THE PARTIAL OXIDATION OF
n-BUTANE

Thesis by
John Joseph Kalvinskas

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1959

ACKNOWLEDGMENT

I would like to acknowledge the guidance and encouragement of Professor William H. Corcoran in directing the research work. The help and guidance of Professor William N. Lacey and Professor Bruce H. Sage in my other academic studies are deeply appreciated. The cooperation and helpful suggestions of Professor Paul A. Longwell were of considerable assistance.

In the construction of equipment, Willard M. DeWitt, George A. Griffith and Frederick A. Wild require special mention for their efforts.

Valuable assistance in conducting the experimental work was provided by Joan L. Beed and Yui-Loong Wang.

Reduction of the experimental data was accomplished with the efforts of Joan L. Beed and my wife, Louanne A. Kalvinskas.

Yui-Loong Wang provided valuable assistance in the correlation of data on the Datatron computer.

Mavis Swan and Lois Schomberg did the typing for the thesis. Virginia Berry made up the graphs and equipment drawing.

Among others who have provided assistance during the course of this work are Roy Sakaida, Richard McKay and Evelyn Anderson.

Financial support of the research program was given by the Dupont Company.

Financial assistance was provided by Stauffer Chemical Company Foundation Fellowships as well as Institute scholarships.

ABSTRACT

The study of the partial oxidation of n-butane was carried out in a porcelain reactor having an inside diameter of 1 inch, and an adjustable length from 0 to 30 inches. The tube was equipped with traverse gear to allow measurement of both temperature and velocity gradients across the outlet section. Electric heaters were mounted on the wall of the reactor tube for obtaining the desired reaction temperatures. Supplementary to the reactor, equipment was provided to meter and preheat the butane and oxygen. A gas chromatograph was developed to provide analysis of the expected product gases, namely CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, CO, CO_2, H_2, H_2O and O_2. The composition of the product stream from the reactor was correlated with the reaction variables of time, temperature, and inlet oxygen composition by means of a multiple regression analysis. Also, by the same technique, the degree of conversion of butane was studied on the basis of assumed rate equations.

The reaction rate data for the n-butane oxidation were correlated on the basis of the following rate equation:

$$r = k\ (C_4H_{10})^{1.5}\,(O_2)^{0.5}$$

Giving: $\log k = -\ 1.1797 - 746.647\ (\frac{1}{T} - 0.00135) + 1.25508 \times 10^7\ (\frac{1}{T} - 0.00135)^2$

Where: r = lb. moles n-butane/ft^3 min.

k = lb. moles/ft^3 min.

(C_4H_{10}) = mole fraction n-butane

(O_2) = mole fraction oxygen

T = temperature, °K.

A minimum reaction rate for the oxidation of n-butane was observed at 452°C.

The thermal decomposition data were found to correlate best on the basis of the following second order rate equation:

$$-\frac{d(C_4H_{10})}{dt} = k\ (C_4H_{10})^2$$

$$k = 1.44 \times 10^{10}\ e^{-\frac{44.3 \times 10^3}{RT}}$$

Where: k = seconds^{-1}

(C_4H_{10}) = mole fraction n-butane

R = gas constant, cal/gm. mole °K.

T = temperature, °K.

The application of the rate equations for the partial oxidation and the thermal decomposition of n-butane is restricted to the range of the experimental investigation, namely one atmosphere, 360°-760°C. and 0-25% inlet oxygen concentration.

The correlation of the product distribution data by means of the multiple regression analysis is represented graphically as moles of component formed per 100 moles of butane feed versus inlet oxygen concentrations for several parametric values of retention time and temperature over the range of conditions investigated.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

I. INTRODUCTION

An investigation of the literature indicated that extensive work had been done on the partial oxidation of hydrocarbons. It was evident, however, that additional data were needed before a thorough understanding of the reaction kinetics of hydrocarbon oxidations is available. In the case of normal butane, much work had been done in the cool-flame region below 350°C. As far as could be determined, Appleby and co-workers (1) and, to a lesser extent, Pease (2) were the principal investigators of the oxidation of normal butane at higher temperatures. The work of Appleby (1), which was the most extensive, covered the region of 486°-526°C. Therefore, a relatively broad temperature region on either side still remained for investigation. It was therefore decided to study the effects of oxygen concentration and retention time on the partial oxidation of n-butane at a pressure of one atmosphere over the temperature region of 360° to approximately 760°C. The purpose was to obtain product compositions as a function of the reaction variables, a correlation of the data in terms of reaction rate equations, and also a possible insight into the controlling mechanisms of reaction. In addition, it was hoped to obtain data on temperature and velocity gradients in the reactor with a view towards using these data to provide an improved correlation of the experimental results.

II. LITERATURE SURVEY

A survey of the literature on the partial oxidation of butane was made by searching "Chemical Abstracts" for the years 1907 to 1958. The literature survey included references to the partial oxidation of hydrocarbons other than butane as well as pyrolysis of butane and related hydrocarbons wherever the specific work appeared to provide useful supplementary knowledge for the study of the oxidation of butane. A general tabulation of references is included in the Bibliography. A review of the most pertinent references is included in the following discussion.

A. EQUIPMENT

The apparatus used for the study of the partial oxidation of butane varied considerably among investigators. However, for those using a flow apparatus, two separate preheater tubes, a mixing chamber and a reactor were standard equipment requirements. Appleby and co-workers (1) used a reactor and preheaters made of pyrex. The reactor was equipped with a thermowell and had a length of 35 mm. and an inside diameter of 15 mm.

Pease (2) used two different sizes of pyrex-glass reactors. The larger reactor had a length of 11 cm. and an inside diameter of 1.65 cm., while the corresponding dimensions for the smaller were 10 cm. and 0.5 cm., respectively. The reactors were used either empty or packed with pyrex.

A conventional way of obtaining temperature control in the various investigations was to immerse the reactor in a constant-temperature bath such as boiling Arachlor (3) and to rely on a high surface-to-volume ratio to obtain sufficiently high heat transfer to hold the reactor temperature at the bath temperature. The reaction temperature was then considered to be identical to the bath temperature. Surface effects were claimed to be minimized by coating the reactor walls (and packing) with KCl by rinsing the reactor with a 20% KCl solution and allowing the moisture to evaporate (1,2).

B. ANALYSIS

Appleby and co-workers (1) analyzed their combustion products by means of multiple isothermal distillations supplemented by chemical and spectroscopic analysis. Pease (2) analyzed only the gaseous products of combustion. No attempt was made by him to analyze the liquid combustion products.

C. PRODUCT COMPOSITION

The products formed in the partial oxidation of butane are a result of (1) cracking of the butane at the elevated temperatures, (2) reaction of butane with oxygen, and (3) secondary oxidation and cracking of reaction products formed from the initial reaction of butane.

Tables I and II contain a summary of operating conditions and product composition from the partial oxidation of n-butane. The lists of components formed in the high temperature region (above 500°C.) include C_4H_8, C_3H_8, C_3H_6, C_2H_4, CH_4, H_2, CO, CO_2, and H_2O (1, 2, 4). At lower temperatures (less than 350°C.) additional components are formed, including HCHO, CH_3CHO, CH_3OH, acids and peroxides, mainly H_2O_2 (4). In addition at 285°C., C_2H_5OH is also formed (4).

Data on the partial oxidation of butane above 500°C. were not found in the literature. However, Burgoyne (5) obtained data on the combustion of CH_4 at temperatures in the vicinity of 1000°C. The data indicated that the reaction proceeds via HCHO to form CO in the first stage and CO_2 in the second stage. This presumably indicates the presence of aldehyde in the oxidation of butane even at high temperatures. In addition, at 500°C. when the KCl coating was removed from the walls, traces of acids, aldehydes, and peroxides were found in the product gas stream (1).

Pyrolysis of butane at 600°C. gave approximately the same product gas composition as the partial oxidation reaction with the exception that no oxygenated compounds were found. Otherwise, the distributions of saturated and unsaturated hydrocarbons in the product streams were similar, as shown in Table III (6).

D. REACTION CHARACTERISTICS

The rates of oxidation of saturated paraffins at temperatures in the low temperature region of 200°C. (and also at somewhat higher temperatures) were highly dependent on structure, i.e., the rates of oxidation increased with increasing chain length and also with unbranched or uninterrupted chain length (7). There were two main types of reactions - oxidation and cracking. As the temperature increased, cracking predominated (4). In the region of 200°

to 300°C., the reactions were autocatalytic and were accelerated by increases of pressure, temperature and the concentration of butane, whereas an increase of the oxygen concentration retarded the velocity of the reaction (8).

For higher temperatures, the work of Appleby and coworkers is very informative. A summary of some of their conclusions is included here:

1) <u>Butane to Oxygen Ratio (Temperature 486°-526°C., KCl coated wall)</u>

At O_2 concentrations of less than 8% by volume, the reaction products consisted of detectable amounts of only hydrocarbons and water. No oxygenated hydrocarbons or carbon oxides were found (1). At O_2 concentrations greater than 10% by volume, CO appeared, and the amount increased with increasing O_2 concentrations (1). The concentration of CO and CO_2 was principally affected by O_2 concentration and increased with increasing O_2 concentration (2). No other carbon compounds containing O_2 were found (1). When KCl was removed from the wall for one run, however, detectable amounts of acids, aldehydes, and peroxides were found.

With only 0.5% O_2 (by volume), the decomposition rate of butane was found to be approximately one-hundred-fold greater than that obtained in the absence of O_2 (1).

Oxygen has the effect of decreasing the production of saturates and propylene and increasing the production of ethylene and 1-butene relative to the values observed in the absence of oxygen (1), as indicated by a comparison of data in Tables I, II, and III.

Extrapolation of the product composition to zero residence time indicated that O_2 in low concentration at 500°C. acted predominantly as a dehydrogenation agent for butane, water and butene being formed as products (1). In addition, there was a small amount of induced cracking.

Data obtained at 503°C. and 1 atmosphere showed that the rate of the n-butane oxidation was approximately proportional to the square root of the O_2 concentration and to the 3/2 power of the butane concentration. The reaction-rate equation may then be written as:

$$-d\ (C_4H_{10})/dt = k\ (C_4H_{10})^{3/2}\ (O_2)^{1/2}.$$

The rate constant was found to be 2.70×10^4 cc./mole-sec. at 503°C., and the apparent activation energy was 21 kcal/g.mole (1).

2) The Effect of Residence Time on the n-Butane Oxidation (486°-526°C., KCl coated walls)

Increased retention time gave increased reaction of butane and O_2 and increased the concentration of CH_4 with a corresponding decrease in unsaturates and CO_2. Also, longer reaction times resulted in marked reduction in the concentration of butene with an accompanying increase in methane and propylene. In addition, a small increase in ethylene occurred accompanied by a slight decrease in ethane (1).

Times required to react as much as 10% of the butane at temperatures in the region of 300°-1000°C. were 10 millisec. at 1000°C. (5), 1 sec. at 500°C. (1), and 1 min. at 300°C. (4).

3) Surface Effects on n-Butane Oxidation Reaction

The data included in Table I (1) were obtained in a pyrex reactor having a wall coated with KCl. One run was made in the same reactor at 503°C. and 1 atmosphere without the KCl coating on the walls. In the latter case there were a greater production of CH_4, lower production of C_2H_6, and an appearance of a slight amount of peroxides accompanied by a small amount of acids and aldehydes. The absence of peroxides in the products from the reactor with KCl-coated walls indicated that KCl either destroyed peroxide formed in the gas phase or prevented a surface reaction on pyrex involving peroxide formation (1).

