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I hereby recommend that the thesis prepared under my supervision by LAWRENCE E. SWABB, JR.

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be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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A KINETIC STUDY OF THE CATALYTIC VAPOR PHASE ADDITION OF HYDROGEN CHLORIDE TO PROPYLENE

A dissertation submitted to the

Graduate School of Arts and Sciences

of the University of Cincinnati

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requirements for the degree of

DOCTOR OF PHILOSOPHY

1951

by

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Ch.E. University of Cincinnati 1948

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ABSTRACT

This thesis is a kinetic study of the vapor phase addition of hydrogen chloride to propylene using activated alumina as a catalyst. Preliminary work on this reaction showed first, that isopropyl chloride is the only gaseous product formed at temperatures of 80°C or less when this catalyst is used. Second, the catalyst activity decreases with time possibly due to the formation of non-volatile polymerized product on the surface. The rate of decreasing catalyst activity is dependent on the temperature and on the conversion.

From the results of the kinetic study it is shown that the addition reaction is not controlled either by the adsorption of hydrogen chloride or by the adsorption of propylene. The reaction may be controlled either by the desorption of isopropyl chloride or by the surface reaction between adsorbed molecules of hydrogen chloride and adsorbed molecules of propylene. The kinetic data are correlated by rate equations derived by two different methods based on the surface reaction as the controlling mechanism. The reaction constants in these equations are expressed as functions of process time and temperature.

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INTRODUCTION

CHAPTER I

In the chemical industry continuous processes are replacing the batch processes because of their greater capacity, better product control and lower operating expense. The heart of the continuous process is the reactor where the chemical change occurs. In order to intelligently design these reactors the chemical engineer must have in his possession kinetic data for the reaction expressed in some form of rate equation. To be reliable these equations should include all the variables likely to be encountered in operation of the large reactor.

Although classical kinetics is an old subject, the kinetics of catalytic flow systems is relatively new. It has been found that the data obtained from a static system did not apply to the reaction carried out in a flow system, principally because of the effect of diffusion of reactants and products to and from the catalyst mass. Only in 1943 was a general method developed for correlation of catalytic kinetic data obtained in flow systems (4).

The fact that a large number of the chemical industries use catalytic flow reactors indicates that a great number of kinetic studies have been made. Unfortunately, however, these studies which were usually conducted with a limited number of operating variables and the results

correlated empirically, have usually been considered as industrial secrets with the result that relatively few of them have been published. With the development of the general theory of Hougen and Watson (4) has come a slow trickle of catalytic kinetic studies conducted in the universities and thus available for publication. These studies, for the most part, have been limited to simple reactions. Thus, the literature on kinetic studies of catalytic reactions on flow systems, is meager and any attempt to correlate the results with respect to reactants or with respect to catalysts is not possible at this time.

The purpose of the work of this thesis was to study the kinetics of the formation of isopropyl chloride by the catalytic vapor phase addition of hydrogen chloride to propylene over activated alumina. The industrial importance of this work is probably negligible since more efficient catalysts (See Appendix Part VII) than activated alumina are no doubt available for this reaction. However, it is hoped that this work will initiate a program of kinetic studies of hydrogen chloride addition to other members of the olefin series over the same catalyst. Such a program would present an opportunity to compare the effect of structure of one of the reactants upon the kinetics of the reaction.

KINETIC THEORY OF HETEROGENEOUS CATALYTIC REACTIONS

CHAPTER II

By definition, a catalyst is a substance which influences the rate of a reaction but is not one of the original reactants or final products. The catalyst must participate in intermediate steps in such a manner as to facilitate the over-all course of the reaction. Although the catalyst may greatly affect the mechanism of a chemical change, it does not influence the over-all free energy change and thus the equilibrium concentrations. Solid catalysts are believed to function through the occurrence of intermediate reactions on their surfaces. The site of the chemical change is believed to be at points of high chemical activity called "active centers." The nature of these active centers and the conditions which must be fulfilled in order that a point on the surface may become an active center remains the subject of much speculation. It is possible that interatomic spacing of the solid structure, chemical constitutions and lattice structure are important variables affecting the activity and the selectivity of a catalyst. In general, it is desirable that the solid catalyst should have a large surface per unit mass or volume and that this surface should be readily accessible to the reactant mixture through interconnected pores and openings.

In order that reactants in the main fluid phase

may be converted catalytically to a product in the main fluid phase, it is necessary that the following processes occur.

1. The mass transfer of reactants from the gas phase the the surface of the catalyst particle.
2. The adsorption of the reactants on the active centers of the catalyst.
3. The chemical reaction between the adsorbed reactants to form adsorbed products.
4. The desorption of products.
5. The mass transfer of the product from the surface of the catalyst to the gas phase.

The rate at which each of these steps occurs influences the distribution of concentrations in the system and plays a part in determining the over-all rate. Their relative importance in determining the over-all rate varies widely according to the catalyst and according to the conditions under which the reaction is carried out.

Steps 1 and 5 are important only for very rapid reactions or where flow conditions are unfavorable. Steps 2, 3 and 4 are chemical phenomena and are generally highly sensitive to temperature. For a heterogeneous system operating under steady state conditions the rates of each of the five steps is necessarily the same. However, to simplify the interpretation of experimental data it is desirable to minimize the resistance offered by the physical steps of mass transfer and deal only with the chemical aspects of the reaction.

Mass Transfer

The general rate of a catalytic reaction in a flow system based upon unit mass of catalyst is given by the relationship

$$r_A dW = F dx_A \qquad (1)$$

where

r_A = moles of reactant A converted per (unit time) (unit mass of catalyst)

F = flow rate of feed, moles per unit time

W = mass of catalyst

x_A = moles of reactant A converted per mole of feed.

Values of the reaction rate r should be correlated against the conditions prevailing at the surface of the catalyst where the catalytic reaction actually takes place. From equations for mass transfer the film gradients for partial pressures of each component gas can be evaluated. However this correction is difficult and uncertain. In experimental work it is desirable, if possible, to render these gradients insignificant by operating at high mass velocities. A method of relating the film gradients to the variables of the system is given by Yang and Hougen (9) from which the following is taken.

Consider the general equation for the rate of mass transfer.

$$r = k_G a_m \Delta P \qquad (2)$$

where $\Delta p = p_A - p_{Ai}$

Experimental data on mass transfer are related to k_G by the relationship (1,2)

$$j_D = \left(\frac{k_G M_m p_f}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3} \qquad (3)$$

Experimental data on values of j_D were obtained for mass transfer in a granular bed by Gamson, Thodos, Wilke and Hougen (3,7) and related to a modified Reynolds number $\frac{\sqrt{a_p}\, G}{\mu}$ as follows:

$$j_D = \alpha\left(\frac{\sqrt{a_p}\, G}{\mu}\right)^{-n} \qquad (4)$$

By a combination of Equations (2), (3), and (4) there results the expression

$$\frac{\Delta p_A}{p_A} = \frac{1}{\alpha}\left(\frac{\sqrt{a_p}\, r M_m p_f}{p_A \mu a_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}\left(\frac{\sqrt{a_p}\, G}{\mu}\right)^{n-1} \qquad (5)$$

From this equation the magnitude of the film gradient Δp_A at the catalyst surface can be estimated once the reaction rate is known. By proper selection of the range of mass velocity the film gradients can be reduced to a negligible value, and the concentrations at the catalyst surface can be assumed to be the same as in the fluid stream.

General Surface Rate Equation

When a reaction is catalyzed by a solid it is presumed that the actual combination of reactants occurs on the surface of the solid. It is further assumed that the reaction

occurs between adsorbed molecules on adjacently situated active centers, and that the reaction proceeds at rates proportional to the concentrations of adjacently adsorbed reactants. With these assumptions, generalized kinetic equations have been developed by Hougen and Watson (4) upon whose work the following discussion is based.

Consider the bimolecular-monomolecular reaction

$$A + B \rightleftharpoons R$$

The rate of the reaction can be expressed by the equation

$$r = kc_{AB} - k'c_{R1} \qquad (6)$$

where c_{AB} = surface concentration of adjacently adsorbed molecules of A and B

c_{R1} = surface concentration of molecules of R adjacent to vacant active centers.

For the development of the rate equations, it may be assumed that a unit mass of catalyst offers L active centers, each of equal activity, upon which adsorption may occur. It may further be assumed that these centers are arranged on the surface in a regular geometric pattern such that each active center is surrounded by s equidistant adjacent centers. If θ_1 is the fraction of the total centers which is vacant, then an average adsorbed molecule of R has adjacent to it $s\theta_1$ vacant centers. Similarly, $s\theta_B$ molecules of B are adjacent to adsorbed A molecule, where θ_B is the fraction of total

centers which is occupied by adsorbed B molecules. The total concentration of adjacently adsorbed molecules of A and B is then the product of the concentration of centers occupied by A and the average number of adjacent sites occupied by B.

$$c_{AB} = c_A \, s\theta_B \tag{7}$$

Likewise, the total concentration of adsorbed molecules of R and adjacent vacant center is

$$c_{Rl} = c_R \, s\theta_l \tag{8}$$

Since θ_B equals $\frac{c_B}{L}$ and θ_l equals $\frac{c_l}{L}$,

$$c_{AB} = \frac{s}{L} c_A c_B \tag{9}$$

$$c_{Rl} = \frac{s}{L} c_R c_l \tag{10}$$

Substituting these expressions into Equation (6), the rate equation for the surface reaction becomes

$$r = \frac{s}{L} (kc_A c_B - k' c_R c_l) \tag{11}$$

Under steady state conditions the rate of adsorption of the reactants and the rate of desorption of products must equal the net overall rate of reaction.

$$r_{overall} = r_{adsorption} = r_{surface\ reaction} = r_{desorption} \tag{12}$$

Since the type of adsorption which occurs with catalysis is apparently chemical in nature involving the reactant in the

gas phase and an active center, the rate of adsorption of A can be expressed by

$$r = k_A a_A c_1 - k'_A c_A \tag{13}$$

$$r = k'_A (K_A a_A c_1 - c_A)$$

from which the concentration of A on the surface can be obtained.

$$c_A = K_A a_A c_1 - \frac{r}{k_A'} \tag{14}$$

where a_A = fluid phase activity of reactant A

K_A = adsorption equilibrium constant.

Similar expressions for the other reactant and product concentrations can be obtained, and substituted into Equation (11).

$$r = \frac{s}{L}\left[k(K_A a_A c_1 - \frac{r}{k_A'})(K_B a_B c_1 - \frac{r}{k_B'}) - k'(K_R a_R c_1 + \frac{r}{k_R'})c_1\right] \tag{15}$$

The concentrations of vacant centers also may be expressed in terms of fluid phase activities at the interface.

$$c_1 = L - (c_A + c_B + c_R)$$

$$c_1 = L - c_1(K_A a_A + K_B a_B + K_R a_R) + r(\frac{1}{k_A'} + \frac{1}{k_B'} - \frac{1}{k_R'})$$

$$c_1 = \frac{L + r(\frac{1}{k_A'} + \frac{1}{k_B'} - \frac{1}{k_R'})}{(1 + K_A a_A + K_B a_B + K_R a_R)} \tag{16}$$

Combining Equations (15) and (16) yields a complete expression for the rate of reaction in terms only of activities in the fluid and the constants of the system. However, this complete equation involving the rates of all adsorption steps as well as the rate of the surface reaction is so cumbersome as to be

of little value and simplifying assumptions must be made in order to make it usable.

Surface Reaction Controlling

In order to simplify the general rate equation the assumption is made that the overall rate is controlled by one slow step, all other steps being relatively fast. From the standpoint of theoretical kinetics this assumption is not acceptable, but it has served as a satisfactory basis for practical purposes.

Consider the net over-all rate as expressed by the steps of adsorption, surface reaction, and desorption for the reaction $A + B \rightleftharpoons R$.

$$r = k_A a_A c_1 - k_A' c_A = k_B a_B c_1 - k_B' c_B = k c_{AB} - k' c_{R1} = k_R' c_R - k_R a_R c_1 \quad (17)$$

If it is assumed that the surface reaction controls the over-all rate, i.e., it is the slow step whereas the other steps are fast, the magnitude of the terms $k_A a_A c_1$ and $k'_A c_A$ may be assumed to be large when compared to the value of the rate r. In this basis little error is introduced by equating the terms

$$k_A a_A c_1 = k'_A c_A \quad (18)$$

Similarly, for the other adsorption steps

$$k_B a_B c_1 = k'_B c_B$$

$$k_R a_R c_1 = k'_R c_R$$

This assumption implies that the reaction velocity constants for the adsorption steps are very large. Therefore in the general surface rate equations (15) and (16) the terms involving the reciprocals of these constants can be neglected and the equations become

$$r = \frac{s}{L}\left[k(K_A a_A c_1)(K_B a_B c_1) - k'(K_R a_R c_1)c_1\right] \qquad (19)$$

$$c_1 = \frac{L}{1 + K_A a_A + K_B a_B + K_R a_R} \qquad (20)$$

Substituting for c_1, the final rate equation for the case where the surface reaction is the slow step becomes

$$r = \frac{k\ s\ L\ K_A K_B}{(1 + K_A a_A + K_B a_B + K_R a_R)^2}\left(a_A a_B - \frac{a_R}{K}\right) \qquad (21)$$

where K is the overall equilibrium constant for the reaction.

Adsorption of A Controlling

If the adsorption of reactant A is the rate controlling step, Equation (18) may be assumed to hold for the other adsorption steps. Similarly, the magnitudes of the quantities kc_{AB} and $k'c_{R1}$ for the surface reaction may be assumed very large when compared to the magnitude of r so that little error is introduced by equating the quantities

$$kc_{AB} = k'c_{R1} \qquad (22)$$

As developed previously

$$c_{AB} = \frac{s}{L} c_A c_B \qquad (23)$$

$$c_{R1} = \frac{s}{L} c_R c_1$$

so that

$$kc_A c_B = k' c_R c_1$$

$$c_A = \frac{k'}{k} \frac{c_R c_1}{c_B} = \frac{c_R c_1}{c_B K} \qquad (24)$$

where K is the equilibrium constant for the surface reaction.

For the other reactant and the product the following expressions can be obtained from Equation (18)

$$c_B = K_B a_B c_1$$

$$c_R = K_R a_R c_1 \qquad (25)$$

where K_A and K_B are adsorption equilibrium constants.

The concentration of adsorbed A can now be expressed in terms of the activities of B and R and the concentration of vacant centers by combining Equations (24) and (25)

$$c_A = \frac{K_R a_R c_1^2}{K_B K a_B c_1} = \frac{a_R c_1}{a_B} \frac{K_A}{K} \qquad (26)$$

The concentration of vacant active centers can also be expressed in terms of the activities of B and R.

$$c_1 = L - (c_A + c_B + c_R)$$

$$c_1 = L - \left(\frac{a_R c_1}{a_B} \frac{K_A}{K} + K_B a_B c_1 + K_R a_R c_1\right)$$

$$c_1 = \frac{L}{1 + \frac{a_R}{a_B} \frac{K_A}{K} + a_B K_B + a_R K_R} \qquad (27)$$

The absorption rate equation from Equation (17) is

$$r = k_A a_A c_1 - k_A' c_A \qquad (28)$$

and when the values of c_A and c_1 are substituted, and the equation rearranged, the final rate equation that applies when the adsorption of A controls becomes

$$r = \frac{L\, k_A}{\left(1 + \frac{a_R}{a_B}\frac{K_A}{K} + a_B K_B + a_R K_R\right)}\left(a_A - \frac{a_R}{a_B K}\right) \qquad (29)$$

Desorption of R Controlling

By an analogous procedure the rate equation for the case where the desorption of R is controlling can be developed.

$$r = \frac{k_R\, L\, K}{1 + a_A K_A + a_B K_B + a_A a_B K_R K}\left(a_A a_B - \frac{a_R}{K}\right) \qquad (30)$$

Alternate Approach to Surface Reaction Kinetics

Recently an alternate method of developing rate equations for the reaction on the surface of a catalyst was developed by Wynkoop and Wilhelm (8). This method involves the assumption of the forms of adsorption isotherms for reactants and products on the catalyst under consideration. Rate equations assuming the surface reaction controls can then be developed with the surface concentrations in accord with the stated adsorption equilibria. The method is the same in principle as the method previously discussed except for the form of the adsorption equilibrium equation. For the simplified case for the irreversible reaction A + B → C, where the

fraction of surface covered by the reactants can be expressed by the Langmuir type isotherms,

$$\theta_A = b_A y_A \pi$$

$$\theta_B = \frac{b_B y_B \pi}{1 + b_B y_B \pi} \qquad (31)$$

where θ represents the fraction of surface covered, Wynkoop and Wilhelm developed an equation that could be integrated over a flow reactor. They found that the kinetic data for the hydrogenation of ethylene over a reduced copper catalyst fit this equation quite well.

This method of approach, although theoretically sound, is difficult to apply to most reactions. For the alternate cases where both isotherms are of the type of θ_B and when the reaction is reversible, the differential equation becomes so complex that it cannot be integrated. Evaluation of the constants by differential rate measurements is possible in some cases, but the method is not as general as the method previously discussed. If, however, adsorption studies are available for the reactants on the catalyst under consideration and if simplification can be made in the expressions for the adsorption equilibria, the method should give satisfactory results for simple reactions.

For the reaction $A + B \rightleftharpoons C$ various rate equations can be written for different forms of the adsorption isotherms.

The equation in terms of fraction of surface covered is

$$r = k\theta_A\theta_B - k'\theta_C \tag{32}$$

If $\theta_i = \frac{\alpha_i p_i}{1 + \alpha_i p_i}$, the rate equation becomes

$$r = \frac{k\alpha_A\alpha_B p_A p_B}{(1 + \alpha_A p_A)(1 + \alpha_B p_B)} - \frac{k'\alpha_C p_C}{(1 + \alpha_C p_C)} \tag{33}$$

This form of the rate equation is too cumbersome to permit evaluation of the constants. However, in many cases the adsorption isotherms may be approximated by the expression

$$\theta_i = \alpha_i p_i \tag{34}$$

and the rate equation becomes, in terms of mole fractions,

$$r = k\alpha_A\alpha_B\pi^2 y_A y_B - k'\alpha_C\pi y_C \tag{35}$$

By a material balance around the reactor, the mole fractions of any two of the components can be expressed in terms of the third. In addition the rate can be expressed in terms of one reactant by

$$\frac{d(Fy_C)}{dW} = \frac{F_o(y_{Ao} - 1)}{(1 - y_A)^2}\frac{dy_A}{dW} \tag{36}$$

where y_{Ao} is the mole fraction of A entering the reaction. Making these substitutions in Equation (35) and rearranging the following equation is obtained.

$$F_o\frac{dy_A}{dW} = k'\alpha_C\pi\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A) - k\alpha_A\alpha_B\pi^2 y_A\frac{(1-y_A)^2}{(1-y_{Ao})^2}(1+y_A y_{Ao}-2y_{Ao}) \tag{37}$$

A complete derivation of this equation will be found in the Appendix Part III.

The term $F_o \frac{dy_A}{dW}$ is the slope of the curve when the mole fraction y_A is plotted vs $\frac{W}{F}$ for a constant feed rate. Indicating this slope by R, combining the constants and rearranging, the following equation is obtained:

$$\frac{1}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A) = \frac{B}{A}\frac{y_A}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(1 - 2y_{Ao} + y_A y_{Ao}) + \frac{1}{A} \qquad (38)$$

where $A = k' \alpha_c \pi$

$B = k \alpha_A \alpha_B \pi^2$

A plot of the two variable terms $\frac{1}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A)$ versus $\frac{y_A}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(1 - 2y_{Ao} + y_A y_{Ao})$ should be a straight line if the assumptions which were made are valid. The slope and intercept of this line permit the evaluation of the reaction velocity constants.

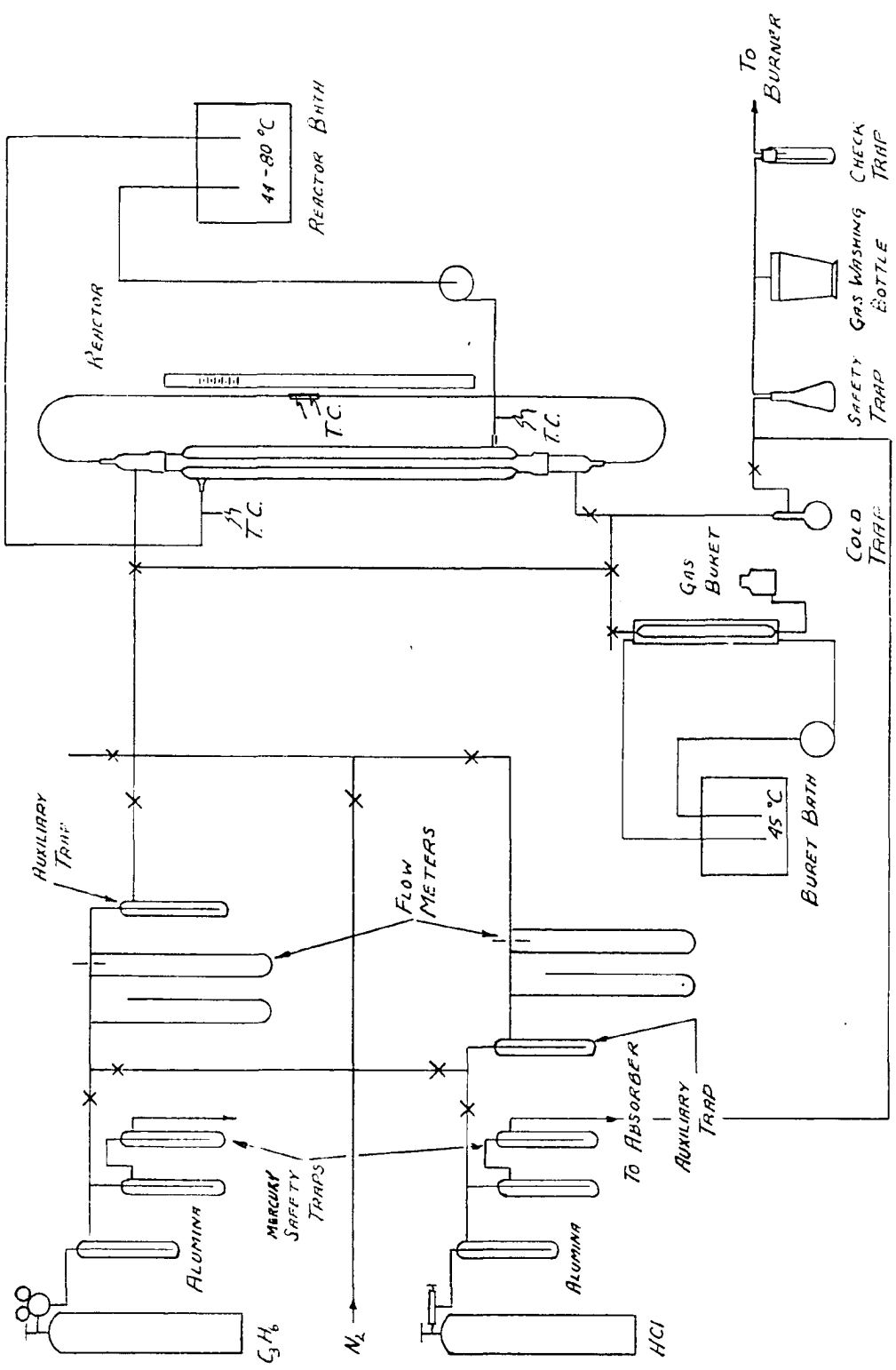
DESCRIPTION OF EXPERIMENTAL EQUIPMENT

CHAPTER III

The general layout of the experimental equipment is shown in Figure 1. Figure 2 is a photograph of the equipment as it was set up for operation.

Reactor

The reactor, shown in a close-up view in Figure 3, consisted of a condenser fitted with ₹24/40 joints and a 50 cm. water jacket. Water was circulated through the jacket at a rate of 0.22 gal/min. from a constant temperature bath by a Model A-1, Type 100 Eastern rotary pump. Chromel-alumel thermocouples placed in the water line before and after the reactor measured inlet and exit water temperatures. Under normal operation, the difference between the inlet and out water temperature was no more than 2°C. The I.D. of the reaction tube was 10 mm. A 2 mm. O.D. glass tube was supported coaxially within the reaction tube by means of 5 mm. O.D. glass tubing aligning supports which were joined to the standard taper joints. Sealing wax provided a gas-tight seal between the 2 mm. and 5 mm. tubes. A 26 gage chromel-alumel thermocouple, drawn within the 2 mm. glass tube was used to measure axial temperature gradients within the catalyst bed which in turn was located in the annular space between the reactor wall and the small tubing. By means of two glass



Layout of Experimental Equipment

Figure 1

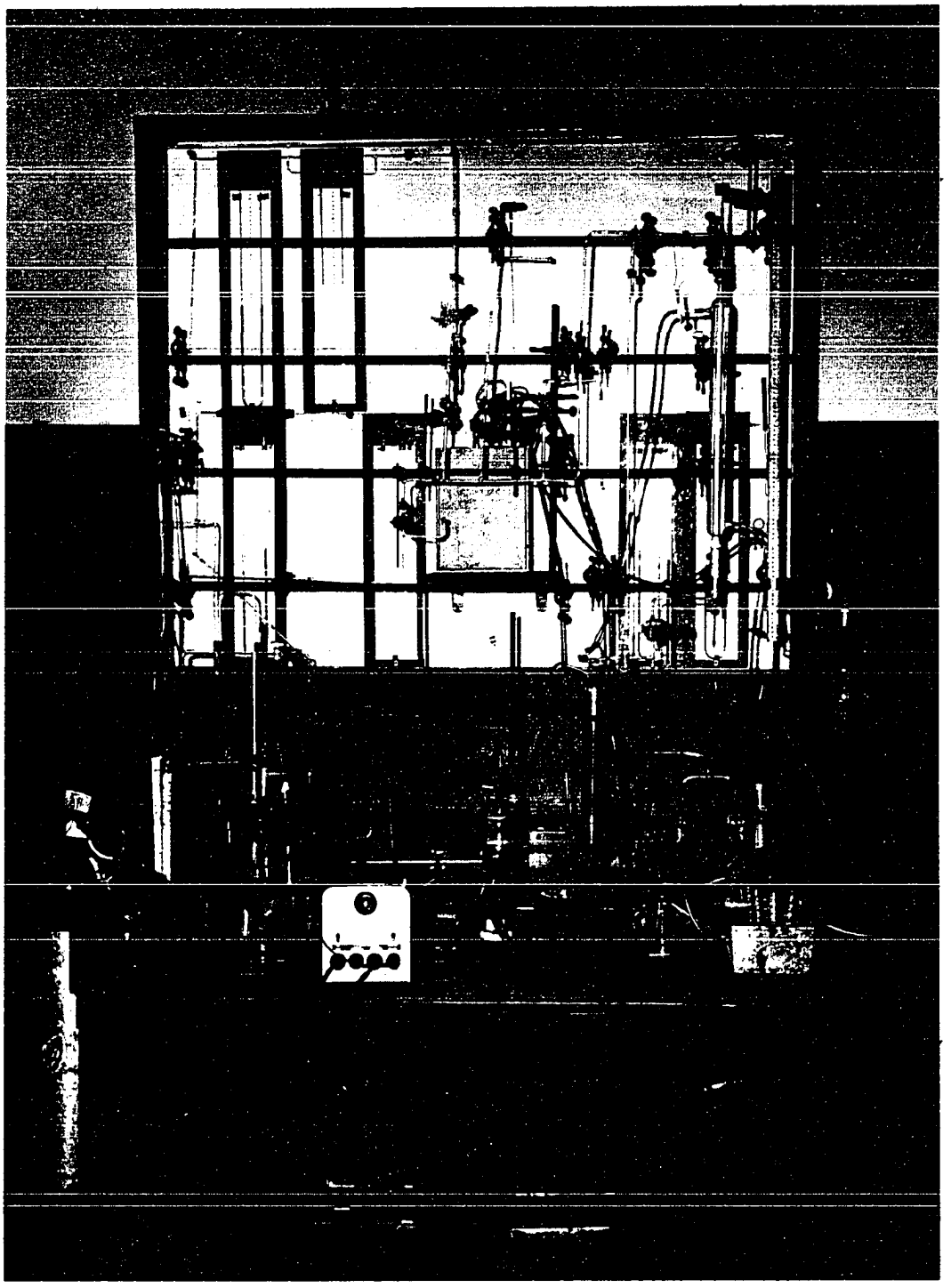


FIGURE 2
EXPERIMENTAL EQUIPMENT

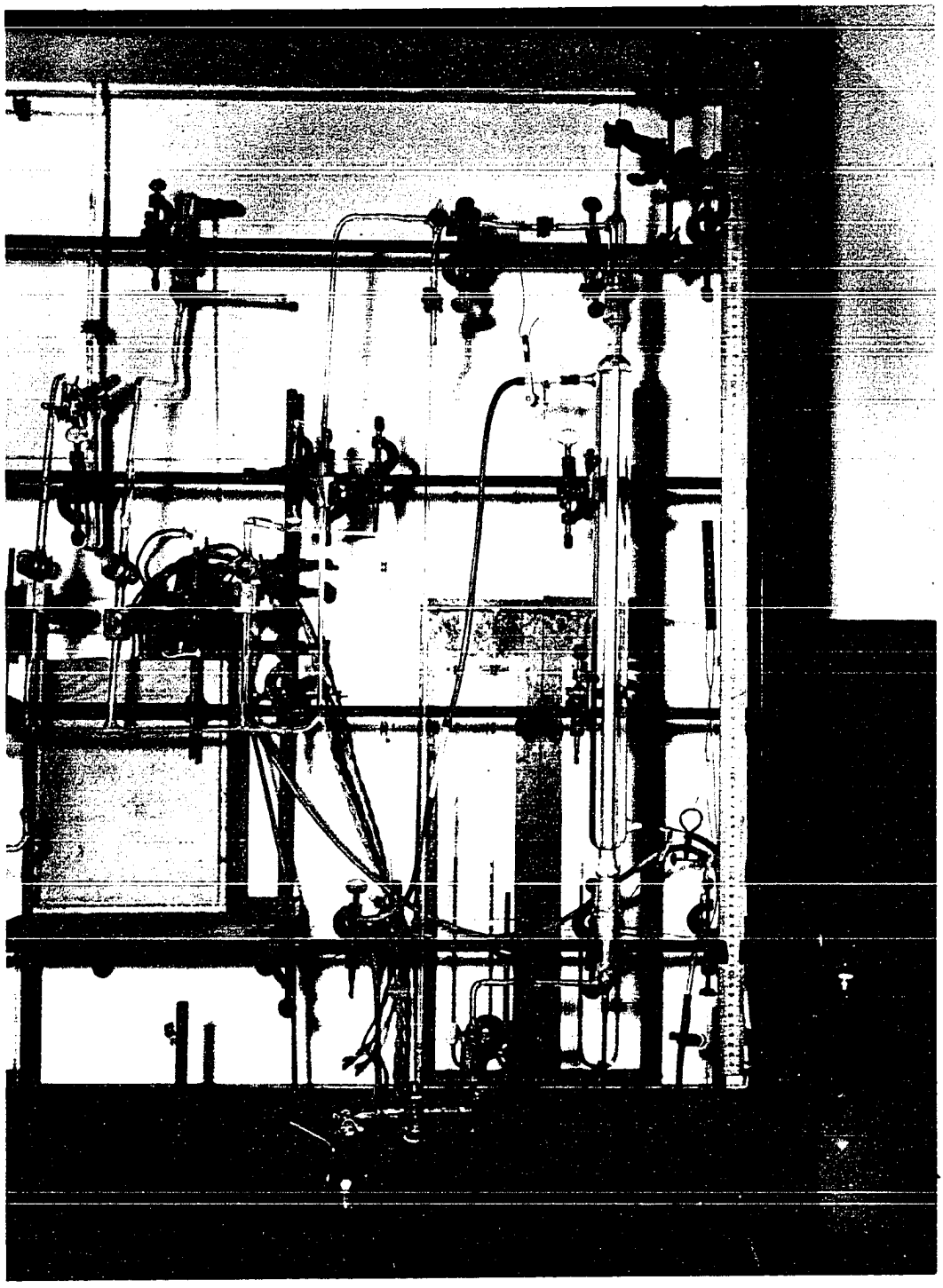


FIGURE 3
REACTOR AND SAMPLING SYSTEM

tube guides, a Formica terminal board, and a scale the thermocouple was centered within the 2 mm. tube and was capable of axial travel and precise positioning within the reactor.

