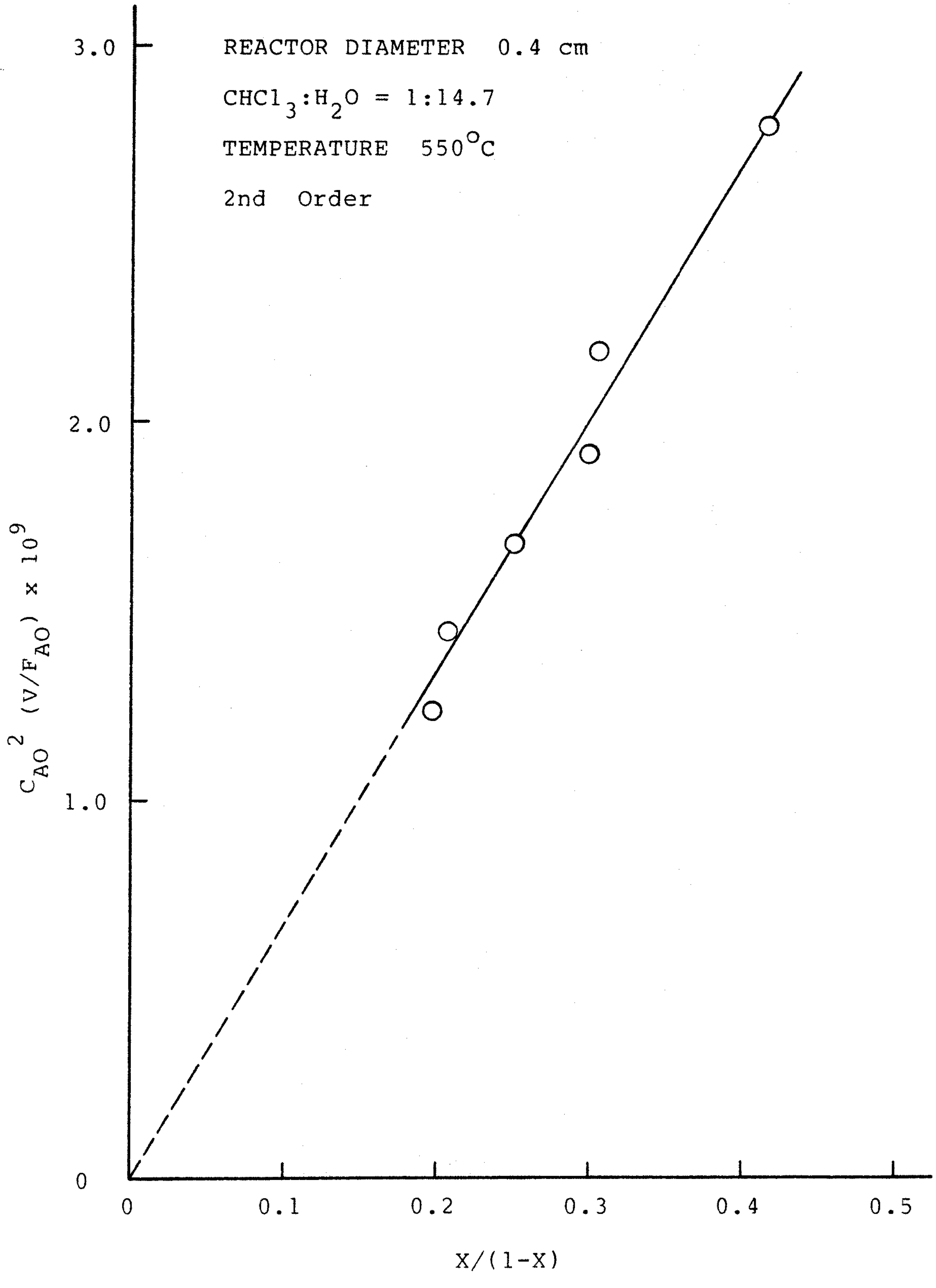

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O = 1:14.7$
TEMPERATURE 550°C
⬡ 1/2 order
△ 1st order
○ 2nd order
$[-\ln(C_A/C_{Ao})]$ or $[C_{Ao}^{1/2} - C_A^{1/2}]$
$[1/C_A - 1/C_{Ao}]$
RESIDENCE TIME-SECONDS
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.2
0.4
0.6
0.8
1.0

Figure 19´.



REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O = 1:14.7$
TEMPERATURE 550°C
2nd Order
3.0
2.0
1.0
0
$C_{AO}^2 (V/F_{AO}) \times 10^9$
0
0.1
0.2
0.3
0.4
0.5
X/(1-X)

Figure 20.

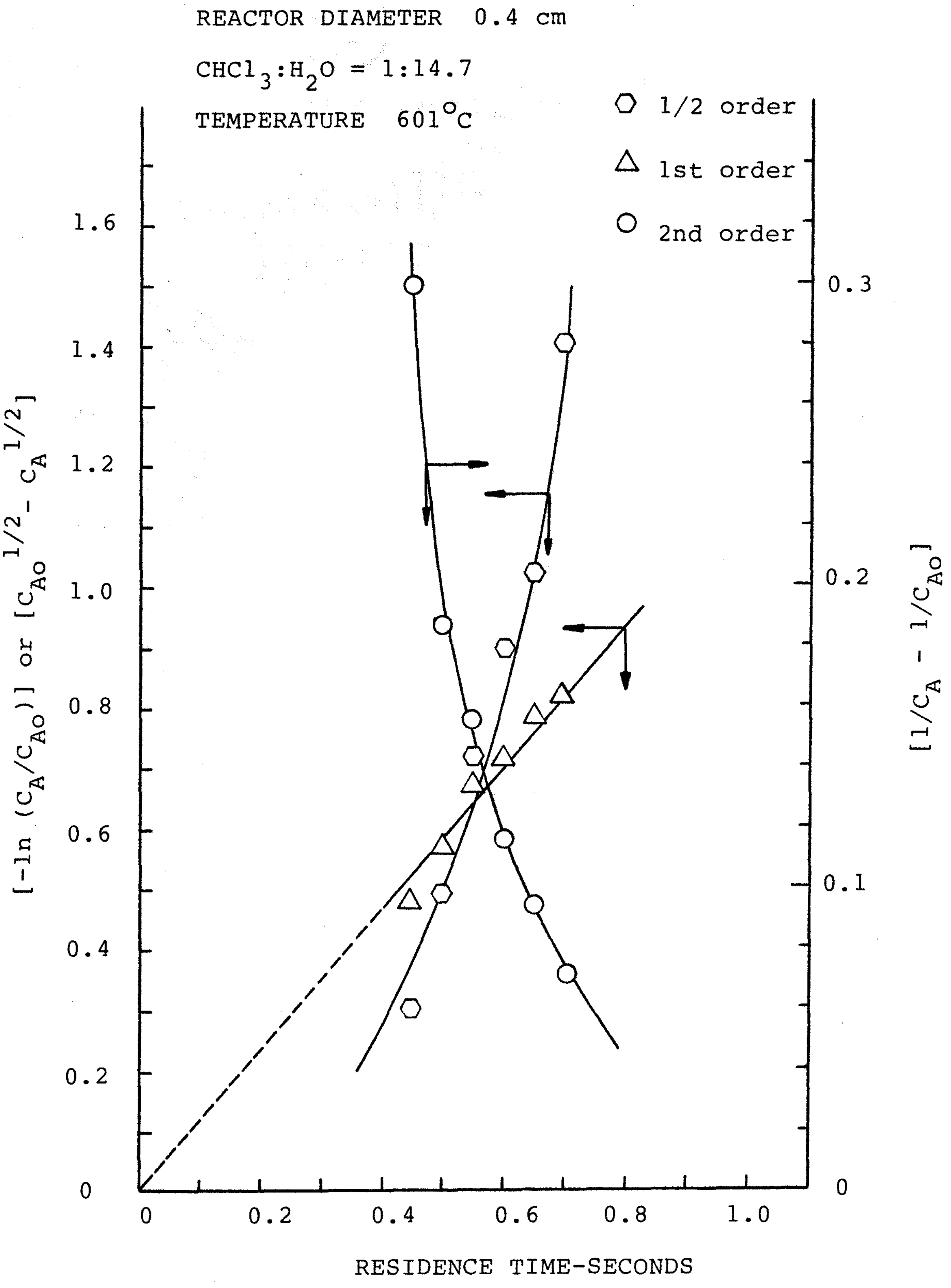
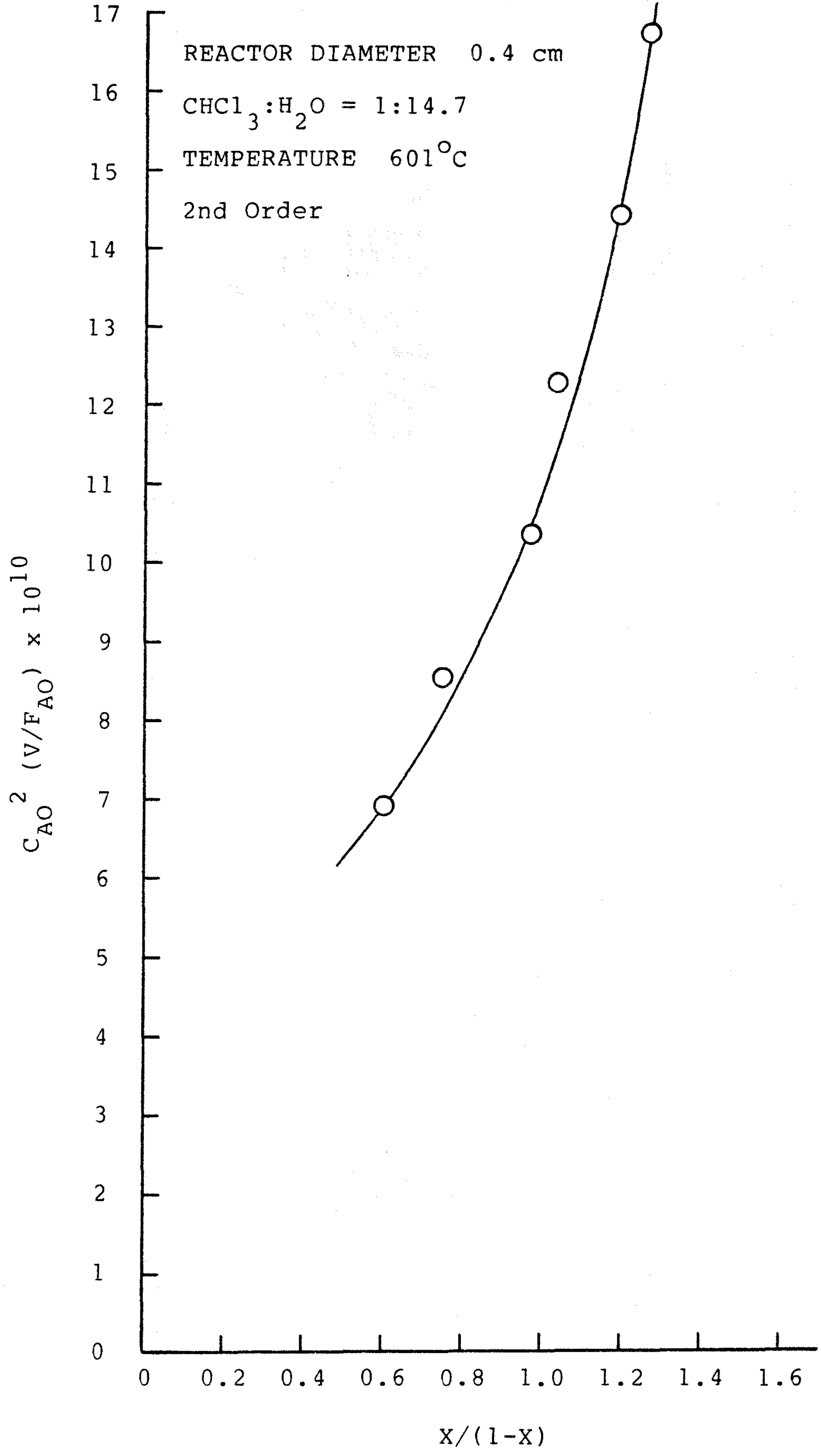

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 601°C
1/2 order
1st order
2nd order
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
$[-\ln (C_A/C_{Ao})]$ or $[C_{Ao}^{1/2} - C_A^{1/2}]$
$[1/C_A - 1/C_{Ao}]$
RESIDENCE TIME-SECONDS

Figure 20´.



REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 601°C
2nd Order
$C_{AO}^2\ (V/F_{AO}) \times 10^{10}$
X/(1-X)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Figure 21.

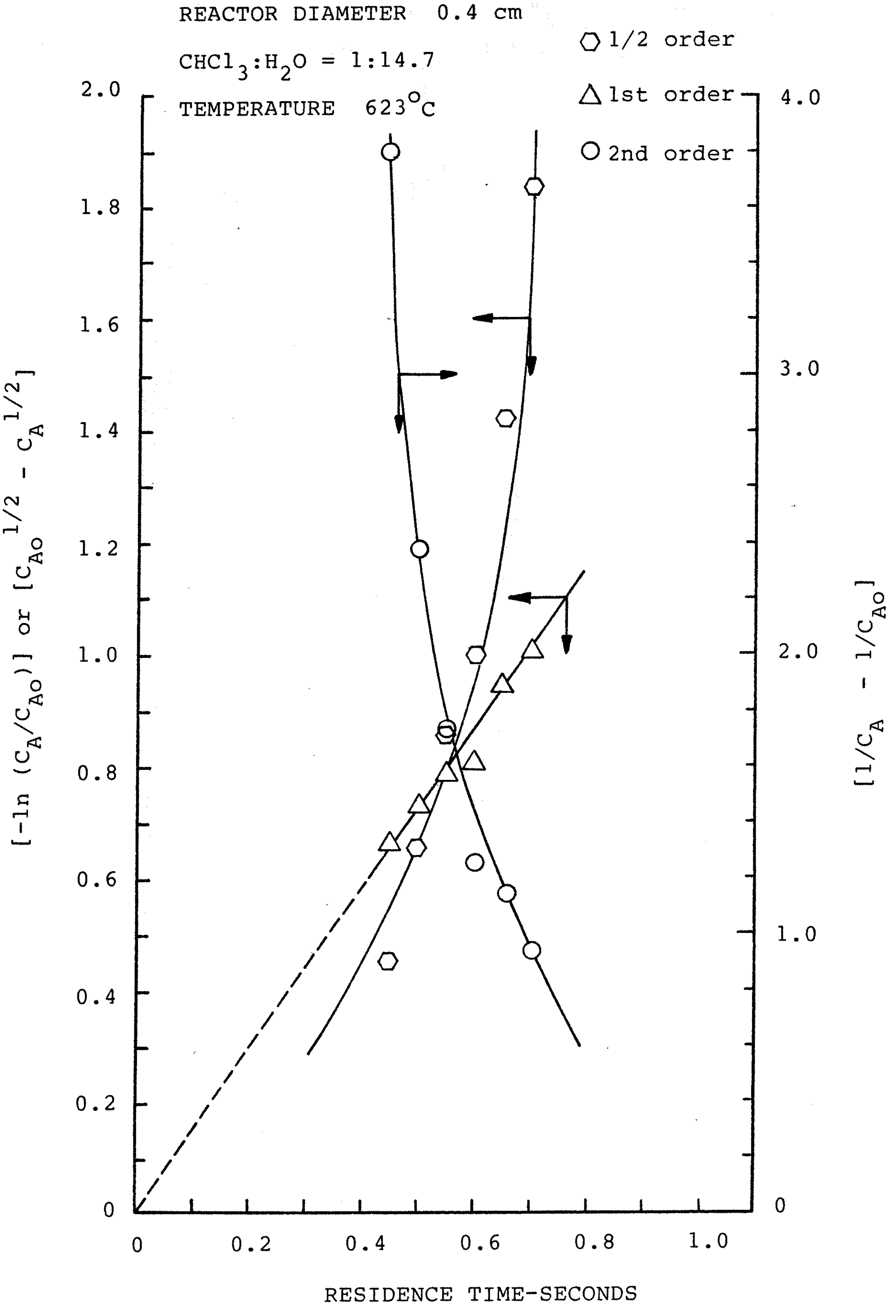

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 623°C
⬡ 1/2 order
△ 1st order
○ 2nd order
$[-\ln(C_A/C_{AO})]$ or $[C_{AO}^{1/2} - C_A^{1/2}]$
$[1/C_A - 1/C_{AO}]$
RESIDENCE TIME-SECONDS
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1.0
2.0
3.0
4.0

Figure 21´.

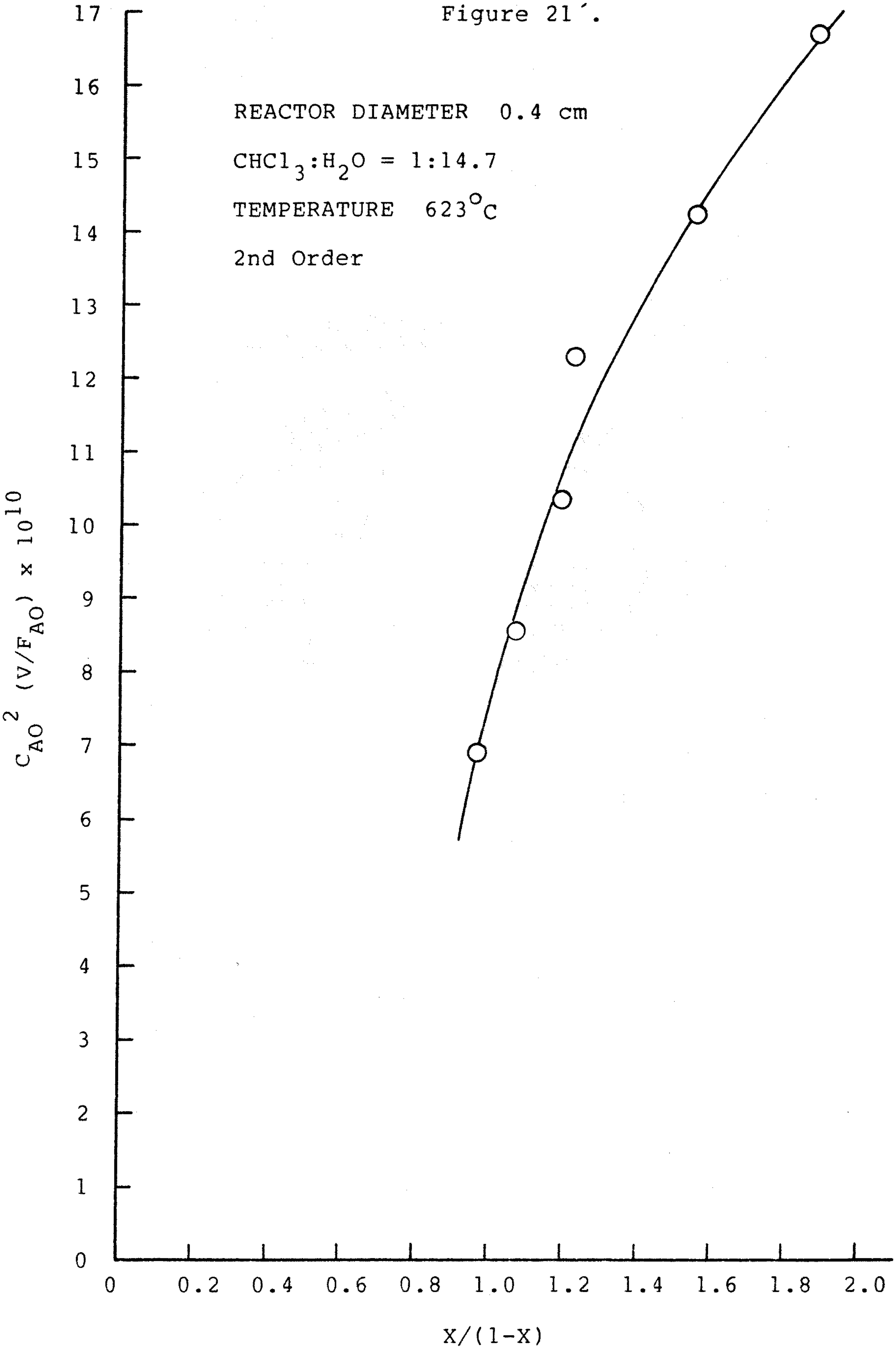

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O = 1:14.7$
TEMPERATURE 623°C
2nd Order
$C_{AO}^2 (V/F_{AO}) \times 10^{10}$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
X/(1-X)

Figure 22.

REACTOR DIAMETER 0.4 cm

$CHCl_3:H_2O$ = 1:14.7 TEMPERATURE 550°C

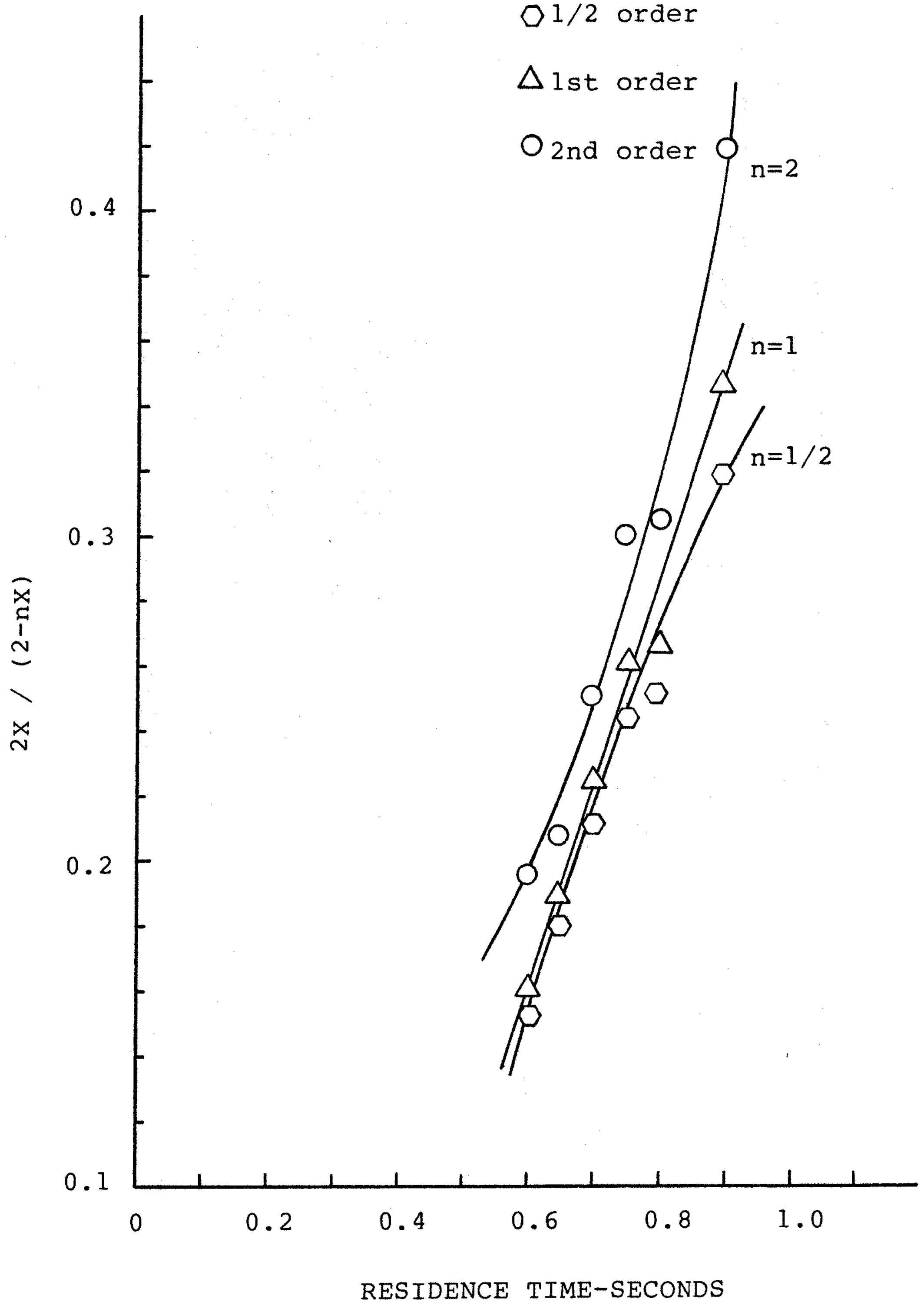


Figure 23.