Effects of KCl-coated surfaces and surface-to-volume ratios on the reaction of butane and oxygen were also found to be significant in the work of Pease (2). His investigation was made in the region of 300o-625oC. using the two sizes of pyrex-glass reactors which were mentioned previously in this report. The reactors were used both as empty tubes and packed with pyrex glass. He observed that in the large, empty-tube reactor, the butane-oxygen reaction was approximately complete at 325°C. In the pyrex, glass-packed, KCl-coated tube there was no reaction below 500°C. In the packed, KCl-coated, smaller tube the reaction set in at 500°-600°C. instead of at 300°-400°C., the latter range prevailing at the part of the reaction in the empty tube (2).

Schmit (8) noted that KCl on the walls retards the reaction mainly by a lowering of k in the Semenoff relation

$$\Delta P = Ae^{kt}$$

The ΔP is equal to the change in reactor pressure. The k in the Semenoff relation is approximately proportional to the negative value of activation energy in the Arrhenius equation. The value of A in the Semenoff relation is proportional to the collision frequency factor (A) in the Arrhenius equation. (t equals temperature.)

Indications were also found that it was possible to poison the walls in such a way that the value of A in the Semenoff relation was also decreased (8). It can be increased by the addition of small amounts of alkyl nitrites and nitrates as well as diethyl ether and butyraldehyde (8).

4) Additives

The addition of 10% butene (by volume) decreases the butane conversion by 20% (1).

E. REACTION MECHANISM

In the field of hydrocarbon oxidation there are three main postulations for the mechanism (3). They are presented as follows:

1) Hydroxylation

An oxygen atom attacks the carbon-hydrogen bond at the end of the hydrocarbon chain to produce an alcohol. This step is followed by further oxygen attack and, subsequently, by thermal decomposition. One of the weaknesses of this theory is that the formation of atomic oxygen is difficult to explain.

2) Peroxide

An oxygen molecule attacks a carbon-hydrogen bond to give a peroxide which, being inherently unstable, decomposes to yield alcohols, aldehydes, acids, water and carbon oxides. Both mechanisms 1) and 2) have chain-initiating and chain-terminating steps to account for inhibition by surfaces.

3) Atomic Chain Theory of Norrish

The reaction is propagated by atoms and radicals formed in the hydrocarbon oxidation reaction rather than by an energy-rich chain mechanism.

Hinshelwood (7) reported that the rate of oxidation of saturated paraffins in the region of 183°-368°C. is highly dependent on structure, i.e., the rate of oxidation increases with increasing chain length. The relation between structure and ease of oxidation appears to be quite anomalous compared with most other hydrocarbon reactions. Experimental results indicate that this anomalous reaction behavior is associated particularly with the fate of the energy-rich peroxide radical, whose formulation and reaction are generally written (9):

(a) $R\cdot + O_2 \rightarrow RO_2\cdot$ (exothermic)

(b) $RO_2\cdot + RH \rightarrow R\cdot + ROOH$ (endothermic)

Factors which may favor reaction (b) include a low energy requirement for transferring H from RH to $RO_2\cdot$ and a high energy content made available for activation by vibration coupling within the hydrocarbon molecule. In addition to possible activation of vibrational energy, it is suggested that $RO_2\cdot$ may exist in more than one electronic state with different energy contents (9).

Satterfield (10) noted that many published studies of the partial oxidation of propane are brought into harmony when the log of the ratio (moles propylene formed)/(moles of propane forming oxygenated organic species) is plotted against 1/T. The results lend support to the hypothesis that the following three reactions are the predominant ones in the oxidation of propane:

(1) $C_3H_7\cdot + O_2 = C_3H_7OO\cdot$

(2) $C_3H_7\cdot + O_2 = C_3H_6 + HO_2\cdot$

(3) $C_3H_7\cdot = C_2H_4 + CH_3\cdot$

In all probability, the results indicated by Satterfield for propane oxidation may be extrapolated to aid in verifying the mechanism of the oxidation of butane. Consequently, a similar correlation of data may be attempted for the butane oxidation.

Appleby and co-workers (1) considered the primary reaction mechanism for the partial oxidation of butane in the region of 486°-526°C. to be the following:

(1) $C_4H_{10} + O_2 \rightarrow C_4H_9\cdot + HO_2\cdot$

(2) $C_4H_9\cdot + O_2 \rightarrow C_4H_8 + HO_2\cdot$

(3) $HO_2\cdot + C_4H_{10} \rightarrow H_2O_2 + C_4H_9\cdot$

(4) $2HO_2\cdot \rightarrow H_2O_2 + O_2$

(5) $H_2O_2 \xrightarrow{\text{wall}} H_2O + \frac{1}{2}O_2$

(6) $2HO_2\cdot \xrightarrow{\text{wall}} H_2O + 1\frac{1}{2}O_2$

(7) $C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6$

(8) $CH_3\cdot + C_4H_{10} \rightarrow CH_4 + C_4H_9\cdot$

(9) $C_4H_9\cdot \rightarrow C_2H_5\cdot + C_2H_4$

(10) $C_2H_5\cdot + C_4H_{10} \rightarrow C_2H_6 + C_4H_9\cdot$

In view of the data presented in the preceding literature references, it seems entirely plausible that both a peroxide and free radical mechanism prevail in the oxidation of butane. The data of Appleby and co-workers (1) and Pease (2) indicated that peroxides are present when KCl-coating on walls is absent and that the reaction can be retarded and stopped at temperatures below 500°C. by a high surface/volume ratio in the reactor, a possible indication of a peroxide mechanism, whereas the reaction will occur at the higher temperatures despite the high surface/volume ratio, a possible indication of atomic or free-radical mechanism. The supporting data for a peroxide mechanism at low temperature are very significant. In addition, the fact that the oxidation of butane will occur at elevated temperatures where there is no evidence of peroxide formation indicates a necessary second mechanism, which can be a free-radical mechanism, to explain the reaction.

The existence of two different reaction mechanisms provides an explanation for an observed negative temperature coefficient in the oxidation reaction of propane and ethane (7, 11). The rate constant for propane was observed to be at a maximum at 320°C. and then for the next 40°C. showed a negative temperature coefficient until 360°C., when the reaction rate started to increase again (7). A well-defined negative temperature coefficient was also observed in the rate of the slow oxidation of ethane between 350° and 410°C. (11). An obvious explanation for the negative temperature coefficient is the one that was tendered above: the peroxide mechanism predominates at low temperature and falls off in importance at higher temperature, whereas the free-radical mechanism is significant only in the higher temperature regions. The region of negative temperature coefficient is a region where the importance of the peroxide mechanism has decreased, but reaction as a result of the free-radical mechanism is not substantial enough to supplement the reaction fall-off because of the decreasing effect of the peroxide reaction.

F. <u>THERMAL DECOMPOSITION OF n-BUTANE</u>

The higher the temperature of the partial-oxidation reaction of butane, the greater is the importance of thermal cracking in the overall reaction of butane. For this reason, the data of Egloff and co-workers (6) on the pyrolysis of n-butane in the region of 600°-700°C. are cited in Table III and the reaction characteristics and mechanism of thermal decomposition are considered.

Propane, n-butane, and isobutane were pyrolyzed in non-catalytic metal tubes in the region of 600°-700°C. and pressures from 1-7 kg./cm.^{2} (6). Data are cited in Table III. The reaction characteristics noted were:

1) Increasing the reaction time increased the amount of hydrocarbon reacting.
2) The olefin concentration in the exit gas increased up to a maximum with increasing time of contact, after which it decreased.
3) When two or more olefins were formed, the conditions for their maxima were different from those for the case of a single olefin component.
4) An increase in temperature increased the maximum olefin concentration obtainable at all pressures. An increase of the pressure from 1 through 7 kg./cm.^{2} increased the reaction rate at 600°C., but this effect disappeared at higher temperatures.

The experimental results are readily understandable if one assumes the reaction takes place according to a group of equations, part of which are unimolecular and part bimolecular. The equations, postulated by Egloff and co-workers to explain the thermal decomposition reaction are included below:

	ΔF^{o}_{298} (cal/mol)
(1) $n\text{-}C_4H_{10} \longrightarrow C_4H_8 + H_2$	19,080
(2) $n\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_6$	7,100
(3) $n\text{-}C_4H_{10} \longrightarrow C_2H_4 + C_2H_6$	12,140
(4) $2\ n\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_8 + n\text{-}C_4H_8$	5,140
(5) $2\ n\text{-}C_4H_{10} \longrightarrow 2\ C_2H_6 + n\text{-}C_4H_8$	7,840

G. MECHANISM OF THERMAL REACTION OF n-BUTANE

Hinshelwood (12) noted that the decomposition of paraffin hydrocarbons was lowered to a limiting value by the addition of nitric oxide or of propylene. The fact that the limiting rates with the two inhibitors were identical and that extra nitric oxide added during the reaction had no further effect, indicated that the residual reaction rate corresponded to a molecular reaction.

The rate of decomposition of olefins increased rapidly with the number of carbon atoms; propane decomposed more rapidly than propylene; butane and 1-butene decomposed at the same rate; and 1-hexene decomposed faster than hexane. In the initial stages of the paraffin hydrocarbon decomposition, the concentration of olefins was small and further decomposition of the product was negligible. As products occurred, however, the olefin decomposition became important. It was inferred from the apparent chain length that the process of molecular rearrangement increased in importance relative to the chain reaction with the ascent of the series and for a given hydrocarbon with increased pressure (12).

For each hydrocarbon studied, the order of thermal decomposition reaction varied between first and second, which is compatible with Egloff's reaction equations. Hinshelwood reports the thermal decomposition reactions were not consistent with a constant order of 1.5, nor was the pressure dependence consistent with the uniform transition from second order to first, which was predicted for unimolecular reactions that were dependent on a single mode of activation by collision. There appeared to be a contribution to the overall reaction from processes that remained second order up to high pressures (12). The decomposition rate for a given pressure of the hydrocarbon tended to a limiting value as the paraffin hydrocarbon series was ascended (12).

The kinetics of the thermal decomposition of n-butane was studied in a pressure range of 1-30 in. Hg and a temperature range of 548°-573°C. by observing the change of pressure with time (13). The addition of traces of propane and isobutene was found to inhibit the n-butane decomposition reaction. Isobutene was the more effective inhibitor. Both inhibitors became less effective as the temperature was increased. The work indicated that the decomposition was a self-inhibiting chain reaction involving free methyl radicals (13).

The rate of decomposition of C_2H_6 in the presence of 0-16% isobutylene was studied at pressures near 10 mm. and at a temperature of 635°C. (14). Runs were made in a clean SiO_2 tube and also in the same tube when thermal decomposition products of isobutylene had been adsorbed on the wall. The amount of decomposition of C_2H_6 in 45 sec. decreased from 3.9% to 2.4% in the clean tube when the concentration of isobutylene in the reaction mixture was increased from 0 to 8%. In the treated tube the decomposition decreased from 7.4% to 5.2% for an increase in isobutylene from 0 to 11.5%. Any further increase in isobutylene had no effect on the reaction (14). This is in agreement with previous data cited in the literature. The conclusion was that the reaction was a chain process in which the inhibiting mechanism, where an H atom was removed from an olefin molecule by an active radical, was more probable than that involving addition to the olefin (14).

Additional work was done on the thermal decomposition of isobutane at 548°-573°C. and 10 mm.Hg. pressure in the presence of 0-20% propylene or isobutylene (15). The decomposition process was considered to be a free-radical chain reaction. The concentration of free methyl radicals was believed to be inhibited according to the following reaction:

$$R_{active} + M \longrightarrow RH + R_{inactive}$$

(where M is the inhibiting olefin molecule)

The activation energy for this type of reaction is small compared to that of reactions between saturated molecules (15). Quantitative information as to the specific-rate equation and values of rate constants is included in the reference. The equations and data included in the above reference are in agreement with previous work cited.