Purification System

The reactor was supplied with hydrogen chloride and propylene from tank sources. Each gas was purified by 4 to 8 mesh activated alumina located in a trap immediately following the tanks. The alumina was degassed and reactivated at the end of each day's run.

Safety Traps

Safety traps on the individual gas lines prevented large pressures from developing in the system. Also, since the hydrogen chloride flow rate could be adjusted only by a needle valve, slowly bubbling the gas through the mercury safety trap permitted, through the use of a stopcock on the main line following the trap, a constant flow rate of the gas at a constant delivery pressure.

Flowmeters

The flow rates of both gases were measured by glass capillary flow meters of conventional design. The propylene meter was calibrated with a precision wet test meter. The hydrogen chloride meter calibration was based on the propylene meter by analyzing mixtures of propylene and hydrogen chloride at different flow rates. Corrections for absolute pressure

changes on the capillary flow meters were made by the method of Whitewell (6). No temperature corrections were made since there was little variation in room temperature. The manometer fluid was a silicone liquid sold by the Wilkens-Anderson Company of Chicago, Illinois. At 20°C its density was 1.0256 gm./cc.

Cold Trap

Following the reactor was a cold trap to collect the liquid isopropyl chloride product. This trap was a modified 250 cc. round bottom flask, which in addition to the inlet and outlet joints, was provided with an exit line fitted with a stopcock. The exit line touched the bottom and came out the tap of the trap. Since the system was under a slight pressure during operation, this arrangement permitted withdrawal of the liquid product with no disruption in operating conditions.

Gas Washing Bottles

A safety trap preceded the Milliken gas washing bottles to eliminate the possibility of water backing into the system when feed gases containing large amounts of hydrogen chloride were used. The gas washing bottles, operated two in parallel, removed all of the hydrogen chloride from the product gases by absorption in water.

Check Trap

The product gases from the gas washing bottles passed through a check trap and then to a burner. The check trap consisted of a large test tube fitted with a rubber stopper. The inlet tube was placed just below the surface of a small amount of mercury. Thus the product gases could pass through the trap, but the natural gas used for the burner could not pass back into the equipment.

Sampling and Analyzing Equipment

The sampling apparatus consisted of a 100 cc. gas buret so arranged that samples of feed gas and product gas could be bled from the system. Mercury was used as the leveling material. Water was circulated through the buret jacket from a constant temperature bath at a rate of 0.25 gal./min. by means of a Model A-1 Type 100 Eastern rotary pump. The jacket temperature was maintained at 45°C to eliminate the possibility of condensation of product.

The analytical apparatus consisted of an absorption tube and leveling bottle shown in Figure 4. The absorption tubes, constructed of 15 mm. O.D. glass tubing, had a capacity of approximately 95 cc. They were fitted with three stopcocks to permit draining and washing of the tube. The leveling bottles, joined to the absorption tubes by Tygon tubing, provided a reservoir for the water used as the absorbing media and also provided a receptacle in which the titration of absorbed hydrogen chloride could be carried out.

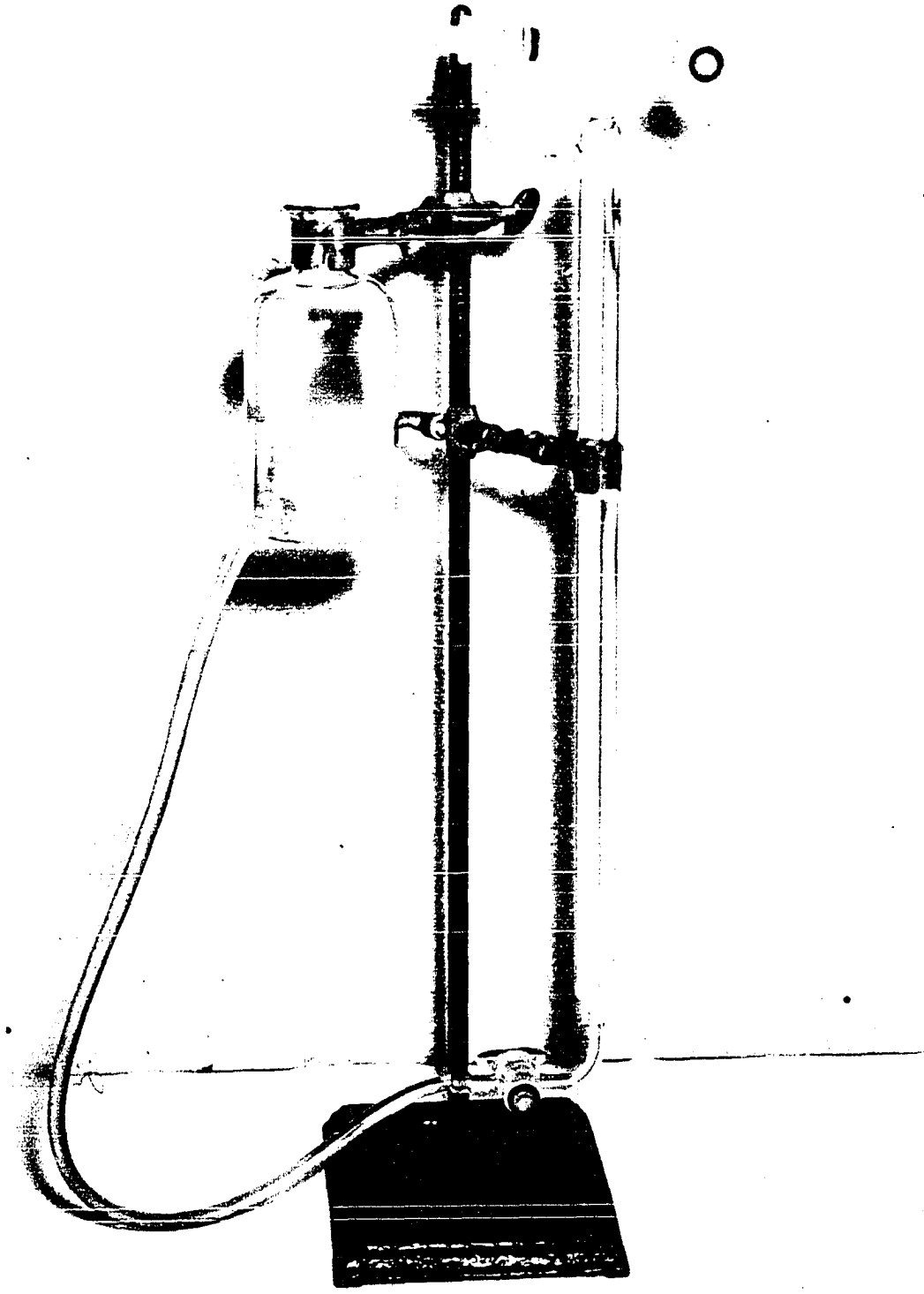


FIGURE 4
ABSORPTION TUBE AND RESERVOIR BOTTLE

MATERIALS

CHAPTER IV

Propylene

The propylene was c.p. grade purchased from the Matheson Company of East Rutherford, New Jersey. The gas had a listed purity of 99% with the principal impurity being propane. Mass spectrographic analysis of the cylinder gas indicated no other impurity.

Hydrogen Chloride

The hydrogen chloride was c.p. grade purchased from the Matheson Company. The gas had a listed purity of 99.5% with the claimed impurities being 0.2% acetylene and 0.3% chlorinated hydrocarbon. Mass spectrographic analysis of the cylinder gas, however, showed that the principal impurity was 5 to 10% of a C_2 hydrocarbon, probably ethylene, and that traces of impurity at masses 63, 64 and 65, were also present. These latter impurities correspond to ethyl chloride. Mass spectrographic analysis showed that the alumina trap in the hydrogen chloride line removed all of these impurities.

Catalyst

The catalyst was activated alumina Alcoa Grade H-41. The 4-8 mesh granular particles were ground and screened, and the fraction passing 20 mesh and retained on 28 mesh screens used for the kinetic study. The catalyst was

activated by heating in a furnace at 750°F for 16 hours.

Heat Transfer Material

An inactive form of alumina was obtained from the Aluminum Company of America in the form of 1/4 inch balls. These were ground and screened. The 20 to 28 mesh size was used as catalyst diluent, and the 20 to 16 mesh size was used as heat transfer material in the preheating section of the reactor and as a catalyst support in the lower section of the reactor.

EXPERIMENTAL PROCEDURE

CHAPTER V

Preliminary Work

In the preliminary work with this reaction, two major difficulties arose. First, the reaction was strongly exothermic so that very large radial and axial temperature gradients were present when an undiluted catalyst charge was used. When these high temperatures occurred, the catalyst became coated with a deposit that varied in color from light orange to black, and the activity of the catalyst decreased rapidly. To minimize these temperature gradients, which were as high as 50°C in a few centimeters, the catalyst charge was diluted with 20 to 28 mesh tabular alumina which was inactive as a catalyst for this reaction. The ratio of volume of catalyst to volume of tabular alumina was 0.4 in all the kinetic runs. With the diluted catalyst charge the maximum radial and axial gradients were not more than 10°C each. The average axial temperature was taken as the temperature of the run.

The second difficulty was the decreasing activity of the catalyst with process time. Placing alumina traps in the individual gas lines after the cylinders and reducing the temperature gradients in the reactor reduced the rate of decreasing catalyst activity a great deal. However, it was

never entirely eliminated. For this reason all kinetic runs were made by measuring the conversion obtained over a period of time for each change of variables. In order to obtain comparable runs it was imperative that the operating procedure be standardized. A detailed operating procedure will be found in Appendix V.

Operation of Equipment

The reactor was assembled with the thermocouple tube in place and sealed with sealing wax to the lower aligning support. The lower standard taper joint was lightly packed with glass wool to provide a support for the catalyst bed. The reactor was filled to a depth of approximately 10 cm with 16-20 mesh tabular alumina, and the hot catalyst charge poured into the chamber. The remaining reactor volume was filled with 16-20 mesh tabular alumina to act as a preheating section for the feed gas. The reactor was quickly closed, connected to the inlet and exit lines, and sealed at the top aligning support. The catalyst bed was cooled to room temperature before the feed gases were introduced by circulating water in the reactor jacket.

After the equipment was completely assembled and tested for leaks the feed gases were turned on. The propylene was always turned on first in order that the water in the gas washing bottles would not back into the system when the hydrogen chloride was turned on. As soon as the propylene was flowing through the system, the hydrogen chloride was introduced. Since the heat of adsorption of hydrogen chloride

or activated alumina is high, the hydrogen chloride was introduced slowly at first in order to prevent initial overheating of the catalyst. After the catalyst temperature had ceased to rise, the flow rates were adjusted to the desired values and the reactor constant temperature bath brought to the desired temperature. It was necessary that this latter operation not be too rapid in order to prevent formation of large temperature gradients.

Since the runs were made on a time basis it was necessary that the start-up period be standard for each run. The zero time was taken at that moment when propylene started to flow through the system. The flow rates were adjusted to the desired feed composition within ten minutes. The reactor was brought to the desired temperature within forty-five minutes so that there was a period of at least fifteen minutes of operation under steady operating conditions before the first sample was taken one hour from the start-up time.

Runs were made at a constant feed gas rate of 0.032 gram moles per minute with slight variations between runs due to pressure differences. A series of runs were made with a given feed composition using 2, 3, and 4 grams of catalyst. A complete series of runs were made at feed compositions of 37% HCl and 63% C_3H_6, and 66% HCl and 34% C_3H_6. The temperatures of operation were 44°C, 60°C, and 80°C. Two supplemental series of runs were made with feed gases of 50% HCl and 50% C_3H_6, and 19% HCl and 81% C_3H_6.

Analytical Procedure

Samples of the gas to be analyzed were drawn slowly into the gas buret by lowering the mercury leveling bottle. Careful manipulation was required in order that the pressure of the system was not affected with subsequent disruption of flow rates of the hydrogen chloride and propylene. A sample of approximately 95 cc was taken, and after allowing the gases to come to temperature, the volume was measured accurately. The gas was then transferred to an absorption tube which had previously been filled with distilled water. After the solution of the hydrogen chloride in the water was assured by repeated shaking of the absorption tube, the acid solution was drained into the leveling bottle and the tube washed twice with distilled water. The acid was titrated directly in the leveling bottle with 0.05N sodium hydroxide using brom thymol blue indicator. Since the ratio of hydrogen chloride to propylene in the feed gas and the total volume of sample were known, the product composition could be calculated by a material balance assuming isopropyl chloride to be the only product formed. This latter fact was substantiated by mass spectrographic analysis of product gases obtained at 44°C and 80°C.

Sufficient samples of product gases were analyzed to establish a conversion vs time plot for each run. The feed gases were analyzed periodically to insure proper feed gas composition.

EXPERIMENTAL RESULTS

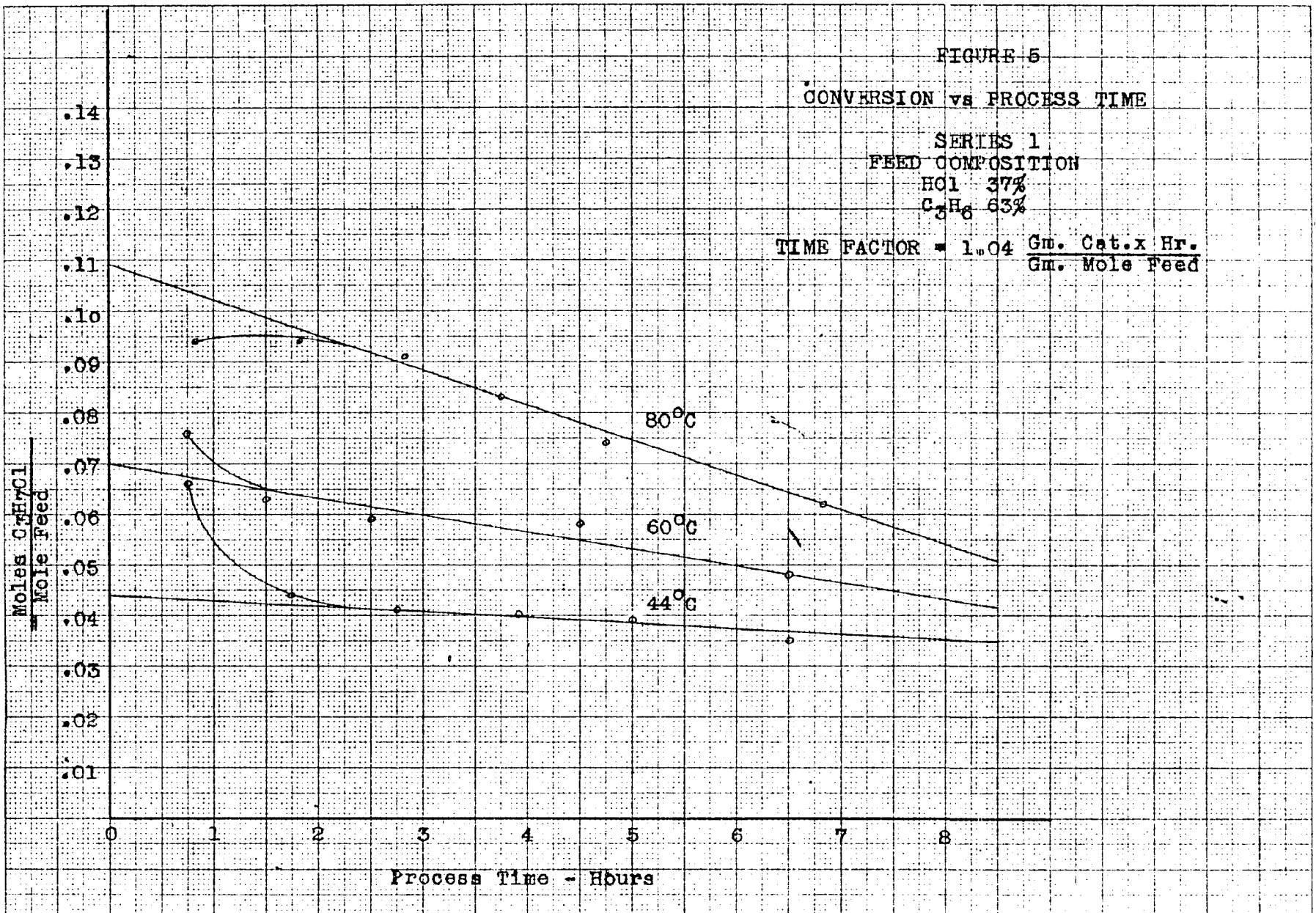
CHAPTER VI

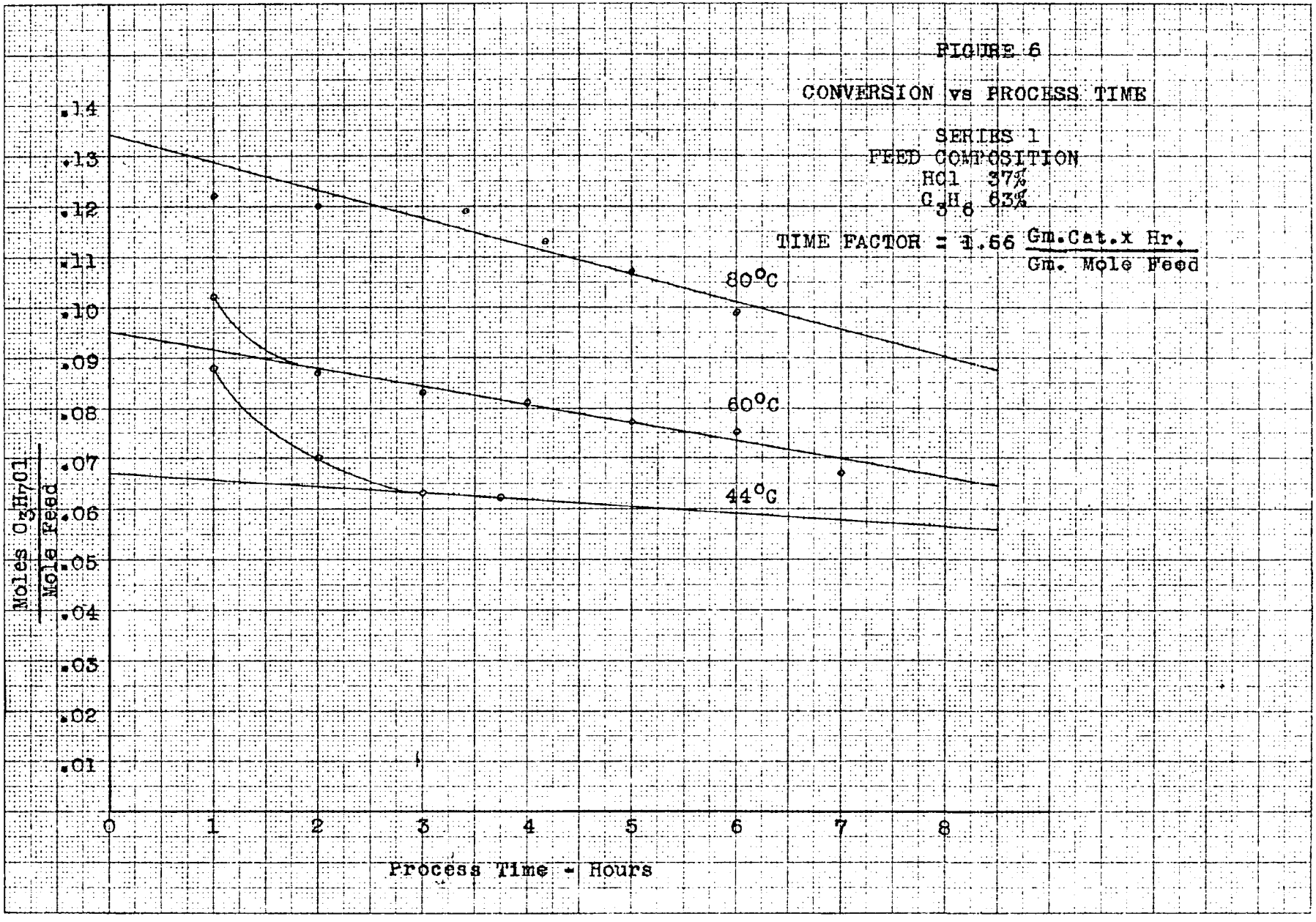
The experimental results are presented in the form of plots of conversion versus process time shown in Figures 5 through 15. The runs of Series 1 were made with a feed composition of 37% HCl and 63% C_3H_6 at time factor of 1.04, 1.56, and 2.08 (gm.cat.)(hr.)/Gm. mole feed at temperatures of 44°C, 60°C and 80°C. Two additional runs of Series 1 were made at a time factor of 0.52 at the temperatures of 60°C and 80°C. The runs of Series 2 are identical with those of Series 1 except that the feed composition was 66% HCl and 34% C_3H_6.

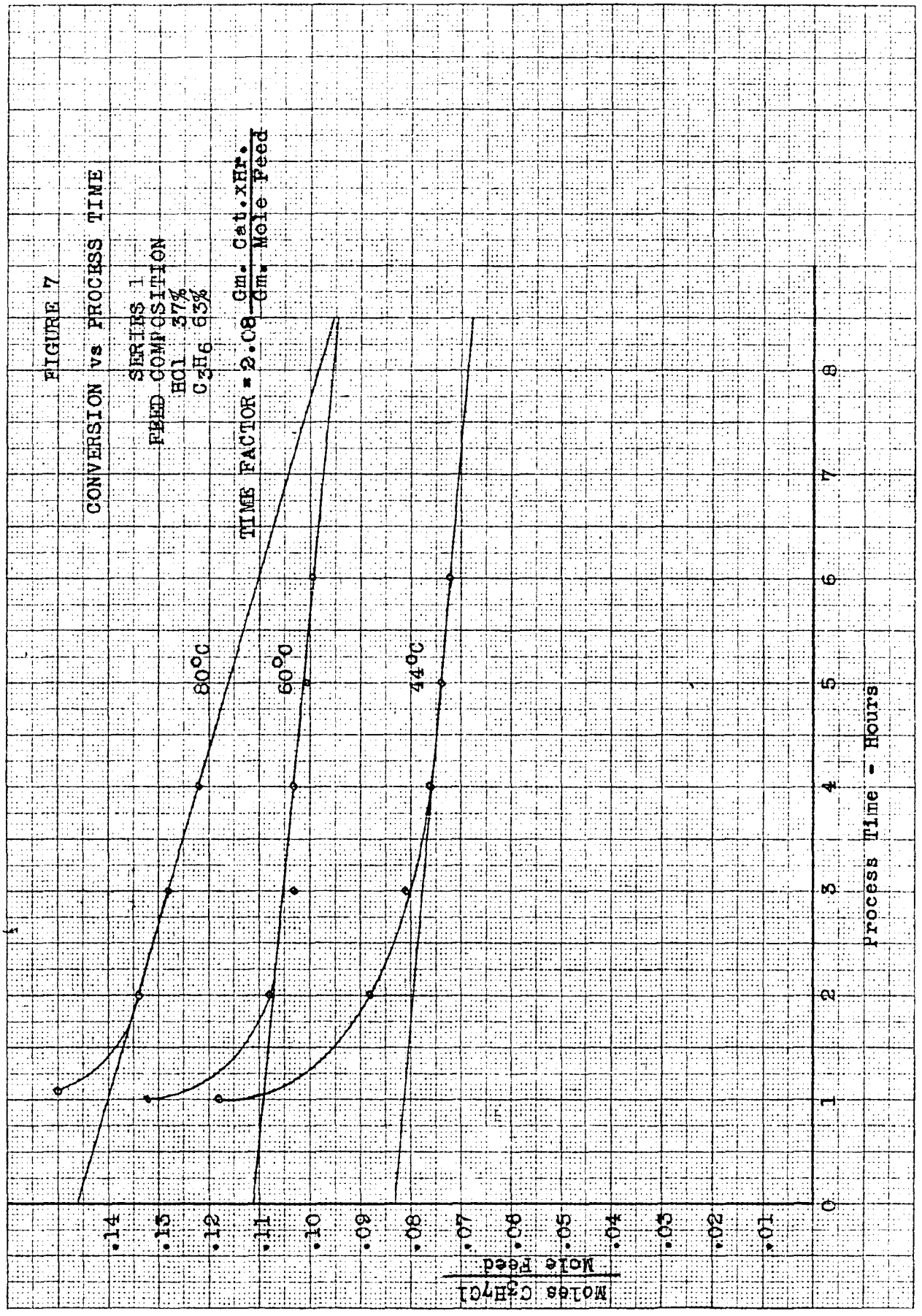
Series 3 runs were made at a time factor of 1.04 with a feed composition of 50% HCl and 50% C_3H_6. Since runs at 44°C, 60°C and 80°C gave substantially the same conversions as were obtained in Series 1 and 2, no additional runs were made at different time factors. Series 4 consisted of two runs with a feed composition of 19% HCl and 81% C_3H_6. These runs gave conversions much lower than previously obtained.

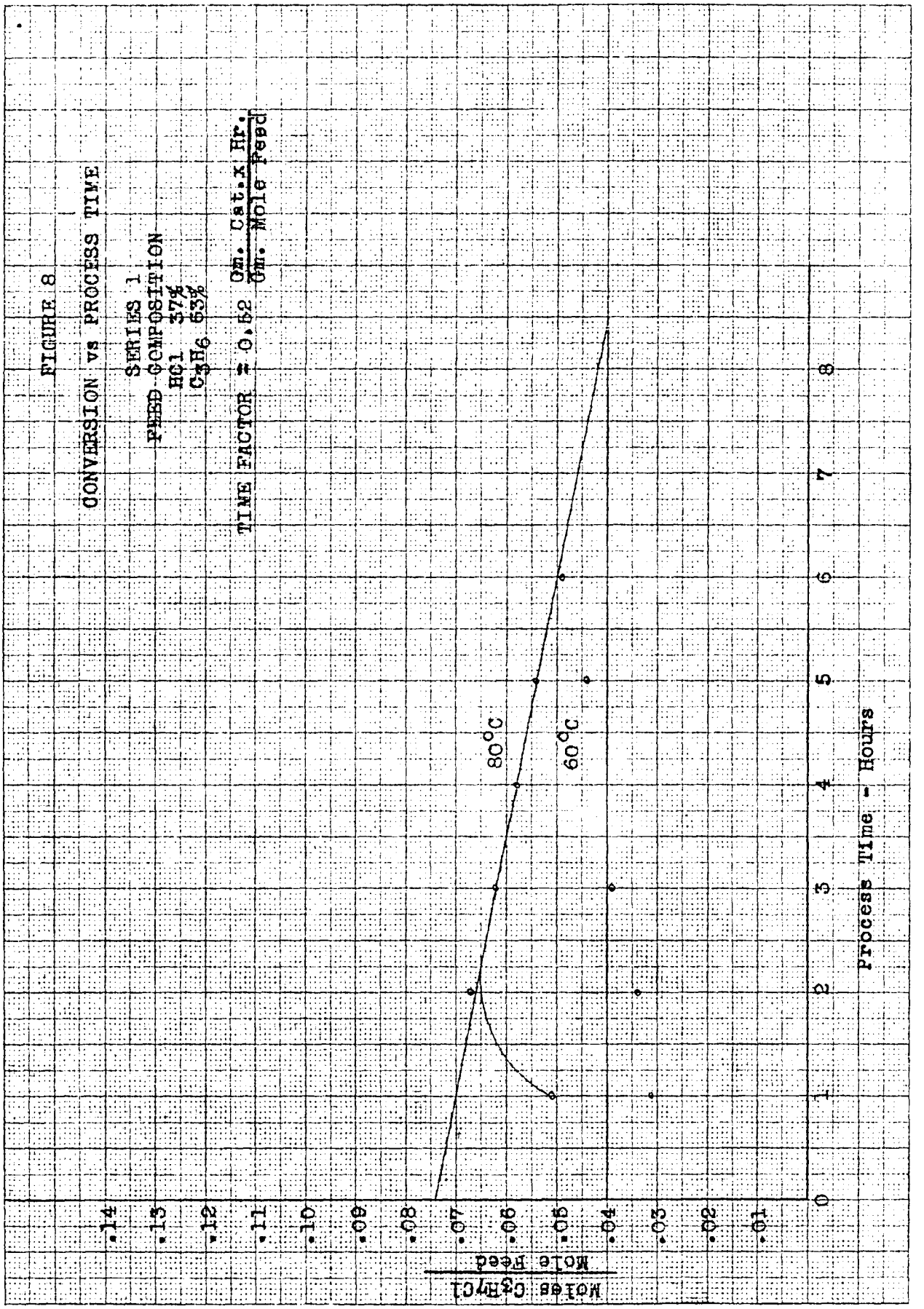
It was characteristic of these plots that after an initial unsteady period the conversion decreased linearly with process time, and the rate of decrease was dependent on the temperature. Thus, for each run a straight line could be drawn through the points, if the points in the unsteady period were neglected. Those lines were extrapolated to zero

process time in order to provide a standard basis for comparison between runs at different temperatures when no fouling of the catalyst occurred.