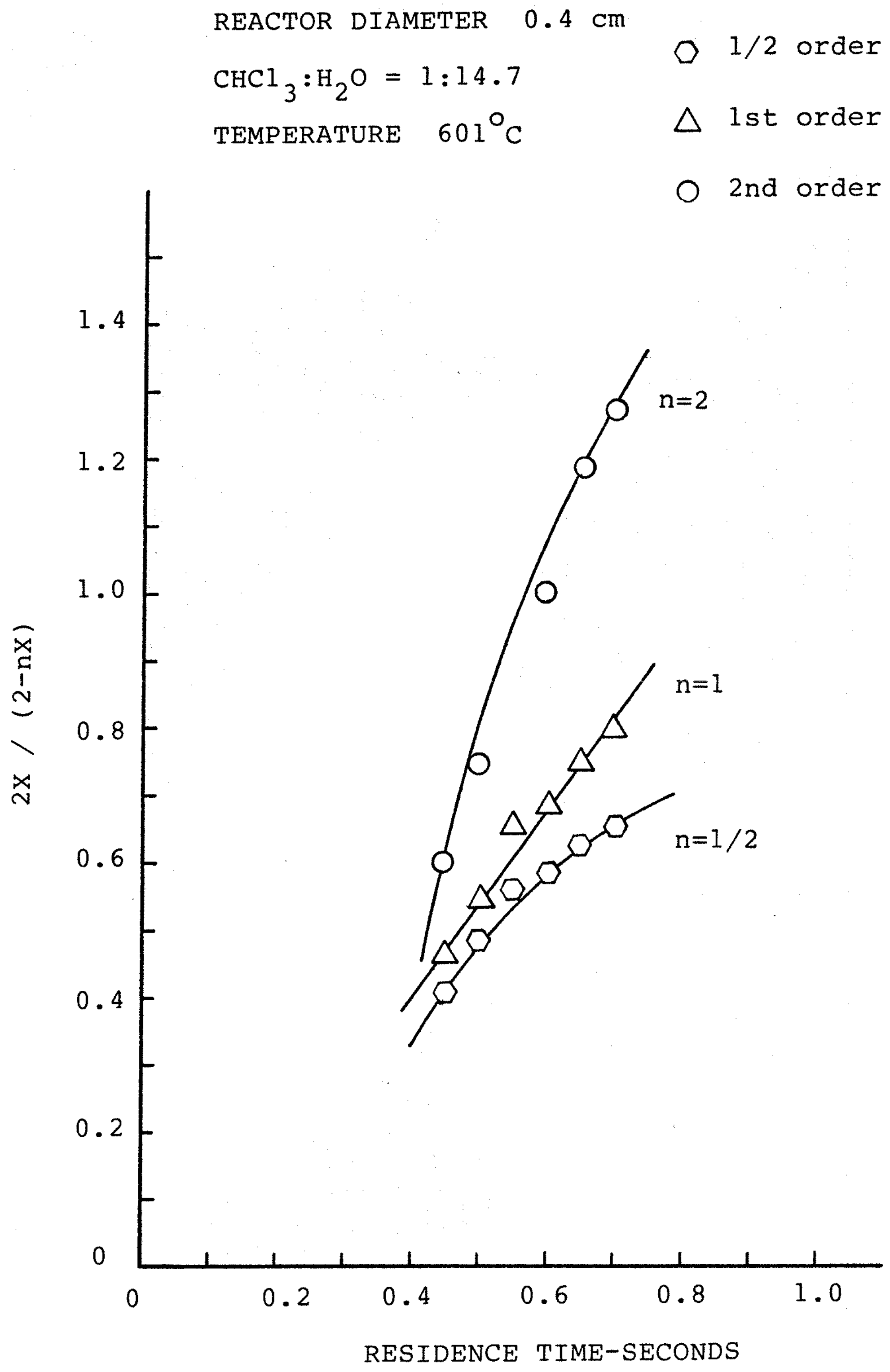

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 601°C
⬡ 1/2 order
△ 1st order
○ 2nd order
n=2
n=1
n=1/2
2X / (2-nX)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

Figure 24.

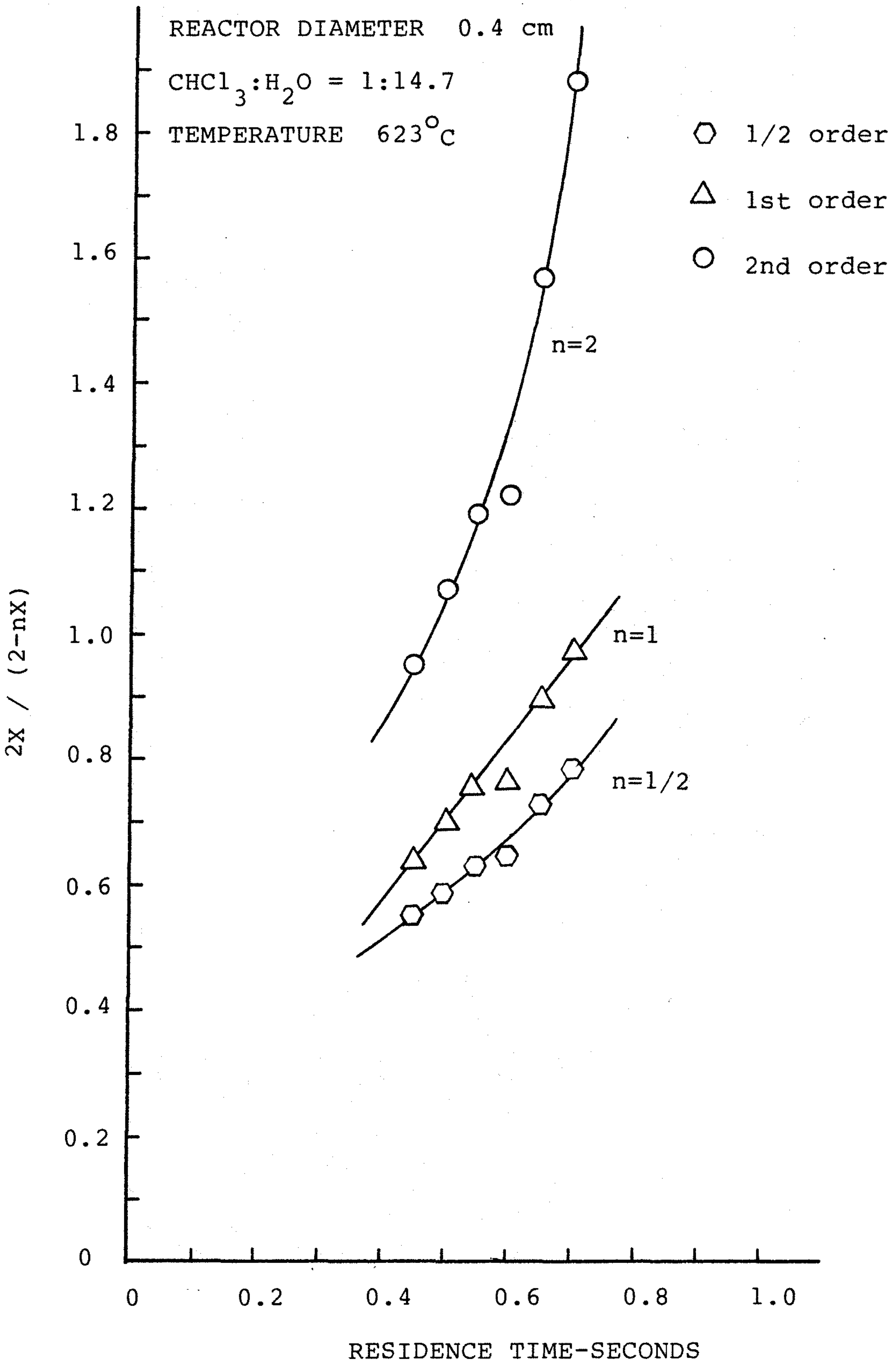

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
TEMPERATURE 623°C
⬡ 1/2 order
△ 1st order
○ 2nd order
n=2
n=1
n=1/2
2X / (2-nX)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

Figure 25.

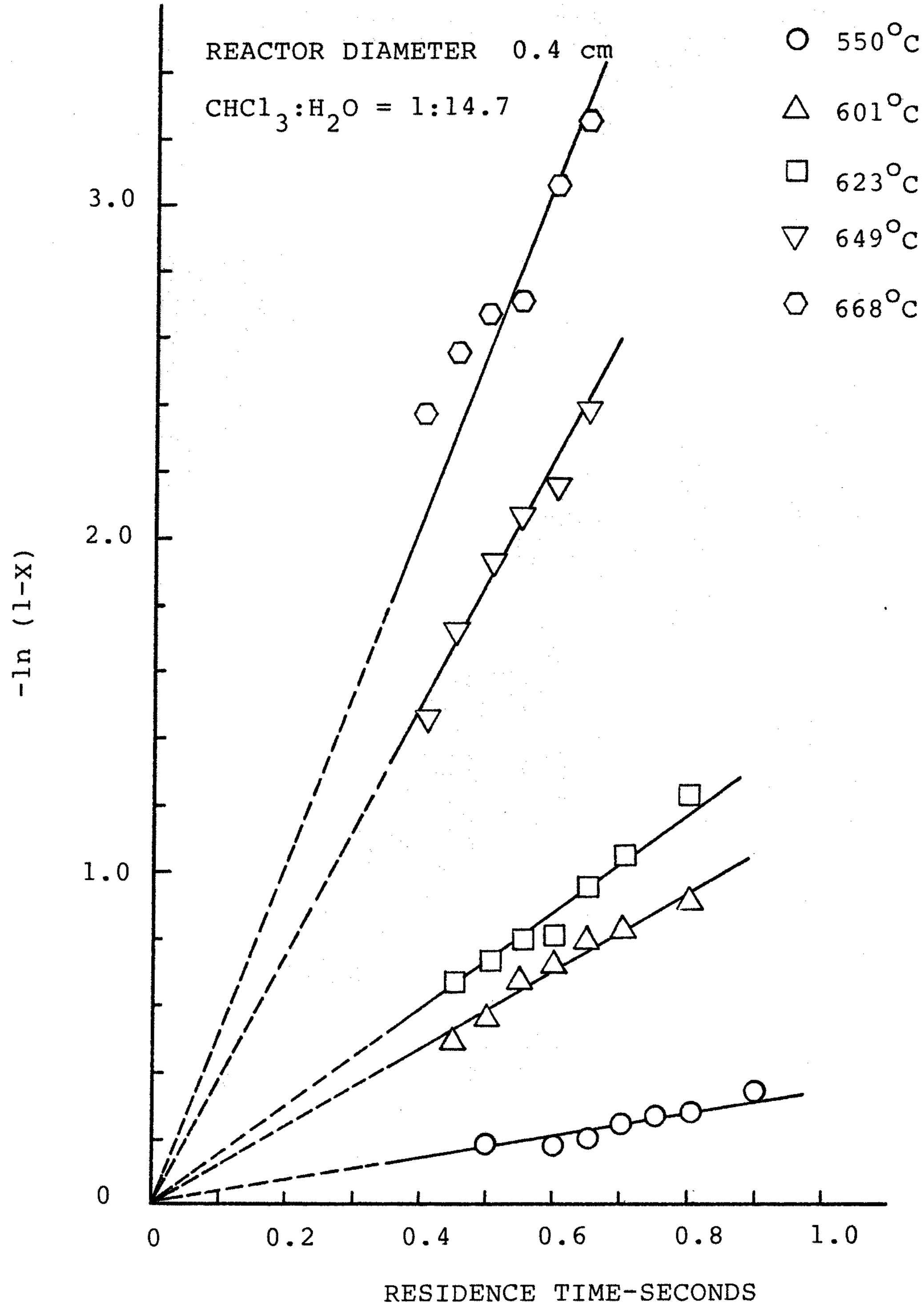
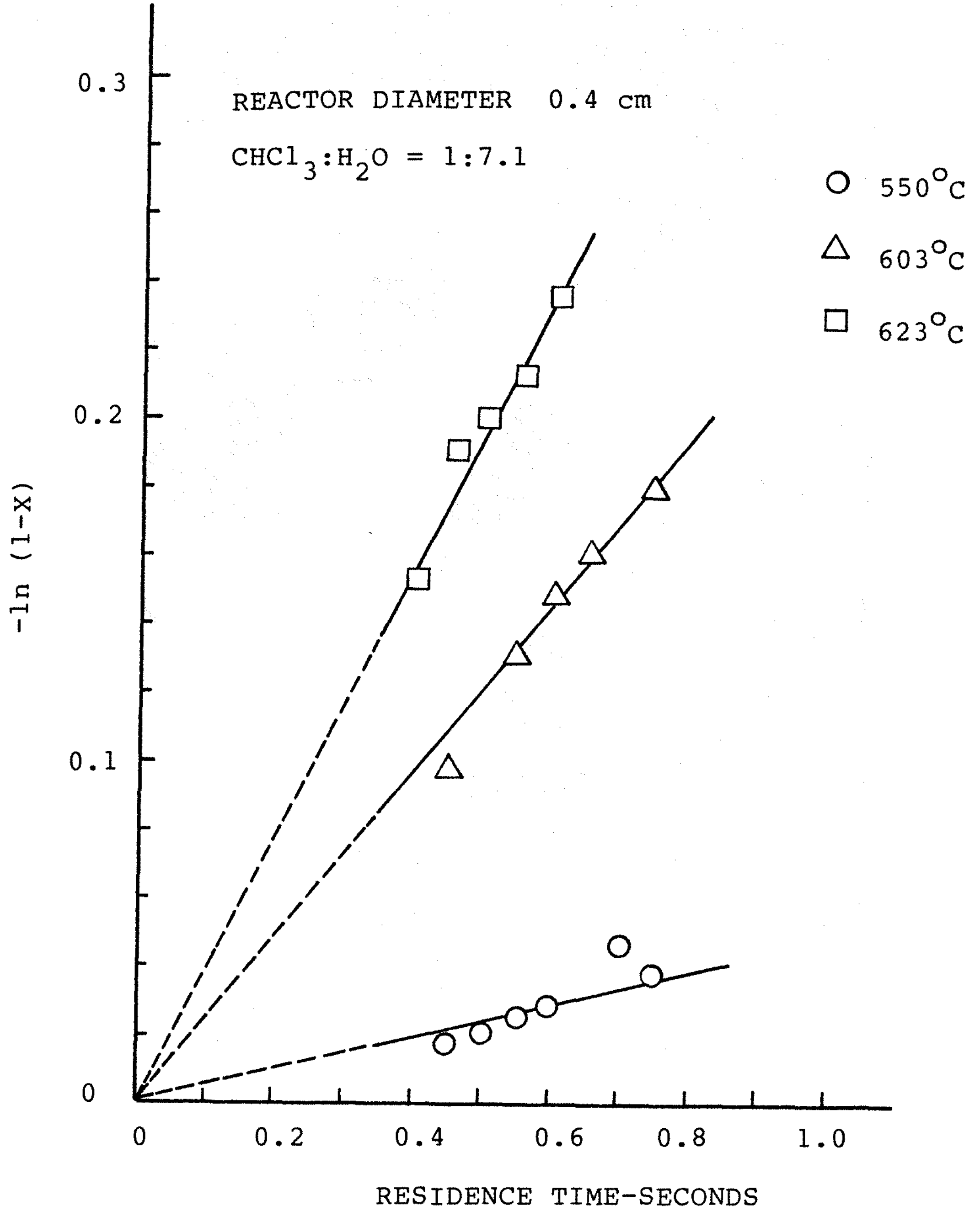