Rice (16) provided a theory for the thermal decomposition of hydrocarbons from the standpoint of free radicals. He assumed that when a hydrocarbon decomposed it dissociated into two free radicals which moved apart. Because the bond energy of a C-H bond is 93.3 kcal and that of a C-C bond is 71.0 kcal, the probable dissociation occurred through rupture of the C-C bond. The probability that the two radicals would collide again after the initial bond rupture is remote. Consequently, the free radical could either decompose or react with the surrounding hydrocarbon molecules. A free methyl group could take an H atom from its surroundings and form CH_4 and a hydrocarbon radical. An ethyl group produced in this way could undergo two reactions - the first, being similar to the methyl group reaction, producing C_2H_6 and a hydrocarbon radical, and the second possibility being a dissociation into C_2H_4 and H atoms. Radicals higher then ethyl could decompose in a similar manner into C_2H_4 and either a H atom or a free radical.

The dissociation of free radicals is possible because, in the process, a single bond becomes a double bond which releases 52,800 calories which contribute to the minimum activation energy (93,000 cal.) necessary to break a C-H bond or to the minimum activation energy (71,000 cal.) necessary to break a C-C bond. The decomposition of paraffin hydrocarbons can be represented as a chain reaction in which free H atoms or free radicals combine with an H atom of a surrounding hydrocarbon molecule. The hydrocarbon radical decomposes, as noted, into a compound and another free radical or H atom. Thus the cycle is continued as a chain reaction (16).

Rice (17) brought the reaction products from the thermal decomposition of propane and butane into contact with metallic Hg. Analyses of the resultant Hg alkyls produced showed that they contained more than 95% of Hg $(CH_3)_2$, indicating that the methyl groups are the principal alkyl radicals formed. Ethyl and higher radicals were shown to be absent.

H. HIGH TEMPERATURE OXIDATION

Burgoyne and Hirsch (5) studied the combustion of methane-air mixtures at approximately 1000°C. using a flow reactor. The concentration of CH_4 in the air mixture was of the order of 5%. The reaction took place in a few milliseconds, and was little influenced by surface effects at high temperatures. The surface effect did increase at lower temperatures.

The reaction was retarded by increased CH_4 concentrations and accelerated by increased O_2 concentrations. It proceeded via HCHO and CO. There was an accumulation of CO in the latter stages of the reaction, which oxidized rapidly or ignited when HCHO and CH_4 had been consumed. CO_2 appeared to a slight extent before the final stage of the reaction.

In the presence of H_2, the oxidation temperature of CO was reduced to that of H_2, but on addition of CH_4 the H_2 and CH_4 were oxidized together, and the CO remained until CH_4 disappeared. Ethane also inhibited the combustion of CO, but less effectively than CH_4.

There were two distinct stages in the reaction as noted above - first, the conversion to CO, and second, the combustion of the CO formed. With lean mixtures, approximately 36% of the CH_4 oxidized was present as HCHO at the first part of the reaction. As the reaction proceeded, however, the proportional conversion to HCHO decreased. The actual concentration of HCHO reached a maximum at a later point in the reaction and then dropped. With richer mixtures at lower temperatures, the HCHO concentration fluctuated about a mean value during the main course of the reaction. Approximately 5% of the CH_4 reacted appeared as an unidentified intermediate near the midpoint of the reaction which was postulated to be either methanol or ethane (5).

I. CARBON FORMATION

At temperatures of 1000°C. and above, and also lower temperatures, the formation of carbon in combustion processes is a possibility. Porter (18) presented three basic conclusions on the mechanism of carbon formation:

(1) The pyrolysis of hydrocarbons led to more rapid decomposition than to polymerization reactions at high temperature.

(2) Decomposition processes resulted in dehydrogenation and cracking to smaller molecules until the least stable hydrocarbon, C_2H_2 is formed, and

(3) Solid carbon is formed from C_2H_2 by simultaneous condensation and dehydrogenation processes.

III. EQUIPMENT AND OPERATING PROCEDURE

A schematic diagram of the apparatus is shown in Figure 1, and photographs in Figures 2, 3, 4, 5, 6, 7, 8, and 9. The principal features are: (A) a gas-metering system for butane and oxygen, (B) a preheater section, (C) a variable-length reactor, (D) a micrometer-mounted pitot tube and thermocouple for obtaining velocity and temperature traverses, respectively, at the exit section of the reactor, (E) a gas-sampling system, (F) a vacuum system, and (G) a gas chromatograph for analysis of product gases.

A view of the gas chromatography cabinet and reactor equipment bays is presented in Figure 2. Figures 3 and 4 provide front angle views of the reactor bays. The reactor is located behind the one-eighth inch steel shield. A rear view of the reactor is provided by Figure 5. The reactor is covered with magnesia insulation. The traverse mechanism is located above the reactor. A front view of the chromatography unit including a Varian Recorder is provided by Figure 7. In Figure 8 there are the stripping column, refrigeration unit, and air compressor which comprise a portion of the vacuum system. Figure 9 provides a view of the upper portion of the stripping column. The water-jet exhauster is located on the side of the column. An afterburner is located at the top of the column.

A. GAS METERING

Pressure regulators on the gas cylinders controlled the flow of butane and oxygen. For the first 46 runs, gas dryers were included in the flow line to insure the removal of residual traces of moisture. The driers were stainless-steel vessels with inside diameters of 3 inches and lengths of 12 inches, and were packed with Drierite ($CaSO_4$). For runs 46 through 167 the gas driers were removed. This was done to facilitate the rapid purging of the inlet gas lines of residual air that would contaminate the n-butane and oxygen flow streams.

The gas flow from the cylinders was directed to a temperature conditioner which consisted of 20 feet of $\frac{1}{4}$-inch 304-stainless-steel tubing, wound in a helical coil and submerged in a constant-temperature water bath. The bath temperature was controlled by proportioning incoming hot and cold water streams. A constant overflow of water from the bath ensured an even bath temperature. The bath temperature was measured by means of a mercury thermometer. The temperature of the bath was held constant within $\pm$ 0.5°C.

From the temperature conditioner, the gases entered the flowrators directly. The flowrators are rotameters made by Fischer and Porter, and are equipped with either stainless-steel, glass, or sapphire floats. The range of flowrator measurement was 0.0005 to 1.0 standard cubic foot of gas per minute (standard conditions were 70°F. and 760 mm. Hg.) The accuracy of the flowrator measurements was primarily dependent on the accuracy of reading the flowrator scales. It was estimated that the scales could be read to approximately one-half of a scale division, which in the case of the size 3 flowrator would indicate a possible error of 0.1% in high flowrate-measurements and 2.0% at low rates.

A 6 inch mercury manometer and a 0 to 30 psig Bourdon gage were connected to the exit side of the flowrators for obtaining the pressures of the gases flowing through the flowrators.

Although the flow rates were measured at other than standard conditions of temperature and pressure, they were in all cases corrected back to the standard conditions.

B. PREHEATER

The preheater section consisted of two separate preheaters in series. The first preheater was 7 feet of stainless-steel tubing having an inside diameter of ¼ inch and a wall thickness of 0.035 inch. The second preheater was 30 inches of stainless-steel tubing with an inside diameter of 1/8 inch and an outside diameter of 3/16 inch. Each was wrapped with asbestos tape to provide electrical insulation for a layer of 30 feet of No. 20 B and S gage nichrome IV wire. Thermal insulation was provided by a layer of micro-quartz insulation over the wire. The nichrome wire was connected to a 0-135 volt, 860 watt, type V-5 Variac. The entire preheater assembly was made movable, since it was connected to the inlet-gas nozzle which could be adjusted in position inside the procelain reactor tube. Each preheater was controlled by a separate Variac. The volume of the first preheater was 0.0012 cubic feet which was equivalent to a 2.7 inch length of the

1-inch inside diameter reactor tube. The volume of the second preheater was 0.00025 cubic foot which was equivalent to a 0.56 inch length of the reactor tube.

The butane and oxygen were fed through separate preheaters and were brought together in the mixing chamber.

C. GAS MIXING CHAMBER

Butane and oxygen were mixed by direct impingement of the two gas streams upon each other at the entrance to the mixing chamber. The volume of the mixing chamber was small (0.00005 cubic foot) and was equivalent to 0.1 inch of reactor length.

D. INLET NOZZLE

An inlet nozzle was provided between the mixing chamber and the reactor tube to provide potential flow of gases into the reactor. A stainless-steel nozzle was provided for runs 1 through 32. It was a 1-inch length of a stainless-steel tube and was packed with hypodermic tubing having an outside diameter of 0.032 inch and an inside diameter of 0.019 inch in lengths of 0.5 inch. The volume of the stainless-steel nozzle, including mixing chamber, was .00029 cubic foot and was equivalent to a reactor length of 0.63 inch. No nozzle was used for runs 33 through 45 and 92 through 99. A quartz nozzle with 0.040 inch inside diameter and 0.5 inch length tubing was employed for runs 46 through 91 and 100 through 109. A quartz nozzle using 0.25 inch outside diameter by 0.5 inch length tubing was used for runs 110 through 167. The volume of the quartz nozzle with 0.040 inch inside diameter tubing was 0.00015 or an equivalent of 0.32 inch of reactor.

The nozzle material was changed from stainless-steel to quartz because there was heavy carbon deposition on the nozzle after each set of runs. It was thought that the stainless-steel surface had some effect on the n-butane reaction which could be minimized by using a quartz nozzle. At temperatures above 600°C., carbon deposits were found on the quartz nozzle. In order to minimize the effect of the quartz nozzle on the n-butane reaction, a nozzle with larger diameter tubing was used. The new nozzle had a 0.25 inch outside diameter and a 0.19 inch inside diameter in place of the 0.050 inch outside diameter by 0.040 inch inside diameter. As a further means of checking nozzle effects on the n-butane reaction, some runs were made without any inlet gas nozzle.

E. REACTOR

The reactor tube was a McDanel high-temperature, porcelain tube with an inside diameter of 1 inch, an outside diameter of 1.25 inches and a length of 30 inches. The reactor tube for runs 62 through 167 had an inside diameter of 1.03 inches with an outside diameter of 1.25 inches. The inlet nozzle to the reactor was fitted inside the reactor tube and could be adjusted in position to allow use of any fraction of the total 30 inches of reactor length. Asbestos packing was used to provide a gas-tight seal between the movable nozzle and the reactor wall. The reactor tube was located inside a second porcelain tube which had an inside diameter of 1.50 inches and an outside diameter of 1.75 inches. The outer tube was wrapped with 5 electric heaters for maintaining the reactor wall at the desired temperature. The heaters were 30 foot lengths of No. 22 nichrome IV wire wound in 6-inch sections. Each heater was connected to a 135 volt, 860 watt, V-5 Variac for separate temperature control of each section. To maintain the wire in place, asbestos tape was used. For purposes of insulation, several layers of 0.50 inch thick micro-quartz insulation were used. At the longitudinal center of each heater section, there was a chromel-alumel thermocouple inserted through the heater tube and mounted at the wall of the reactor tube. In operation, the Variacs controlling the heaters were set to give uniform thermocouple readings along the length of the reactor.

F. TEMPERATURE AND VELOCITY TRAVERSES

At the exit section of the reactor tube, a pitot tube and thermocouple were located for the purpose of obtaining radial temperature and velocity traverses.

The traverse thermocouple was made of 0.003 inch diameter Platinum and 90% platinum-10% rhodium wires. It was enclosed in a quartz tube having an outer diameter of 0.1 inch. The quartz tube was made in the form of a right-angle with the leg containing the thermocouple junction having a length of 3 inches and the other, which was joined to a micrometer head for positioning, a length of 5 inches.