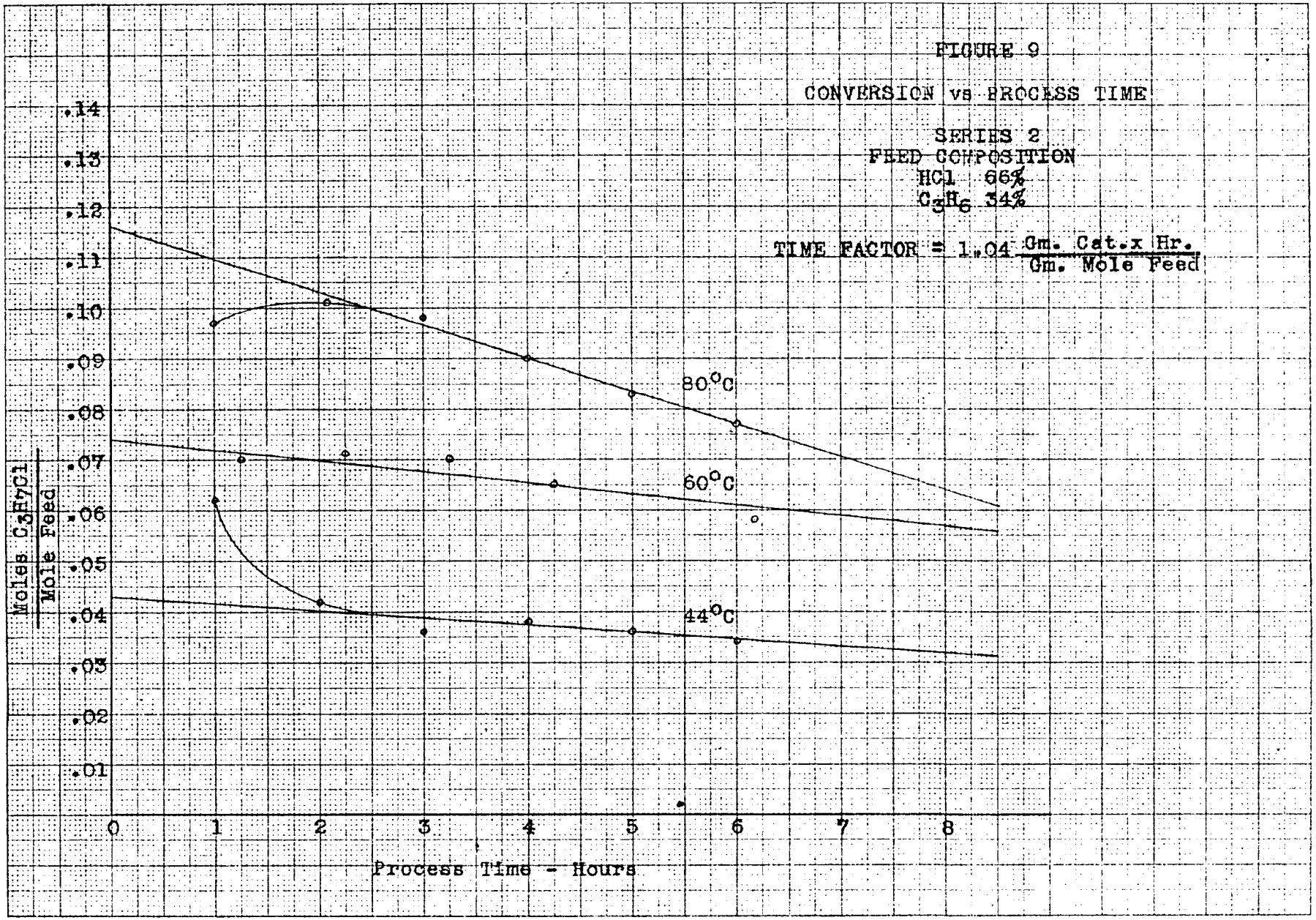


FIGURE 12

CONVERSION vs PROCESS TIME

SERIES 2

FEED COMPOSITION

HCl 66%

C_3H_6 34%

TIME FACTOR = 0.52 Gm. Cat.x Hr. / Gm. Mole Feed

FIGURE 16

CONVERSION vs PROCESS TIME

SERIES 4

FEED COMPOSITION

HCl 19%

C_3H_6 81%

TIME FACTOR = 1.56 $\frac{\text{Gm. Cat.} \times \text{Hr.}}{\text{Gm. Mole Feed}}$

DETERMINATION OF THE MECHANISM

CHAPTER VII

Mass Transfer

The film gradients at the catalyst surface were estimated using Equation (5) with conversion data at 80°C. The largest gradient present was of the order of magnitude of 0.0002 atmospheres so that the effect of mass transfer could be neglected, and the concentrations at the catalyst surface could be assumed to be the same as that in the fluid stream.

Adsorption of Hydrogen Chloride Controlling

The equation which applies to the case where adsorption of one of the reactants controls was developed on Page 13 . Applying it to the adsorption of hydrogen chloride the equation becomes

$$r = \frac{k_{HCl} \; L \left(a_{HCl} - \frac{a_{C_3H_7Cl}}{K} \right)}{1 + a_{C_3H_6} K_{C_3H_6} + \frac{a_{C_3H_7Cl}}{a_{C_3H_6}} \frac{K_{HCl}}{K} + a_{C_3H_7Cl} K_{C_3H_7Cl}} \qquad (39)$$

For the initial rate the activity of the isopropyl chloride is zero. Replacing activities by partial pressures expressed in mole fraction, the equation for the initial rate becomes

$$r_o = \frac{k_{HCl} L \pi y_{HCl}}{1 + y_{C_3H_6} \pi K_{C_3H_6}} \qquad (40)$$

At the initial time $y_{C_3H_6} = 1 - y_{HCl}$

Making this substitution and rearranging, the following equation is obtained:

$$\frac{y_{HCl}}{r_o} = -\frac{K_{C_3H_6}}{k_{HCl} L} y_{HCl} + \frac{1 + \pi K_{C_3H_6}}{k_{HCl} L \pi} \qquad (41)$$

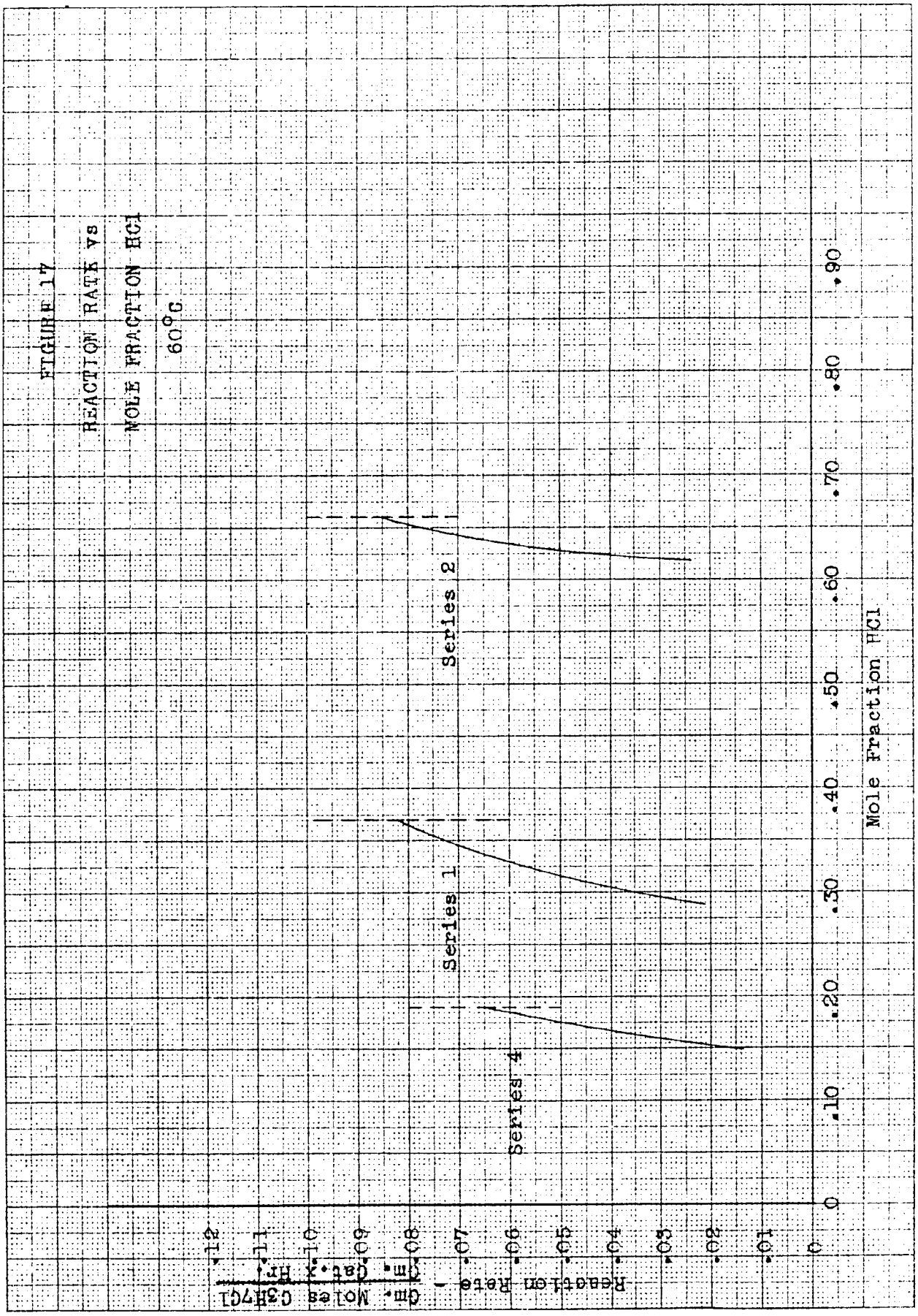
The plot of $\frac{y_{HCl}}{r_o}$ versus y_{HCl} at the same temperature for different feed compositions should give a straight line with a negative slope.

The extrapolated values of conversion at zero time were plotted versus time factor for the runs of Series 1, 2 and 4. The rates of reaction, which are represented by the slopes of these curves, were measured graphically and plotted versus mole fraction of hydrogen chloride. These curves which are shown in Figures 16 and 17 were then extrapolated to the feed composition to give the initial rates.

The plots of $\frac{yHCl}{r_o}$ versus y_{HCl} are shown in Figure 18 for 60° and 80°C. These plots show that although they are straight lines they have positive slopes. According to Equation (41) the slope of these lines should be negative if the adsorption of hydrogen chloride were the controlling mechanism. Therefore the adsorption of hydrogen chloride is not the controlling step.

Adsorption of Propylene Controlling

An equation of the same form as Equation (41) can



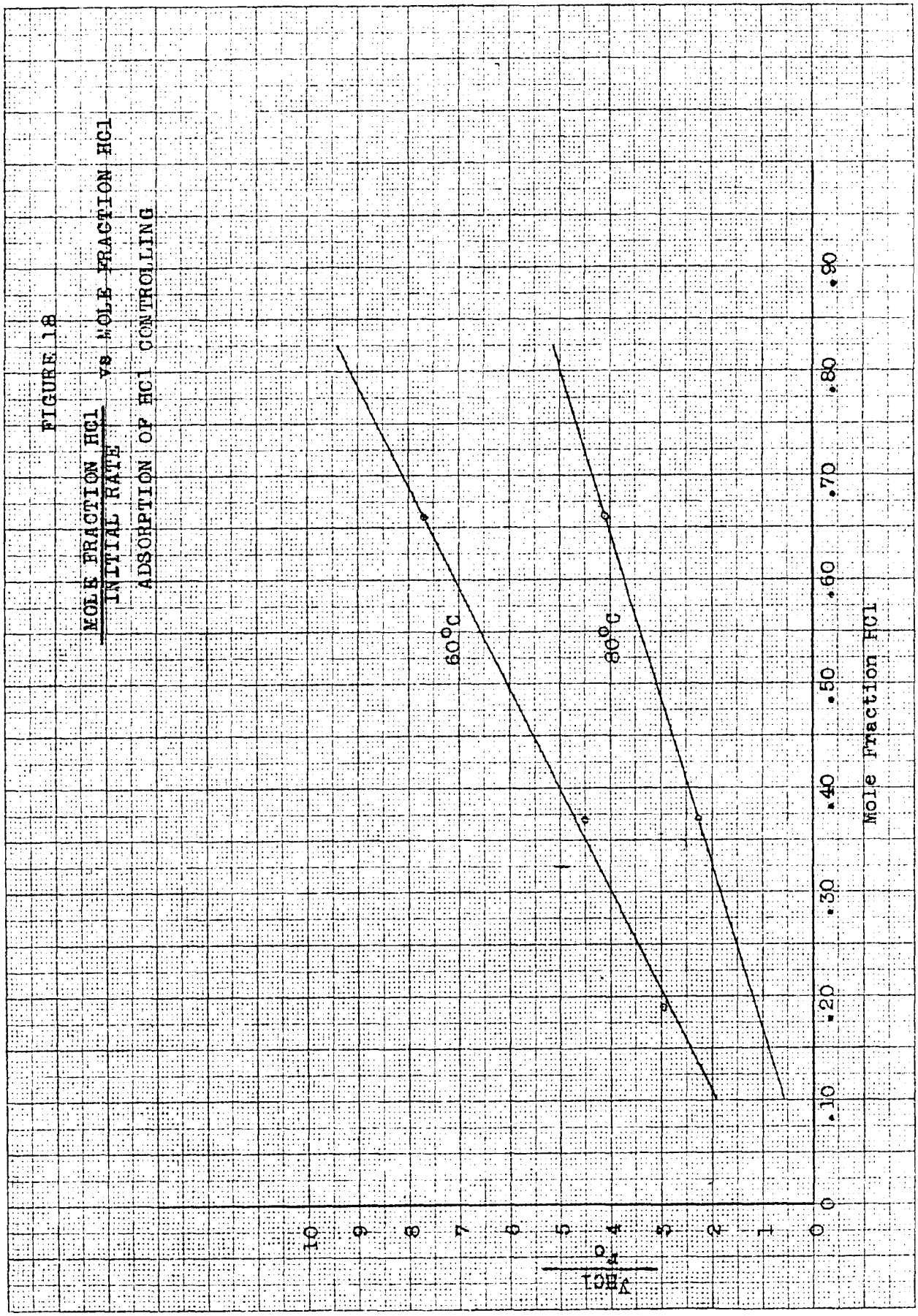


FIGURE 18

MOLE FRACTION HCl vs MOLE FRACTION HCl

INITIAL RATE

ADSORPTION OF HCl CONTROLLING

be developed for the case where the adsorption of propylene controls.

$$\frac{y_{C_3H_6}}{r_o} = -\frac{K_{HCl}}{k_{C_3H_6}L}\, y_{C_3H_6} + \frac{1 + \pi K_{HCl}}{k_{C_3H_6}L\pi} \qquad (42)$$

The plot of this equation, shown in Figure 19, shows that a straight line drawn through the experimental points has a positive slope whereas Equation (42) indicates that the slopes would be negative if the adsorption of propylene were the controlling mechanism. Therefore, the adsorption of propylene is not the controlling step.

Desorption of Isopropyl Chloride Controlling

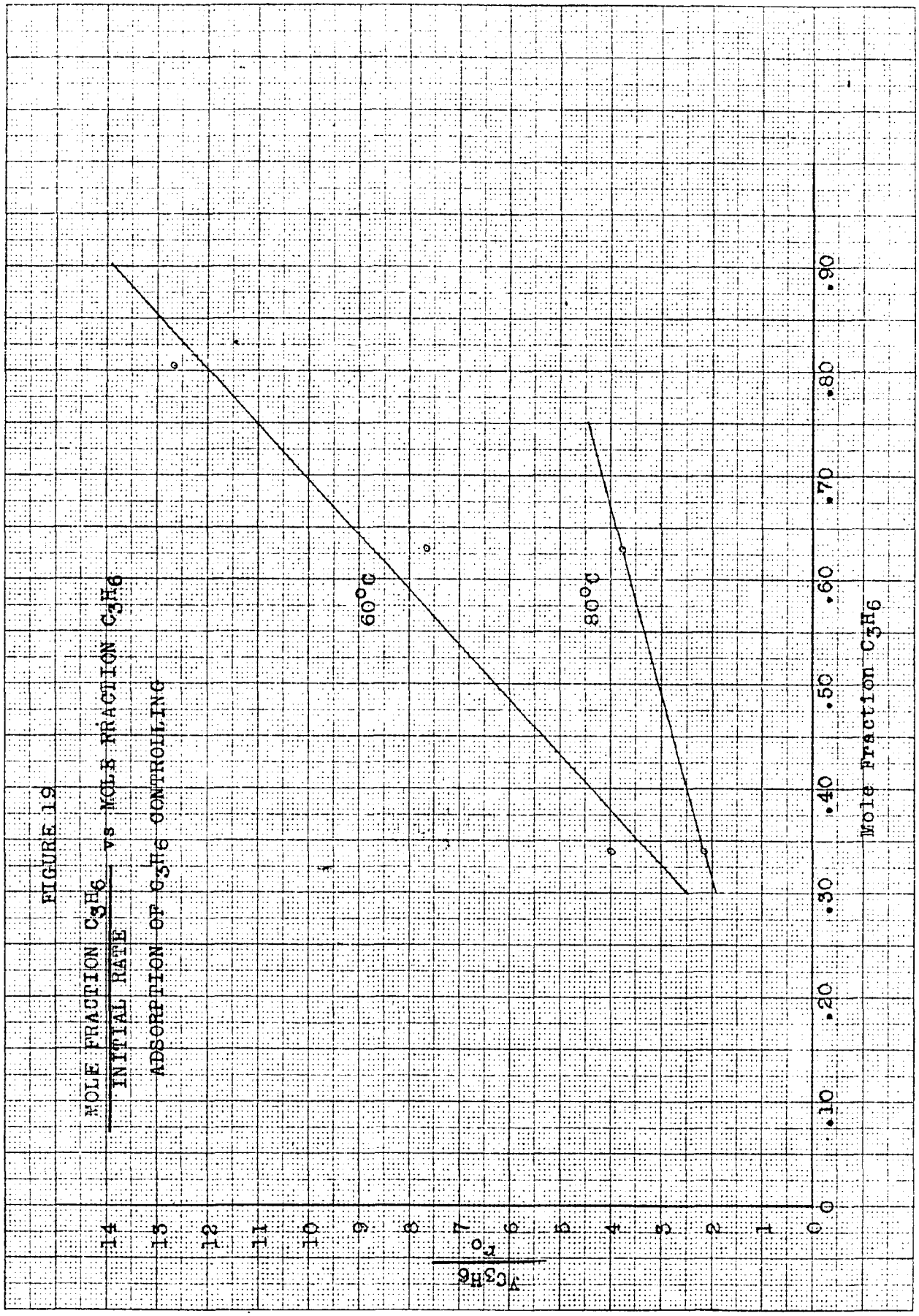
By Equation (30) when desorption of isopropyl chloride is the controlling step, the following equation for the reaction rate applies.

$$r = \frac{k_{C_3H_7Cl}\, L\, K\, (a_{HCl}\, a_{C_3H_6} - \frac{a_{C_3H_7Cl}}{K})}{1 + a_{HCl}K_{HCl} + a_{C_3H_6}K_{C_3H_6} + a_{HCl}a_{C_3H_6}K_{C_3H_7Cl}K} \qquad (43)$$

If only the initial rate is considered and the equation expressed in terms of mole fraction of hydrogen chloride, the following equation is obtained.

$$\frac{y_{HCl}(1-y_{HCl})}{r_o} = -\frac{K_{C_3H_7Cl}}{k_{C_3H_7Cl}L}y_{HCl}^2 + \frac{K_{HCl}K_{C_3H_6} + \pi K_{C_3H_7Cl}K}{\pi k_{C_3H_7Cl}\, L\, K}\, y_{Ao} + \frac{1 + \pi K_{C_3H_6}}{\pi^2 k_{C_3H_7Cl}\, L\, K}$$

$$\frac{y_{HCl}(1-y_{HCl})}{r_o} = \alpha\, y_{HCl}^2 + \beta\, y_{HCl} + \gamma \qquad (44)$$



The constants in Equation (44) were evaluated with the initial rate data at 60°C. The final equation is as follows:

$$\frac{y_{HCl}(1-y_{HCl})}{r_o} = -7.12\ y_{Ao}^2 + 6.64\ y_{Ao} + 1.335 \qquad (45)$$

Since the signs of the constants α, β, and γ are in agreement with those of Equation (44), the desorption of isopropyl chloride is a possible controlling mechanism.

Evaluation of the individual constants of Equation (43) by the method of least squares has been suggested (4). If partial pressures in terms of mole fraction are substituted for activities and the equation rearranged, the following expression results.

$$\frac{y_{C_3H_7Cl}}{r} = \pi K \frac{y_{HCl}y_{C_3H_6}}{r} - \frac{K_{HCl}}{k_{C_3H_7Cl}L}\, y_{HCl} - \frac{K_{C_3H_6}}{k_{C_3H_7Cl}L}\, y_{C_3H_6} - \frac{\pi K_{C_3H_7Cl}K}{k_{C_3H_7Cl}L}\, y_{HCl}y_{C_3H_6} - \frac{1}{k_{C_3H_7Cl}L\,\pi}$$

$$\frac{y_{C_3H_7Cl}}{r} = \alpha \frac{y_{HCl}y_{C_3H_6}}{r} + \beta\, y_{HCl} + \gamma y_{C_3H_6} + \delta\, y_{HCl}y_{C_3H_6} + \epsilon \qquad (46)$$

The constants of Equation (46) were evaluated at 60°C and 80°C from the experimental conversion versus time factor curves by the method of least squares. The results are shown in Table I.

Table I

Values of Constants in Equation (46)

		80°C	60°C
α	πE	1.414	-0.358
β	$-\frac{K_{HCl}}{k_{C_3H_7Cl}{}^L}$	1.436	-0.269
γ	$-\frac{K_{C_3H_6}}{k_{C_3H_7Cl}{}^L}$	0.058	-1.071
δ	$-\frac{\pi K_{C_3H_7Cl}{}^K}{k_{C_3H_7Cl}{}^L}$	0.300	-0.867
ϵ	$-\frac{1}{k_{C_3H_7Cl}{}^L \pi}$	-2.479	+3.768

As seen in Table I the signs of these constants are not only inconsistent at the two temperatures, but they do not agree with the definitions of the individual constants. Normally, this latter fact would eliminate this mechanism as a possible controlling step. However, it is believed that since the data *are* over a limited range of composition of isopropyl chloride this method of evaluation of the constants is not reliable and the mechanism of desorption of isopropyl chloride controlling is still possible based upon the results of Equation (45).

Surface Reaction Controlling

As developed in Equation (21) the reaction rate equation for the case of the surface reaction controlling is as follows:

$$r = \frac{ks\ L\ K_{HCl}K_{C_3H_6}}{(1 + a_{HCl}K_{HCl} + a_{C_3H_6}K_{C_3H_6} + a_{C_3H_7Cl}K_{C_3H_7Cl})^2}\left(a_{HCl}a_{C_3H_6} - \frac{a_{C_3H_7Cl}}{K}\right) \quad (47)$$

If the activities are expressed in terms of mole fraction of hydrogen chloride and if only the initial rate considered, the following equation is obtained.

$$\left[\frac{y_{HCl}(1-y_{HCl})}{r_o}\right]^{1/2} = \frac{K_{HCl}-K_{C_3H_6}}{(ksLK_{HCl}K_{C_3H_6})^{1/2}}\ y_{HCl} + \frac{1 + \pi K_{C_3H_6}}{(\pi^2 ksLK_{HCl}K_{C_3H_6})^{1/2}}$$

$$\left[\frac{y_{HCl}(1-y_{HCl})}{r_o}\right]^{1/2} = \alpha\, y_{HCl} + \beta \quad (48)$$

This equation is plotted in Figure 20 which shows that straight lines drawn through the experimental points have either positive or zero slopes and positive intercepts. This is consistent with Equation (48). On this basis the surface reaction is a possible controlling mechanism.

If activities are expressed in terms of mole fraction, Equation (47) can be rearranged to give the following equation:

$$\left[\frac{y_{HCl}y_{C_3H_6} - \frac{y_{C_3H_7Cl}}{\pi K}}{r}\right]^{1/2} = \frac{1}{\pi(ksLK_{HCl}K_{C_3H_6})^{1/2}} + \frac{K_{HCl}^{1/2}}{(ksLK_{C_3H_6})^{1/2}} y_{HCl}$$

$$+ \frac{K_{C_3H_6}^{1/2}}{(ksL\,K_{HCl})^{1/2}} y_{C_3H_6} + \frac{K_{C_3H_7Cl}}{(ksLK_{HCl}K_{C_3H_6})^{1/2}} y_{C_3H_7Cl}$$

$$R = \alpha + \beta y_{HCl} + \gamma y_{C_3H_6} + \delta y_{C_3H_7Cl} \qquad (49)$$

The constants in Equation (49) were evaluated by the method of least squares from data from the experimental conversion versus time factor curves. The results are given in Table III. The values of the equilibrium constant, K, were obtained from known and estimated thermodynamic properties for the reactants and products. The values of K at each of the temperatures is given in Table II.

Table II

Values of Equilibrium Constant, K

	44°C	60°C	80°C
K	22.4	7.61	2.32

Table III

Values of Constants in Equation (49)

		80°C	60°C	44°C
α	$\frac{1}{\pi(ksLK_{HCl}K_{C_3H_6})^{1/2}}$	+1.975	-7.280	+2.670
β	$\frac{K_{HCl}^{1/2}}{(ksLK_{C_3H_6})^{1/2}}$	-1.377	+8.559	-0.324

Table III (cont.)

Values of Constants in Equation (49)

		80°C	60°C	44°C
γ	$\frac{K_{C_3H_6}}{(ksLK_{HCl})^{1/2}}$	-1.0072	+8.959	-0.557
δ	$\frac{K_{C_3H_7Cl}}{(ksLK_{HCl}K_{C_3H_6})^{1/2}}$	+4.6736	+14.238	+0.401

The values of the constants in Table III are much the same as were obtained with the desorption of isopropyl chloride controlling in that there is no consistency in sign between the values of the constants and their definitions. This inconsistency is again believed to be due to the small range of composition values for the isopropyl chloride rather than due to the inapplicability of the equation to the mechanism. Thus, based on the results obtained from the initial reaction rates the surface reaction is a possible controlling mechanism.

CORRELATION OF KINETIC DATA

CHAPTER VIII

The kinetic data for the addition of hydrogen chloride to propylene over activated alumina were correlated by two methods assuming that the surface reaction is the rate controlling step.

Method A

In Equation (49) the mole fraction of isopropyl chloride can be expressed in terms of the mole fractions of the other two components of the system, and the constants combined to give the following equation:

$$R = (\alpha + \beta) + (\beta - \delta) y_{HCl} + (\gamma - \delta) y_{C_3H_6}$$

$$R = A + B\, y_{HCl} + C\, y_{C_3H_6} \qquad (50)$$

$$A = \frac{1}{(ksLK_{HCl}K_{C_3H_6})^{1/2}} \left(\frac{1}{\Pi} + K_{C_3H_7Cl}\right)$$

$$B = \frac{1}{(ksLK_{HCl}K_{C_3H_6})^{1/2}} \left(K_{HCl} - K_{C_3H_7Cl}\right)$$

$$C = \frac{1}{(ksLK_{HCl}K_{C_3H_6})^{1/2}} \left(K_{C_3H_6} - K_{C_3H_7Cl}\right)$$

$$R = \left[\frac{y_{HCl} y_{C_3H_6} - \frac{y_{C_3H_7Cl}}{\pi K}}{r} \right]^{1/2}$$

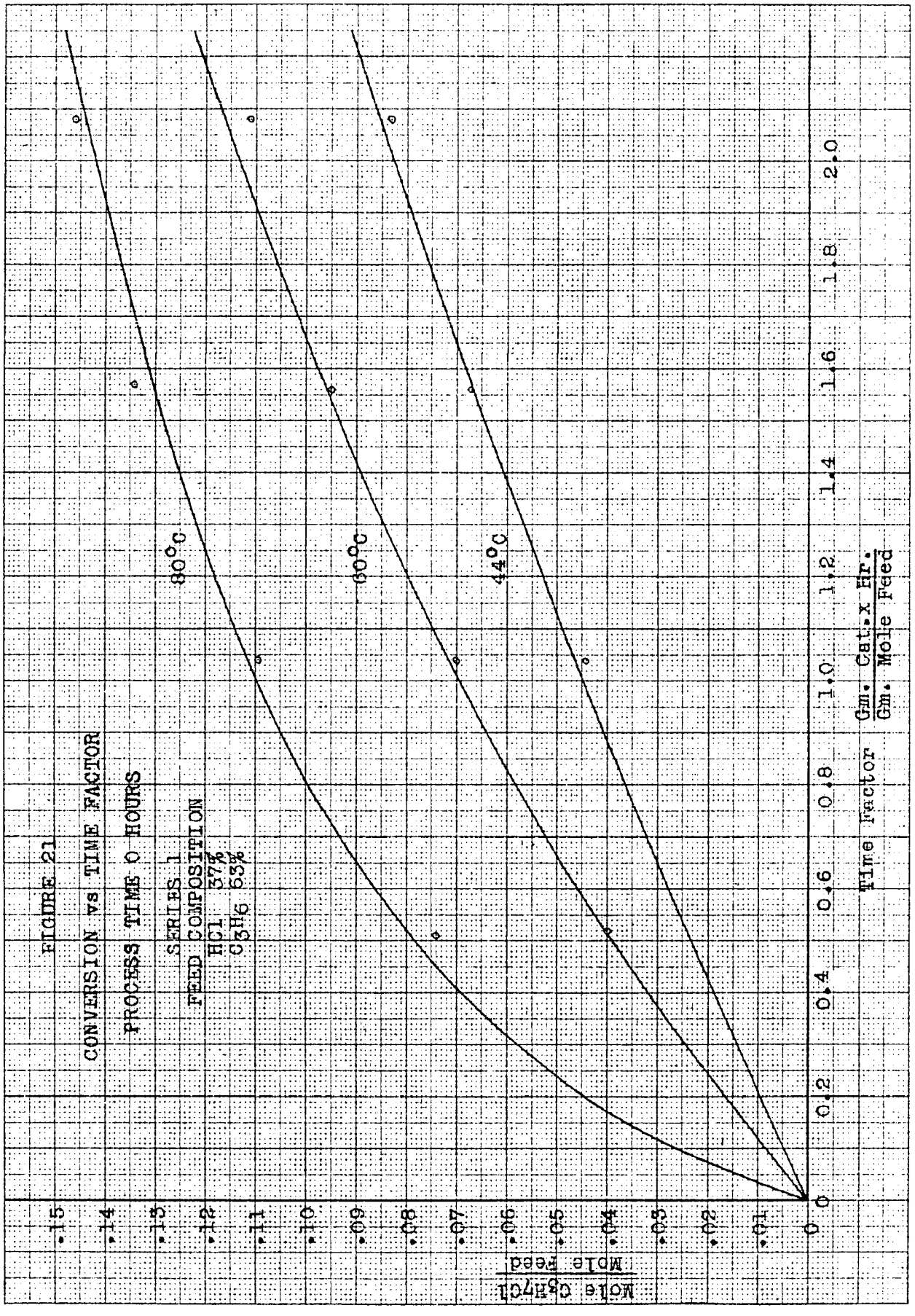
Upon evaluating the constants A, B, and C by the method of least squares from the experimental conversion versus time factor curves for all three temperatures, it was found that the sign of the constants were in all cases consistent with the definitions above.