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
○ 550°C
△ 601°C
□ 623°C
▽ 649°C
⬡ 668°C
3.0
2.0
1.0
0
-ln (1-X)
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

Figure 26.


REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:7.1
○ 550°C
△ 603°C
□ 623°C
-ln (1-X)
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
RESIDENCE TIME-SECONDS

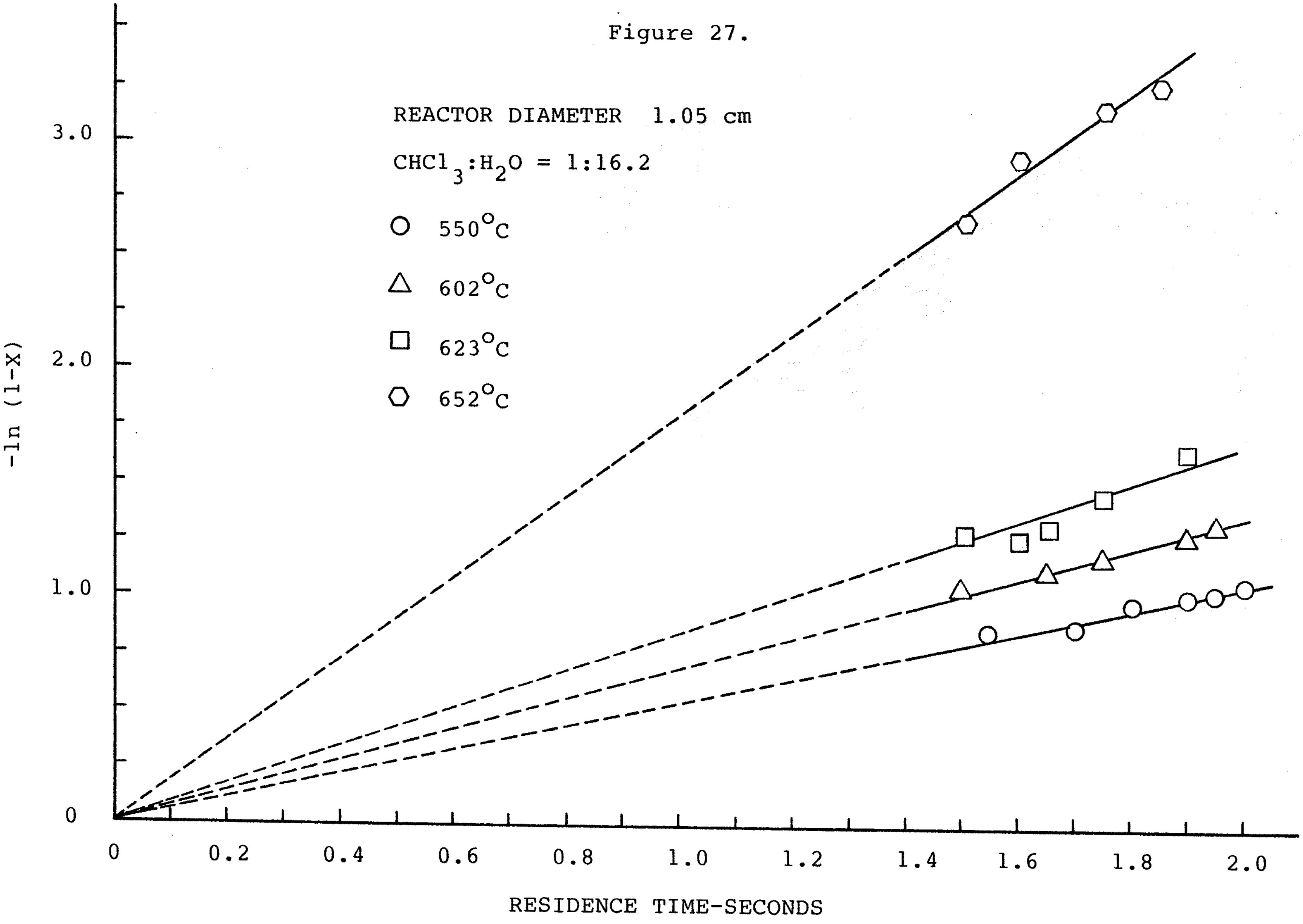


Figure 27.

REACTOR DIAMETER 1.05 cm
$CHCl_3:H_2O = 1:16.2$
○ 550°C
△ 602°C
□ 623°C
⬡ 652°C
-ln (1-X)
3.0
2.0
1.0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
RESIDENCE TIME-SECONDS

Figure 28.

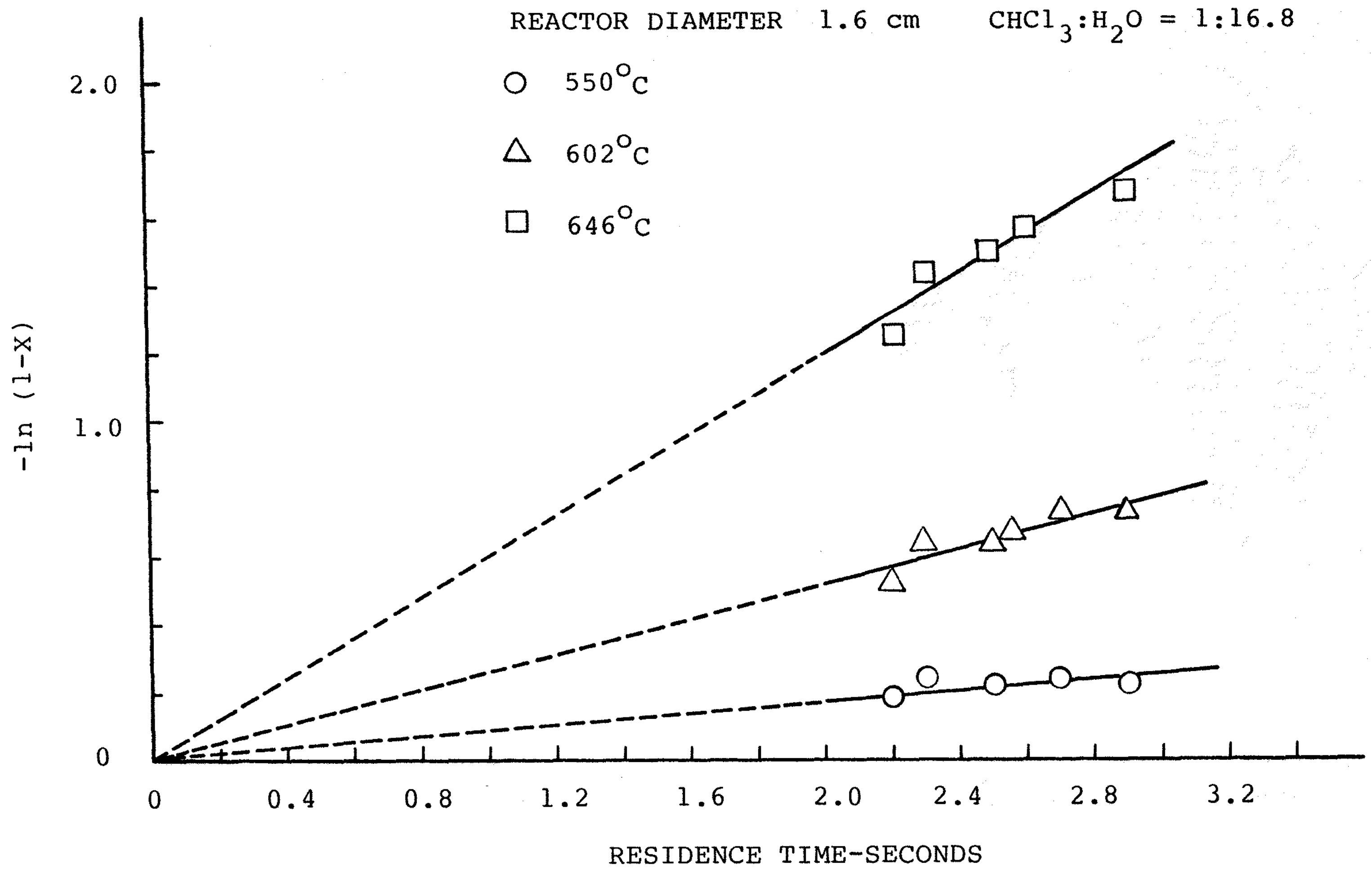

REACTOR DIAMETER 1.6 cm
$CHCl_3:H_2O = 1:16.8$
○ 550°C
△ 602°C
□ 646°C
-ln (1-X)
2.0
1.0
0
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
RESIDENCE TIME-SECONDS

Figure 29.