For velocity measurements, a pitot tube made of quartz with an inside diameter of approximately 0.060 inch and outside diameter of 0.080 inch was used. The length and the arrangement of the pitot tube in the reactor were similar to those for the thermocouple. The two traverse assemblies were mounted on opposite sides of the reactor, and permitted traverses to reach within 0.1 inch of the adjacent wall and 0.3 inch of the opposite wall. The major error in determining the exact traverse location was in the initial positioning of the probe with respect to the wall. The estimated error of position was ±0.01 inch. Otherwise, the micrometer heads enabled the positioning of the probes to within ±0.001 inch.

The temperature probe had an axial length of 3 inches inside the reactor for the purpose of minimizing conduction effects along the wire and quartz tube. It was estimated from the temperature data for the traverse and gas temperatures that the traverse temperature read low by approximately 20°C. at low flowrates. The low temperature readings appeared to be independent of traverse location as indicated by the similarity of traverse temperatures on either side of center in the reactor. At sufficiently high flowrates, the temperature-traverse reading was approximately that of the gas temperature as measured by thermocouples inside the reactor. A part of the low temperature reading on the traverse thermocouple was attributed to the greater heat conduction effects at the end of the reactor tube.

G. THERMOCOUPLE CALIBRATIONS

The platinum vs. 90% platinum-10% rhodium and chromel-alumel thermocouples were calibrated by the National Bureau of Standards over the range of 0-1100°C. The calibration values are included in Appendix L. The Bureau of Standards considered the calibration of the platinum vs. 90% platinum-10% rhodium thermocouple to be accurate to within 0.5°C. The calibration of the chromel-alumel thermocouple was considered to be accurate to within 1°C.

All thermocouples were made from either the platinum and 90% platinum-10% rhodium wire or the chromel and alumel wire calibrated by the Bureau of Standards.

H. VELOCITY MEASUREMENTS

A micro-manometer was connected to the pitot tube to measure the impact pressure of the gas. It was designed to measure liquid heads within 0.0001 inch. With kerosene as a manometer fluid (at 25°C. = 0.803 g./cc.), gas velocities as low as 1 foot per second may be measured. In practice, it was found that somewhat higher gas velocities were needed before measurements could be made. Since the gas velocities present in the reactor were generally lower than 1 foot per second, no velocity traverses were obtained.

I. SAMPLING SYSTEM

The reaction gases left the reactor through a stainless-steel nozzle that converged to a minimum diameter of 1/8 inch. There was a sampling port with a diameter of 0.030 inch located 2 inches downstream of the nozzle in the sidewall of the

1/8 inch diameter section. This was connected to a gas sampler by means of an 8 inch length of stainless steel tubing having an outside diameter of 0.072 inch. All gas samples were obtained at this location during the first 61 runs. Samples were obtained from the pitot tube for runs 62 through 167 by approximately isokinetic sampling.

The procedure for obtaining gas samples was: (1) the gas sampler and attached tubing were evacuated by means of a vacuum pump until the vacuum indicated on a 0-30 inch mercury manometer was constant, (2) the valve to the reactor was opened and the gas was purged through the sampling system for several minutes, (3) the valve was then closed, the system re-evacuated, and a sample taken. When a sample was taken through the pitot tube, isokinetic conditions were accomplished by throttling the gas through a valve at the desired rate. That rate was indicated by observing the rate of pressure change on a mercury manometer connected to the sampling system. The final sample was always at 1 atmosphere. This prevented air contamination of the samples prior to analysis. The sample bulbs had a capacity of 250 cc. A total of 12 bulbs were used to permit consecutive sampling of as many as 12 runs and allow later analysis of the samples.

One of the principal considerations in obtaining the gas samples was that they be representative of the gas composition in the reactor. In order to accomplish this, the gas sample had to be cooled rapidly below the reaction temperature so that the reaction during the cooling period would be negligible. Heat-transfer calculations indicated that the passage of the gas sample at an initial temperature of 500°C. through the 0.072 inch outside diameter stainless steel tube held at room temperature would result in a cooling of the gas from 500°C. to 150°C. in 10 millisec. and to 100°C. in 20 millisec. These calculations were based on an overall heat-transfer coefficient from the gas to stainless-steel tubing of 1.5 B.t.u./(hr.)(ft.^{2})(°F.).

The residence time for 10-20% reaction of butane at 500°C. was in the range of 1-2 seconds and in the range of minutes at 200°C. (4). Consequently, the amount of reaction that occurred in the short cooling period was negligible. For cooling gases from 1000°C. to 500°C., 1 millisec. was required which was short with respect to the reaction time of 10 millisec. for significant reaction at 1000°C. This illustrated that the sample cooling period was too short for significant reaction to occur even at initially high reaction temperatures.

J. VACUUM SYSTEM

A diagram of the vacuum system is included as a part of the main equipment diagram (Figure 1).

A Schutte and Koerting multi-nozzle, water-jet exhauster was used to obtain a vacuum on the downstream side of the exit-gas nozzle. A feed rate of approximately 100 gpm of water was needed to operate the jet exhauster. Its capacity was indicated by the fact that it could draw a 27 inch Hg. vacuum under a load of 0.1 cubic foot of gas per minute, measured at 70°F., 760 mm. Hg. Because of the large water requirement, it was continuously recirculated. Since the exit-water stream from the jet exhauster was contaminated with the reaction gases, which would reduce the efficiency of the jet exhauster, the absorbed gases were stripped from the water before recirculation. In addition, provision was made to remove the energy added to the water system by the hot exit gases and the energy added by the pump for the recirculation of the water. The stripper was a steel column with a length of 10 feet and an inside diameter of 20 inches. It was packed with Dowpac FN-90 Polystyrene packing obtained from Fluor Corp. Air for stripping was provided by a DeVilbis air compressor with a 1/2 horsepower motor. The heat exchanger was a shell-and-tube unit with a rating of 3 tons. It was connected on the tube side to a 3 ton, air-cooled refrigeration unit.

The water stream leaving the jet exhauster went directly to the top of the stripping column. Air entered at the bottom of the stripping column and flowed countercurrent to the water stream, thus stripping out the reaction gases. Water leaving the bottom of the column went to a 7.5 horsepower centrifugal pump from which it circulated to the heat exchanger and then back to the inlet side of the jet exhauster.

K. AFTERBURNER

To minimize contamination of the atmosphere from unburned combustion gases, an afterburner was mounted on top of the stripper column. The afterburner was equipped with an air-feed line and a pilot flame. For ignition of the pilot flame a spark-plug system was used.

L. GAS CHROMATOGRAPHY

The unit for analyses consisted of 2 columns, each of which was followed by a thermal conductivity cell, as shown in Figure 10. The first of the 2 columns was a 30 foot length of copper tubing having an outside diameter of 0.25 inch packed with 35-48 mesh Sil-O-Cel coated with tetraisobutylene. The column consisted of 7.5 foot sections connected by U tubes for a total of 30 feet. The second column was a 20 foot length of stainless-steel tubing having an outside diameter of 0.25 inch packed with 35-48 mesh molecular sieves (type 13X).

The columns and thermal conductivity cells were located in a constant-temperature cabinet, which controlled to within 0.05°C. The cabinet temperature was controlled at some fixed temperature to ±0.05°C. within the temperature range of 28° to 32°C. The cabinet temperature was kept relatively uniform by means of a blower for air recirculation. Both a refrigeration unit and heater system were used to obtain the desired cabinet temperature. A 15-foot loop of stainless-steel tubing having an outside diameter of 0.19 inch was filled with mercury and used as a sensing device. This was combined with a mercury switch and an electrical relay to control the cabinet temperature.

Helium was used as the carrier gas for the general analyses of the majority of the reaction components. The inlet pressure was normally 40-42 psig. The flow rate was usually 60 cc./min. measured at 70° F. and 760 mm. Hg. For the analysis of hydrogen, nitrogen was used as the carrier gas at an inlet pressure of 35 psig.

The thermal conductivity cell was a combination of a thermistor (G106 probe, Fenwal Electronics) and an aluminum block. The thermistor was part of a Bridge network as shown in Figure 11. The output of the circuit was fed to a G-10 Varian Recorder which had full-scale deflection at 10 mv. The Varian Recorder was operated at a chart speed of 48 inches per hour. An attenuator switch was included in the output from both the first and second thermal conductivity cells. The attenuation of peaks on the first detector was 0.195. The attenuation on the second detector was 0.265.

Gas samples sent through the chromatography columns were made up in the sampling network indicated in Figure 10. The procedure was to evacuate the stainless-steel coil (34.88 cc.) and the interconnecting tubing by means of a vacuum pump. A gas sample was then admitted to the stainless-steel coil from the sampling bulb. The sample in the coil was closed off, the interconnecting tubing re-evacuated and the sample in the coil switched into the helium carrier-gas-line. The flow of helium through the sample coil purged the gas sample to the chromatography columns.

The components were identified by the elution time (measured from the time the component sample was introduced into the chromatography unit until the time the leading edge of the peak appeared on the chromatogram. Calibration of the chromatography columns with known samples was necessary in order to determine the elution time for various components as well as the relative response. Calibration of the chromatography unit with respect to the relative peak of each component is indicated in Appendix A. Elution times for various components are indicated in Appendix B.

In order to obtain a more sensitive determination of sample components in small concentrations, an attenuator was included as a part of the detector circuit. The operating procedure was to insert a large sample so that components in large concentrations had to be attenuated to avoid recording off scale. Then, by leaving the components in small concentrations unattenuated, an amplification of the components present in small concentrations was achieved. This required running two aliquot samples through in some cases - the first to determine the order of magnitude of the peaks and the second to use the optimum sample size and attenuator setting to achieve maximum sensitivity for detecting small peaks.

The components of methane, nitrogen, oxygen and carbon monoxide were not resolved on the first column (35-48 mesh Sil-O-Cel coated with tetraisobutylene) and consequently a second column of molecular sieves was placed in series with the first column for the resolution of these components. The first column provided resolution of the carbon dioxide, ethylene, ethane, propylene, propane, butene and butane peaks. They were eluted in that respective order from the first column. These components were irreversibly adsorbed on the molecular sieves and did not pass through this second column. As a consequence of this adsorption, the molecular-sieve packing had to be reactivated by heating to elevated temperatures (500°F.) which desorbed the gases. The need for reactivation of the molecular sieves was indicated by a decrease in the resolution between the nitrogen and oxygen peaks.

M. GENERAL OPERATING PROCEDURE

The general operating procedure for making a given series of runs was as follows:

(1) The vacuum system was turned on and the vacuum valve to the reactor system was opened slightly to provide a slight vacuum in the reactor (as indicated by a mercury manometer connected to the reactor).

(2) The inlet butane and oxygen lines were evacuated by a vacuum pump and a small flow of butane started through the reactor.

(3) The Variacs controlling heat input to the reactor and preheater were turned on and adjusted to achieve the desired reaction temperature.

(4) The reactor wall, gas and traverse temperatures were measured periodically on a temperature bench.

The Variacs were adjusted to give a uniform temperature level. When the desired temperature level was nearly achieved, the butane flow rate was adjusted to the desired level. Also, oxygen flow was started into the reactor in order to purge any residual air out of the inlet oxygen line.

(5) Temperatures and flow rates were adjusted until the desired operating conditions were attained for the first run.

(6) With operating conditions set, flow rates and temperatures were recorded on data sheets while simultaneously obtaining a sample of the reaction gases.

(7) A gas sample was obtained by (a) evacuating the sample bulb and interconnecting tubing to the reactor by means of a vacuum pump (using a mercury manometer as an indication of the vacuum level), (b) allowing the reaction gases to purge through the sample bulb, and (c) re-evacuating the system and then taking the gas sample.