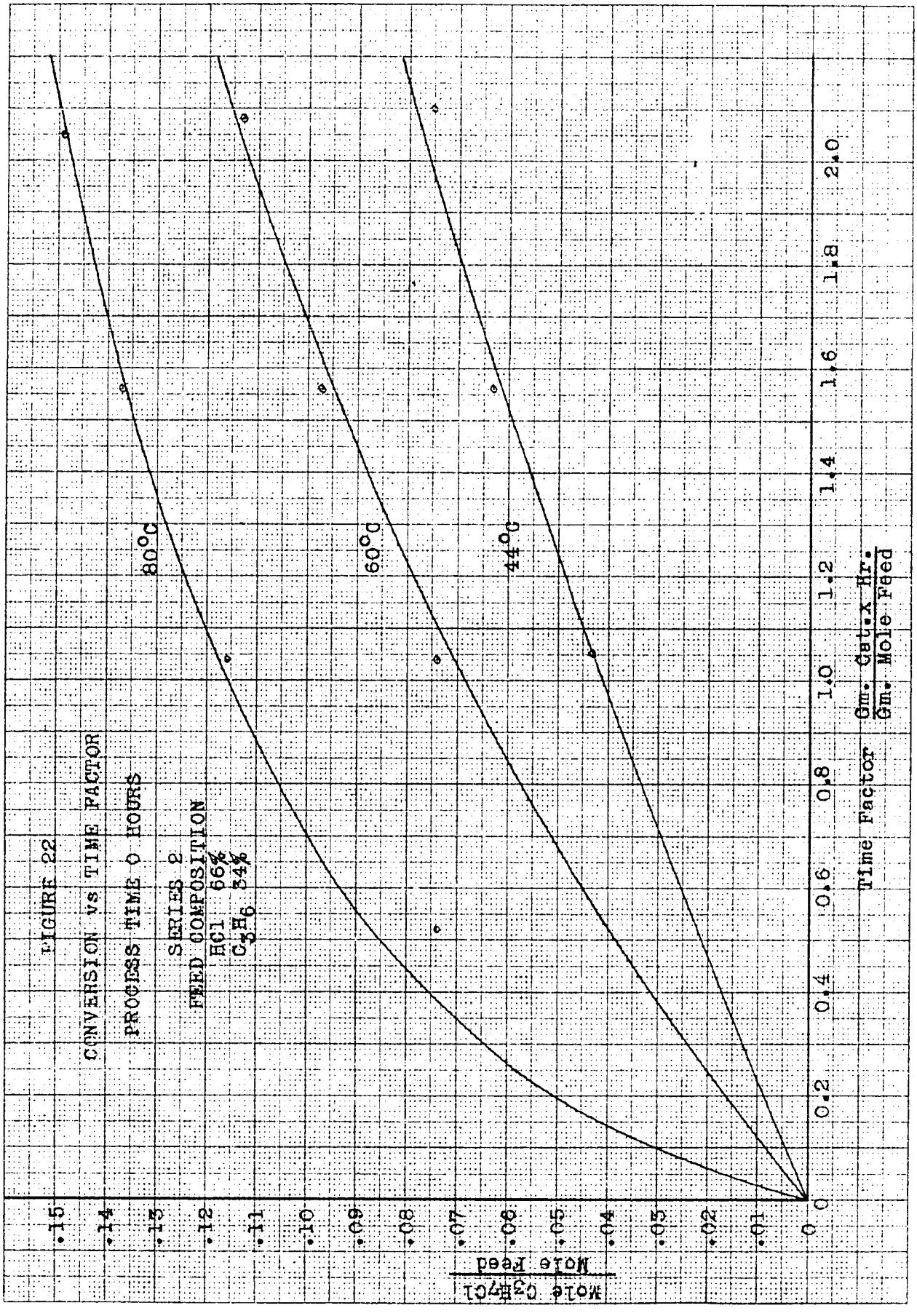
In a steady flow system the relationship between conversion and time factor can be obtained by integration of Equation (1)

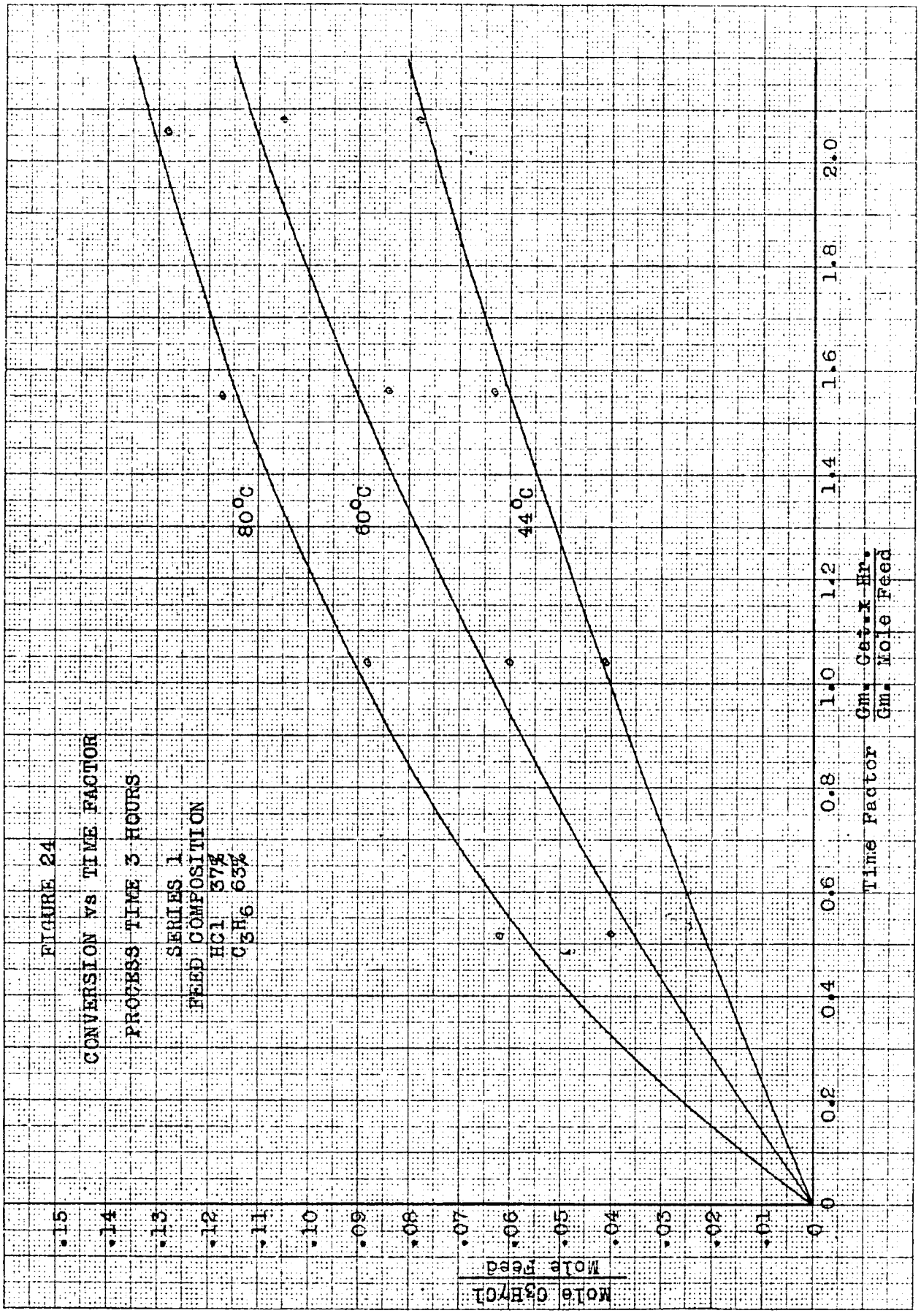
$$\frac{W}{F} = \int_0^x \frac{dx}{r} \qquad (51)$$

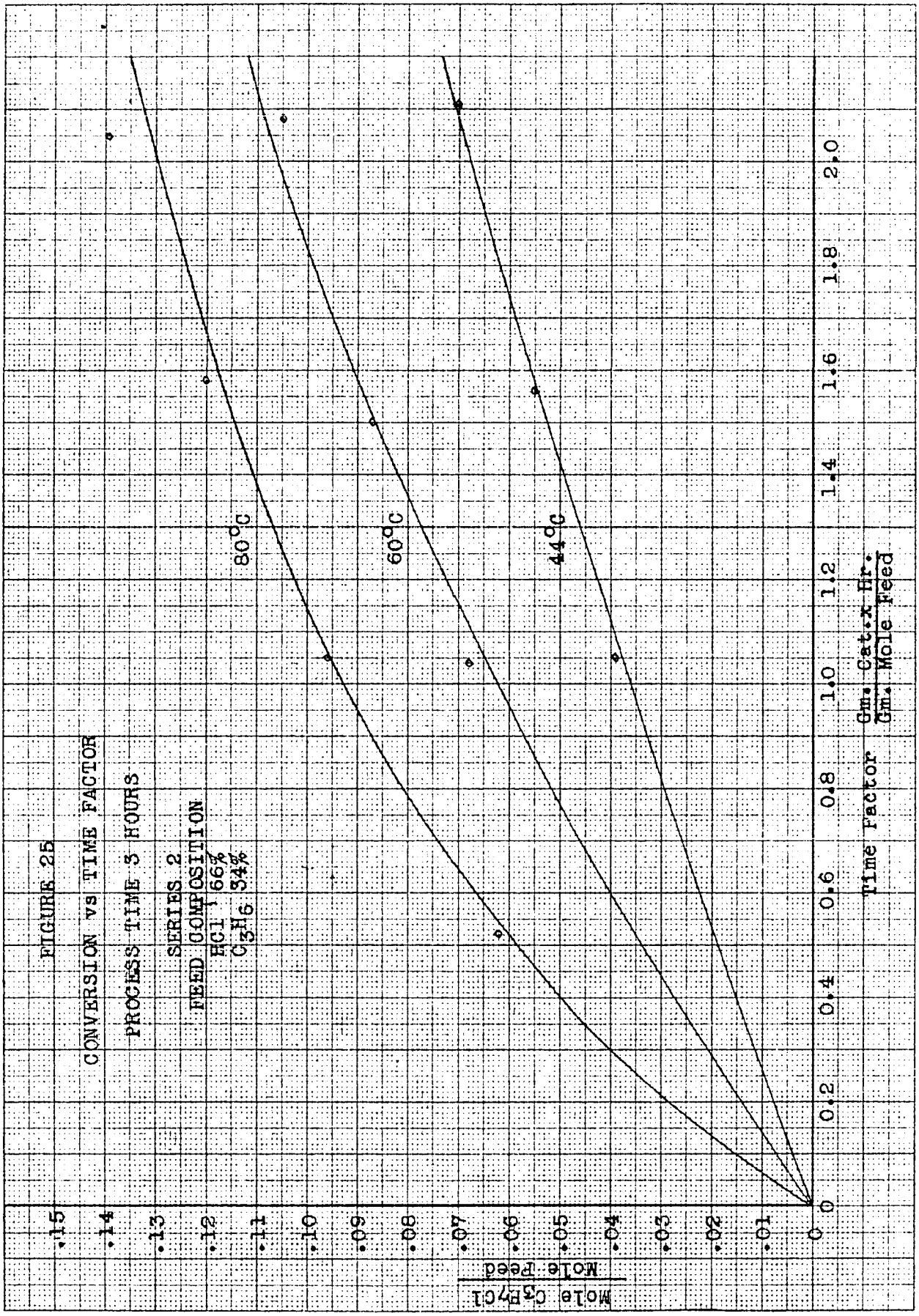
Graphical integration of Equation (51) was carried out to reproduce the experimental conversion versus time factor curves. The values of the constants found by the method of least squares were adjusted by trial and error, and the integration repeated until an equation for the reaction rate was found that would best fit the experimental data. Only the data from Series 1 and 2 were used for this work. The conversion curve for Series 4 was then checked using the final rate equation.

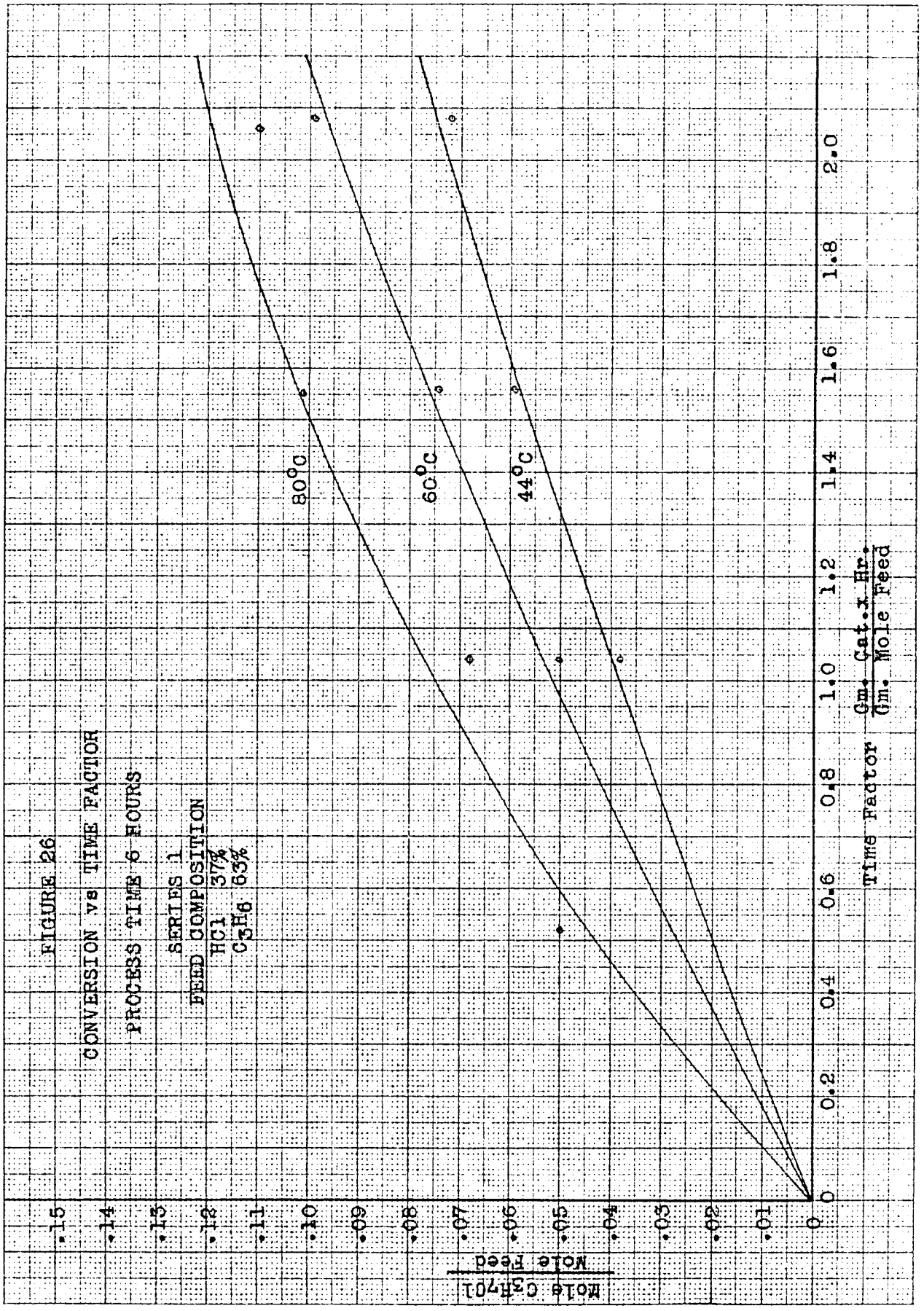
The final conversion curves are shown in Figures 21 through 27 for the various feed compositions at process times of zero, three, and six hours. The experimental points are indicated on each curve. Figure 23 shows that there is fair

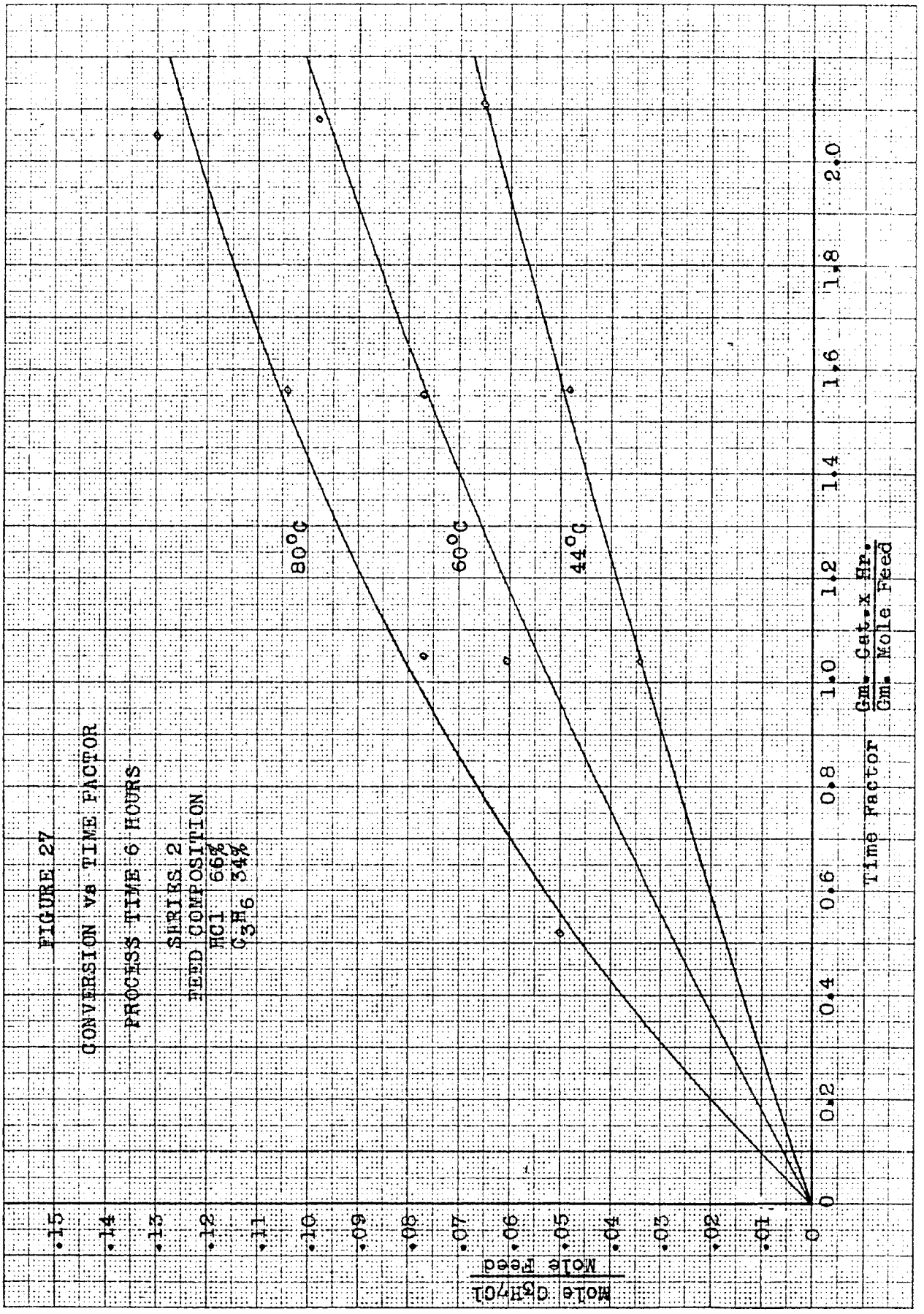












agreement between the derived equation at 60°C and process time zero hours and the experimental data of Series 4, even though this series was not used to evaluate the constants in the equation.

Plots of the values of the constants versus temperature at various process times are shown in Figures 28 through 30. Values of the constants at the various temperatures are plotted versus process time in Figures 31 through 33. These plots show the linearity of the values of the constants with time and temperature. On the basis of these plots the following equations were derived for each constant in terms of the process time τ, in hours and the temperature t, in degrees centigrade.

$$\begin{aligned} A &= (0.330 - 0.0111\ t)\ \tau - 1.32 + 0.100\ t \\ B &= (0.0128\ t - 0.351)\ \tau + 5.78 - 0.148\ t \\ C &= (0.0136\ t - 0.415)\ \tau + 4.82 - 0.131\ t \end{aligned} \qquad (52)$$

Values of the constants calculated by these equations are compared with the experimental values in Table IV (see next page).

Method B

Equation (38), developed using the method of Wynkoop and Wilhelm, can also be used to correlate the kinetic data. The values of the variable terms

Table IV

Calculated and Experimental Values of Constants A, B, and C

$$r = \frac{(y_{HCl}y_{C_3H_6} - \frac{y_{C_3H_7Cl}}{\pi K})}{(A + By_{HCl} + Cy_{C_3H_6})^2}$$

Process Time 0 Hours

	80°C			60°C			44°C		
	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.
A	6.65	6.68	+0.3	4.68	4.68	0.00	3.07	3.08	+.01
B	-6.05	-6.06	-.01	-3.12	-3.10	+.02	-0.73	-0.73	.00
C	-5.68	-5.66	+.02	-3.00	-3.04	-.04	-0.96	-0.94	+.02

Process Time 3 Hours

	80°C			60°C			44°C		
	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.
A	5.04	5.01	-.03	3.60	3.67	+.07	2.58	2.61	+.03
B	-3.97	-4.04	+.07	-1.90	-1.85	+.05	-0.04	-0.09	-.05
C	-3.70	-3.64	+.06	-.180	-1.84	-.04	-0.35	-0.39	-.04

Process Time 6 Hours

	80°C			60°C			44°C		
	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.	Exp.	Calc.	Dev.
A	3.30	3.33	+.03	2.65	2.66	+.01	2.05	2.16	+.11
B	-1.93	-2.02	-.09	-0.70	-0.60	+.10	0.72	0.54	-.18
C	-1.68	-1.62	+.06	-0.60	-0.63	-.03	0.17	0.16	-.01

FIGURE 28

REACTION CONSTANT A
vs
TEMPERATURE

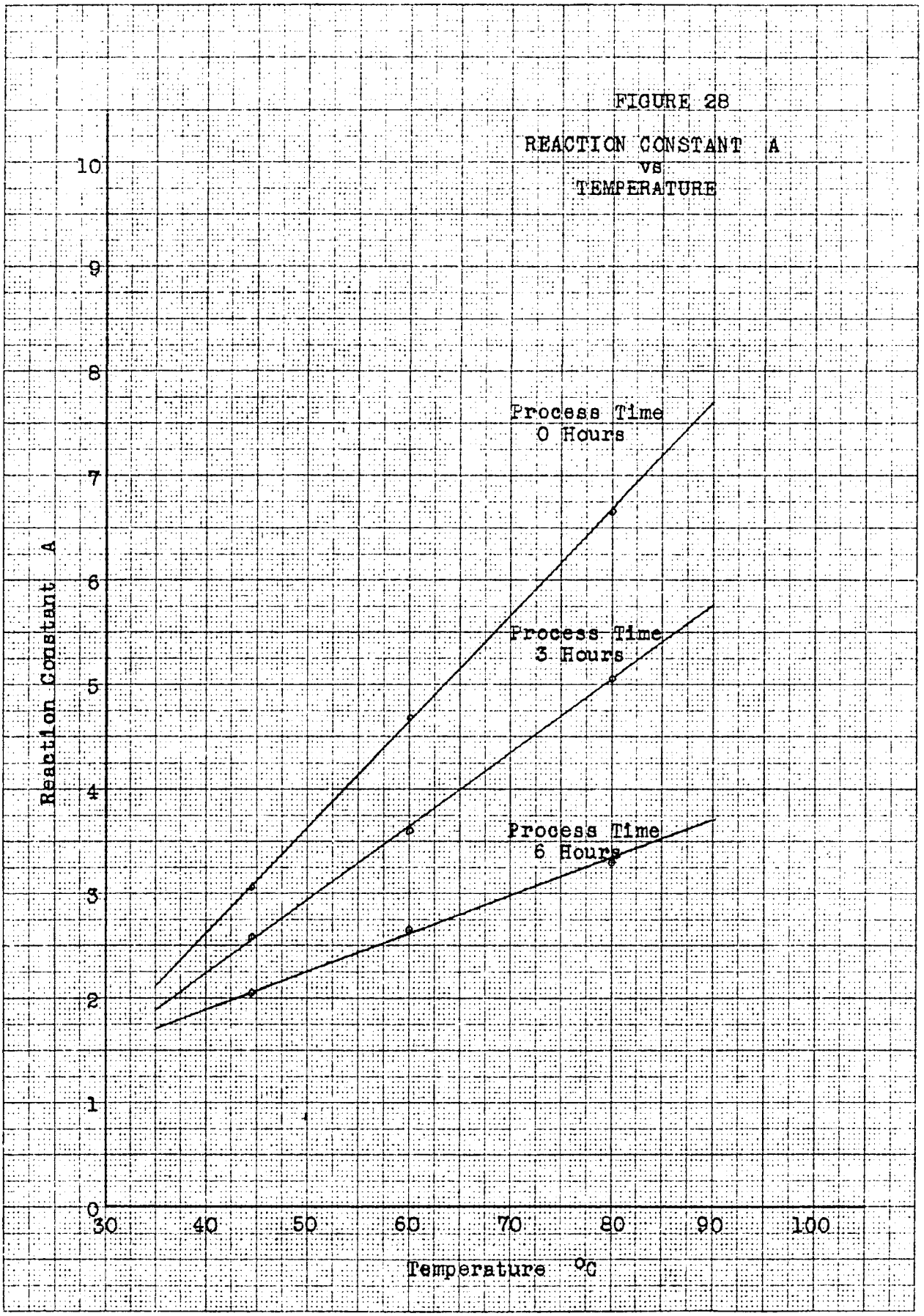


FIGURE 29

REACTION CONSTANT B
vs
TEMPERATURE

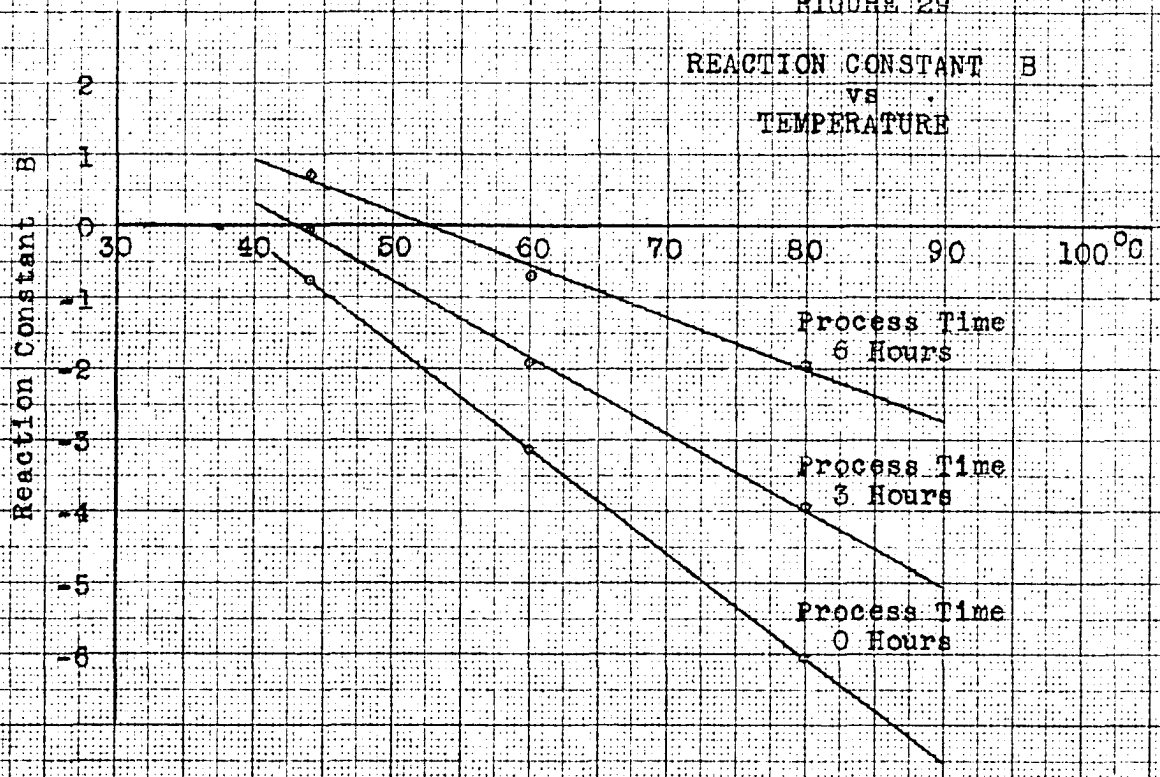
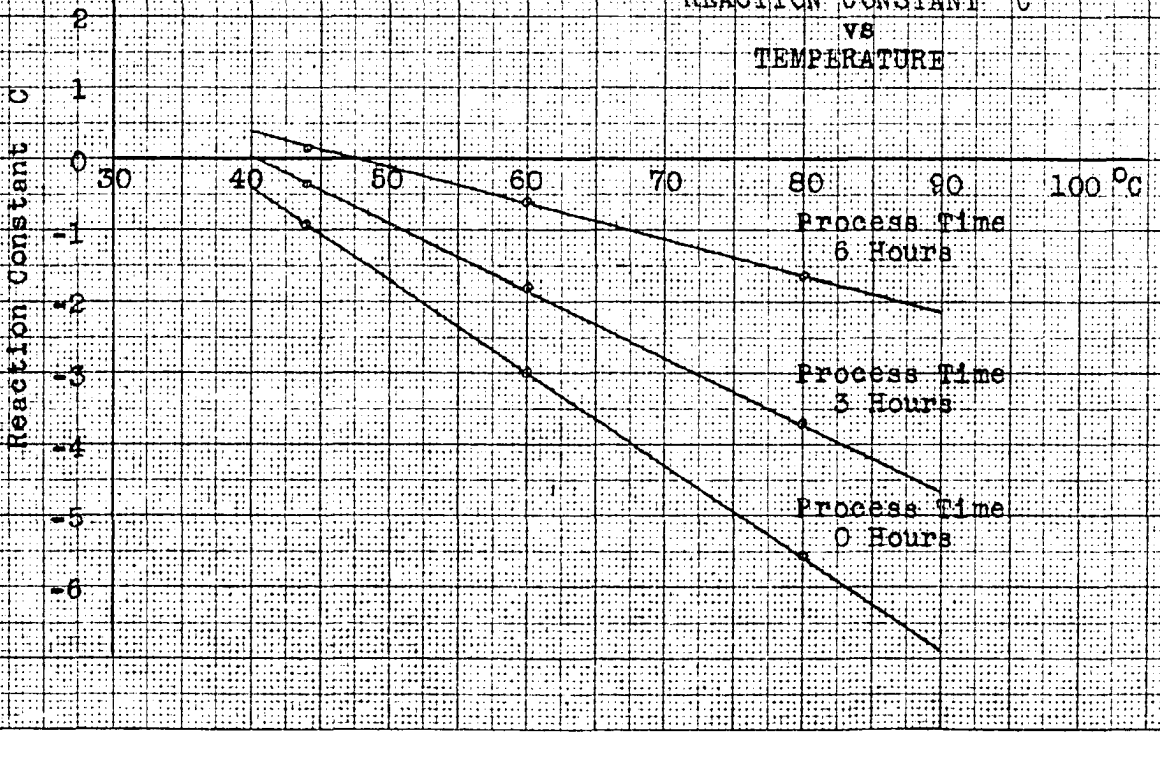