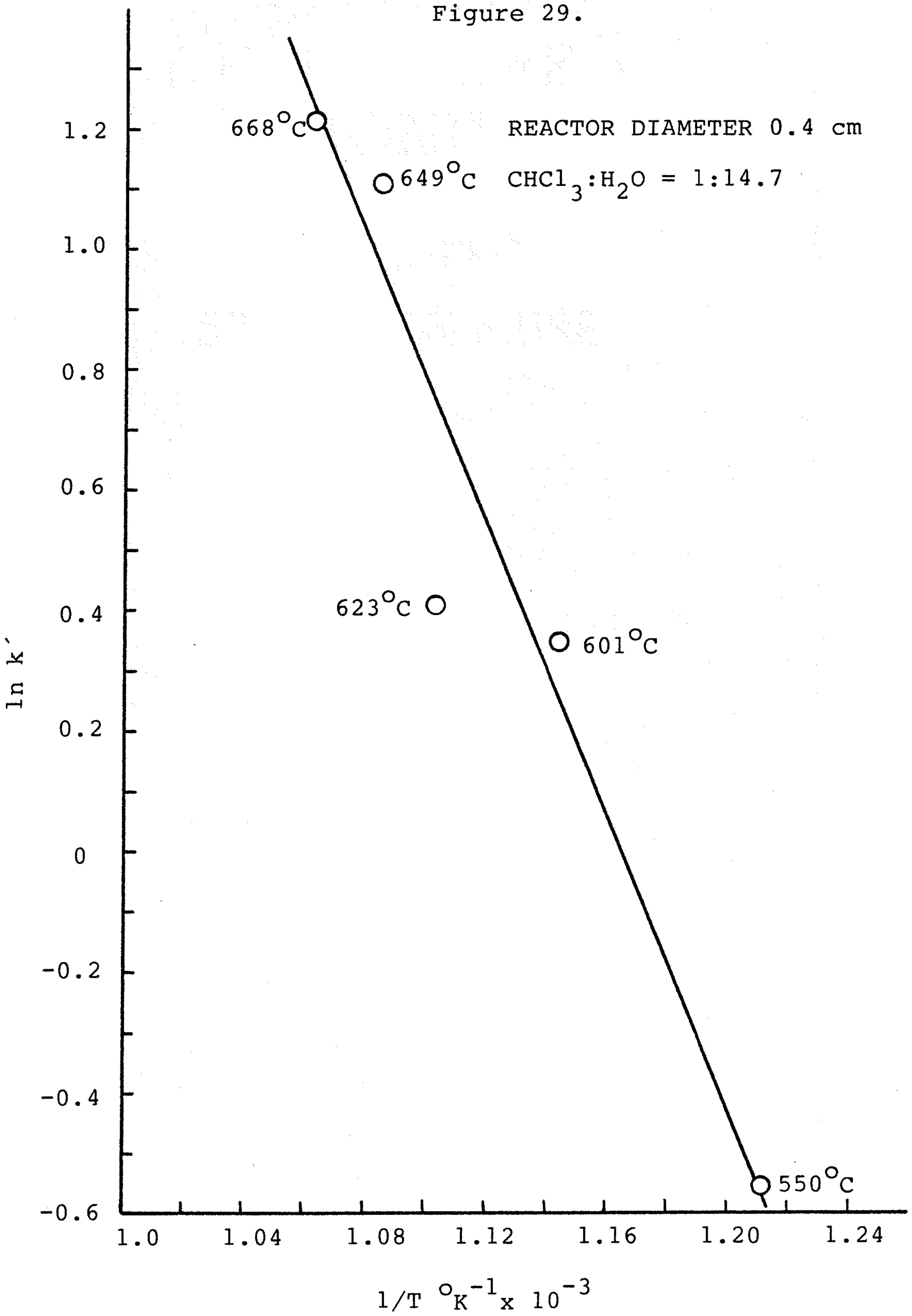

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:14.7
668°C
649°C
623°C
601°C
550°C
ln k´
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
1.0
1.04
1.08
1.12
1.16
1.20
1.24
1/T $°K^{-1}$ x 10^{-3}

Figure 30.

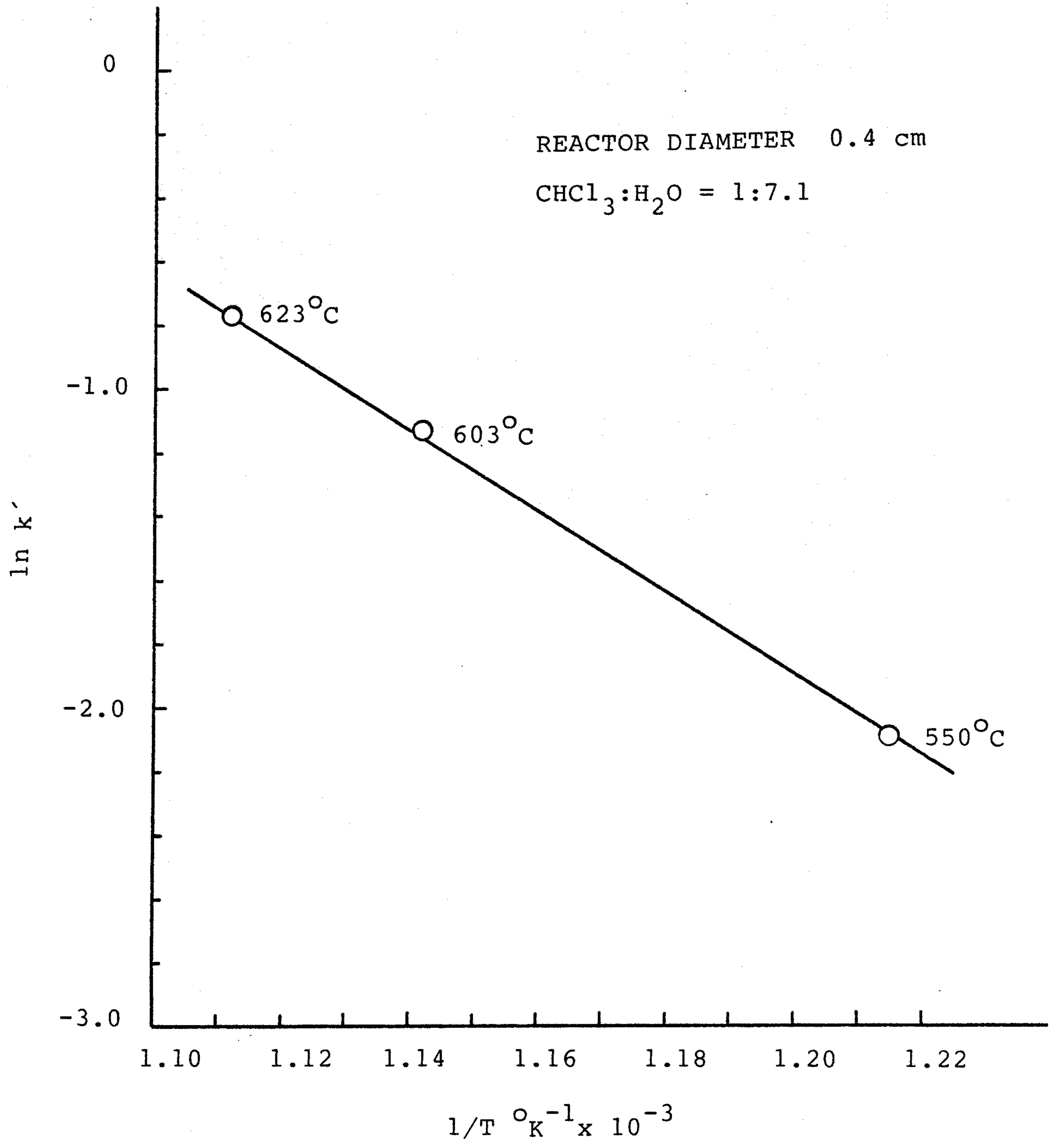
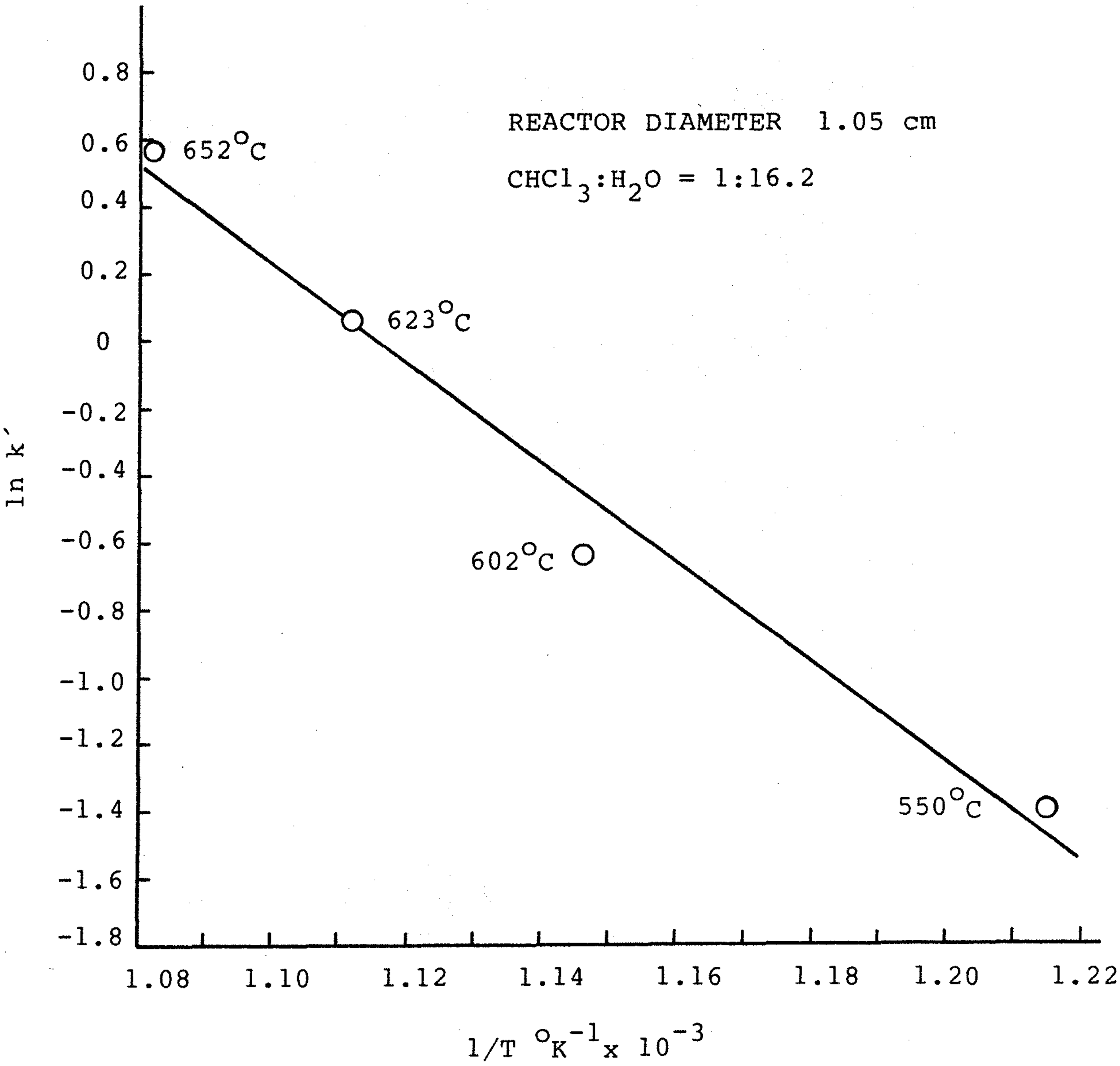
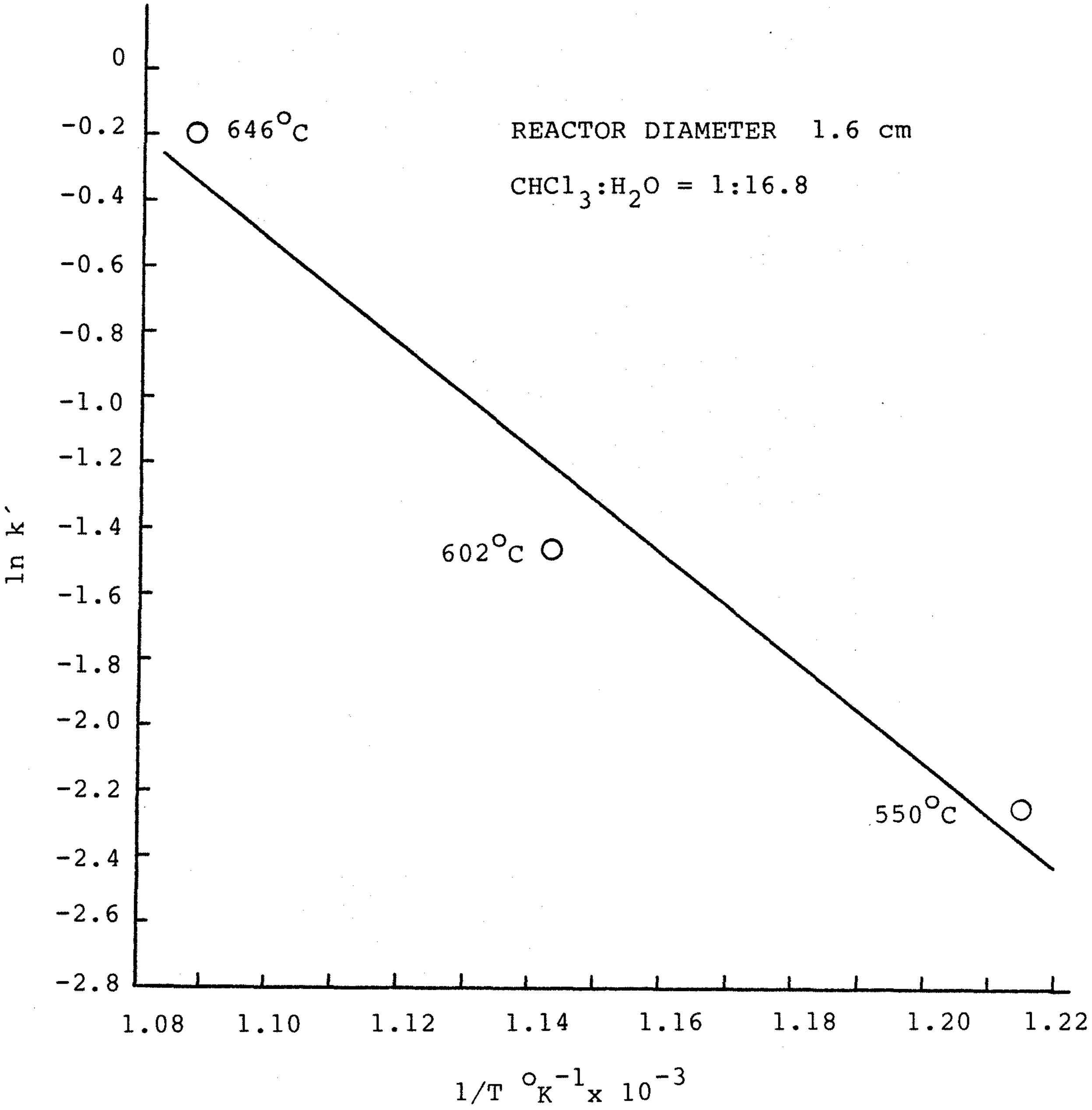