(8) The operating conditions were then changed to those desired for the succeeding run. Generally, a series of 4 runs was made at the same temperature but at different inlet oxygen concentrations, which meant that the next set of run conditions could be achieved by merely changing the oxygen

flowrate. The second set of 4 runs was generally at a different temperature level. This involved adjustment of the Variac heaters and required a longer period for attainment of steady operating conditions.

(9) At high oxygen concentrations (greater than 20%) the reaction was highly exothermic. Consequently, it was sometimes necessary to set the initial temperature of the reaction gases and reactor wall below the desired reaction temperature so that at the end of the run the reaction gas temperature had not risen too far above the desired level. The overall rise of temperature could generally be kept to within 20°C. during the course of the run.

(10) During the course of the reaction the pressure was kept slightly positive (0.02-0.05 inch kerosene). This minimized leakage of air into the reactor at the inlet nozzle. The space between the inlet nozzle and reactor wall was packed with asbestos string wound around the nozzle. This did not prove, apparently, to be a completely gas-tight seal in all runs.

IV. RAW MATERIALS

The reactant gases were n-butane and oxygen. For the first 30 runs instrument grade n-butane (minimum purity 99.5%) was obtained from Phillips Petroleum Company. For runs 31-141, C.P. grade n-butane (99.0% minimum purity) was obtained from the Matheson Company, Inc. For runs 142-167, instrument grade n-butane (99.5% minimum purity) was obtained from the Matheson Company, Inc. For all the runs oxygen (99.5% minimum purity) was obtained from Linde Air Products. The principal impurity in the oxygen was nitrogen.

Nitrogen used in the gas chromatography unit as a carrier gas was obtained from Linde Air Products. It was dry and of extra-high purity (99.7%). Helium used in the gas chromatograph as a carrier was obtained from Air Reduction Pacific. Its purity was 99.97%. Calibration gases were obtained in lecture bottles (generally 99.0% minimum purity) from the Matheson Company, Inc.

V. EXPERIMENTAL PROGRAM

Temperature, inlet oxygen concentration and retention time were the variables that were investigated. Pressure was held constant at one atmosphere.

A. Temperature

The temperature region investigated for the reaction of n-butane with oxygen was 360°C. to 760°C. The temperature range was divided into three regions centering about 400°, 500° and 700°C. respectively. An attempt was made to keep a minimum temperature interval of 30°C. between given runs. This temperature interval was maintained to insure that the temperature between runs was greater than the temperature deviation of any given run. In practice, the desired temperature spread between runs was maintained although the precision of reproducing the same reactor temperature for a series of runs was poor because of the difficulty of attaining uniform temperatures at a predesignated temperature within a reasonable time. When a set of uniform temperatures was attained, a run was generally made even though it deviated a few degrees from the desired operating temperature. A discussion of determining a representative reaction temperature on the basis of the measured traverse, wall and gas temperatures is provided in Appendix C.

B. Inlet Oxygen Concentration

Investigations were carried out over a range of inlet oxygen concentrations of 0-25%. Generally, 0, 5, 10 and 20 mole % oxygen concentrations were used. In practice, however, intermediate levels of oxygen concentration were run due to air leakage into the reactor (when it occurred, it was calculated as shown in Appendix H and indicated in Table XI). Sometimes flowrates were altered slightly to facilitate the reactor operation. The pattern of oxygen concentrations was not strictly adhered to in such cases. Operation at these relatively low levels of oxygen concentration kept the reactor conditions outside the explosive limits for the butane-oxygen mixture. The explosive limits are between 2.8 and 31.4 volume % of butane in oxygen (22). Also, the heat of reaction was limited to levels permitting reasonable attainment of isothermal operating conditions.

C. Reaction Time

The reaction times were adjusted to correspond to the particular temperature levels of operation. A combination of reactor length and butane and oxygen flowrates was used to obtain the desired retention time. Since the retention time was also a function of the number of moles of product formed, the retention time was set only approximately. In practice, for each temperature the butane and oxygen flowrates were held approximately constant while the total reactor length was varied between 7, 14 and 28 inches.

The retention times corresponding to the several temperature levels of operation were: 700°C. - (0.5-2.0 sec.)
500°C. - (4.0-8.0 sec.)
400°C. - (4.0-16.0 sec.)

These times were chosen to provide a significant level of butane conversion without providing complete conversion. With the exception of the low temperature operation at 400°C. without oxygen, there generally was a significant amount of reaction.

D. Product Gas Analysis

The principal products of the partial oxidation of butane in the region of 360°- 760°C. were butene, propylene, ethylene, ethane, methane, hydrogen, carbon monoxide, carbon dioxide, water and carbon. The chromatography unit was calibrated with each of the component gases to be analyzed, as shown in Appendix A, D, and E. The chromatograms were reproduced and the component peaks cut out and weighed. By following the procedure outlined in Appendix F, sample concentrations were obtained. In addition to the chromatography analysis, 3 samples were analyzed by mass spectrometer. A comparison of the 2 sets of analyses is shown in Table IV. For purposes of comparison, the chromatographic analyses were reported on the same basis as the mass spectrometer analysis.

VI. CORRELATION OF DATA

The data obtained in a given run were the reactor wall temperatures, traverse temperatures and reactor gas temperatures, butane and oxygen flow rates, reactor length, and chromatograms of the product sample. The reactor operating conditions are summarized in Table XI. The temperature of the reaction was generally taken to be the average gas temperature in the reactor, as measured by thermocouples present inside the reactor. A more detailed discussion of the choice of a representative reaction temperature on the basis of the temperature data is indicated in Appendix C.

The butane and oxygen flow rates were corrected for pressure and temperature, and the values reported on the basis of flow at 70°F. and 760 mm. Hg. In the case where air leakage was indicated on the basis of the chromatogram and where the oxygen coming in with the air had at least partially reacted, as shown in Appendix G, the amount of air leaking into the reactor was calculated, as reported in Appendix H, and included in determining the oxygen flowrate as well as the inlet butane concentration.

The reactor length was generally set at 7 inches, 14 inches, and 28 inches. For a given flowrate, changing the length of the reactor was a means of changing the retention time. Although the flow was in the laminar region as indicated by the Reynolds number which was generally less than 500, the sample composition across the reactor as shown in Table V did not vary significantly with respect to radial distance from the reactor wall. The heat transfer between the reactor wall and the gas stream appeared to be high as shown by a comparison of the calculated and measured values of traverse temperature in Table VI. The temperature gradient in the radial direction across the reactor was relatively low as shown by the data in Table VII.

The chromatographic unit was calibrated to give the sample concentration in volume percent. In some cases, the sample bulbs were contaminated by air leakage. This was indicated by the presence of nitrogen in the chromatogram and the fact that the ratio of oxygen to nitrogen was proportional to, or somewhat greater than, that found in air. It was generally possible to make a reasonable assumption whether a given sample was contaminated by air leakage at the time of sampling or by leakage of air into the reactor at the inlet gas nozzle. As indicated above, the ratio of oxygen to nitrogen was used as a primary index for this determination. In general, any air contamination was slight and did not affect the run conditions or the sample analyses to a significant extent. The assumption as to the source of air contamination on a given run is indicated in Appendix G. In the cases where it was shown that the sample was contaminated with air during sampling, the nitrogen and corresponding oxygen were subtracted from the sample composition and the sample compositions reported on an air free basis. The sample compositions in mole percent, obtained directly from chromatograms and uncorrected for air contamination are listed in Table VIII.

Material balances were made on each run using the mole ratios of carbon and hydrogen (obtained from butane), the mole ratios of carbon to oxygen which were obtained from the ratio of flow rates of butane and oxygen, and the sample composition data to obtain the amount of water formed and the carbon unaccounted for in each run. The equations and method of calculation are shown in Appendix I. It was assumed for purposes of calculation that all the carbon unaccounted for was present as carbon deposited in the reactor. This assumption was made because, in a large portion of the runs, carbon was found deposited in the reactor. An analysis of carbon deposited in the reactor indicated that the mole ratio of carbon to hydrogen (as H) was 10:1 as indicated in Table IX. The hydrogen accompanying the carbon was included in the material balance. The material balances for the carbon and water determination are interdependent. Both water and carbon were obtained by solution of the simultaneous equations describing the material balance.

To obtain the concentration of the reaction gases in the product stream, the sample composition was recomputed on the basis that it included water obtained from the material balance. These data are reported in Table X.

In order to provide an indication of the variation of the product composition as well as the amounts of individual components with respect to the reaction variables, the sample concentration data were recomputed on a basis of moles of component formed per hundred moles of butane feed. These data are included in Table XII.

For correlation of the butane conversion in terms of a reaction rate equation, several rate equations for the oxidation of n-butane for various orders of butane and oxygen were considered. The equations used for the correlation of data were:

$$r = k\ (C_4H_{10})^{1.5}\ (O_2)^{0.5} \qquad (1)$$

and,

$$r = k\ (C_4H_{10})^{1.0}\ (O_2)^{1.0} \qquad (2)$$

Rate constants calculated for the n-butane oxidation on the basis of rate equation (1) are presented in Table XIII. The derivation of the integrated form of this rate equation (1) is indicated in Appendix J. The correlation of the rate constant on a log k vs. 1/T plot for the above rate equation is shown in Figure 12. It appeared that the scattering of the data on the log k vs. 1/T plot for the above rate equation could be reduced by increasing the order of oxygen and decreasing the order of n-butane. Rate constants were calculated, therefore, on the basis of rate equation (2). The scatter of data on a log k vs. 1/T plot based on rate equation (2) was considerably greater than before. Based on the above comparison of the correlation of reaction rate constants with respect to 1/T, the reaction equation with butane to the 1.5 order and oxygen to the 0.5 order provided the better correlation of reaction rate data.

In obtaining the integrated form of the rate equation, it was necessary to obtain the stoichiometric ratio of of oxygen to n-butane and also a value for the increase in the number of moles per mole of n-butane reacted. Both of these values were determined from the experimental data for each run and are shown in Appendix K. It was assumed that these values remained constant over the course of the run. The correlation of the log k with respect to 1/T data for the 1.5 order for butane and 0.5 order for oxygen was made by a least squares fit of a second order equation using the program written by Darwin W. Smith for the Datatron 205. Temperatures were substituted back into the equation to obtain k values which were then plotted on Figure 12.

The thermal decomposition data were correlated for zero, first, second and third orders for butane on log k vs. 1/T plots as shown in Figures 13, 14, 15, and 16, respectively.

The correlation of the product composition data in the form of moles of component per 100 moles of butane feed for the operating variables of temperature, time, and inlet oxygen concentration was made by using the least squares program written by Darwin W. Smith and also the linear regression code written by Jack Varga and George Gerson. The equations used to compute the data are included in Table XV. For carbon, ethane, ethylene, propylene, butene, and butane conversion, second order equations in terms of temperature, time and inlet oxygen concentration were used. For carbon monoxide and carbon dioxide, a second order equation in terms of the three variables multiplied by the inlet oxygen concentration was used. The multiplication by oxygen concentration fixed the value of CO and CO_2 at zero for zero oxygen concentration. For methane and hydrogen, a second order equation with respect to time and oxygen concentration and third order with respect to temperature was written. It also included the cross product terms of time-temperature and oxygen-time. Values obtained for butane conversion and for moles of component per 100 moles of butane feed, were plotted against inlet oxygen concentration for parametric values of time and temperature, as shown in Figures 17 to 32. These values were obtained by substituting temperature, time and inlet oxygen concentration back into linear regression equations. The range of these variables was kept within the range of the experimental conditions. The temperatures were 670, 770, 870, and 970°K. Inlet oxygen concentrations were 0, 10, and 20 mole percent. The range of retention time was 0.5 to 16.0 seconds. At any given temperature level the average change in retention time was considerably less than the overall range of retention time indicated for the investigation. Original data points which most closely corresponded to the operating conditions were plotted on each graph to provide some comparison of the original data with the result of the multiple regression correlation. These data are included in Table XII.