FIGURE 30

REACTION CONSTANT C
vs
TEMPERATURE



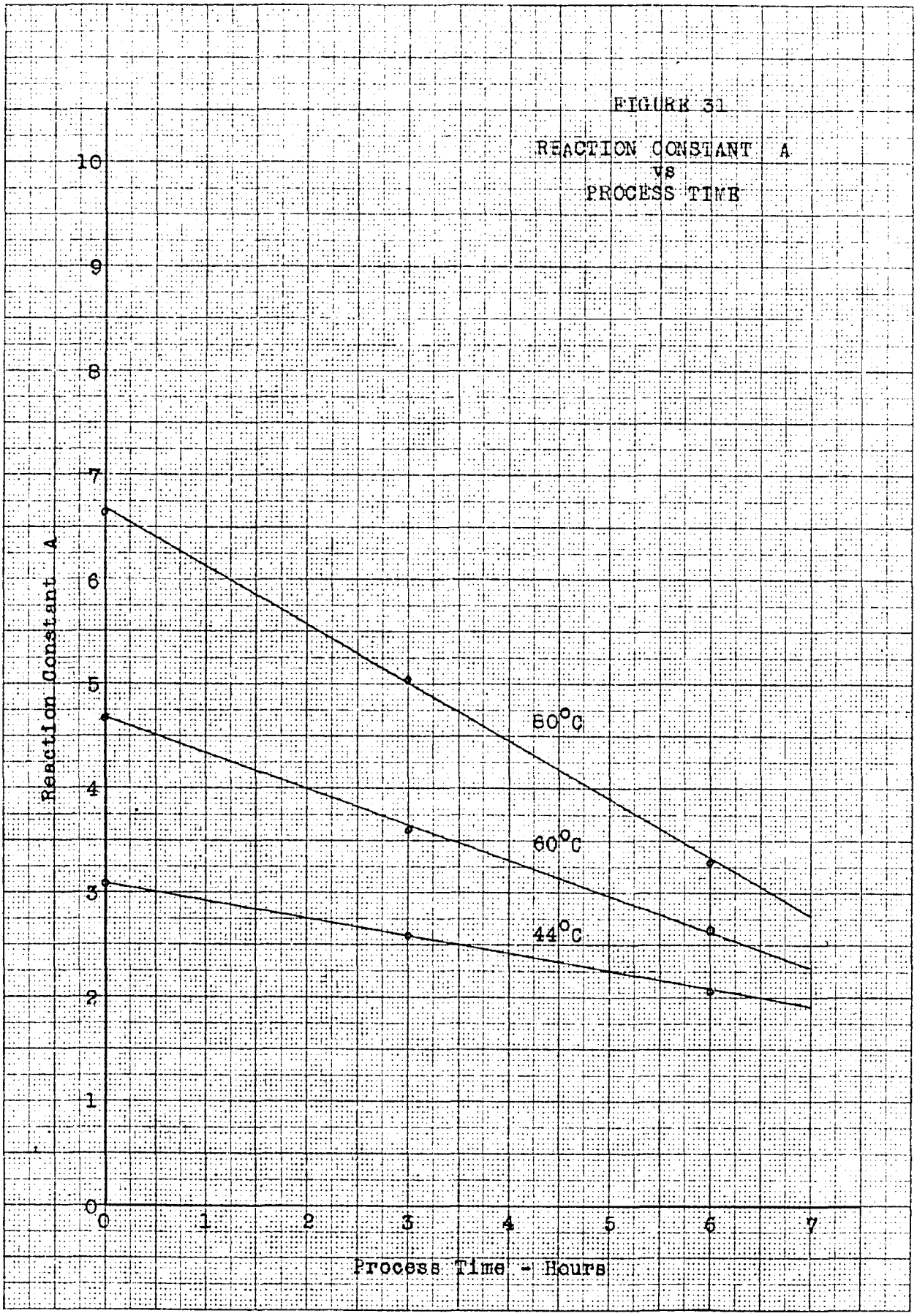


FIGURE 32

REACTION CONSTANT B
vs
PROCESS TIME

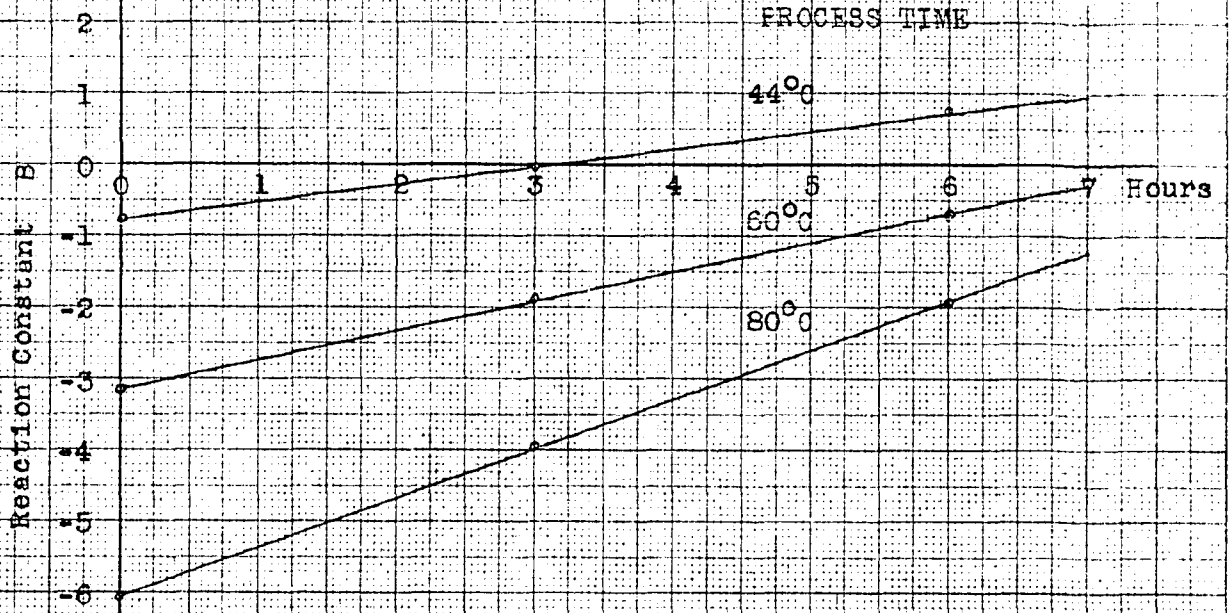
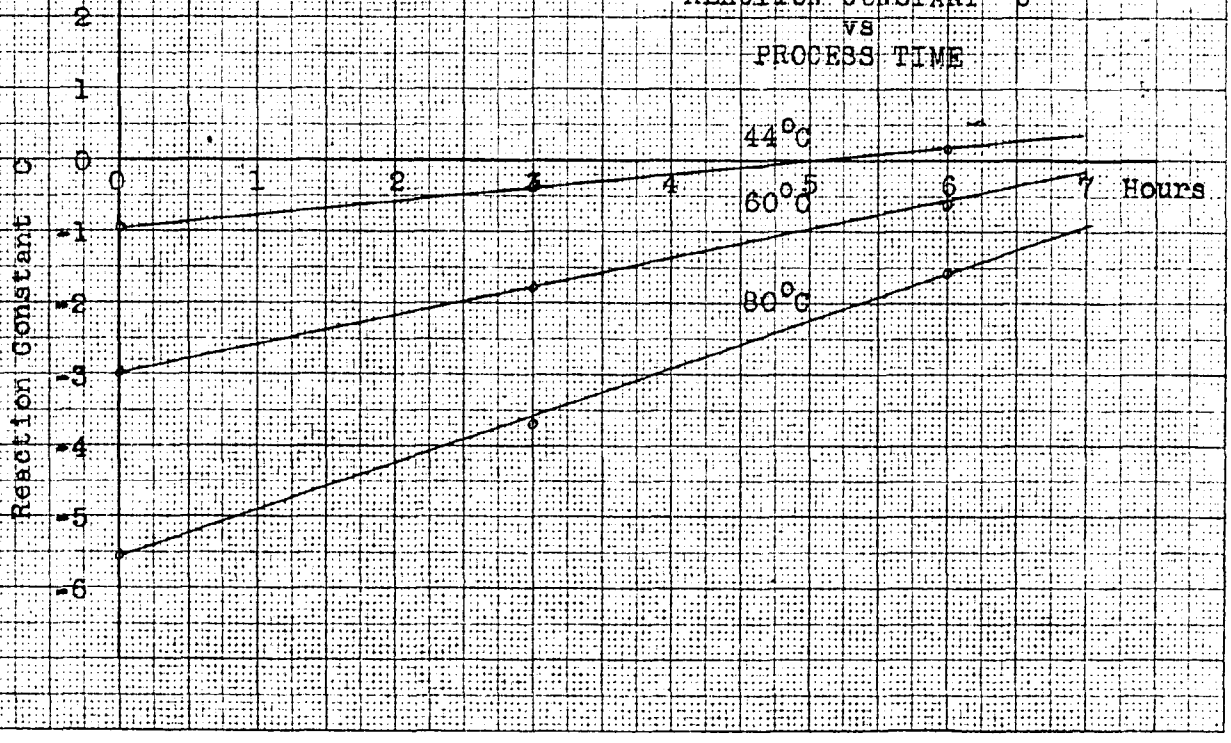


FIGURE 33

REACTION CONSTANT C
vs
PROCESS TIME



$$\frac{1}{R}\frac{(1 - y_{HCl})^2}{(1 - y_{HCl_o})^2}(y_{HCl_o} - y_{HCl})$$

and

$$\frac{y_{HCl}}{R}\frac{(1 - y_{HCl})^2}{(1 - y_{HCl_o})^2}(1 - 2y_{HCl_o} + y_{HCl}y_{HCl_o})$$

were plotted for Series 1 and 2 for each temperature, and the best straight line drawn through the points. The slopes and intercepts of these lines gave the values of the constants shown in Table V.

Table V

Values of Constants for the Equation

$$r = k\alpha_A\alpha_B\pi^2 y_{HCl}y_{C_3H_6} - k'\alpha_C\pi y_{C_3H_6}$$

	Process Time 0 Hours			Process Time 3 Hours			Process Time 6 Hours		
°C	80	60	44	80	60	44	80	60	44
$k\alpha_A\alpha_B$	0.736	0.342	0.198	0.538	0.302	0.176	0.364	0.244	0.151
$k'\alpha_C$	0.577	0.241	0.083	0.420	0.215	0.076	0.208	0.114	0.058

To obtain the conversion curves, Equation (37) was graphically integrated for each set of conditions.

$$\int_{y_{HCl_o}}^{y_{HCl}} \frac{dy_{HCl}}{k'\alpha_C\pi\frac{(1-y_{HCl})^2}{(1-y_{HCl_o})^2}(y_{HCl_o}-y_{HCl}) - k\alpha_A\alpha_B\pi^2 y_{HCl}\frac{(1-y_{HCl})^2}{(1-y_{HCl_o})^2}(1-2y_{HCl_o}+y_{HCl}y_{HCl_o})} = \int_0^W \frac{dW}{F}$$

$$\int_{y_{HCl_o}}^{y_{HCl}} \frac{dy_{HCl}}{f(y_{HCl})} = \frac{W}{F} \qquad (53)$$

The results of this integration are shown in Figures 34 through 39, for Series 1 and 2 at process times of zero, three and six hours. The experimental points are indicated on these plots. Figure 40 shows the agreement of the equation at 60°C with the experimental data of Series 4.

The values of the constants given in Table V are plotted versus reciprocal absolute temperatures in Figures 41 and 42 and are plotted versus process time in Figures 43 and 44. Since the logarithms of the constants are linear functions of the reciprocal absolute temperature, the velocity constants can be expressed in the form of the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}}$$

The values of the frequency factor, A, and the activation energy, E, for the process times of zero, three, and six hours are listed in Table VI and plotted in Figures 45 and 46. From these plots can be seen that the constants are not simple linear functions of the process time.

Table VI

Values of A and E in Arrhenius Equation

$$k = Ae^{-\frac{E}{RT}}$$

	$k\alpha_A\alpha_B$		$k'\alpha_C$	
Process Time	E $\frac{\text{K. cal}}{\text{Gm.mol}}$	A $\frac{\text{Gm.Mol}}{\text{Gm.catxHr.}}$	E $\frac{\text{K. cal}}{\text{Gm.mol}}$	A $\frac{\text{Gm.Mol}}{\text{Gm.catxHr.}}$
0	8.02	6.64×10^4	11.80	1.25×10^7
3	6.98	1.13×10^4	11.02	3.03×10^6
6	5.48	9.48×10^2	8.56	4.58×10^4

In order to express the velocity constants as a function of process time and temperature, the slopes of the lines in Figures 43 and 44 were plotted versus absolute temperature. This plot was a straight line for both velocity constants on a semi-log plot. The intercepts of the lines of Figures 43 and 44 were plotted versus reciprocal absolute temperature and the equation of the curves obtained. These calculations gave the following empirical expressions for the reaction velocity constants as a function of process time, τ, in hours and temperature, T, in degrees Kelvin.

$$k\alpha_A\alpha_B = 6.64 \times 10^4 e^{-\frac{8020}{RT}} - 9.29 \times 10^{-11}\,\tau\, e^{0.0576T}$$

$$k'\alpha_C = 8.91 \times 10^5 e^{-\frac{10,000}{RT}} - 6.00 \times 10^{-10}\,\tau\, e^{0.0524T} \qquad (54)$$

Values of the velocity constants calculated by Equation (54) are compared with the experimental values in Table VII.

Table VII

Calculated and Experimental Values of the Reaction Velocity Constants $k\alpha_A\alpha_B$ and $k'\alpha_C$

	Process Time 0 hours					
	80°C		60°C		44°C	
	Exp.	Calc. Dev.	Exp.	Calc. Dev.	Exp.	Calc. Dev.
$k\alpha_A\alpha_B$	0.736	.706 -.030	0.342	.361 +.019	0.198	.190 -.008
$k'\alpha_C$	0.577	.583 +.006	0.241	.239 -.002	0.083	.111 +.028
	Process Time 3 hours					
	80°C		60°C		44°C	
	Exp.	Calc. Dev.	Exp.	Calc. Dev.	Exp.	Calc. Dev.
$k\alpha_A\alpha_B$	0.538	.520 -.018	0.302	.300 -.002	0.176	.158 -.018
$k'\alpha_C$	0.420	.384 -.036	0.215	.170 -.045	0.076	.082 +.006
	Process Time 6 hours					
	80°C		60°C		44°C	
	Exp.	Calc. Dev.	Exp.	Calc. Dev.	Exp.	Calc. Dev.
$k\alpha_A\alpha_B$	0.364	.333 -.031	0.244	.240 -.004	0.151	.126 -.025
$k'\alpha_C$	0.208	.185 -.023	0.114	.101 -.013	0.058	.053 -.005