REACTOR DIAMETER 0.4 cm
$CHCl_3:H_2O$ = 1:7.1
623°C
603°C
550°C
0
-1.0
-2.0
-3.0
ln k´
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1/T °K^{-1}x 10^{-3}

Figure 31.



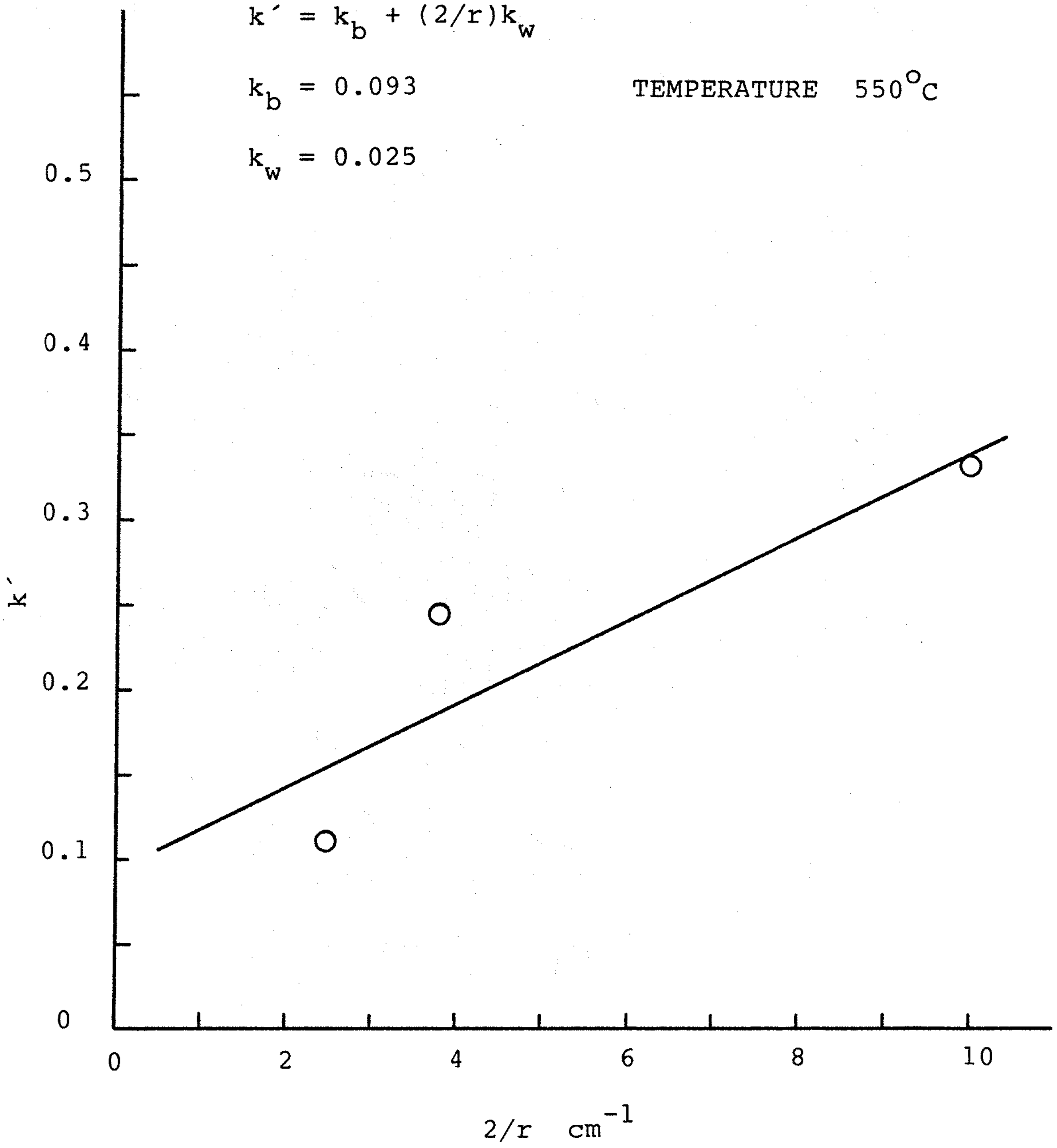
REACTOR DIAMETER 1.05 cm
$CHCl_3:H_2O$ = 1:16.2
652°C
623°C
602°C
550°C
ln k´
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1/T °K^{-1}x 10^{-3}

Figure 32.



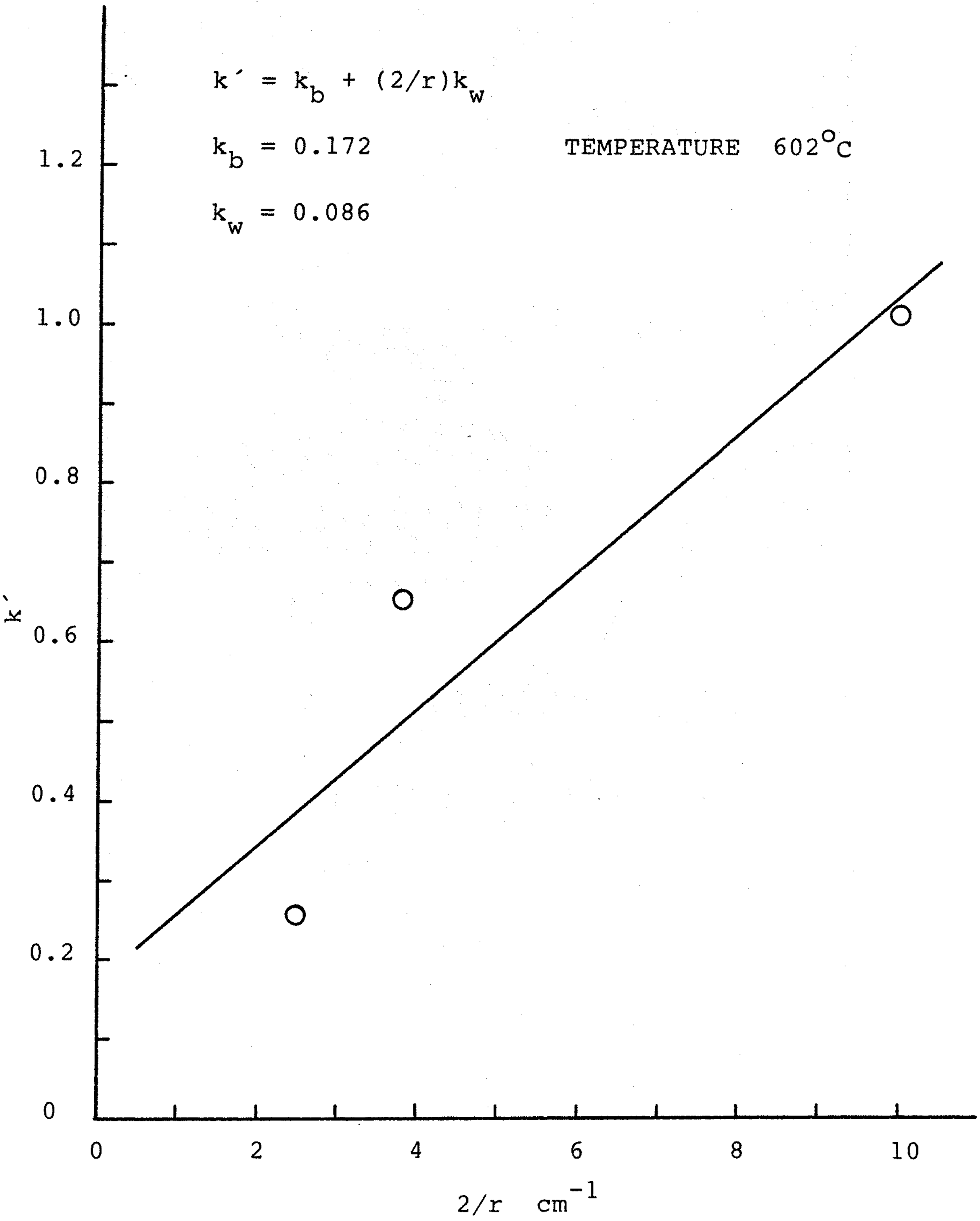
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
ln k´
646°C
602°C
550°C
REACTOR DIAMETER 1.6 cm
CHCl$_3$:H$_2$O = 1:16.8
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1/T °K^{-1}x 10^{-3}

Figure 33.