In plotting the data obtained in runs using a stainless steel inlet gas nozzle, it was found that these data scattered more widely and, in general, showed a somewhat greater conversion of butane than data obtained with either a quartz nozzle or no nozzle. These data consisted of only 32 runs, of which the first 11 runs were not completely reduced because of insufficient calibration data on the chromatography unit. The reactor operating condition, as well as the results of sample analyses for runs 11 to 32, are reported in Tables XVII to XIX. Reaction rate constants for both the oxidation and thermal decomposition reaction have been calculated for these data and are to be found in Tables XX and XXI, respectively.

VII. RESULTS AND DISCUSSION OF RESULTS

A. Analysis

A comparison of duplicate analyses is shown in Table XXII in order to indicate the reproducibility of the sample analysis. The comparison includes sources of errors that may come from calibration of the chromatograph, errors in non-uniformity of the paper used in reproduction of the chromatograms, and errors incurred in cutting out and weighing the component peaks. In general, the error in duplicating the analysis was of the order of 5%. In some cases, such as carbon dioxide where the peak was located between two generally large peaks (methane and ethylene), the peak resolution was poor. As a consequence, the reliability of the analysis for carbon dioxide was inferior to that of the other components. A further indication of the accuracy of the analysis is indicated by comparison of air calibration data and hydrogen calibration. These data consist of calibration of the chromatograph before and after a set of analyses. The calibrations coincided very well at times, within 1%. In other cases, the calibration differed by as much as 10%. The larger deviation probably resulted from slight changes in carrier gas flow rate and also changes in the response of the thermal conductivity cell due to slight changes in thermistor current. The average difference in calibrations was approximately 5%. A change in the chromatograph calibration does not cause a proportionate error in analysis unless the change occurs during the analysis of a sample. Otherwise, the change in calibration causes the response of the chromatograph to change proportionately for all components, thus cancelling out this effect.

Three samples were analyzed by means of a mass spectrometer and the analyses compared with those obtained by the gas chromatograph. The comparison is shown in Table IV. In order to put both analyses on the same basis for purposes of comparison, the total percent of sample accounted for on the gas chromatography unit was made equal to the sample total that these same components represented in the mass spectrometer analyses. The mass spectrometer analyses indicated that approximately 95% to 97% of the total sample was accounted for by the gas chromatograph. The components unaccounted for were small concentrations of components such as C_4 and C_5 acetylenes and/or diolefins. A complete list of the components is presented in Table IV.

The samples that were analyzed were deemed to be representative of the reaction gases at the sampling location in the reactor. Sampling of the gases at 0.1 inch, 0.3 inch and 0.5 inch from the reactor wall gave no significant difference in composition as shown in Table V. Rapid sampling, 45 seconds for a 250 cc. sample, and slow sampling, 8 minutes for a 250 cc. sample, gave no significant difference in sample composition. Runs 166-3 and 166-4 were sampled rapidly and runs 166-1 and 166-2 were sampled slowly. Both sets of runs were obtained under the same set of operating conditions. A comparison of the sample compositions obtained for these runs is included in Table IV.

Since samples were sometimes stored for a period of several days before analyses, it was necessary to establish the fact that no change occurred in sample composition prior to analysis. To establish this, several samples were analyzed within one day after sampling and reanalyzed approximately one month later. The results are shown in Table XXIII. No significant change in sample composition had occurred during this period.

The values of carbon and water formed during the reaction were obtained by means of material balances. They are consequently less reliable than the values obtained directly from the analysis. The value for carbon represents unaccounted for carbon. At low temperatures, 500°C. and less, the carbon value probably represents carbon components not picked up in the analysis. At high temperatures the carbon value probably represents carbon deposited in the reactor, as indicated qualitatively in Table XXIV.

B. Oxidation Rate Equation

The oxidation data for n-butane were correlated on the basis of the following rate equation:

$$r = k\ (C_4H_{10})^{1.5}(O_2)^{0.5}$$

This rate equation was found by Appleby and co-workers (1) to fit their data for the oxidation of n-butane in the region of 486° to 526°C. It was decided, therefore, to use this as a basis for the initial correlation of the rate data on the oxidation of n-butane. Some theoretical justification for using the above rate equation is based on the reaction mechanisms for n-butane proposed by Appleby (1). The proposed mechanism is included under the literature section. Greater emphasis in the reaction mechanism proposed by Appleby is placed on the butane and less on oxygen, which is in accord with a 1.5 order of butane and a 0.5 order of oxygen. After plotting the calculated rate constants on the basis of the above rate equation, it appeared that a higher order of oxygen and lower order of butane would provide a more satisfactory correlation. It was decided to attempt a correlation of the rate data on the basis of a first order for butane and a first order for oxygen since data on the propane oxidation were found to have a second order dependence, first order for propane and first order for oxygen (19). A plot of the calculated rate constants for these orders of butane and oxygen on a log k vs. 1/T plot was found to have more scatter than the correlation of reaction rate data on the basis of 1.5 order for butane and 0.5 order for oxygen. As a consequence, it was decided that the 1.5 order for butane and 0.5 order for oxygen gave the best correlation of the n-butane reaction rate data.

The correlation of the reaction rate constants for the 1.5 order for butane and 0.5 order for oxygen on a log k vs. 1/T plot indicated that the reaction rate constants passed through a minimum with respect to temperature. A correlation of the above data using a least squares fit of a second order equation to the data gave the following equation:

$$\log k = -1.1797 - 746.647 \left(\frac{1}{T} - 0.00135\right) + 1.25508$$
$$\times 10^7 \left(\frac{1}{T} - 0.00135\right)^2$$

Where: k = pound moles/(minute)(ft^3)

T = temperature (°K.)

Taking the first derivative of log k with respect to 1/T and setting the derivative equal to zero gave a minimum at 452°C. The occurrence of this minimum in the oxidation of n-butane is not surprising in view of the fact that a reaction rate minimum has been reported for the oxidation of ethane between 350° and 410°C. (20) and also for propane at 430°C. (19). (Cullins and Hinshelwood (7) have reported a minimum reaction rate for propane at 360°C.) A reasonable explanation for the minimum, which results from a decrease in the reaction rate with respect to increasing temperature, is that the mechanism of reaction is changing in this region.

The postulated mechanism in the low temperature region involves the fate of a peroxide radical. The postulated reactions are:

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + RH \longrightarrow R\cdot + ROOH$$

As the temperature of reaction increases, the importance of the reaction attributed to the peroxide radical decreases, perhaps as a result of the instability of the peroxide radical at elevated temperatures. This instability would reduce the concentration of the peroxide radical, thus decreasing the amount of reaction attributed to it. It is postulated that as the temperature increases, other free radicals govern the reaction. The following equations are illustrative:

$$RH + O_2 \rightarrow R\cdot + HO_2$$

$$R\cdot + O_2 \rightarrow R' + HO_2$$

$$R\cdot \rightarrow R''\cdot + R'''$$

It is postulated that a decrease in reaction attributed to the peroxide free radical is not compensated by a corresponding increase in reaction attributed to the other free radicals. Over a short temperature range the reaction rate can, therefore, decrease with increasing temperature.

Reaction rate constants obtained from the work of Appleby (1) are plotted on the log k vs. 1/T plot in Figure 12 for 486°, 503°, and 526°C. At 503°C. Appleby's rate constant is 0.0419 lb. moles/min. ft.^{3} as compared to 0.085 lb. moles/min. ft.^{3} found in the present work. The activation energy reported by Appleby was 21 kcal./gm. mole. This is greater than the 10.52 kcal./gm. mole found here. Differences in the reactor designs can provide a basis for these differences in rate constants and apparent activation energies. As the curvature of the log k vs. 1/T plot indicates the so-called "activation energy" is changing throughout this region as a result of the changing mechanism as shown in Figure 33. At 1000°K. the apparent activation energy is 43.68 kcal./gm. mole and falls off to zero at 724.8°K. Consequently, the value of an apparent activation energy cannot be considered too meaningful since it cannot be related directly to the activation energy that would be expected on the basis of a single reaction mechanism. Pease (19) has suggested that the value of activation energy found by Appleby (1) is low, since he would expect, on the basis of the reaction mechanism postulated for butane oxidation, a value of no less than 30 kcal./gm. mole. It is evident from the previous explanation that the activation energy reported is only an apparent one and cannot be related directly to the values of activation energy expected on the basis of a single reaction mechanism as Pease had attempted to do.

C. Thermal Decomposition

Twenty-five thermal decomposition runs of n-butane were made in the range of 360° to 760°C. These data were correlated on the basis of zero, first, second and third orders of reaction for n-butane and plotted on log k vs. 1/T plots as shown in Figures 13, 14, 15 and 16, respectively. A comparison of the plotted data indicated that the best correlation, especially at high temperatures, was obtained on the basis of a second order reaction for n-butane. There appeared to be a greater scatter of data points on each of the other plots, although the scatter of data was not too widespread. The thermal decomposition data obtained with the stainless-steel nozzle were not included in the above correlations, since it appeared to give a greater conversion of butane and also provided a larger scatter of data than indicated for runs using the quartz nozzle. Catalytic effects of stainless-steel on the n-butane thermal decomposition have been reported by Egloff (6). Apparently, the stainless-steel nozzle provided some catalytic effect on the n-butane thermal decomposition.

A second order thermal decomposition reaction for n-butane is readily explained on the basis of the thermal decomposition equations proposed for n-butane by Egloff (6), since part of them, Equations 4 and 5, are bimolecular. The assumed reactions to explain the thermal decomposition are:

$$(1)\ n\text{-}C_4H_{10} \rightarrow C_4H_8 + H_2$$

$$(2)\ n\text{-}C_4H_{10} \rightarrow CH_4 + C_3H_6$$

$$(3)\ n\text{-}C_4H_{10} \rightarrow C_2H_4 + C_2H_6$$

$$(4)\ 2\ n\text{-}C_4H_{10} \rightarrow CH_4 + C_3H_8 + n\text{-}C_4H_8$$

$$(5)\ 2\ n\text{-}C_4H_{10} \rightarrow 2C_2H_6 + n\text{-}C_4H_8$$

The work of Hinshelwood (7) also indicated that the decomposition reaction is second order at low pressures.

The activation energy calculated for the assumed second order thermal decomposition reaction of n-butane is 44.3 kcal./gm. mole. The value of the activation energy does not appear to vary greatly with respect to the assumed reaction order. For example, it amounts to approximately 34 kcal./gm. mole on the assumption of a first order reaction and 45 kcal./gm. mole on the assumption of a third order reaction. All of these values are significantly below that reported by previous investigators (20 & 21) which were reported to be between 58.7 and 73.9 kcal./gm. mole. Since the present data from which the activation energies were calculated were obtained over a wide temperature range, 360° to 760°C., combined with a relatively accurate determination of the n-butane conversion, it is felt that the values of activation energies obtained here are reliable. Possible explanations for the difference in activation energy reported by previous investigators and that reported here may be based on differences in reactors. The high values of activation energy reported by Paul and Marek (21) were calculated from data obtained in a reactor of 0.125 inch outside diameter and having copper and fused silica surfaces. The diameter of the present reactor was 1 inch inside diameter and the wall surface was porcelain. This difference in reactor geometry and wall surface could provide a basis for explaining the differences in activation energies.