FIGURE 34

MOLE FRACTION HCl vs TIME FACTOR

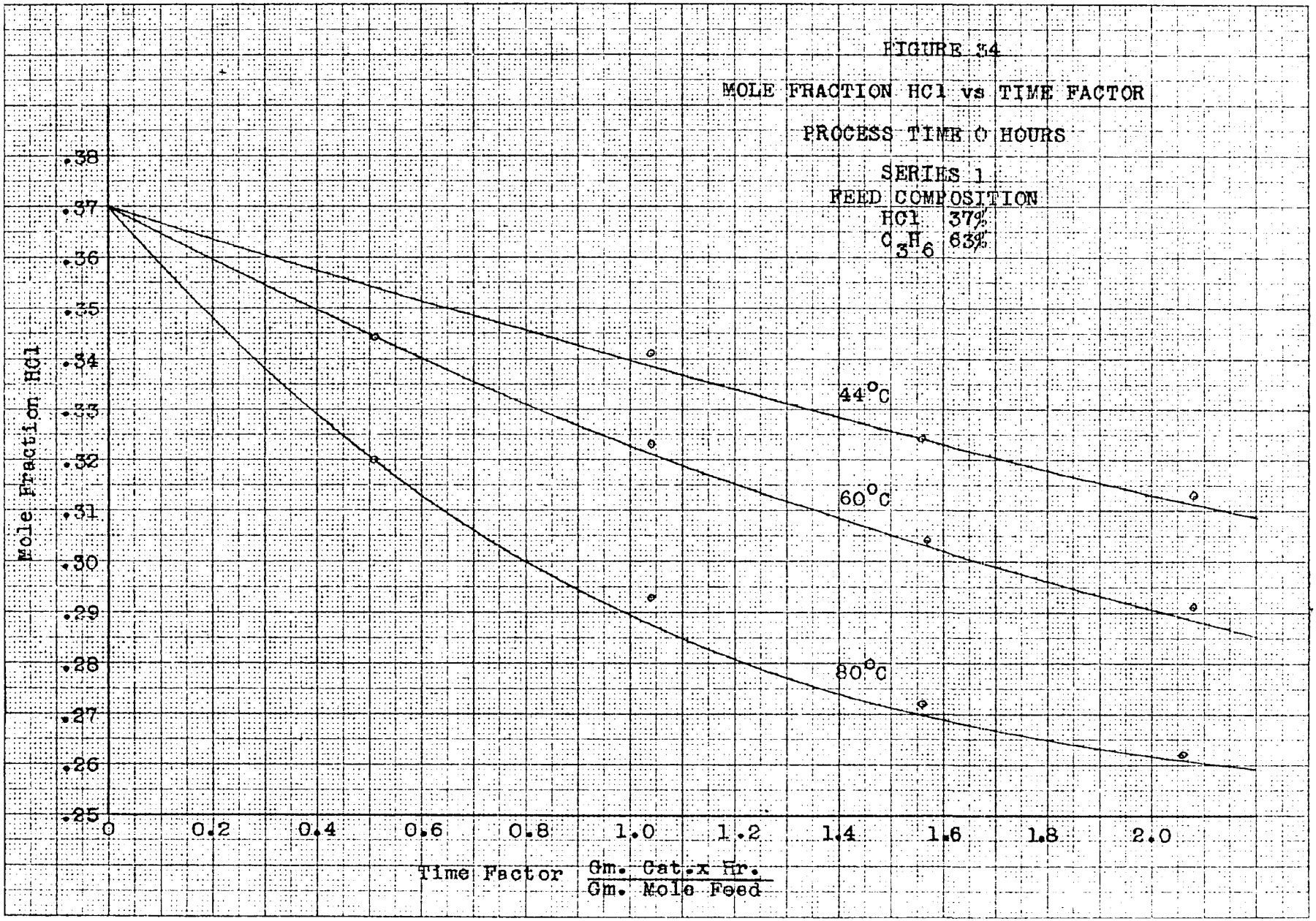
PROCESS TIME 0 HOURS

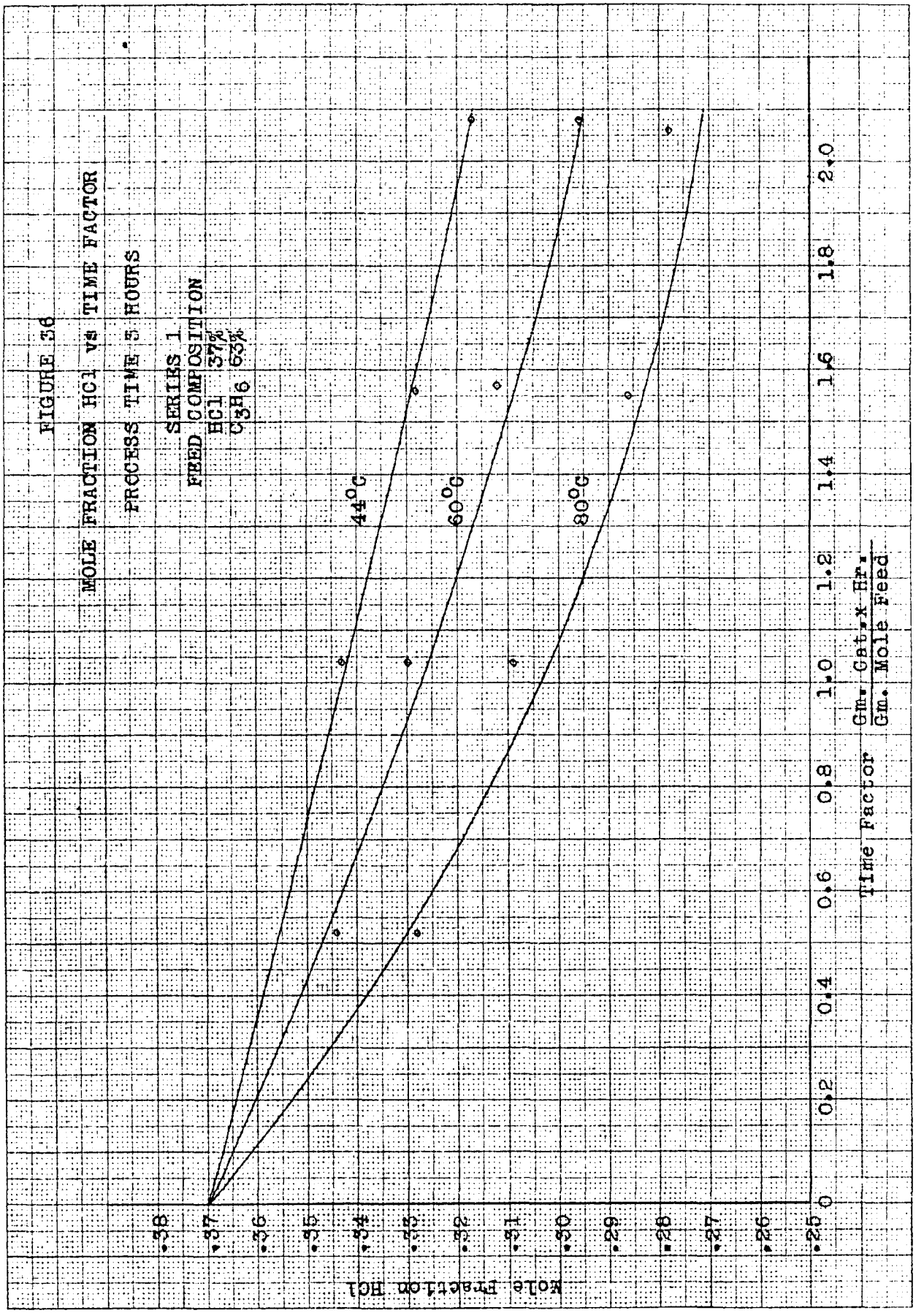
SERIES 1

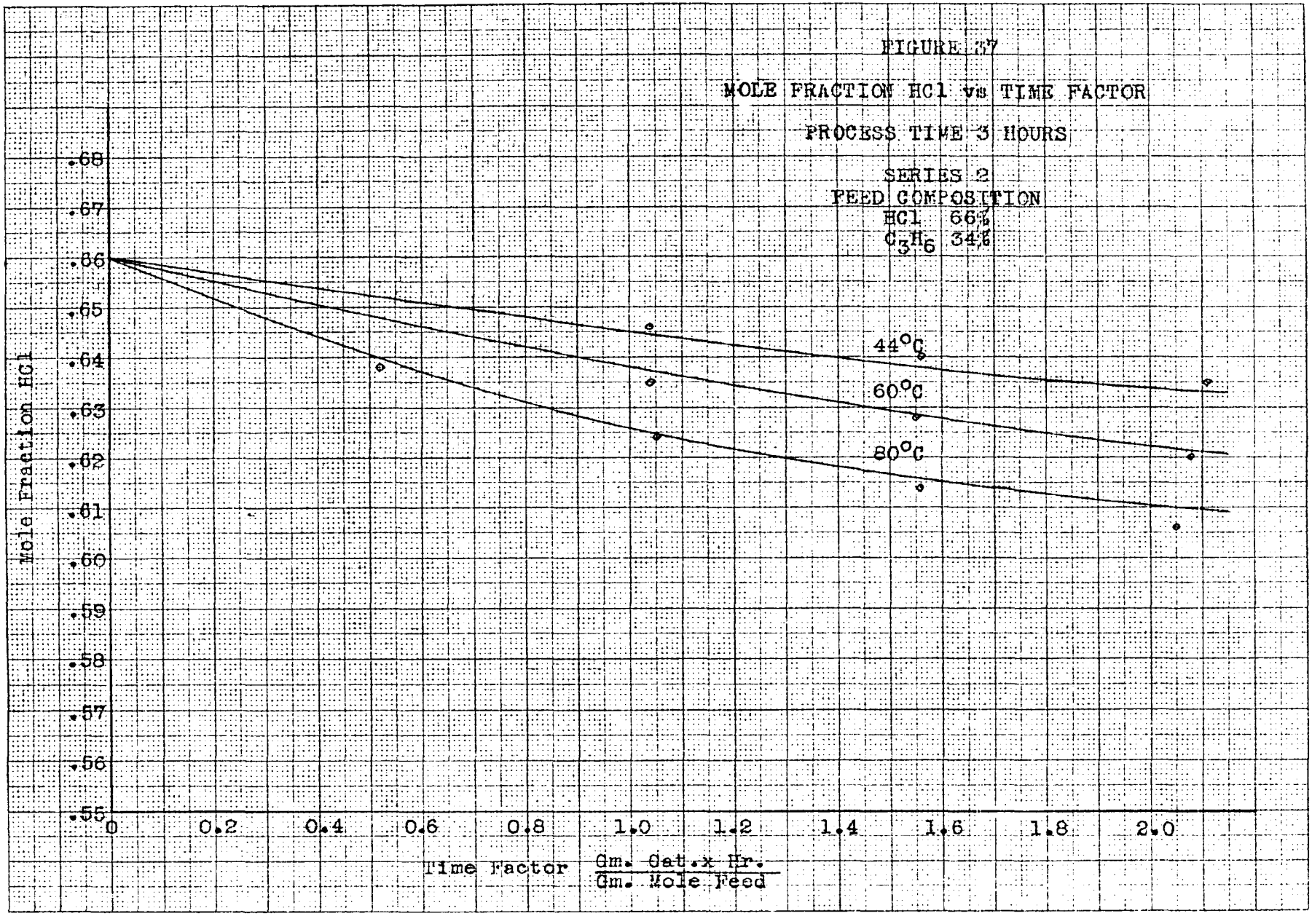
FEED COMPOSITION

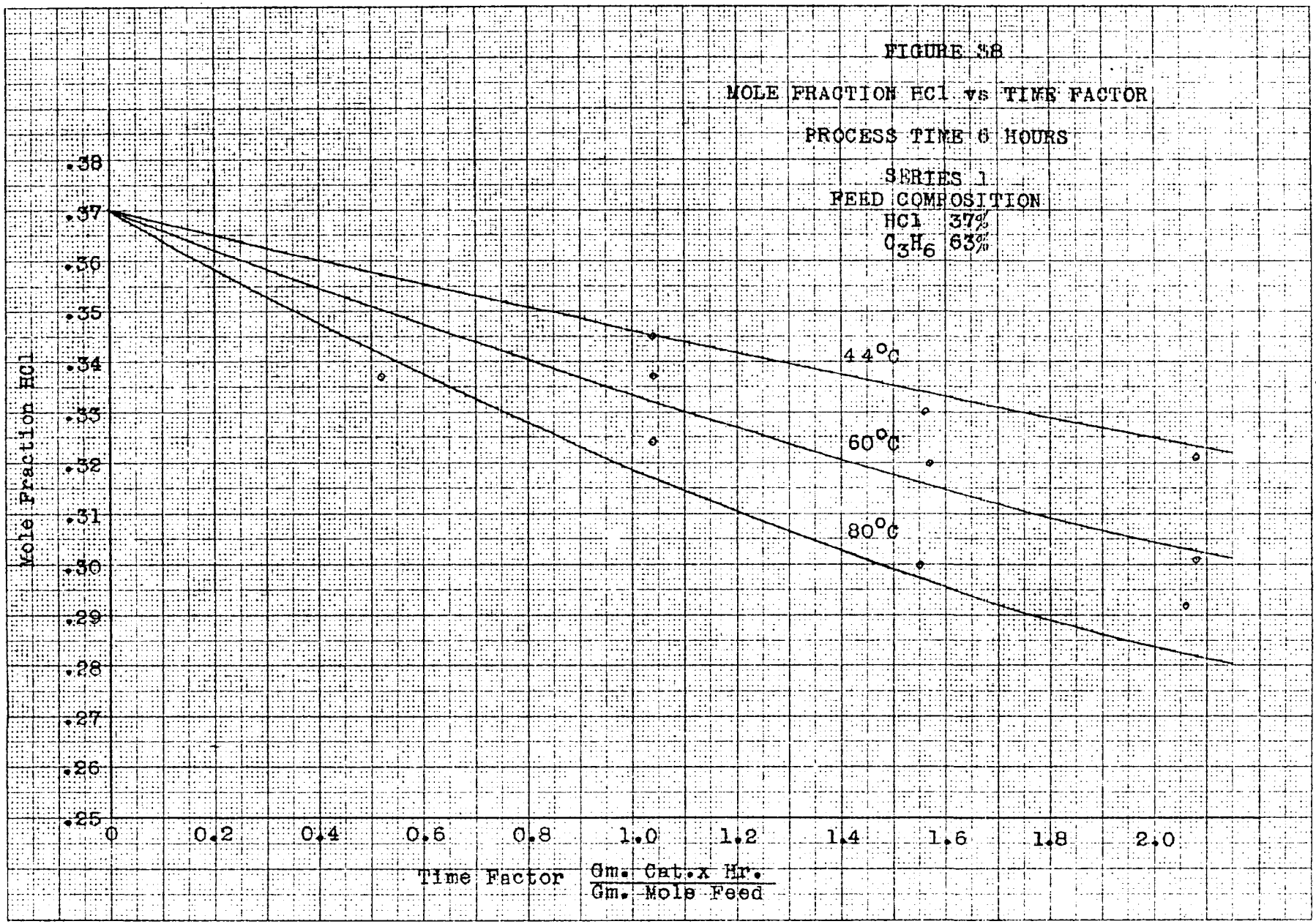
HCl 37%

C_3H_6 63%









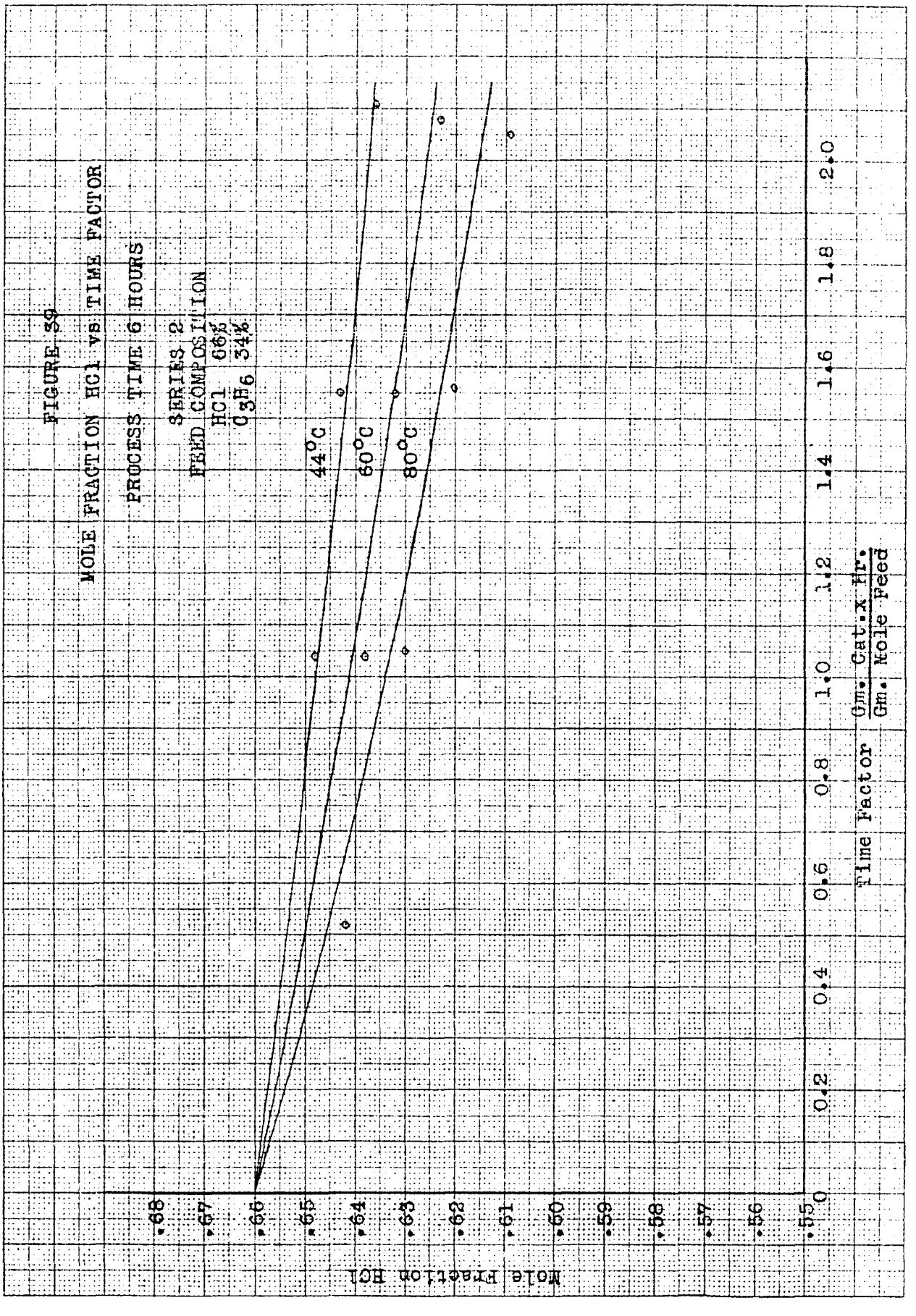
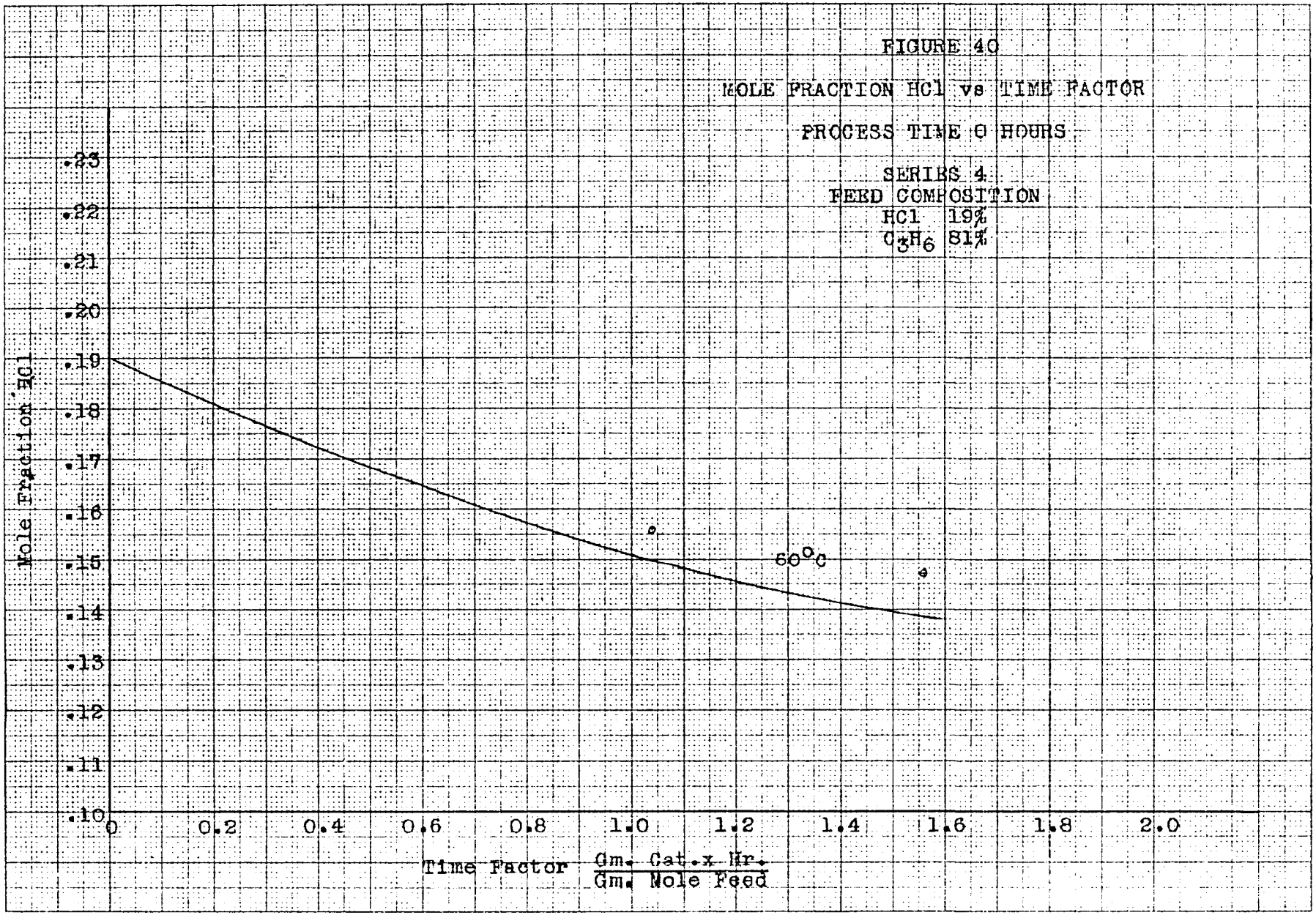


FIGURE 40

MOLE FRACTION HCl vs TIME FACTOR

PROCESS TIME 0 HOURS

SERIES 4
FEED COMPOSITION
HCl 19%
C_3H_6 81%



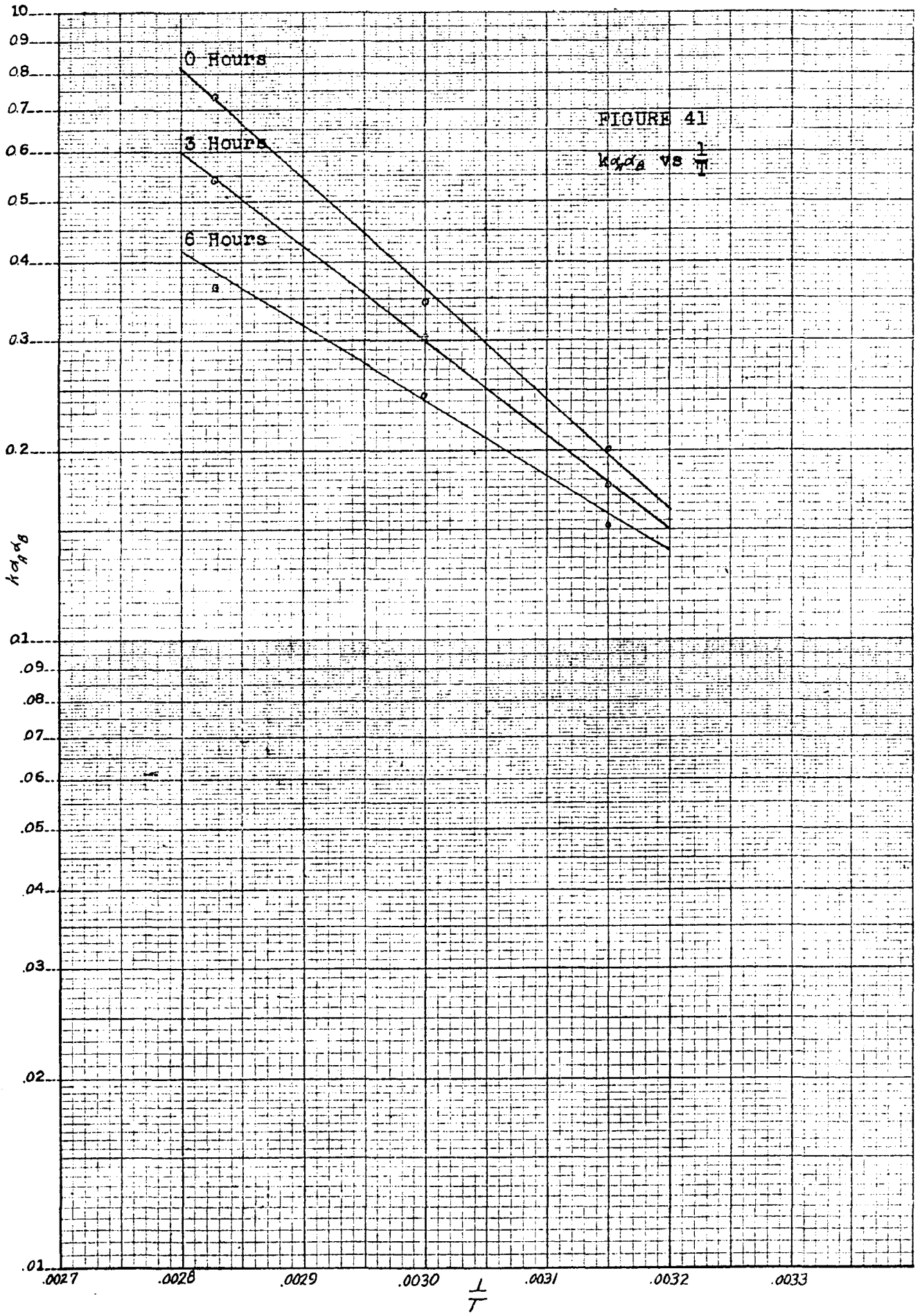


FIGURE 41

$k\alpha_A\alpha_B$ vs $\frac{1}{T}$

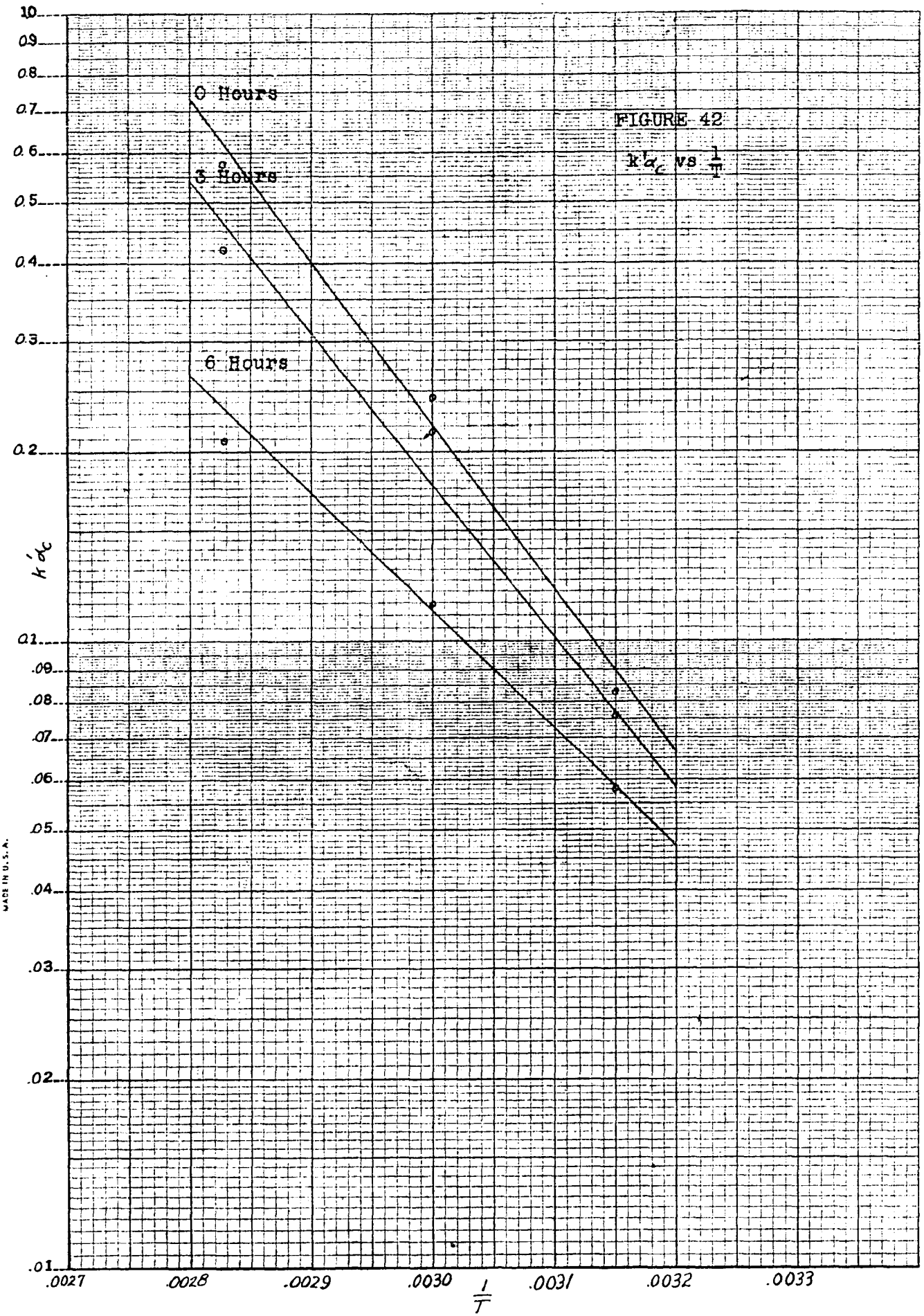


FIGURE 42

$k'\alpha_c$ vs $\frac{1}{T}$

FIGURE 43

$k'\alpha_c$ vs PROCESS TIME

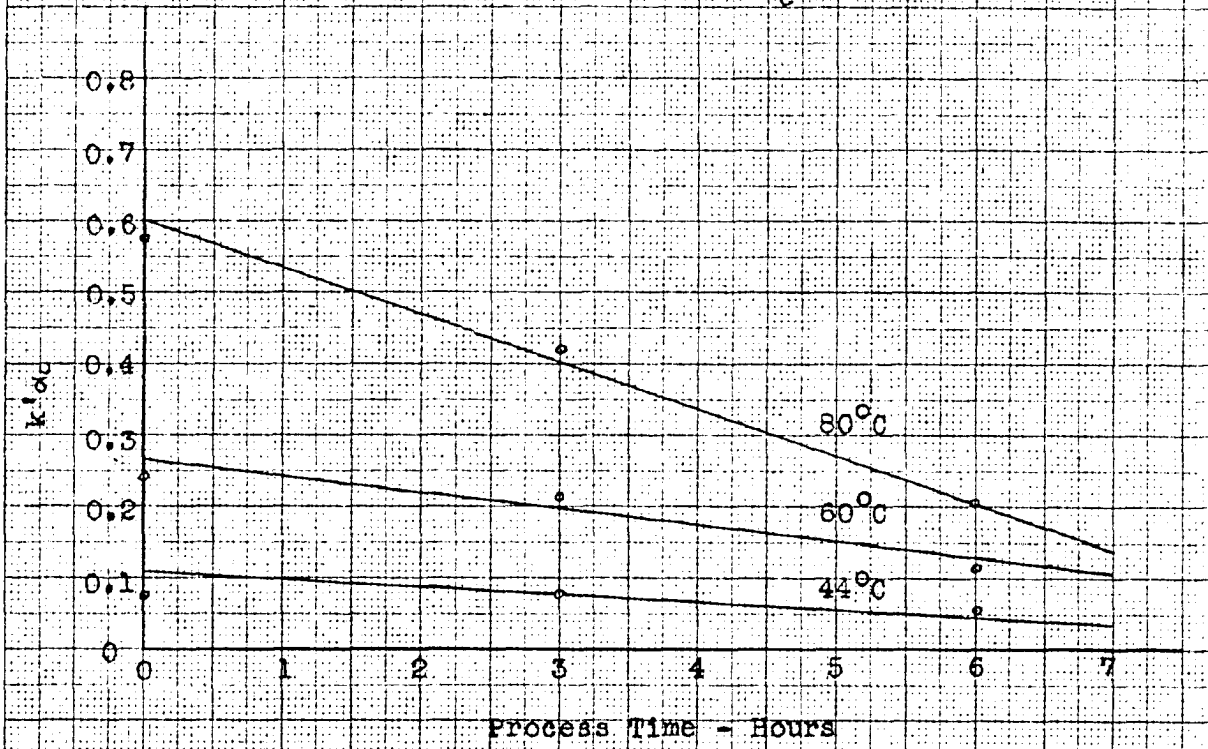
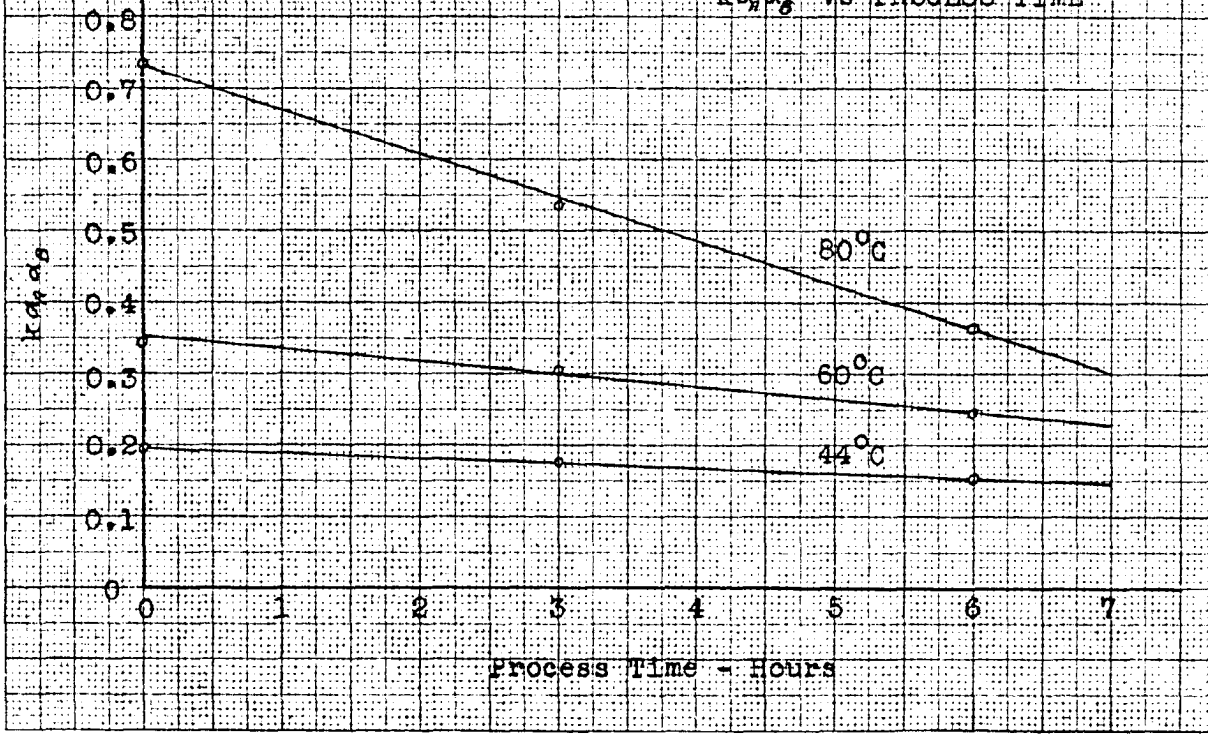


FIGURE 44

$k\alpha_n\alpha_B$ vs PROCESS TIME



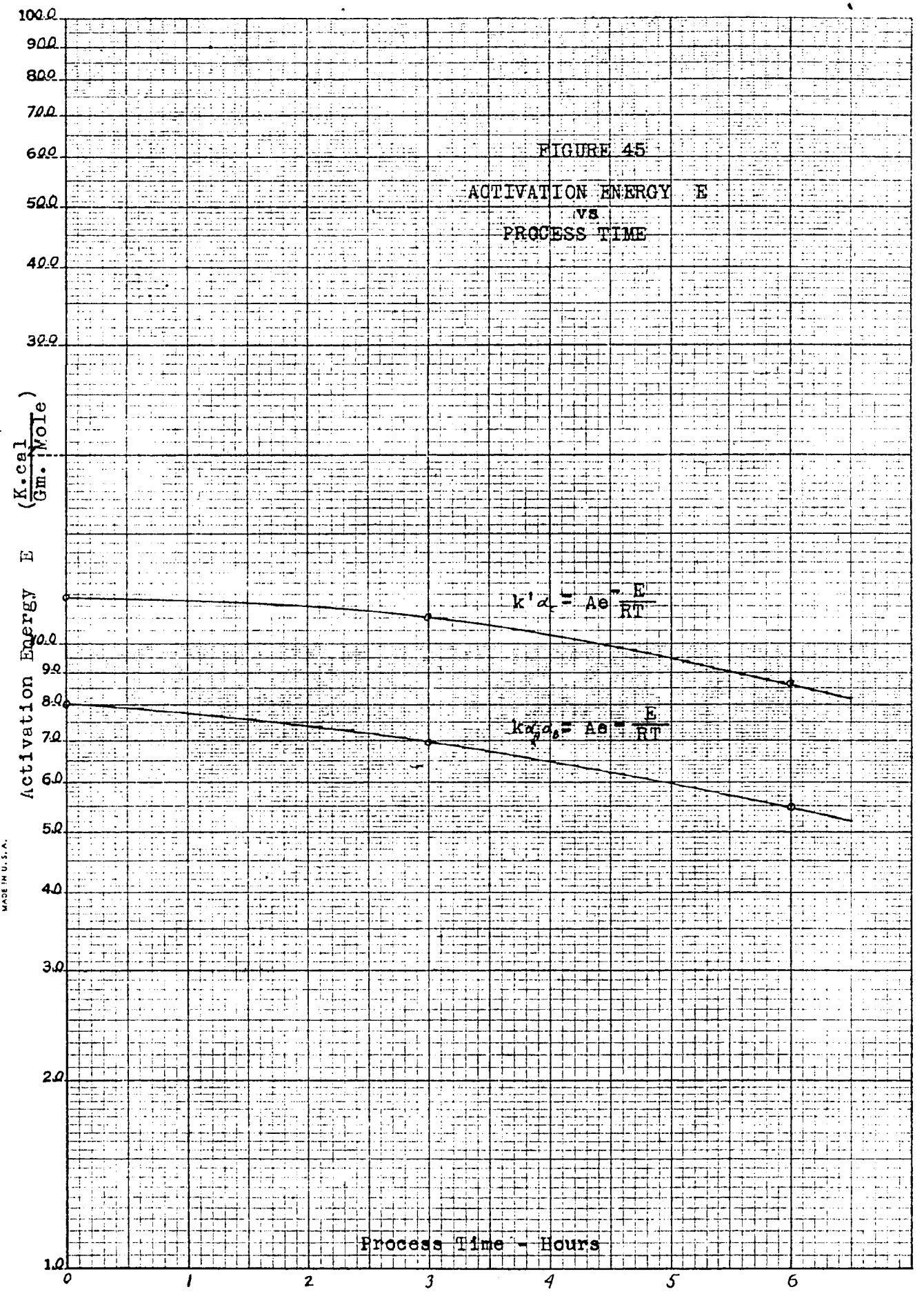
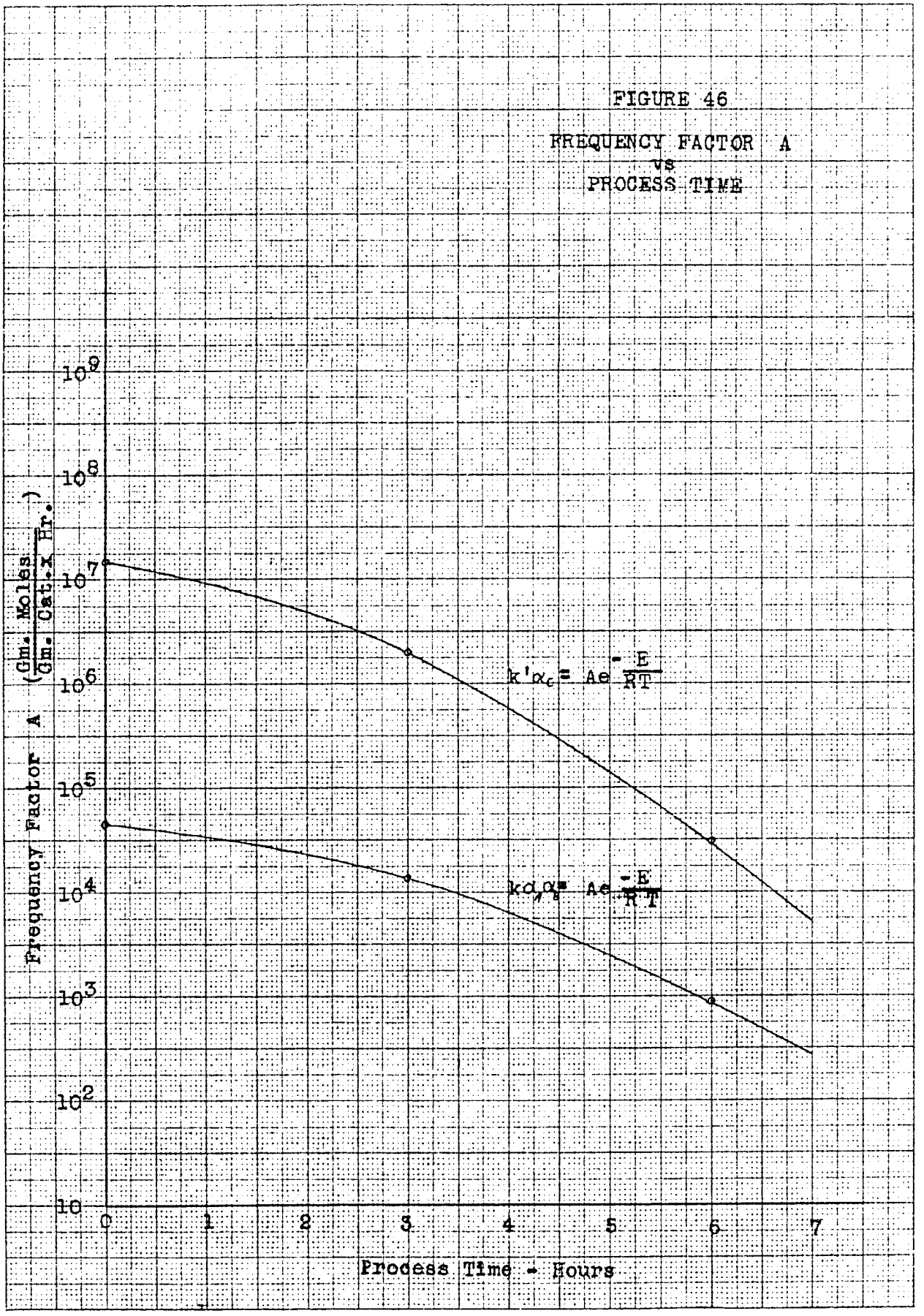


FIGURE 46

FREQUENCY FACTOR A
vs
PROCESS TIME



DISCUSSION OF RESULTS

CHAPTER IX

Both Method A and Method B give satisfactory correlations of the kinetic data over the range of variables used in this study. Method A possibly is the better of the two since the agreement of the equations to the experimental data is better throughout the range of time factors. This is especially true at process times other than zero hours. By comparing Figures 23 and 40 it can be seen that the two methods give essentially the same results when used with a feed composition of 19% hydrogen chloride. Figures 34 through 39 show that the curves obtained from Method B deviate appreciably from the experimental values at high time factor. The fact that this deviation is low for Series 1 and high for Series 2 in all cases indicates that use of the correlationship for feed compositions greater than 66% hydrogen chloride and less than 37% hydrogen chloride would tend to give erroneous results at high time factors.

In addition, Method B can be considered only as an empirical equation because of the value of the ratio $\frac{k\alpha_A\alpha_B}{k'\alpha_C}$. From Equation (35) it can be seen that this ratio should be the overall equilibrium constant if the surface reaction were the controlling step. In Table VIII the ratio $\frac{k\alpha_A\alpha_B}{k'\alpha_C}$ is compared with the value of the overall equilibrium constant, K,

as calculated from the thermodynamic properties of the constituents of the system. Although the values of the ratios are nearly the same at the different process times, the variation of the ratio with temperature does not correspond

Table VIII

Values of $\frac{k\alpha_A\alpha_B}{k'\alpha_C}$ and the Equilibrium Constant, K

	Process Time 0 Hours			Process Time 3 Hours			Process Time 6 Hours		
°C	80	60	44	80	60	44	80	60	44
$\frac{k\alpha_A\alpha_B}{k'\alpha_C}$	1.28	1.42	2.39	1.28	1.41	2.32	1.75	2.14	2.60
K	2.32	7.61	22.4	2.32	7.61	22.4	2.32	7.61	22.4

to the variation of the equilibrium constant with temperature. Thus, the original assumptions as to the expressions for the adsorption isotherms are probably not correct for these components, and Equation (35) can not be considered the true kinetic equation for this reaction. The correlation by Method A incorporates the equilibrium constant when evaluating the reaction constants so that a similar comparison can not be made.

Although the reaction velocity constant and the individual adsorption constants of Equation (21) can not be evaluated with these data, conclusions of a general nature may be drawn. The definitions of the reaction constants are

listed here for convenience.

$$A = \frac{1}{(k_s L K_{HCl} K_{C_3H_6})^{1/2}} \left(\frac{1}{\pi} + K_{C_3H_7Cl}\right)$$

$$B = \frac{1}{(k_s L K_{HCl} K_{C_3H_6})^{1/2}} \left(K_{HCl} - K_{C_3H_7Cl}\right)$$

$$C = \frac{1}{(k_s L K_{HCl} K_{C_3H_6})^{1/2}} \left(K_{C_3H_6} - K_{C_3H_7Cl}\right)$$

Referring to Table V, it can be seen that the ratio of B to C is approximately 1.1 in nearly every case. This would indicate that the values of the adsorption equilibrium constants K_{HCl} and $K_{C_3H_6}$ are nearly equal with K_{HCl} being slightly larger. This is substantiated by the slopes of the lines in Figure 20. Also since B and C are usually negative, $K_{C_3H_7Cl}$ must be larger than either K_{HCl} or $K_{C_3H_6}$. The fact that A increases while B and C become more negative with increased temperature would indicate that $K_{C_3H_7Cl}$ increases with temperature at a faster rate than $(k_s L K_{HCl} K_{C_3H_6})^{1/2}$ and also at a faster rate than either K_{HCl} or $K_{C_3H_6}$. If all the adsorption equilibrium constants increased with temperature at the same rate, the values of B and C would become more positive at increased temperature since $(k_s L K_{HCl} K_{C_3H_6})^{1/2}$ must increase with temperature. This would also be the case if K_{HCl} and $K_{C_3H_6}$ increased with temperature at a greater rate than $K_{C_3H_7Cl}$.

Proper interpretation of the effect of process time on the values of the constants A, B, and C is not apparent from these definitions. The effect of fouling of a catalyst may be introduced into the rate equation by either of two ways. First, a "fouling factor" may be introduced as a multiplying factor on the reaction velocity constant, ksL, considering that fouling merely reduces L, the total member of active centers on the catalyst surface. The second method is the introduction of another term in the denominator, or adsorption term, of the rate equation with the view that fouling has the same effect as the adsorption of a constituent on the active centers. This latter procedure has been used successfully (5). In either case the fouling factor would be a function of temperature, conversion, and process period length.