$k' = k_b + (2/r)k_w$
$k_b = 0.093$
$k_w = 0.025$
TEMPERATURE 550°C
0.5
0.4
0.3
0.2
0.1
0
k´
0
2
4
6
8
10
$2/r \ \ cm^{-1}$

Figure 34



$k' = k_b + (2/r)k_w$
$k_b = 0.172$
$k_w = 0.086$
TEMPERATURE 602°C
k´
0
0.2
0.4
0.6
0.8
1.0
1.2
0
2
4
6
8
10
2/r cm^{-1}

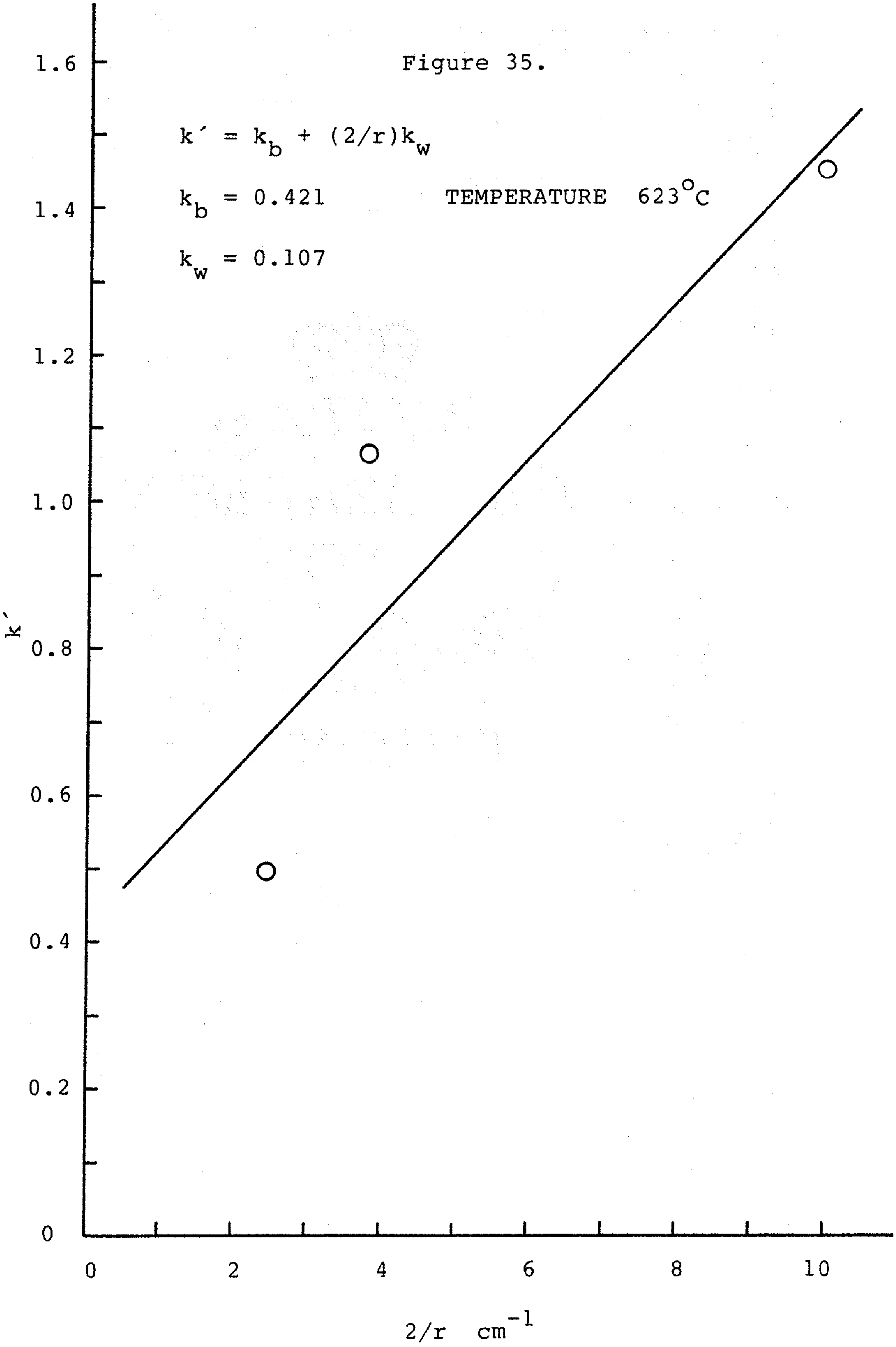


Figure 35.

$k' = k_b + (2/r)k_w$
$k_b = 0.421$
$k_w = 0.107$
TEMPERATURE 623°C
k'
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
$2/r$ cm^{-1}

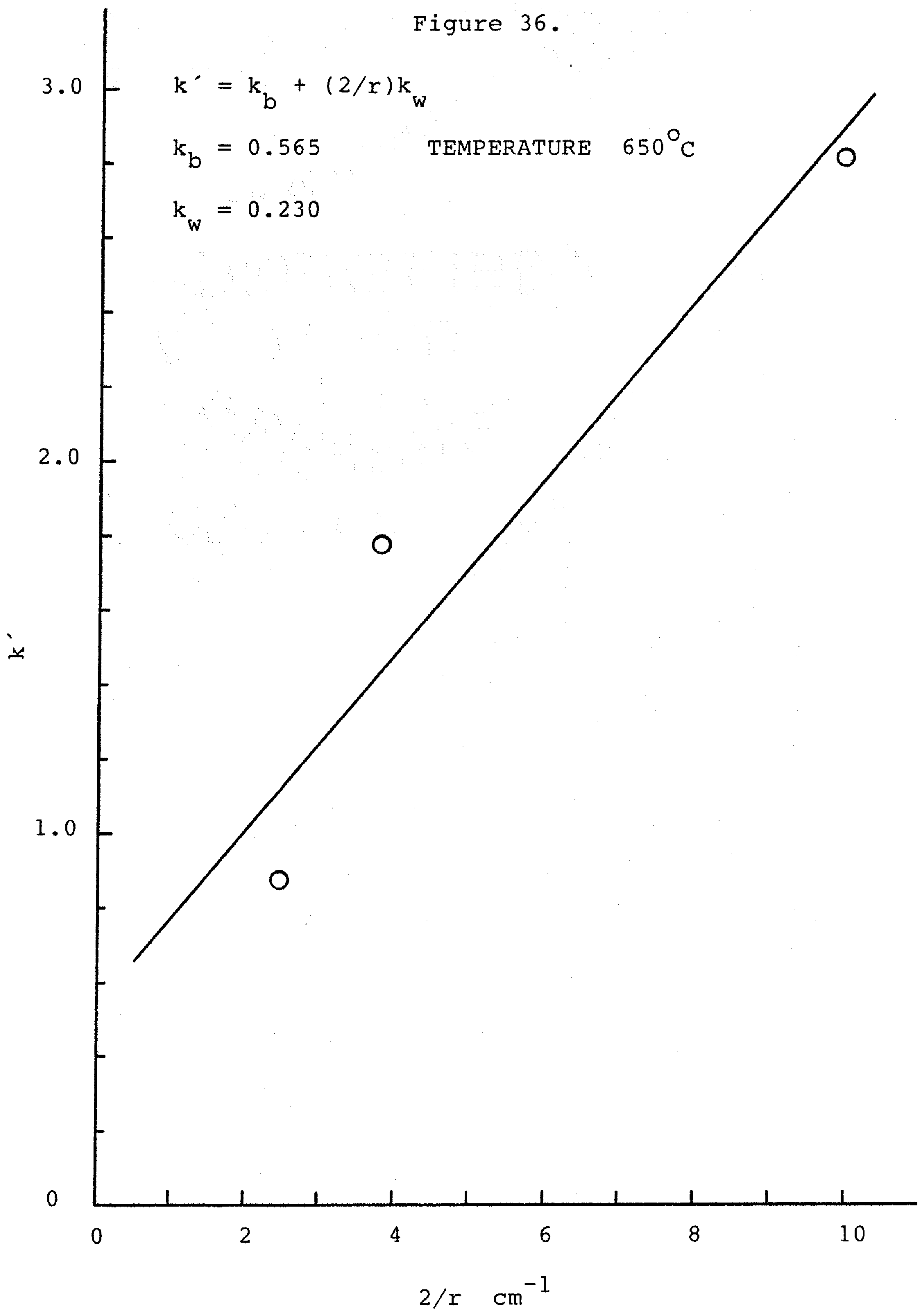


Figure 36.

$k' = k_b + (2/r)k_w$
$k_b = 0.565$
TEMPERATURE 650°C
$k_w = 0.230$
3.0
2.0
1.0
0
k′
0
2
4
6
8
10
2/r cm^{-1}

Figure 37.

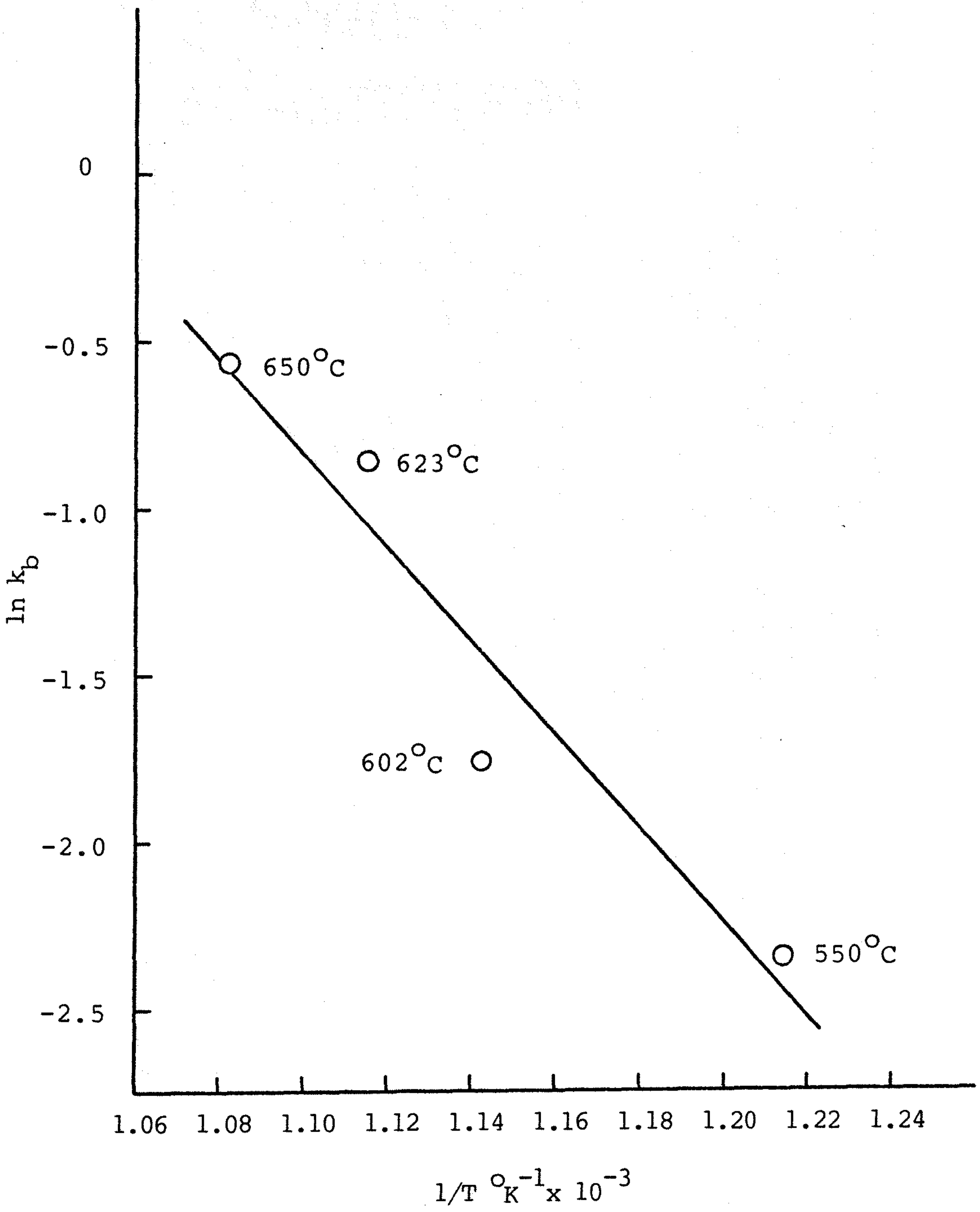
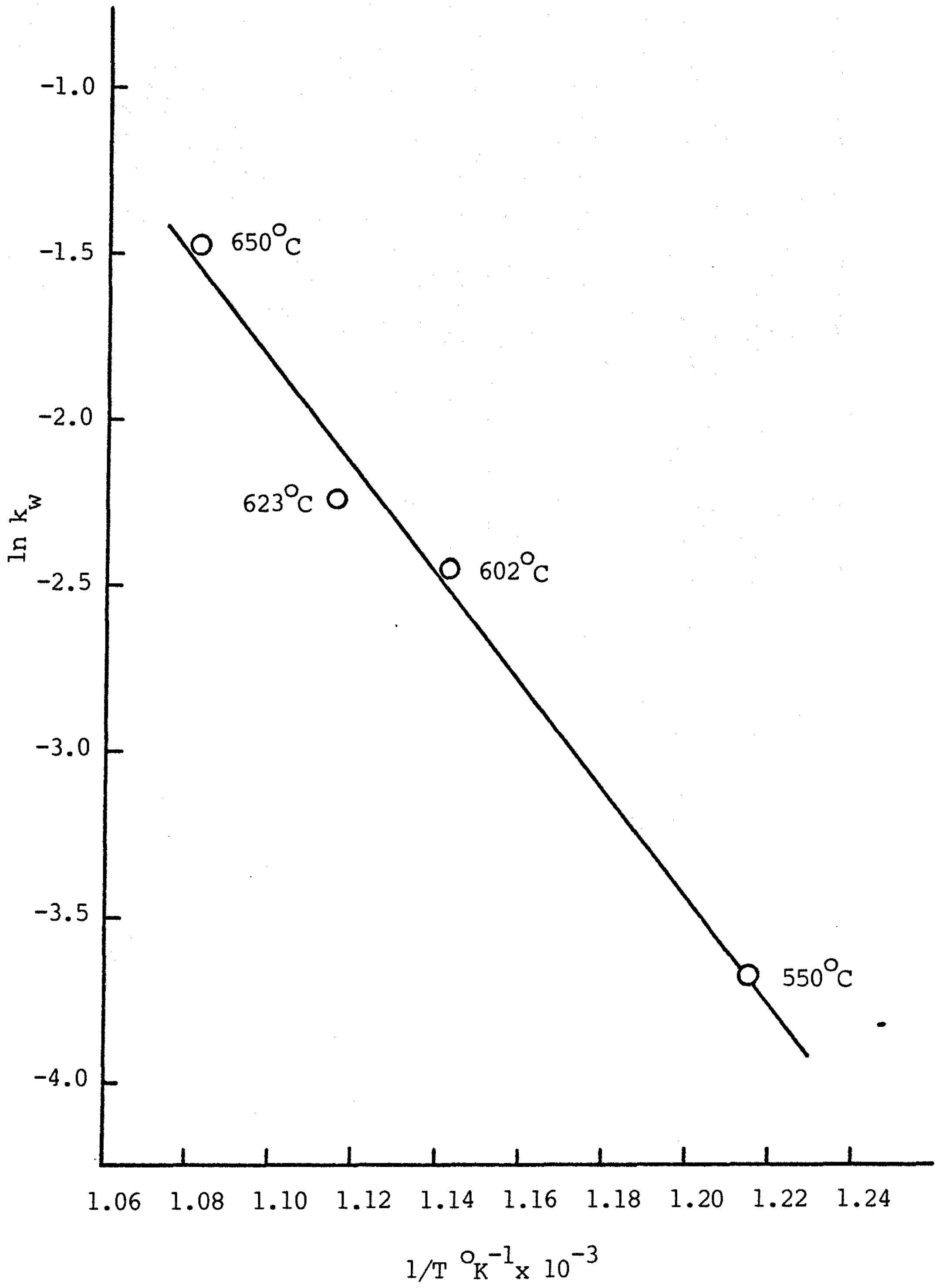