D. Correlation of Butane Conversion

The data of butane conversion with respect to retention time, inlet oxygen concentration and temperature were correlated by means of a multiple regression analysis run on the Datatron. A second order equation in terms of temperature, time and oxygen concentration was used. The equation is indicated in Table XV. Several levels of the independent variables were substituted back into the equation and the resulting values of butane conversion plotted with respect to inlet oxygen concentration for parametric values of retention time and temperature as shown in Figures 17, 18, 19 and 20. Experimental data points whose run conditions coincide at least approximately with the indicated operating conditions on the graphs were plotted. They provide a comparison of the experimental data with the result of the correlation analysis. Only a few experimental points were found to correspond to operating conditions listed on the graphs. The points plotted on the graph are too few in number to provide a sufficiently accurate representation of the results of the 124 runs that were used as a basis for the correlation. Consequently, too much emphasis should not be placed on the correspondence of the data points. In general, the data points provide a basis for seeing an order of magnitude agreement between the data and the correlation curves.

The correlation of butane conversion with the reaction variables provides the following indications within the range of the variables investigated. Butane conversion for a given temperature and retention time is directly proportional to the inlet oxygen concentration. The effect of changing inlet oxygen concentration is approximately a doubling of the butane conversion in going from 10 to 20 mole percent oxygen. The influence of temperature on butane conversion is also very pronounced. The butane conversion is tripled for a 300°C. increase in temperature at constant retention time and inlet oxygen concentration. This increase in conversion with respect to temperature appears to hold true independent of oxygen concentration and retention time. The effect of retention time on the level of butane conversion appears to be less pronounced than that of the other variables. There is approximately a 25% relative increase in conversion level with a 200% increase in retention time at 670°K. At 970°K., there is apparently a 2% increase in butane conversion with a 200% increase in retention time. This trend appears to follow a uniform pattern with respect to temperature.

E. Product Composition

The components methane, ethane, ethylene, propylene, butene, hydrogen, carbon monoxide, carbon dioxide, and carbon were correlated on the basis of moles formed per hundred moles of butane feed with respect to the operating variables, retention time, inlet oxygen concentration and temperature, by means of a multiple regression analysis. The Datatron was used for the correlation of the data. The regression equations are included in Table XV. The operating variables were substituted back into these equations and the resulting data plotted in Figures 21-32. Each figure is a plot of the moles of each component formed in the product stream per 100 moles of butane feed with respect to the inlet oxygen concentration for a given value of temperature and retention time. To illustrate the effect of retention time, separate graphs were plotted for three levels of retention time while keeping temperature constant. To illustrate the effect of temperature, separate graphs were made up at 670°, 770°, 870°

and 970°K. In view of the fact that the retention time was decreased during the investigation as the temperature was increased, it was not possible to illustrate the effect of temperature in all cases at identical retention times. All of the graphs were plotted for zero to 20% oxygen. At 670°K. the retention times considered were 4, 8, and 16 seconds, at 770°K. 4, 6 and 8 seconds, at 870°K. 2, 4 and 6 seconds, and at 970°K. 0.5, 1 and 2 seconds. The range of the operating variables was kept within the range of the experimental conditions investigated.

Butene

The average production of butene is relatively low, less than $2\frac{1}{2}$ moles/100 moles of butane feed. This is in contrast to the relatively large amount of butene found by Appleby (1). An explanation for this discrepancy is that Appleby operated at generally shorter retention times. His work indicated that there was a falling off of butene at longer retention times. This would explain the difference in results. In addition, much of the present work was done at higher temperatures, which is reported to be conducive to a lower butene concentration in the reaction products (1).

The results of the present correlation indicated that the butene levels appear to be relatively independent of temperature but a strong function of oxygen concentration. Although the effect of temperature indicated here appears to be in contradiction to the effect of temperature indicated by Appleby, it should be borne in mind that the retention times of the two operations were different. Consequently, the effect of temperature may have been pronounced at low retention times as indicated by Appleby, but at increased retention times the influence of temperature could have decreased. The influence of oxygen on butane production that is indicated here was also found by Appleby. Butene was generally low or zero at zero oxygen and increased to approximately 1 mole/100 moles of butane feed at 10% oxygen, levelling off to a slightly higher value at 20% oxygen. In the range of retention times investigated here, retention time appeared to have very little effect on the concentration of butene except at 670°K. At 670°K. and short retention time and low oxygen concentration, apparently very little butene was present. With longer retention times, the butene level had increased to approximately 0.2 to 0.5 moles/100 moles of butane feed.

Propylene

The effect of temperature on propylene was pronounced. At 670°K. propylene varied between 0 and 3½ moles/100 moles of butane feed, being a strong function of both retention time and oxygen concentration. At 670°K. and high retention times, propylene was approximately zero. At short retention times (4 seconds) the propylene level was zero at zero oxygen and increased to a level of approximately 4 in the range of 10-20% oxygen. At 8 seconds and 670°K. the propylene appeared to go through a maximum of 3½ moles/100 moles of butane feed at 10% oxygen and dropped to zero at both zero and 20% oxygen. At higher temperatures the amount of propylene increased and the influence of time and oxygen concentration on the production of propylene was reduced from that observed at the lower temperatures. At the elevated temperatures, the level of propylene production was highest at the shorter retention time and there appeared to be a slight maximum at 10% oxygen concentration. This maximum of propylene production with respect to oxygen concentration almost completely disappeared by increasing the temperature to 970°K. At 970°K. the propylene level was higher than at the lower temperatures. It was approximately 25 moles/100 moles of butane feed at 970°K.

Appleby (1) has reported a decrease of propylene with increased oxygen, which tends to agree with the present observations at the higher inlet oxygen concentration. He did not observe the initial increase of propylene with increased oxygen concentration. However, this initial increase of propylene with respect to oxygen could be expected on the basis of an increased conversion of butane. The observed maximum of propylene with respect to oxygen concentration can be explained on the basis of the relative rate of formation of propylene from butane as opposed to the decomposition rate of propylene.

Ethylene

At 670°K. ethylene appeared to be a strong function of both retention time and oxygen concentration. The amount of ethylene increased proportionately to the oxygen concentration and decreased with respect to retention time in going from 4 to 8 and 16 seconds. The maximum ethylene production was approximately 4½ moles/100 moles butane feed at 670°K. At 770°K. the ethylene production increased to a maximum of 15 moles/100 moles of butane feed and followed to a lesser degree the decrease in ethylene production with respect to retention time exhibited at 670°K. It appeared to increase appreciably with oxygen concentration. At 970°K. the effects of oxygen and retention time on ethylene production had almost disappeared. Ethylene production was greater than that of propylene at all reaction conditions. In Appleby's work the proportion of propylene was greater. This probably resulted from his operating at shorter retention times (1). It also appeared that, whereas propylene appeared to go through a maximum at 10% oxygen, the ethylene kept increasing with increasing oxygen concentration through 20%. Appleby (1) also indicated an increase of ethylene with increased oxygen concentration.

Ethane

The formation of ethane with respect to time, temperature and inlet oxygen concentration appeared to parallel the formation of ethylene except that the production of ethane was 1/3 to 1/2 the amount of ethylene.

Methane

The correlation of data for methane was poor, especially at high temperatures and high oxygen concentration where the correlation indicated values of methane greater than that actually encountered. At 670°K. methane was found to decrease with an increase in retention time. At elevated temperatures the effect of retention time was negligible. The effect of temperature on methane production was drastic, the amount of methane going from approximately zero at 670°K. and zero oxygen concentration to 45 moles/100 moles of butane feed at 970°K. and zero oxygen concentration. Increasing the oxygen concentration increased the methane level proportionately.

Hydrogen

The hydrogen production was a strong function of temperature. It increased from less than 1 mole/100 moles of butane feed at 670°K. to 80 at 970°K. At the higher temperatures, the hydrogen production appeared to be relatively independent of retention time over the region investigated. Undoubtedly if a wider range of retention times were investigated, a definite influence of retention times on hydrogen production would have been perceived. The hydrogen formation is independent of inlet oxygen concentration between zero and 10%, but between 10% and 20% oxygen, the hydrogen goes up slightly. At lower temperatures, 670° and 770°K., hydrogen appeared to go through a minimum with respect to oxygen. The minimum was at 5% oxygen. Hydrogen also appeared to increase with retention time at the lower temperatures, although the behavior was such that there was an apparent maximum with respect to time.

Carbon Monoxide and Carbon Dioxide

The experimental data for these two components were such that they appeared to undergo relatively random formation with respect to time and temperature, and were solely a function of oxygen concentration. The strong influence of oxygen was indicated by the correlation of data. Carbon monoxide production was slightly below that of carbon dioxide, and both appeared to increase from zero at zero oxygen to approximately 1 mole/100 moles of butane feed at 20% oxygen. The relative ratio of carbon monoxide to carbon dioxide in the experimental data varied significantly for individual runs from that indicated in the correlation. Also, on the basis of the experimental data the initial appearance of carbon monoxide and carbon dioxide was at approximately 10% oxygen concentration instead of increasing from zero percent oxygen as indicated by the correlation.

Carbon

At 670°K. and 4 seconds, the carbon goes from zero at zero oxygen to 10 moles/100 moles of butane feed at 10% oxygen and levels off at approximately $12\frac{1}{2}$ at 20% oxygen. Increasing the retention time sharply increased carbon production at zero oxygen. At higher oxygen concentration, carbon production did not increase as rapidly with increasing retention time. At 770° and 870°K. carbon production was zero at zero oxygen and increased rapidly with an increase in oxygen through 10% oxygen and levelled off at 20%

oxygen. A retention time increase appeared to increase the carbon production slightly. At 970°K. carbon formation was between 3 and 4½ moles/100 moles of butane feed for zero oxygen and increased to a value of 20 at 20% oxygen. Apparently, carbon production goes through a minimum with respect to temperature for zero oxygen concentration. The explanation for this minimum may be that at low temperatures the carbon value is in reality represented by carbon containing compounds which are not detected on the gas chromatograph. At slightly higher temperatures, these compounds are not formed, which accounts for the zero carbon value. At even higher temperatures, carbon is deposited in the reactor and accounts for the increase in the carbon value.

Propane

In general, propane was not found in the product gases. This is in agreement with the findings of Appleby (1).

Water

Water was the principal oxygen containing compound found in the product gases. The value of water was obtained from material balance equations. Apparently, as indicated by Appleby, the role of oxygen is predominantly that of a dehydrogenation agent.

In general, the product distribution at 770°K. and above appeared to be fairly uniform between the various products with the exception that carbon, butene, carbon monoxide, and carbon dioxide tend to follow a more pronounced increase with respect to increased oxygen concentration than the remaining components. At 670°K. the behavior is more complex, in view of the fact that the variables of time and oxygen concentration have a more pronounced effect.

The reaction mechanism proposed by Appleby for the oxidation of n-butane provides for the formation of all of the products indicated in the reaction. The equations representing the proposed reaction mechanism are included in the literature section. The relative ratios of butene, propylene, and ethylene are dependent on the fate of the butyl radical. If this radical is attacked by oxygen, butene is formed. On the other hand, if the butyl radical undergoes thermal decomposition, propylene or ethylene are formed, depending on the bond cleavage. On the basis of bond energies, since the central bond in the butyl radical has the lowest value, the probability is that the cleavage of the center bond would occur first. This would then provide an explanation for the greater value of ethylene with respect to that of propylene. The formation of ethane results from the attack of the ethyl radical, which is formed in the production of ethylene, on butane. It would be expected that only a fraction of the ethyl radicals that are formed would react with butane. On this basis, the amount of ethane formed would be less than the amount of ethylene. This is discounting the further reaction of ethylene and ethane. The formation of methane occurs through the attack of a methyl free radical on the butane molecule. The methyl radical comes from the reaction of a butyl radical to form propylene plus the methyl radical. It would appear that the relative proportion of propylene to methane should be high since methane results from a secondary reaction following the initial reaction to form propylene. However, the further reaction of propylene cannot be discounted. The decomposition reaction is indicated by the decrease of propylene production with increased oxygen concentration as shown on Figure 22. Relative to the other components, very little butene was formed which is in contrast to the findings of Appleby (1). The apparent disagreement can be explained on the basis of differences in operating conditions. The present investigation was made at longer retention times. This would allow decomposition of butene formed in the reaction, thus resulting in a lowered butene concentration. The decrease of butene with increased retention time is indicated by Appleby (1).