If the first method of correcting for catalyst fouling were applicable in this case, the absolute values of all three constants should increase with process time. Since this is not the case, the first method does not apply to the reaction constants obtained in the correlation by Method A. It should be noted, however, that the reaction constants $k\alpha_A\alpha_B$ and $k'\alpha_C$ do decrease with time indicating that this type of correction is applicable in the case of Method B.

From Equations (21) and (50) it can be shown that the following equation is true.

$$A + By_A + Cy_B = \frac{1}{(ksLK_AK_B)^{1/2}} \left(\frac{1}{\Pi} + y_AK_A + y_BK_B + y_RK_R\right) \qquad (55)$$

According to the second method of introducing a fouling factor, a term J, which is a function of conversion, temperature, and time, can be introduced into the adsorption term in the right-hand side of Equation (55). Eliminating y_R, the equation becomes

$$A + By_A + Cy_B = \frac{1}{(k_s L K_A K_B)^{1/2}} \left[\left(\frac{1}{\pi} + K_R\right) + (K_A - K_R)y_A + (K_B - K_R)y_B + J \right] \tag{56}$$

Each of the terms in Equation (56) are functions of temperature, and J is a function of y_A, y_B, and time as well as temperature.

If the expressions for A, B, and C given by Equation (52) are substituted into the left-hand side of Equation (56) and the terms rearranged, the following expression results.

$$\begin{aligned} A + By_{HCl} + Cy_{C_3H_6} = {} & (-1.32 + 0.100t) + (5.78 - 0.148t)y_{HCl} \\ & + (4.82 - 0.131t)y_{C_3H_6} + \left[(0.330 - 0.0111t)\right. \\ & + (0.0128t - 0.351)y_{HCl} + (0.0136t - 0.415)y_{C_3H_6} \end{aligned} \tag{57}$$

Equations (56) and (57) are of the same form indicating that this method of introducing the effect of catalyst fouling applies in this case. Thus the effect of process time on the values of A, B, and C can not be interpreted on the basis of their original definitions. These definitions can be considered valid only at zero time and would require modifications to be applicable at any other time.

CONCLUSIONS

CHAPTER X

On the basis of this kinetic study of the catalytic vapor phase addition of hydrogen chloride to propylene over activated alumina, the following conclusions can be made.

1. Over the temperature range 44°C to 80°C isopropyl chloride is the only product present in the exit gases.

2. The activity of activated alumina as a catalyst for this reaction decreases with time.

3. The rate of reaction may be controlled either by the desorption of isopropyl chloride or by the surface reaction between adsorbed molecules of hydrogen chloride and adsorbed molecules of propylene.

4. The rate of reaction may be expressed by the equation

$$r = \frac{y_{HCl}y_{C_3H_6} - \frac{y_{C_3H_7Cl}}{\Pi K}}{(A + By_{HCl} + Cy_{C_3H_6})^2}$$

where $A = (0.330 - 0.0111t)\tau - 1.32 + 0.100t$

$B = (0.0128t - 0.351)\tau + 5.78 - 0.148t$

$C = (0.0136t - 0.415)\tau + 4.82 - 0.131t$

5. The rate of reaction may also be expressed by the equation

$$r = k\alpha_A\alpha_B\pi^2 y_{HCl}y_{C_3H_6} - k'\alpha_C\pi y_{C_3H_7Cl}$$

where

$$k\alpha_A\alpha_B = 6.64 \times 10^4 e^{-\frac{8020}{RT}} - 9.29 \times 10^{-11}\gamma e^{0.0576T}$$

$$k'\alpha_C = 8.91 \times 10^5 e^{-\frac{10,000}{RT}} - 6.00 \times 10^{-10}\gamma e^{0.0524T}$$

This equation is probably unreliable when used outside of the range of variables covered by this work.

NOMENCLATURE

A, B, C = constants

a_A, a_B, a_R = gas phase activities of components A, B, and R

a_m = particle area per unit mass of catalyst

a_p = average surface area per particle

b = constant in adsorption isotherm equation

c_A = surface concentration of adsorbed molecules of component A

c_{AB} = surface concentration of adjacently adsorbed molecules of A and B

c_l = surface concentration of vacant active centers

c_{Rl} = surface concentration of molecules of component R adjacent to vacant active centers

D_{Am} = average diffusivity of component A

F = flow rate of feed, gram moles per unit time

G = mass velocity

J = fouling factor

j_D = mass transfer factor

K_A, K_B, K_R = adsorption equilibrium constants

K = surface reaction equilibrium constant

$\mathbb{K}$ = overall equilibrium constant; $\mathbb{K} = \frac{K_A K_B K}{K_R}$

k, k' = reaction velocity constants for the surface reactions

k_A, k'_A = reaction velocity constants for the adsorption reactions

k_G = mass transfer coefficient

L = number of active centers per unit mass of catalyst

M_m = mean molecular weight

n = constant

p_A = partial pressure of component A

p_f = film pressure factor

r = rate of reaction, gram moles converted per (unit time)(unit mass of catalyst)

s = number of equidistant adjacent active centers

T = temperature, degrees Kelvin

t = temperature, degrees Centigrade

W = mass of catalyst

x = moles of reactant converted per mole of feed

y = mole fraction

GREEK SYMBOLS

$\alpha, \beta, \gamma, \delta, \epsilon$ = constants

θ = fraction of total active centers

π = total pressure, atmospheres

ρ = density of gas

τ = time, hours

μ = viscosity of gas

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APPENDIX

PART I

Discussion of Experimental Equipment and Procedure

A great deal of the work of this thesis consisted of developing satisfactory experimental equipment and an analytical procedure. The work can be separated into the development of (1) the reactor, (2) the purification system and improvement of catalyst activity, and (3) the method of analysis. Since reproducibility of results is an indication of the merit of the technique and analysis, a short discussion on reproducibility is included in this appendix.

Reactor

The first reactor used was a glass chromatographic tube 15 mm. I.D. and 150 mm. long. The tube was fitted with female ℔ 15/20 glass joints at each end. The male part of the joint was closed with a perforated glass plate so that when the reactor was assembled, the lower male joint acted as a catalyst support. The tube was wound with seven feet of 1 ohm per foot Nichrome wire and heavily insulated with glass wool. A preheater, made from a chromatographic tube 210 mm long, was wound with 10.5 feet of 1 ohm per foot Nichrome wire. The lower end was fitted with a female ℔ 19/38 glass joint. The preheater and reactor were joined by a connector consisting of a male ℔ 15/20 joint and a male ℔ 19/38 joint.

This intermediate section was fitted with a ball and socket joint on a side tube to permit insertion of a thermocouple which was sealed into one end of the glass joint. The tip of the thermocouple lay in the hollow of the male joint just above the catalyst bed. The preheater and connector were packed with 1/4 inch tabular alumina balls to provide heat transfer surface. Exit gas temperatures were read at the perforated plate of the lower male joint by a thermocouple sealed into a glass ball and socket joint joined to the exit standard taper joint.

The idea behind the design of this reactor was that after the heating element brought the catalyst bed to temperature, the heat of reaction would maintain this temperature with small radial temperature gradients. For this reaction, however, the reactor was unsatisfactory. The heat of reaction was so high that the catalyst became overheated with the result that the particles became coated with a black deposit and the catalyst activity decreased very rapidly. To make a reactor of this type work satisfactorily would require a diluent, such as nitrogen, in the feed gas and high flow rates in order to remove the heat of reaction. It is questionable as to whether axial temperature gradients could ever be reduced to a low value in this type of reactor, since by the nature of catalytic reactions, the entering feed composition would tend toward higher rates of reaction at the bed entrance with subsequent greater evolution of heat. If

the heat of reaction were not removed efficiently, a hot spot would develop at the bed entrance. These hot spots have been known to reach as high as 100°C above the average bed temperature in a very short distance.

A second reactor was made of a chromatographic tube with a 1 inch copper tube jacket 135 mm. long closed at both ends by rubber gaskets made from flexible No. 6 rubber stoppers. The jacket was fitted with 1/4 inch copper inlet and exit tubes soldered into the jacket. Water was circulated through the jacket from a constant temperature bath. The thermocouples were a permanent type placed before and after the bed in the hollow of the male glass joints as before.

This reactor was used for a period of a month without a satisfactory procedure being developed. The catalyst particles were still discolored at the end of a run but not as badly as before. Even though the catalyst was diluted with 20-28 mesh tabular alumina, this discoloration of the catalyst continued especially at the bed entrance.

After the second reactor was made the first reactor was used to activate the catalyst charge at the site of the experimental equipment. The weighed charge was placed in the tube and heated in a stream of nitrogen. When the tube was placed inside a one inch copper tube which in turn was covered with one inch of asbestos paper pipe insulation, temperatures up to 425°C could be obtained on a thermocouple

placed at the bed exit when a nitrogen flow rate of 1000 cc/min was used. This arrangement for catalyst activation proved to be unsatisfactory because at the high temperature of operation the silicone stopcock grease used in the joints of the tube vaporized and formed a black deposit on the catalyst. An arrangement similar to this using a longer tube, so that the heating section would not be close to the ends could probably be developed. Such a system would allow faster catalyst activation and greater convenience.

The second reactor was modified to reduce the effective inside diameter to permit better radial heat transfer and to permit measurement of longitudinal temperatures. A hole was bored in the perforated glass plate of the lower male glass joint and a 2 mm O.D. glass tube inserted. Holes were blown in this tubing to correspond to the top, middle, and bottom of the catalyst bed. Thermocouples were sealed into these holes with porcelain cement. A common lead of the thermocouple was placed inside the tubing and the three external leads wound around the 2 mm tube so that the leads did not touch. The entire assembly was coated with porcelain cement with the result that the outside diameter of the assembly was 4 mm. The glass tube was bent to come out the side of the lower male joint and a glass seal made at the point of exit.

This arrangement permitted for the first time a temperature measurement in the catalyst bed. Previously

the jacket had been brought to the desired temperature of the bed, and the average of the entrance and exit gas temperatures used as the actual bed temperature. With the insertion of a thermocouple in the bed, it was shown that the radial temperature gradients were about 10°C when operating at 80°C. Axial temperatures as measured by the permanent type thermocouples differed by as much as 12°C. Although this arrangement of the thermocouples was not satisfactory due to fragility, the few runs that were made not only indicated the magnitude of the temperature gradients that were being obtained, but also showed that the discoloration of the catalyst was practically eliminated when the bed temperature was held to below 90°C.

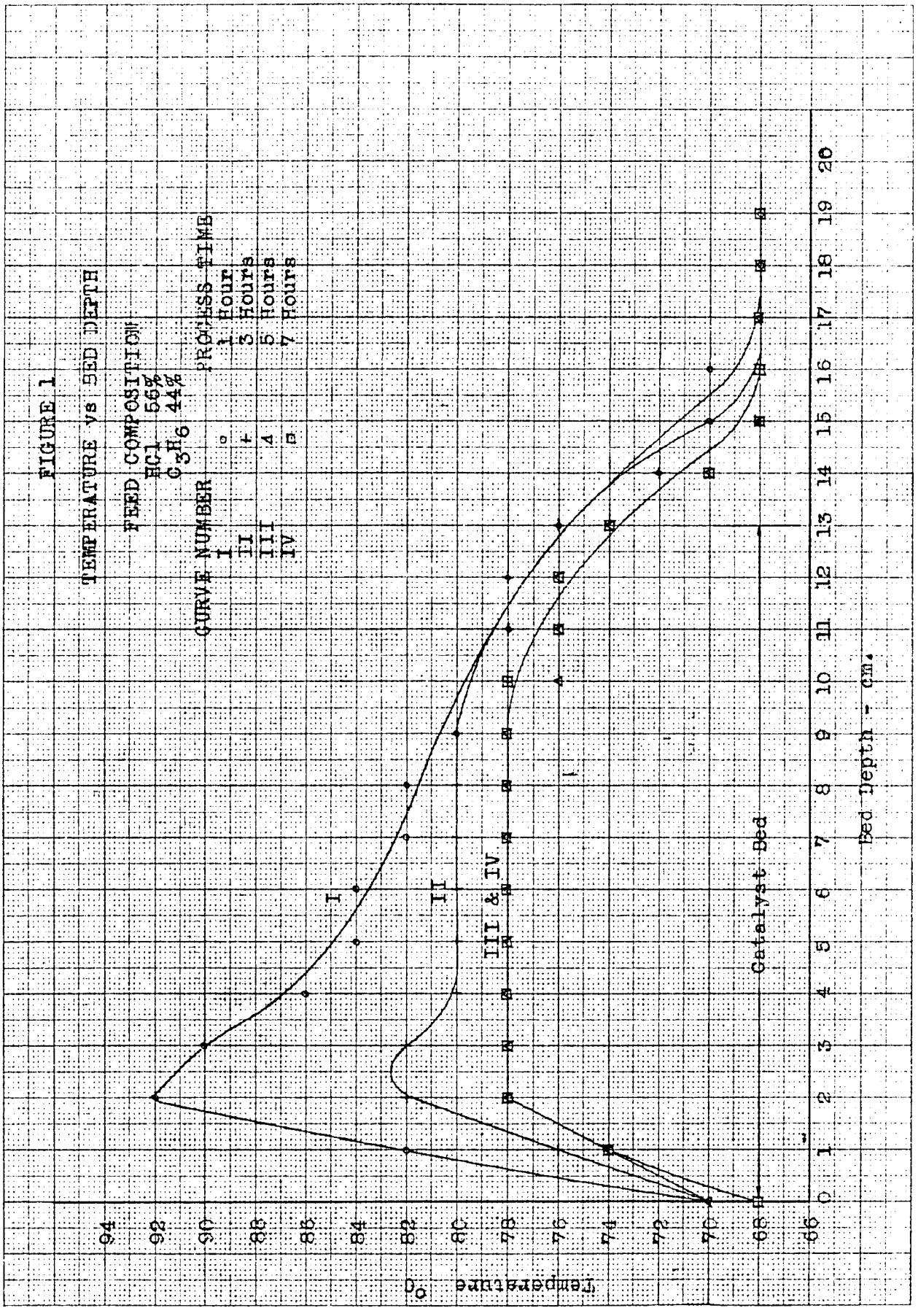
The preheater was also of unsatisfactory design. Although the heated section was very hot, it required a considerable length of time for the packing in the connecting section between the preheater and reactor to reach operating temperature. This was true in spite of heavy insulation wrapped around the section. Furthermore, the temperature of the entering gas could not be controlled with precision due to the lag in heating the packing in the connecting section.

As a result of this preliminary work the condenser-type reactor previously described was used. The reaction tube was long enough so that the preheating section and catalyst bed were adjacent. The thermocouple tube permitted a flexible temperature measuring system in the axial direction, and the

construction was sturdy enough to withstand normal handling.

Temperature gradients were never entirely eliminated from the catalyst bed; a difficulty that is practically impossible to eliminate in a fixed bed reactor especially when the heat of reaction is high and appreciable conversions are obtained. Radial and axial temperature gradients may be reduced by small diameter reactors and good heat transfer at the reactor walls, but they can never be entirely eliminated. By using tabular alumina as a diluent in the catalyst bed, the heat transfer was improved to the point where temperature differences were no more than 10°C above or below the average bed temperature. Without the tabular alumina the temperature rose from 70°C at the bed entrance to 128°C at a distance of one centimeter from the entrance. Diluents in the catalyst bed to improve heat transfer have been used before in kinetic studies (1,2).

Figure (1) shows a typical temperature distribution obtained in the final reactor. These curves were obtained with a feed composition of 55% HCl and 45% C_3H_6 using two grams of catalyst diluted so that the catalyst volume was 0.4 of the diluent volume. The jacket temperature was 70°C. The Leeds and Northrup potentiometer, Catalog No. 8656-D, permitted temperature readings no closer than ± 2°C with chromel-alumel thermocouples so that within the error of the temperature reading the catalyst bed was substantially at a uniform temperature after three hours of operation.



It is of interest to note that the large temperature gradient present after one hour of operation corresponds to the first point obtained on the conversion versus time curves of Figures 5 through 15 in Chapter VI. This first point was invariably off the straight line portion of the curve. In fact, the conversion did not become a linear function of the process time until the temperature of the bed became uniform.

The temperature of a run was taken as the plateau values of curves similar to those of Figure 1. This assumes that the radial temperature gradient is concentrated at the reactor wall. Such an assumption, of course, is probably not entirely true, but the design of the reactor did not permit the determination of the form of the radial temperature gradient. Use of the average axial temperature as the temperature of the catalyst bed is the usual procedure in catalytic vapor phase studies (1, 2, 13). However, Olson, Schuler and Smith (9) assumed a parabolic temperature distribution and calculated an average bed temperature. Such a procedure was not believed to be warranted in this work. Using the plateau temperature rather than the area average temperature over the length of catalyst bed is within the error of the temperature measurement.

The temperature distributions encountered in this work are of the same order of magnitude that others have reported in similar kinetic studies (9, 13). Using very thin

walled, small diameter metal reactors and limiting the reaction to small conversions have failed to reduce these temperatures gradients much below those obtained in this study.

Catalyst Activity and Purification System

The variation of catalyst activity with time was encountered very early in the experimental work. Although the deposition of a visible catalyst deposit was reduced to negligible proportions by the improved reactor design, the catalyst activity continued to decrease with process time although at a reduced rate. A trap containing concentrated sulfuric acid was placed in the hydrogen chloride line to insure the removal of water which would affect the catalyst. This failed to improve the catalyst activity, however. Based on the assumption that the catalyst was being poisoned by an impurity in the feed gases, traps containing the active catalyst were placed in the propylene and in the hydrogen chloride lines. These traps were first placed in the reactor constant temperature bath, but it was discovered later that they were just as effective at room temperature. The activated alumina reduced the rate of decreasing catalyst activity a great deal. Subsequent mass spectrographic analysis showed that the hydrogen chloride contained appreciable amounts of ethylene and traces of ethyl chloride. The fact that these impurities were removed by the alumina traps shows that they were probably poisoning the catalyst in the reactor.

Although ethylene is adsorbed on activated alumina, it does not react with hydrogen chloride over this catalyst at the low temperatures used in this work (10).

Although the impurities in the feed gases were removed, the catalyst activity continued to decrease with process time. As another step in the attempt to locate the source of the trouble, a catalyst charge was exposed at 80°C for forty-eight hours to propylene and its activity determined by a run at 80°C. This was repeated with a fresh catalyst charge exposed to hydrogen chloride and also with a charge exposed to isopropyl chloride vapors obtained from a liquid sample from a previous run. There was essentially no difference in activity between the catalysts. This was true even though the hydrogen chloride bleached the catalyst from a light pink color to a nearly white color. By accident, however, some catalyst particles fell to the bottom of the flask containing the isopropyl chloride product. After the forty-eight hours these particles had turned black whereas the catalyst charge that was exposed to the vapors only were unchanged in color. It is believed that since the liquid product used was obtained from a run where the temperature in the reactor was quite high, possibly some polymerized product had formed and dissolved in the isopropyl chloride when it was condensed. Upon heating this liquid mixture to 80°C the by-product did not vaporize with the isopropyl chloride and thus, lying in the bottom of the flask was able

to form the deposit on the catalyst particles.

With this evidence it is postulated that the decreased activity of the catalyst with time was due to the formation of polymerized propylene material that was not desorbed from the surface of the catalyst at the temperatures at which the kinetic runs were made. Since the activity of the catalyst exposed to propylene at 80°C was not changed, the relatively high local temperatures which were probably developed at the surface of the catalyst particle during the formation of isopropyl chloride were probably necessary in order that the polymerization of the adsorbed propylene could occur.

Method of Analysis

During the preliminary work an analytical procedure was developed that gave reproducible results for the analysis of samples taken within a few minutes of each other. Improvement of the technique involved several steps. First, the sample had to be taken without appreciably affecting the system. It was found that taking a sample by slowly lowering the mercury leveling bottle of the gas buret did not disturb the flow rates of the feed gases as much as throttling the gases to be sampled into the gas buret with the leveling bottle placed in a lowered position. Because the system was maintained at a more uniform pressure, the flow rates were more nearly uniform since they were controlled by constant

delivery pressure devices.

The second step was the transfer of the gas from the gas buret to the absorption tube. The loss of hydrogen chloride in the dead space between the gas buret and the absorption tube could be minimized by washing the inside of the tubing and the stopcock with a stream of water from a washing bottle immediately after separation of the absorption tube from the gas buret. The third step was the washing of the absorption tube after the acid solution was transferred to the reservoir bottle. This was accomplished by adding a third stopcock at the top of the tube to permit the addition of wash water while the stopcock at the bottom of the tube was closed. After two washings with water, the Tygon tubing connecting the absorption tube and the leveling bottle could be completely drained and the acid solution titrated directly in the reservoir bottle.

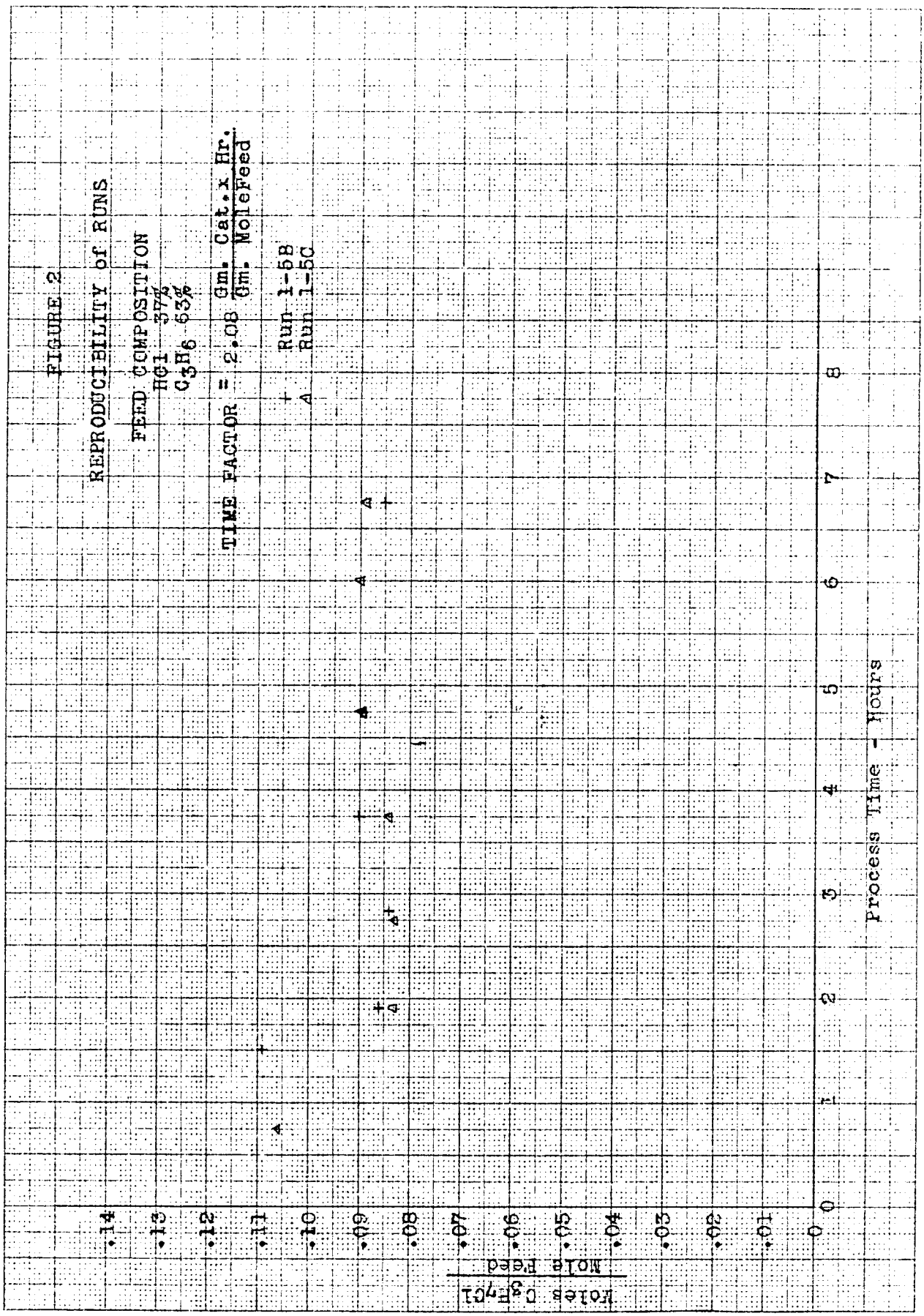
An attempt was made to analyze the feed and product gases using a gas density balance. This proved to be unsuccessful due to the condensation of the isopropyl chloride when the gases were throttled into the very low vacuum of the balance chamber. As drops of isopropyl chloride formed, the hydrogen chloride and propylene dissolved in the liquid so that reliable results were impossible to obtain.

Reproducibility of Results

With proper operating technique the final analytical

procedure gave analyses of isopropyl chloride in terms of mole fraction of product gas to within ±.005, which is surprisingly good when the number of variables involved is considered.

Figure 2 compares two runs made under the same conditions of feed composition and temperature. These runs were made at a 0.28 weight ratio of catalyst to tabular alumina. From this plot it can be seen that under identical operating conditions reproducible results were obtained.



APPENDIX

PART II

Evaluation of Film Gradients Due to Mass Transfer

As shown in Chapter II, Hougen and Watson (6) and Yang and Hougen (14) have developed the following equation for evaluating the film gradient for mass transfer.

$$\frac{\Delta p_A}{p_A} = \frac{1}{\alpha}\left(\frac{\sqrt{a_p}\, r\, H_m\, p_f}{p_A \mu\, a_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)_f^{2/3}\left(\frac{\sqrt{a_p}\, G}{\mu}\right)^{n-1} \qquad (1)$$

From the experimental work of Gamson, Thodos, Wilke and Hougen (4, 12) the values of the constants α and n can be evaluated.

$$\text{If} \quad \frac{\sqrt{a_p}\, G}{\mu} < 620, \qquad \alpha = 2.44; \quad n = 0.51 \qquad (2)$$

$$\frac{\sqrt{a_p}\, G}{\mu} > 620, \qquad \alpha = 1.25; \quad n = 0.41$$

In order to evaluate the terms in equation (1) certain assumptions were made.

1. The surface area of the particles are the same as spheres with a diameter of the average particle size. At first this may appear to be a source of large error since the particles are granular and porous. However, the values of the constants α and n given above are based on experiments where similar assumptions as to surface area were used.

2. The equilibrium composition for the reaction exists at the gas-solid interface. This, in effect, is assuming a value of Δp_A. However, some value of p_{Ai} must be chosen in order that the pressure factor p_f may be determined.

Only the reaction at 80°C was considered. Since the reaction rate is greater at the higher temperatures, the larger film gradients would be expected. Rates of mass transfer are little affected by temperature. The exit of the catalyst bed was chosen as the point of calculation.

Pressure Factor, p_f

For the complex system $aA + bB \rightleftharpoons rR + sS$, in which diffusion occurs, Hougen and Watson (6) assumed for estimation purposes that the diffusional gradient established for the component A is equal to the sum of the gradients which would result from the separate diffusion of A with each of the other components in separate binary systems in which the concentrations and rates are the same as the complex system. This assumption leads to the expression for the rate of diffusion as follows.

$$r_A = \frac{D_{A_m} \pi}{RTB_G p_f} (p_A - p_{Ai})$$

where p_f is defined as

$$p_f = \frac{(\pi + \delta_A p_A) - (\pi + \delta_A p_{Ai})}{\ln \frac{\pi + \delta_A p_A}{\pi + \delta_A p_{Ai}}}$$

and where

$$\delta_A = \frac{r + s - a - b}{a}$$

For the addition of hydrogen chloride to propylene p_A is the partial pressure in the fluid stream, and p_{A_i} is assumed to be the equilibrium partial pressure at the interface. From the definition, $\delta_A = -1$.

Average Diffusivity

In this same development of the diffusion equation for complex mixtures the average diffusivity D_{Am} is defined as

$$(1 - N_A)D_{A_m} = N_B D_{AB} + N_R D_{AR} + N_S D_{AS}$$

The values of the individual diffusivities were estimated by the Gilliland equation for each binary system.

$$D_{AB} = 0.0043 \frac{T^{3/2}}{\pi (V_A^{1/3} + V_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

Viscosity

The viscosity of the gas was estimated from the generalized relationship given by Uyehara and Watson (11) using pseudo-critical properties of temperature, pressure and viscosity. The critical viscosity of isopropyl chloride was estimated by the equation proposed by Licht and Stechert (7)

$$\mu_c = 7.70 \frac{\sqrt{M} (p_c)^{3/2}}{T_c^{1/6}}$$

The critical constants for isopropyl chloride were estimated also by the method of Meissner and Redding (8).

Calculation of Diffusional Gradients

The values of the various terms and the final diffusional gradients for Run 1-6 are shown in Table I (see next page.).

From the values of Δp for each component it can be seen that the concentration gradients assumed originally were considerably in error. However, the error in p_f is not great and therefore the values of $\frac{\Delta p_A}{p_A}$ are not greatly in error due to this assumption. Since much of the data was estimated in order to evaluate the film gradients, the values of Δp_A can be considered only as approximations. Errors in the assumptions and estimates made would have to be in error in the order of magnitude of one hundred percent before concentration corrections would have to be applied to the experimental data. The errors are not believed to be that large so that the effect of mass transfer can be considered negligible for the conditions used. Therefore, the concentrations of the reactants and product at the solid-gas interface can be considered essentially the same as the average concentrations in the fluid stream.

Table I

Calculation of Diffusional Gradients

$$\frac{\Delta p_A}{p_A} = \frac{1}{\alpha}\left(\frac{\sqrt{a_p}\ r\ K_m\ p_f}{p_A \mu\ a_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)_f^{2/3}\left(\frac{\sqrt{a_p}\ G}{\mu}\right)^{n-1}$$

Term	Unit	HCl Diffusional Gradient	C_3H_6 Diffusional Gradient	C_3H_7Cl Diffusional Gradient
a_p	$ft.^2$	1.73×10^{-5}	1.73×10^{-5}	1.73×10^{-5}
a_m	$ft.^2/lb.$	34.2	34.2	34.2
K_m	--	46.9	46.9	46.9
r	$\frac{\text{Gm-Mols } C_3H_7Cl}{\text{Gm Cat x Hrs}}$	0.0196	0.0196	0.0196
p_f	atm.	0.803	0.472	0.826
p_A	atm.	0.275	0.594	0.181
μ	lb./hr.xft.	0.038	0.038	0.038
ρ	gm/cc	0.00170	0.00170	0.00170
D_{Am}	$cm^2/sec.$	0.128	0.114	0.101
G	$lb./hr.ft.^2$	258	258	258
α	--	2.44	2.44	2.44
n	--	0.51	0.51	0.51
$\frac{\Delta p_A}{p_A}$	--	0.00055	0.000162	0.00101
Δp_A	atm.	0.00015	0.000096	0.000183

APPENDIX

PART III

Derivation of Rate Equation Used in Correlation Method B

The general procedure used in this derivation is outlined by Wynkoop and Wilhelm (13). Consider the reaction:

$$\underset{A}{HCl} + \underset{B}{C_3H_6} \rightleftharpoons \underset{C}{C_3H_7Cl} \qquad (1)$$

The rate of the surface reaction may be written:

$$\frac{d(Ny_C)}{dW} = k\theta_A\theta_B - k'\theta_C \qquad (2)$$

where

N = gm.moles per minute of gas flowing in reactor at any point

W = weight of catalyst in grams

d = differential operator

θ = fraction of available catalyst surface covered

k,k' = specific reaction rate constant; gm.moles/(hr)(gm. catalyst)

Subscripts

A refers to hydrogen chloride

B refers to propylene

C refers to isopropyl chloride

o refers to inlet conditions

It will be assumed that the fraction of surface covered by each component can be expressed by the equation

$$\theta_i = \alpha_i y_i \pi \tag{3}$$

where

α = an adsorption equilibrium constant

π = total pressure in atmospheres.