0
-0.5
-1.0
-1.5
-2.0
-2.5
ln k_b
650°C
623°C
602°C
550°C
1.06
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1.24
1/T °K^{-1} x 10^{-3}

Figure 38.



-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
ln k_w
650°C
623°C
602°C
550°C
1.06
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1.24
1/T °K^{-1} x 10^{-3}

V. CONCLUSION

The reactions of chloroform with water vapor were studied in a tubular reactor at atmospheric pressure, and in the temperature range of 550 to 1050 ^{o}C. The experiments performed to date prove the detoxification applicability of reacting chlorinated hydrocarbons with water vapor in a tubular reactor at constant temperature. Through such a scheme, detoxification occurs by removal of Cl as thermodynamically favorable HCl plus formation of either carbon oxides or hydrocarbons. The gas products were analyzed by on-line gas chromatograph with flame ionization detector (FID), and batch sample were also analyzed by both GC/Mass Spectrometer and thermal conductivity detector (TCD) GC.

The thermal reaction of $CHCl_3$ in the presence of H_2O yields significant quantities of HCl, CO_2, CO, H_2, and a range of $C_1 \sim C_2$ light hydrocarbons with small amounts of non-parent chlorocarbons (at the lower temperature levels), plus some solid graphitic carbon. The major products of this reaction, hydrogen chloride and tetrachloroethylene, in the temperature range 600 to 700 ^{o}C, are similar with those in thermal decomposition of chloroform in Semeluk et. al.(18), for the temperature range 450 to 525 ^{o}C. The more desirable and stable species, HCl and CO_2, are observed at higher temperatures which is in fair agreement with the study by Gaisinovich et. al. (13). Vinly chloride is observed as the most stable chlorocarbon product at the temperature range 600 to 850 ^{o}C. Complete destruction of all chlorocarbon products occured at temperature of 1000 ^{o}C and above. In comparison to the study on the reactions of chloroform with hydrogen(42), smaller amounts of solid graphitic carbon were found probably due to the presence of oxygen or hydroxide radicals which could react with carbon to form CO or CO_2 as observed. The calculated empirical rate constants as well as the reaction order, were determined from regression of data fitted to the integrated rate equations. The data are summarized in Table 3.

The reaction mechanisms for this study is postulated based on observed product distributions, heat of reactions, unimolecular reaction theory, reaction temperature conditions and limited references from related studies. It is hoped that the present research will make future studies on similar reactions and yet more fruitful.

APPENDIX I.

Thermodynamic Equilibria of Selected Reactions*

$$CCl_4 + 4\ H_2 \quad = \quad 4\ HCl + CH_4$$

T(k)	kp
288	3.19×10^{65}
800	6.10×10^{26}
1000	8.70×10^{21}

$$CCl_4 + 2H_2 \quad = \quad 4\ HCl + CO_2$$

T(k)	kp
288	3.77×10^{43}
800	7.56×10^{25}
1000	3.72×10^{23}

$$C_6Cl_6 + 15H_2 \quad = \quad 6\ CH_4 + 6\ HCl$$

T(k)	kp
288	$>10^{50}$
800	8.35×10^{50}
1000	2.5×10^{36}

$$C_6Cl_6 + 12H_2O \quad = \quad 6\ CO_2 + 6H_2O + 9H_2$$

T(k)	kp
288	7.08×10^{41}
800	1.04×10^{45}
1000	1.58×10^{46}

*Ref. (21)

APPENDIX II. SAMPLE CALCULATIONS

A. Calculation of Flow Velocity Through Reactor

Inside diameter of reactor tube = 1.05 cm
Cross-section area of reactor = 0.87 cm^2
Chloroform flowrate = 0.25 cm^3/sec,550°C
Water vapor flowrate = 18.34 cm^3/sec,550°C
Argon flowrate = 4.61 cm^3/sec,550°C
Total flowrate = 23.2 cm^3/sec,550°C
Flow velocity = 23.2/0.07
= 26.67 cm/sec,550°C

B. Calculation of Reagent Concentration Through Reactor

Chloroform flowrate = 0.25 cm^3/sec,550°C
Water vapor flowrate = 18.34 cm^3/sec,550°C
Argon flowrate = 4.61 cm^3/sec,550°C
Total flowrate = 23.2 cm^3/sec,550°C
Total pressure of flow system = 1.0 atm
Partial pressure of chloroform = 1.0x(0.25/23.2)
= 0.01 atm
Partial pressure of water vapor = 1.0x(18.34/23.2)
= 0.79 atm
Partial pressure of argon = 1.0x(4.61/23.2)
= 0.2 atm
Concentration of chloroform(550°C) = 0.01/(82.05x823)
= $1.48\text{x}10^{-7}$ g-mole/cm^3

Concentration of water vapor(550^oC)= 18.34/(82.05x823)

= 1.17×10^{-5} g-mole/cm^3

Concentration of argon(550^oC) = 0.2/(82.05x823)

= 2.96×10^{-6} g-mole/cm^3

C. Calculation of Conversion of Reagent (Chloroform)

Initial concentration of chloroform:

Integrator response (peak area) of chloroform from by-pass run (without reaction) at typical $CHCl_3/H_2O$ ratio and residence time................= C_{AO}

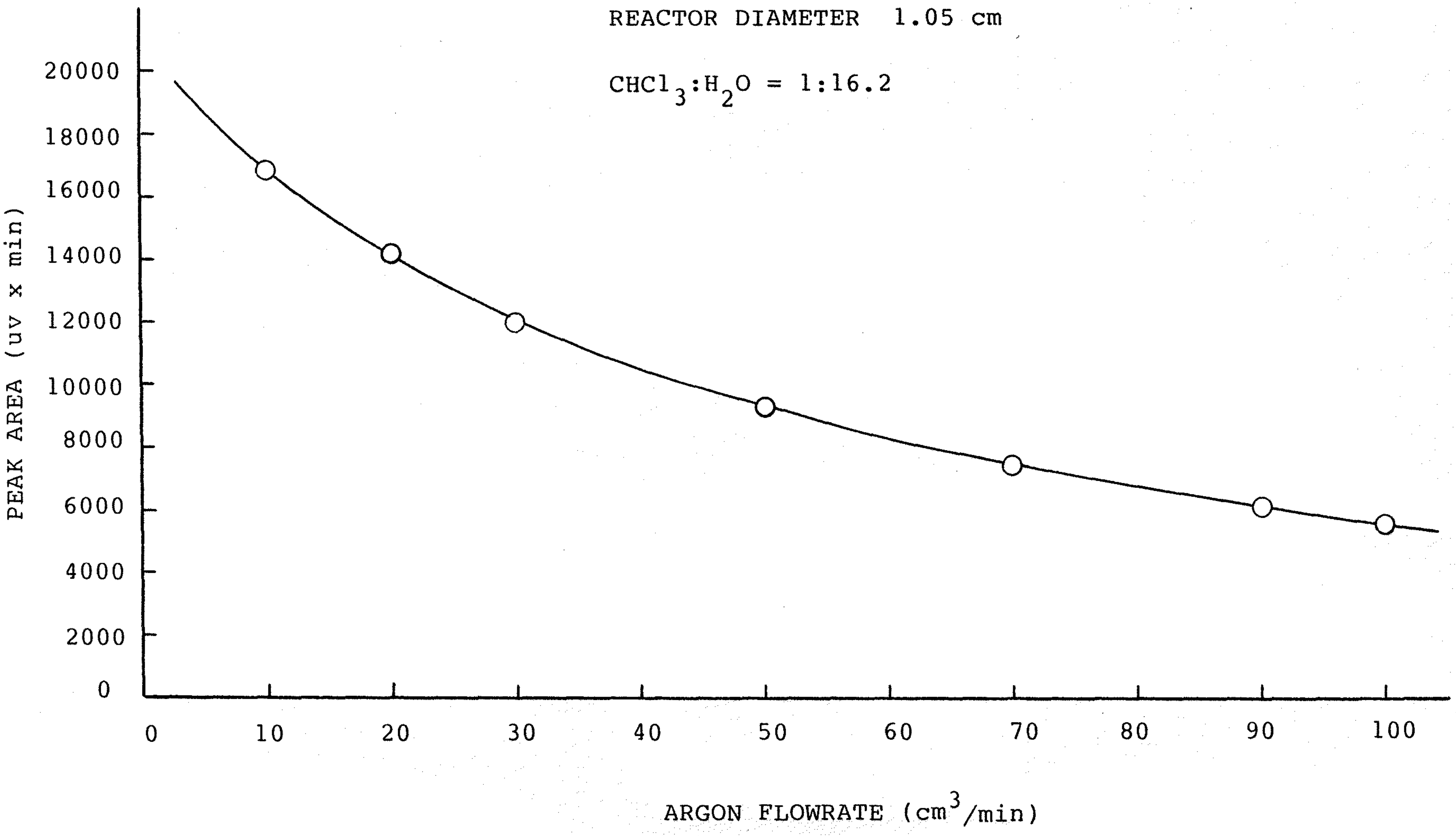
Concentration of chloroform at the point of concideration:

Integrator response (peak area) of chloroform (with reaction) at the same flow condition as by-pass run......................................= C_A

Conversion of chloroform....................= $1 - C_A/C_{AO}$

Since the initial concentration of chloroform changes with respect to residence time (argon flow), a chart (see Figure 39 as example) which showed argon flow rate with respect to integrator response (peak area) of chloroform, from by-pass run was made as a calibration at each ratio between chloroform and water for use in determining the initial concentration of chloroform and conversion.

Figure 39.


REACTOR DIAMETER 1.05 cm
$CHCl_3:H_2O = 1:16.2$
PEAK AREA (uv x min)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
60
70
80
90
100
ARGON FLOWRATE (cm^3/min)

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