Thus Equation (2) becomes

$$\frac{d(Ny_c)}{dW} = k\alpha_A\alpha_B\pi^2 y_A y_B - k'\alpha_C\pi y_C \tag{4}$$

Since no inert material is in the feed gas

$$y_C = 1 - y_A - y_B \tag{5}$$

With this substitution Equation (4) becomes

$$\frac{d(Ny_c)}{dW} - k'\alpha_C\pi(y_A-1) + y_B(k\alpha_A\alpha_B\pi^2 y_A + k'\alpha_C\pi) \tag{6}$$

With the condition that there is no C in the feed it follows from Equation (1) that

$$N_A - N_B = y_{Ao}N_o - y_{Bo}N_o = N_o(2y_{Ao} - 1) \tag{7}$$

and also that

$$N_B + N_C = N_o y_{Bo} = N_o(1 - y_{Ao}) \tag{8}$$

thus

$$\frac{N_A - N_B}{N_B + N_C} = \frac{2y_{Ao} - 1}{1 - y_{Ao}} \tag{9}$$

For any point in the reactor

$$N_A - N_B = N(y_A - y_B) \tag{10}$$

$$N_B + N_C = N(y_B + y_C) \tag{11}$$

thus

$$\frac{N_A - N_B}{N_B + N_C} = \frac{y_A - y_B}{y_B + y_C} = \frac{2y_{Ao} - 1}{1 - y_{Ao}} \tag{12}$$

By definition

$$y_A + y_B + y_C = 1 \tag{13}$$

From Equation (12) and (13) y_B and y_C can be expressed as a function of y_A and y_{Ao}.

$$y_B = \frac{y_{Ao}y_A + 1 - 2y_{Ao}}{1 - y_{Ao}} \tag{14}$$

$$y_C = \frac{y_{Ao} - y_A}{1 - y_{Ao}} \tag{15}$$

A propylene balance across the reactor and the use of Equation (13) leads to

$$N_o y_{Bo} = Ny_B + Ny_C$$

$$N = \frac{N_o(1 - y_{Ao})}{(1 - y_A)} \tag{16}$$

Combining Equations (15) and (16),

$$Ny_C = \frac{N_o(1 - y_{Ao})}{(1 - y_A)} \left(\frac{y_{Ao} - y_A}{1 - y_{Ao}}\right)$$

$$Ny_C = N_o \frac{(y_{Ao} - y_A)}{(1 - y_A)} \tag{17}$$

Differentiating with respect to W gives

$$\frac{d(Ny_C)}{dW} = \frac{N_o(y_{Ao} - 1)}{(1 - y_A)^2} \frac{dy_A}{dW} \qquad (18)$$

Substituting Equations (14) and (18) into Equation (6) the following expression in terms of y_A is obtained.

$$\frac{N_o(y_{Ao}-1)}{(1-y_A)^2} \frac{dy_A}{dW} = k'\alpha_C\pi(y_A-1) + (k\alpha_A\alpha_B\pi^2 y_A + k'\alpha_C\pi)\frac{1+y_A y_{Ao}-2y_{Ao}}{1 - y_{Ao}} \qquad (19)$$

Rearranging Equation (19) the final equation is obtained.

$$N_o \frac{dy_A}{dW} = k'\alpha_C\pi\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A) - k\alpha_A\alpha_B\pi^2 y_A \frac{(1-y_A)^2}{(1-y_{Ao})^2}(1+y_A y_{Ao}-2y_{Ao}) \qquad (20)$$

Due to the complex function of y_A, this equation may not be integrated readily.

Letting $R = N_o \frac{dy_A}{dW}$

$$A = k'\alpha_C\pi$$

$$B = k\alpha_A\alpha_B\pi^2$$

and rearranging Equation (20)

$$\frac{1}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A) = \frac{B}{A}\frac{y_A}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(1 + y_A y_{Ao} - 2y_{Ao}) + \frac{1}{A} \qquad (21)$$

If the variable term $\frac{1}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(y_{Ao}-y_A)$ is plotted versus $\frac{y_A}{R}\frac{(1-y_A)^2}{(1-y_{Ao})^2}(1 + y_A y_{Ao} - 2y_{Ao})$ a straight line of slope $\frac{B}{A}$

and intercept $\frac{1}{A}$ should result if the assumptions underlying the equation were true.

APPENDIX

PART IV

Evaluation of Thermodynamic Properties and Equilibrium Constant

Table II lists the thermodynamic properties of the reactants and product. The standard heat of formation and absolute entropy of isopropyl chloride were estimated by the method of group contributions outlined by Hougen and Watson (5). The molal heat capacity of isopropyl chloride and propylene were estimated by two methods, i.e., the method of group contributions of Hougen and Watson and the method of Dobratz (3). The expressions of the thermodynamic properties as a function of temperature were used to calculate the equilibrium constant as a function of temperature by the usual procedure. Two different equations for **K** shown in Table III were obtained using the expressions for c_p obtained by the two methods. However, both equations gave the same values for **K** at the same temperature as they should.

Table II

Thermodynamic Properties

		Reference
Hydrogen Chloride	$S^{\circ}_{298.1} = 44.66 \pm 0.01$ E.U.	(1)
	$\Delta H^{\circ}_{f_{298.1}} = -22060$ cal/gm mole	(2)
	$c_p = 6.64 + 0.959 \times 10^{-3}T - 0.057 \times 10^{-6}T^2$	(3)
Propylene	$S^{\circ}_{298.1} = 63.80$ E.U.	(4)
	$\Delta H^{\circ}_{f_{298.1}} = 4879$ cal/gm mole	(4)
	$c_p = 1.97 + 49.8\times10^{-3}T - 17.01 \times 10^{-6}T^2$	Est.I
	$c_p = -0.261 + 50.991 \times 10^{-3}T - 15.90 \times 10^{-6}T^2 + 3.28 \times 10^{7}T^{-3}$	Est. II
Isopropyl chloride	$S^{\circ}_{298.1} = 70.5$ E.U.	Est. I
	$\Delta H^{\circ}_{f_{298.1}} = -31,200$ cal/gm mole	Est. I
	$c_p = 4.49 + 63.46 \times 10^{-3}T - 22.53 \times 10^{-6}T^2$	Est. I
	$c_p = 26.73 + 64.94 \times 10^{-3}T - 23.97 \times 10^{-6}T^2 + 1.45 \times 10^{7}T^{-3}$	Est. II

Table III

Equilibrium Constant as a Function of Temperature

Method I Molal heat capacity data estimated by method of Hougen and Watson

$$\ln K = -6.88 + 3.19 \times 10^{-3}T - 0.458 \times 10^{-6}T^2 - 2.095 \ln T + \frac{6690}{T}$$

Method II Molal heat capacity data estimated by method of Dobratz

$$\ln K = -8.50 + 3.27 \times 10^{-3}T - 0.672 \times 10^{-6}T^2 - 0.151 \times 10^{7}T^{-3} + \frac{6810}{T} - 1.87 \ln T$$

References for Thermodynamic Properties

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5. Est. I Estimation by method of Hougen and Watson

6. Est. II Estimation by method of Dobratz

APPENDIX

PART V

Detailed Operating Procedure

Since runs were made on a time basis because the catalyst activity decreased with time, a standard operating procedure had to be followed. If this work were to be continued or if work were to be done with other reactants, the operating procedure would necessarily have to be the same in order that comparable results could be obtained. For this reason the procedure will be described here in detail.

Catalyst Preparation

1. The activated alumina was ground in a mortar and pestle from the 4-8 mesh size to 20-28 mesh. Before being used the screens were carefully cleaned to insure that no foreign material was mixed with the catalyst. The tabular alumina balls were crushed in a roll mill and classified to give 20-28 mesh and 16-20 mesh fractions.
2. The catalyst was activated at 750°F for 16 hours.
3. After cooling, the desired weight of active catalyst was weighed rapidly to the nearest 0.01 gram, and its volume measured in a 10 ml. graduate. The graduate was tapped until the volume of catalyst did not change. Two and one-half times this volume of 20-28 mesh tabular alumina was then weighed. Subsequent catalyst charges were

made up by weighing catalyst and diluent since the measurement by weight was more accurate than the volume measurement. The charge was thoroughly mixed and placed in an open dish in an oven at 750°F for 16 hours.

4. Before removing the catalyst from the furnace the reactor was fastened in place with the lower joint assembled and the thermocouple sealed to the lower aligning support with sealing wax. The lower joint was lightly packed with glass wool to the top of the male joint. The reaction tube was then filled to a depth of approximately 10 cm. with 16-20 mesh tabular alumina, care being taken that the thermocouple tube remained centered in the reactor. The catalyst charge was removed from the furnace, and immediately poured into a bottle which was then tightly stoppered. The catalyst was poured into the reactor while it was still very hot. The remaining volume of the reactor tube was quickly filled with 16-20 mesh tabular alumina, the top glass joint pressed firmly in place, and the thermocouple tube immediately sealed to the upper aligning support with sealing wax. The thermocouple wire was placed under tension by means of the upper and lower guides and the connections made at the terminal board.

Preliminary Starting Procedure

1. Water at room temperature was circulated through the reactor jacket by means of a pump.
2. The gas buret constant temperature bath was brought to temperature, and water circulated through the gas buret jacket by means of a pump.
3. The system was tested for leaks by applying pressure with nitrogen. If no change in the nitrogen pressure manometer occurred in ten minutes, the equipment was assumed to be gas tight.
4. The traps containing activated alumina were placed in the hydrogen chloride and propylene lines. The ball and socket joints on these traps were well greased with stopcock grease to insure a good seal.
5. The Milliken gas washing bottles containing fresh top water were placed in the system by means of rubber connecting hose. The bottles were packed in ice to remove the heat of solution of hydrogen chloride.
6. The gas burner was ignited.
7. The system was completely checked to be sure that all of the necessary stopcocks and clamps were open.

Starting Procedure

1. The propylene was turned on at the cylinder with the propylene regulating stopcock open. A time lag between the opening of the cylinder and the flow of propylene

through the equipment was always present due to the adsorption of the gas on the activated alumina in the trap following the gas cylinder. The propylene flow rate was adjusted to approximately the desired value and the time was noted.

2. The hydrogen chloride was turned on at the cylinder with the hydrogen chloride regulating stopcock closed. There was always a time lag between the opening of the cylinder and the flow of the gas through the mercury safety trap due to adsorption in the activated alumina trap. The hydrogen chloride was introduced slowly by adjusting the regulating stopcock. The temperature at the entrance of the catalyst bed was watched carefully to be sure that it did not rise too rapidly. With careful control of the hydrogen chloride flow rate, it soon rose to a constant value of about 40°C.

3. Ten minutes after the propylene had been turned on the flow rates of propylene and hydrogen chloride were adjusted to the desired values by means of the regulating stopcocks on each line. The needle valve on the hydrogen chloride tank was adjusted so that the gas bubbled at a slow rate through the mercury safety trap. Since the propylene tank was equipped with a constant pressure single stage reducing valve, this procedure was not necessary for the propylene.

4. The heater in the reactor constant temperature bath was turned on. To facilitate the heating to the higher temperatures, the bath was equipped with an auxiliary heater that was not controlled by the temperature regulator. This heater was also used until the temperature of the bath was within five degrees of the desired value.
5. The temperature of the bath was adjusted so that the average temperature of the bed was at the desired value. The catalyst bed was always at the desired temperature within forty-five minutes from the starting time. If the bed were brought to temperature too rapidly, the temperature continued to rise and large gradients developed.
6. Constant attention was required by the flow rates of the feed gases during this starting period in order to maintain constant readings in the capillary meter manometer.

Sampling Procedure

1. The pressure and flow manometers were read and the time noted.
2. The mercury leveling bottle was raised so that the surface of the mercury in the bottle was slightly above the top of the gas buret. The stopcocks to the gas stream to be sampled were opened completely.

3. Seventy-five cubic centimeters of gas were slowly drawn into the gas buret by slowly lowering the leveling bottle. The buret stopcock was opened to the atmosphere and the gas discharged.
4. Approximately ninety-five cubic centimeters of gas were slowly drawn into the gas buret and the stopcock closed.
5. The gas was allowed to come to the temperature of the jacket and the volume was measured.
6. An absorption tube completely filled with distilled water was connected to the gas buret by means of a short length of pressure tubing. The empty reservoir bottle was lowered, the mercury leveling bottle raised and the gas transferred to the absorption tube.
7. As soon as the transfer was complete and the mercury leveling bottle replaced on the rack, the absorption tube was closed and disconnected from the buret. The exit tubing and upper stopcock were immediately washed by opening the stopcock and washing with a stream of water from a washing bottle, care being taken that no wash water was spilled from the tube. The stopcock was then closed and the reservoir bottle placed on the foot of the absorption tube stand so that a slight vacuum was maintained on the gas in the tube.
8. With proper technique three gas samples could be taken in ten minutes.
9. The time and atmospheric pressures were noted.

Analytical Procedure

1. The absorption tube was removed from its stand and vigorously shaken until no change of gas volume occurred.
2. The remaining gas was completely expelled by raising the reservoir bottle, and the absorption tube drained. The lower stopcock was closed as soon as the acid solution was completely out of the absorption tube.
3. The two upper stopcocks were opened and approximately 10 cc. of water from a washing bottle introduced into the tube. The tube was shaken and the water drained out as before.
4. The washing step was repeated.
5. The absorption tube and connecting Tygon tubing were drained completely by slowly lowering the reservoir bottle, and the lower stopcock closed.
6. The acid solution was titrated with 0.05 N sodium hydroxide using brom thymol blue indicator.
7. The product gas composition was calculated by a material balance since the feed gas composition and the volume of sample were known.

Shut-down Procedure

1. The nitrogen gas cylinder was turned on with all the nitrogen stopcocks closed.

2. The hydrogen chloride cylinder valve was closed. After the flow rate had fallen to nearly zero, the regulating stopcock was closed and nitrogen was introduced into the hydrogen chloride line.
3. The propylene cylinder valve was closed. After the flow rate had fallen to nearly zero, the regulating stopcock was closed and nitrogen was introduced into the propylene line.
4. After approximately fifteen minutes the nitrogen was turned off.
5. The burner, temperature regulators, and pumps were turned off.
6. The alumina traps were disconnected and placed in insulation jackets. Air was blown through the traps and heat applied by means of Nichrome wire windings around the traps. An iron-constantan thermocouple placed in the inlet tube of the propylene trap permitted control of the temperature at 750°F by means of a Type 5001, Illinois Testing Laboratories temperature controller. This degassing and reactivating period lasted at least one and one-half hours.

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APPENDIX

PART VIII

Experimental Data

SERIES 1

Feed Composition 37% HCl 63% C_3H_6

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
1-1	0.0320	1.04	78.9	44	42	0.75	32.6	60.3	7.1	0.066
						1.75	34.2	61.2	4.6	0.044
						2.75	34.4	61.3	4.3	0.041
						3.92	34.5	61.3	4.2	0.040
						5.00	34.5	61.4	4.1	0.039
						6.75	34.8	61.6	3.6	0.035
1-2	0.0321	1.04	--	60	54	0.75	31.9	59.9	8.2	0.076
						1.50	32.8	60.5	6.7	0.063
						2.50	33.1	60.6	6.3	0.059
						4.50	33.2	60.6	6.2	0.058
						6.50	33.9	61.1	5.0	0.048
1-3	0.0322	1.04	79.5	80	70	0.83	30.5	59.1	10.4	0.094
						1.83	30.5	59.1	10.4	0.094
						2.83	30.7	59.3	10.0	0.091
						3.75	31.4	59.6	9.0	0.083
						4.75	32.0	60.0	8.0	0.074
						6.83	32.9	60.5	6.6	0.062
1-4	0.320	2.08	79.3	44	42	1.0	28.6	58.0	13.4	0.118
						2.0	31.0	59.4	9.6	0.088
						3.0	31.5	59.7	8.8	0.081
						4.0	31.9	59.9	8.2	0.076
						5.0	32.1	60.0	7.9	0.073
						6.0	32.2	60.0	7.8	0.072

SERIES 1 (cont.)

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
1-5	0.0321	2.08	79.0	60	52	1.0	27.5	57.3	15.2	0.132
						2.0	29.4	58.5	12.1	0.108
						3.0	29.8	58.7	11.5	0.103
						4.0	29.8	58.7	11.5	0.103
						5.0	30.0	58.8	11.2	0.101
						6.0	30.1	58.9	11.0	0.099
1-5B	0.0317	2.11	78.2	60	52	1.0	29.3	58.4	12.3	0.109
						1.83	31.1	59.5	9.4	0.086
						2.83	31.3	59.6	9.1	0.083
						3.75	30.9	59.2	9.9	0.090
						4.75	30.9	59.4	9.7	0.089
						6.75	31.2	59.5	9.3	0.085
1-5C	0.0318	2.14	78.4	60	50	0.75	29.5	58.6	11.9	0.106
						1.83	31.3	59.6	9.1	0.083
						2.75	31.4	59.6	9.0	0.083
						3.75	31.3	59.5	9.2	0.084
						4.75	30.9	59.4	9.7	0.088
						6.00	30.9	59.3	9.8	0.089
						6.75	30.9	59.3	9.8	0.089
1-6	0.0323	2.06	79.8	80	68	1.08	26.0	56.4	17.6	0.150
						2.0	27.3	57.2	15.5	0.134
						3.0	27.8	57.6	14.6	0.128
						4.0	28.3	57.8	13.9	0.122

SERIES 1 (cont.)

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
1-7	0.0323	1.55	80.2	80	69	1.0	27.7	58.4	13.9	0.122
						2.0	27.9	58.5	13.6	0.120
						3.42	28.0	58.5	13.5	0.119
						4.17	28.4	58.8	12.8	0.113
						5.0	28.9	59.1	12.0	0.107
						6.0	29.6	59.4	11.0	0.099
1-8	0.0318	1.57	78.3	60	52	1.0	30.0	58.7	11.3	0.102
						2.0	31.1	59.4	9.5	0.087
						3.0	31.4	59.6	9.0	0.083
						4.0	31.5	59.7	8.8	0.081
						5.0	31.8	59.8	8.4	0.077
						6.0	32.0	59.9	8.1	0.075
						7.0	32.5	60.3	7.2	0.067
1-9	0.0320	1.56	79.9	44	40	1.0	31.0	59.3	9.7	0.088
						2.0	32.4	60.1	7.5	0.070
						3.0	32.9	60.4	6.7	0.063
						3.75	32.9	60.5	6.6	0.062
1-10	0.0323	0.52	79.7	80	71	1.0	33.4	61.2	5.4	0.051
						2.0	32.2	60.6	7.2	0.067
						3.0	32.6	60.8	6.6	0.062
						4.0	32.9	61.0	6.1	0.058
						5.0	33.2	61.1	5.7	0.054
						6.0	33.5	61.4	5.1	0.049

SERIES 1 (cont.)

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
1-11	0.0319	0.52	78.9	60	53	1.0	35.0	61.8	3.2	0.031
						2.0	34.8	61.7	3.5	0.034
						3.0	34.4	61.5	4.1	0.039
						5.0	34.1	61.3	4.6	0.044
						6.0	33.7	61.1	5.2	0.049

SERIES 2

Feed Composition 66% HCl 34% C_3H_6

Run No.	Flow Rate Gm-Mols/Min	Time Factor Gm Cat/Gm Mol/Hr	Total Pressure Gm.Hg	Temperature °C	Jacket Temperature °C	Time Hours	Product Composition Mol Percent HCl	C_3H_6	C_3H_7Cl	Mols C_3H_7Cl / Mol Feed
2-1	0.0317	1.05	80.0	80	68	1.0	62.0	27.3	10.7	0.097
						2.08	61.8	27.0	11.2	0.101
						3.0	62.0	27.2	10.8	0.098
						4.0	62.1	27.8	9.9	0.090
						5.0	62.6	28.4	9.0	0.083
						6.0	62.7	28.9	8.4	0.077
2-2	0.0322	1.04	81.5	60	52	1.25	63.4	29.1	7.5	0.070
						2.25	63.3	29.0	7.7	0.071
						3.25	63.4	29.1	7.5	0.070
						4.25	63.6	29.4	7.0	0.065
						6.17	63.9	30.0	6.1	0.058
2-3	0.0317	1.05	80.0	44	38	1.0	63.7	29.7	6.6	0.062
						2.0	64.5	31.1	4.4	0.042
						3.0	64.8	31.6	3.6	0.035
						4.0	64.6	31.4	4.0	0.038
						5.0	64.7	31.6	3.7	0.036
						6.0	64.8	31.7	3.5	0.034
2-4	0.0320	1.56	80.0	44	38	1.0	63.0	28.3	8.7	0.080
						2.0	63.8	29.8	6.4	0.060
						3.0	64.0	30.4	5.6	0.053
						5.0	64.2	30.7	5.1	0.049
						6.0	64.3	30.9	4.8	0.046

SERIES 2 (cont.)

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
2-5	0.0323	1.55	80.2	60	49	1.0	62.5	26.7	10.8	0.098
						2.0	63.0	27.5	9.5	0.087
						3.0	63.0	27.5	9.5	0.087
						4.0	63.1	27.7	9.2	0.084
						6.0	63.4	28.3	8.3	0.077
2-6	0.0320	1.56	79.7	80	68	1.0	62.1	26.2	11.7	0.105
						2.0	61.6	25.0	13.4	0.118
						3.0	61.2	24.5	14.3	0.125
						4.0	61.6	25.2	13.1	0.116
						6.0	62.2	26.3	11.5	0.103
						7.0	62.6	26.5	10.9	0.098
2-7	0.0326	2.05	80.2	80	69	1.0	61.0	23.9	15.1	0.132
						2.0	60.5	23.2	16.3	0.140
						3.0	60.5	23.1	16.4	0.141
						4.0	60.7	23.4	15.9	0.137
						5.0	60.8	23.8	15.4	0.133
						6.0	61.1	24.2	14.7	0.128
2-8	0.0320	2.08	79.3	60	52	1.0	61.9	25.2	12.9	0.110
						2.0	62.1	25.9	12.0	0.107
						3.0	62.3	25.8	11.9	0.106
						4.0	62.4	26.2	11.4	0.103
						6.0	62.6	26.6	10.8	0.097

SERIES 2 (cont.)

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
2-9	0.0317	2.11	78.9	44	38	1.0	61.7	25.3	13.0	0.115
						2.0	62.9	27.5	9.6	0.088
						3.0	63.3	28.3	8.4	0.077
						4.0	63.6	29.0	7.4	0.069
						5.0	63.8	29.2	7.0	0.066
						6.0	63.7	29.0	7.3	0.068
						7.0	63.9	29.4	6.7	0.063
2-10	0.0321	0.52	79.9	80	69	1.0	63.9	29.8	6.3	0.059
						2.0	63.6	29.1	7.3	0.068
						3.0	63.8	29.3	6.9	0.065
						4.0	64.2	30.2	5.6	0.053
						5.0	64.4	30.6	5.0	0.048
						6.0	64.5	30.7	4.8	0.046

SERIES 3

Feed Composition 50% HCl 50% C_3H_6

Run No.	Flow Rate Gm-Mols/Min	Time Factor Gm Cat/Gm Mol/Hr	Total Pressure Gm.Hg	Temperature °C	Jacket Temperature °C	Time Hours	Product Composition Mol Percent HCl	C_3H_6	C_3H_7Cl	Mols C_3H_7Cl / Mol Feed
3-1	0.0320	1.04	78.7	44	38	1.0	47.2	47.1	5.7	0.054
						2.0	47.9	47.9	4.2	0.040
						3.0	48.2	48.2	3.6	0.034
						4.0	48.1	48.1	3.8	0.036
						5.0	48.3	48.3	3.4	0.033
						6.0	48.2	48.2	3.6	0.035
3-2	0.0322	1.04	79.5	60	52	1.0	46.4	46.4	7.2	0.067
						2.0	45.4	45.4	9.2	0.084
						3.0	47.1	47.1	5.8	0.055
						4.0	46.9	46.9	6.2	0.058
						5.0	46.8	46.8	6.4	0.060
						6.0	47.1	47.1	5.8	0.055
3-3	0.0324	1.03	79.7	80	68	1.0	44.4	44.4	11.2	0.101
						2.0	44.0	44.0	12.1	0.108
						3.0	44.7	44.7	10.7	0.097
						4.0	45.3	45.3	9.4	0.086
						5.0	45.8	45.8	8.4	0.077
						6.0	46.1	46.1	7.8	0.072

SERIES 4

Feed Composition 19% HCl 81% C_3H_6

Run No.	Flow Rate	Time Factor	Total Pressure	Temperature	Jacket Temperature	Time	Product Composition			Mols C_3H_7Cl / Mol Feed
							HCl	C_3H_6	C_3H_7Cl	
	Gm-Mols / Min	Gm Cat / Gm Mol/Hr	Gm.Hg	°C	°C	Hours	Mol Percent			
4-1	0.0321	1.04	79.1	60	54	1.0	15.8	80.0	4.2	0.040
						2.0	16.1	80.1	3.8	0.037
						3.0	15.9	80.0	4.1	0.039
						4.0	15.7	80.0	4.3	0.041
						5.0	15.4	79.9	4.7	0.045
4-2	0.0320	1.56	79.3	60	55	1.0	13.9	80.0	6.1	0.058
						2.0	15.4	80.4	4.2	0.040
						3.0	15.5	80.4	4.1	0.039
						4.0	15.6	80.4	4.0	0.038
						6.0	15.1	80.3	4.6	0.044

CONVERSION AT PROCESS TIME 0 HOURS

SERIES 1

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
1-1	1.04	44°C	.044	.341	.613	.046
1-2	1.04	60	.070	.323	.602	.075
1-3	1.04	80	.109	.293	.584	.123
1-4	2.08	44	.083	.313	.596	.091
1-5	2.08	60	.111	.291	.584	.125
1-6	2.06	80	.146	.262	.567	.171
1-7	1.55	80	.134	.272	.573	.155
1-8	1.57	60	.095	.304	.591	.105
1-9	1.56	44	.068	.324	.603	.073
1-10	0.52	80	.074	.320	.600	.080
1-11	0.52	60	.040	.344	.614	.042

SERIES 2

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
2-1	1.05	80°C	.116	.615	.254	.131
2-2	1.04	60	.074	.633	.287	.080
2-3	1.05	44	.043	.645	.310	.045
2-4	1.56	44	.063	.637	.296	.067
2-5	1.55	60	.097	.624	.269	.107
2-6	1.56	80	.137	.606	.235	.159
2-7	2.05	80	.149	.601	.224	.175
2-8	2.08	60	.113	.617	.256	.127
2-9	2.11	44	.075	.633	.286	.081
2-10	0.52	80	.074	.633	.287	.080

CONVERSION AT PROCESS TIME 0 HOURS (cont.)

SERIES 3

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
3-1	1.04	44°C	.040	.479	.479	.042
3-2	1.04	60	.063	.466	.466	.068
3-3	1.04	80	.113	.436	.436	.128

SERIES 4

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
4-1	1.04	60°C	.04	.156	.802	.042
4-2	1.56	60	.05	.147	.800	.053

CONVERSION AT PROCESS TIME 3 HOURS

SERIES 1

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
1-1	1.04	44°C	.041	.343	.614	.043
1-2	1.04	60	.060	.330	.606	.064
1-3	1.04	80	.088	.309	.594	.097
1-4	2.08	44	.078	.317	.598	.085
1-5	2.08	60	.105	.296	.587	.117
1-6	2.06	80	.128	.278	.575	.147
1-7	1.55	80	.117	.286	.581	.133
1-8	1.57	60	.084	.312	.596	.092
1-9	1.56	44	.063	.328	.605	.067
1-10	0.52	80	.062	.328	.606	.066
1-11	0.52	60	.040	.344	.614	.042

SERIES 2

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
2-1	1.05	80°C	.096	.624	.270	.106
2-2	1.04	60	.068	.635	.292	.073
2-3	1.05	44	.039	.646	.313	.041
2-4	1.56	44	.055	.640	.302	.058
2-5	1.55	60	.087	.628	.277	.095
2-6	1.56	80	.120	.614	.250	.136
2-7	2.05	80	.139	.606	.233	.161
2-8	2.08	60	.105	.620	.263	.107
2-9	2.11	44	.070	.635	.290	.075
2-10	0.52	80	.062	.638	.296	.066

CONVERSION AT PROCESS TIME 6 HOURS

SERIES 1

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
1-1	1.04	44°C	.038	.345	.615	.040
1-2	1.04	60	.050	.337	.610	.053
1-3	1.04	80	.068	.324	.603	.073
1-4	2.08	44	.072	.321	.601	.078
1-5	2.08	60	.099	.301	.589	.110
1-6	2.06	80	.110	.292	.584	.124
1-7	1.55	80	.101	.300	.588	.112
1-8	1.57	60	.074	.320	.600	.080
1-9	1.56	44	.059	.330	.607	.063
1-10	0.52	80	.050	.337	.610	.053
1-11	0.52	60	.040	.344	.614	.042

SERIES 2

Run No.	Time Factor	Temp.	Mols C_3H_7Cl / Mol Feed	Mol Fraction HCl	Mol Fraction C_3H_6	Mol Fraction C_3H_7Cl
2-1	1.05	80°C	.077	.632	.285	.083
2-2	1.04	60	.061	.638	.297	.065
2-3	1.05	44	.034	.648	.317	.035
2-4	1.56	44	.047	.643	.307	.049
2-5	1.55	60	.077	.632	.285	.083
2-6	1.56	80	.104	.620	.264	.116
2-7	2.05	80	.130	.609	.242	.149
2-8	2.08	60	.098	.623	.268	.109
2-9	2.11	44	.065	.636	.294	.070
2-10	0.52	80	.050	.642	.305	.053

Results of Mass Spectrographic Analyses

The mass spectrographic analyses were made on a General Electric Analytical Mass Spectrometer by the sensitivity method by Mr. S. Huven Smith of Ohio State University.

Sample No.	Description	Analysis
1	Hydrogen chloride directly from cylinder.	Contains 5-10% impurity of a C_2 group hydrocarbon probably ethylene, also an impurity at masses 63, 64, 65.
2	Hydrogen chloride after passage through activated alumina.	Above impurities removed.
3	Propylene directly from cylinder.	
4	Propylene after passage through activated alumina.	Identical to Sample 3
5	Product gases at 44°C	C_3H_7Cl 15.8 ±0.1% C_3H_6 55.7 ±0.6% HCl 29.3 ±1.4% The listed products comprised the total spectrum of the sample. No peaks are unaccounted for.
6	Product gases at 80°C	C_3H_7Cl 17.6% C_3H_6 60.7% HCl 22.7%