VIII. CONCLUSIONS AND RECOMMENDATIONS

The experimental program provided a broad study of the effects of temperature as well as retention time and inlet oxygen concentration. The gross effect of these variables on the butane conversion and product composition was amply delineated. A limitation to the correlation of the product composition data was that the reaction is a complicated function of the independent variables of time, temperature and oxygen concentration. Consequently, the correlation of data had to be made by means of a multiple regression analysis. This method provided a statistical correlation of the data on the basis of a least squares fit of the experimental data for assumed equations. A limitation of the present correlation is that the assumed equations which are used for the data correlation are solely on an empirical basis rather than a theoretical basis. When a knowledge of the reaction rate equations for each of the components present in the normal butane reaction is available, an attempt should be made to correlate the composition data on the basis of a summation of these rate equations. This would allow a more direct correlation of the n-butane oxidation reaction with postulated reaction mechanisms.

The reaction rate data for the n-butane oxidation were correlated by the following rate equation:

$$r = k\ (C_4H_{10})^{1.5}(O_2)^{0.5}$$

Where: k = lb. moles/ft.^{3} min.

r = lb. moles/ft.^{3} min. (based on butane)

(C_4H_{10}) = mole fraction, n-butane

(O_2) = mole fraction, oxygen

The correlation of the rate constants for the above rate equation using a least squares fit of a second order equation to the data yielded the following equation:

$$\log k = -1.1797 - 746.647\,(1/T - 0.00135) + 1.25508 \times 10^7\,(1/T - 0.00135)^2$$

Where: k = lb. moles/ft.^{3} min.

T = temperature, °K.

The equation correlates rate constants over the temperature range of 360°-760°C. and at atmospheric pressure.

The correlation of the log k with respect to 1/T for the above rate equation indicates a minimum reaction rate at 452°C. The only plausible explanation is that there are two competing reaction mechanisms, one of which is falling off while the other is increasing with temperature. Since the reaction attributed to the one mechanism is decreasing, there must be an inflection point at a lower temperature region where the reaction rate goes through a maximum. As a consequence, it would prove interesting to operate in this lower temperature range in order to find this maximum.

The thermal decomposition data for n-butane were correlated on the basis of zero, first, second and third orders for n-butane. It was concluded that the second order equation yielded the best correlation of the thermal decomposition data. The correlation of the rate constants on the basis of the second order equation:

$$\frac{-d(C_4H_{10})}{dt} = k\ (C_4H_{10})^2$$

Where: (C_4H_{10}) = mole fraction, n-butane

t = time, sec.

k = sec.$^{-1}$

gave a value for the rate constant over the range of 360°-760°C. at atmospheric pressure:

$$k = 1.44 \times 10^{10}\ e^{-\frac{44.3 \times 10^3}{R\,T}}$$

Where: k = rate constant, sec.$^{-1}$

R = gas constant, cal/gm. mole °K.

T = temperature, °K.

The activation energy for the second order thermal decomposition reaction of n-butane was found to be 44.3 kcal./gm. mole.

IX. PROPOSED WORK

1. It is proposed that the investigation of the partial oxidation of n-butane be continued at temperatures below 360°C. in order to find the predicted maximum for reaction rate with respect to temperature.

2. For the investigation of the n-butane oxidation at lower temperatures, it is proposed that a third chromatography column be developed for the analysis of oxygenated compounds such as methanol, ethanol, formaldehyde, etc. which will be found in this region.

3. It is proposed that the oxidation of each of the components occurring in the n-butane reaction be investigated separately to determine the individual reaction rate equations. These could then be grouped to describe the n-butane oxidation reaction in terms of these individual rate equations.

REFERENCES

1. Appleby, W. G.; Avery, W. H.; Meerbott, W. K.; and Sator, A. F., J. Am. Chem. Soc. (1953) Vol. 75, pp. 1809-14.
2. Pease, Robert N., J. Am. Chem. Soc. (1929) Vol. 51, pp. 1839-56.
3. Quon, D.; Dalla Lana, I.; and Covier, G. K., Can. J. Chem. (1954) Vol. 32, pp. 880-95.
4. Cheruzak, N. Ya; Antonovkii, V. L.; Revzin, A. F.; and Shtern, V. Ya, Zhur. Fiz. Khim., (1954) Vol. 28, pp. 250-53.
5. Burgoyne, J. H. and Hirsh, H., Proc. Roy. Soc. (London) (1954) Vol. A 227, pp. 73-93.
6. Egloff, Gustav; Thomas, Charles L.; and Linn, Carl B., Ind. Eng. Chem., (1936) Vol. 28, pp. 1283-94.
7. Cullis, C. F. and Hinshelwood, C. N., Discussion Faraday Soc., (1947) pp. 117-28.
8. Schmit, G. C. A., Rec. Trav. Chim. (1941) Vol. 60, pp. 29-49.
9. Small, N. J. H. and Ubbelohde, A. R., J. Appl. (Chem. London), (1953) Vol. 3, pp. 193-8.
10. Satterfield, Charles N. and Reid, Robert C., J. Phys. Chem., (1955) Vol. 59, pp. 283-5.
11. Knox, J. H. and Norrish, R. G. W., Trans. Faraday Soc. (1954) Vol. 50, pp. 928-33.
12. Stubbs, F. J. and Hinshelwood, Cycil N., Proc. Roy. Soc. London (1950) Vol. A 200, pp. 458-73.

13. Stepukhovich, A. D. and Chaikin, A. M., Zhur. Fiz. Khim., (1953) Vol. 27, pp. 1737-47.

14. Stepukhovich, A. D. and Derevenskikh, Zhur. Fiz. Khim., (1954) Vol. 28, pp. 199-203.

15. Stepukhovich, A. D. and Vorobeve, G. P., Zhur. Fiz. Khim., (1954) Vol. 28, pp. 1361-70.

16. Rice, F. D., J. Am. Chem. Soc., (1931) Vol. 53, pp. 1959-72.

17. Rice, F. C., and Evering, B. L., J. Am. Chem. Soc., (1934) Vol. 56, pp. 2105-7.

18. Porter, George, Advisory Group Aeronaut. Research and Development, AGB/M9, (1954) pp. 1-16.

19. "Combustion Processes", Vol. II. High Speed Aerodynamics and Jet Propulsion, Editor B. Lewis, R. N. Pease, and H. B. Taylor, Princeton Press, Princeton, N. J. (1956) Section E. Kinetics of Several Oxidation Reactions, R. N. Pease, p. 160.

20. Steacie, E. W. R., Atomic and Free Radical Reactions, The Kinetics of Gas-Phase Reactions Involving Atoms and Organic Radicals, Reinhold Publishing Corp., New York, p. 106 (1946).

21. Paul, R. E. and Marek, L. F., Ind. Eng. Chem., (1934) Vol. 26, pp. 454-57.

22. Breton, Jean and Laffitte, Paul, Compt. Rend, (1936) Vol. 202, pp. 316-18.

LIST OF FIGURES

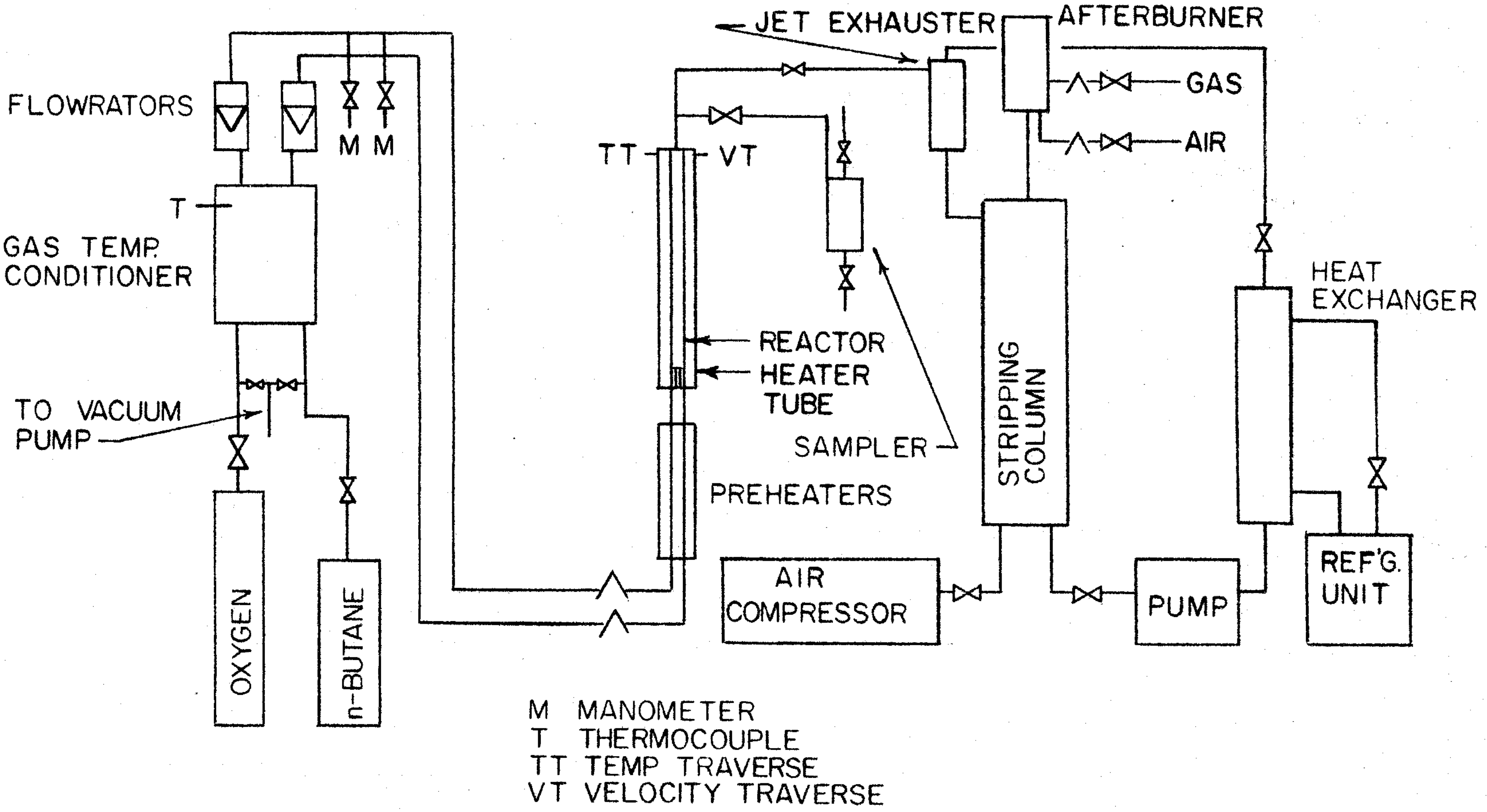


Fig. 1 FLOWSHEET OF n-BUTANE PARTIAL OXIDATION APPARATUS

Figure 2. View of Gas Chromatography Unit and Reactor Equipment Bays

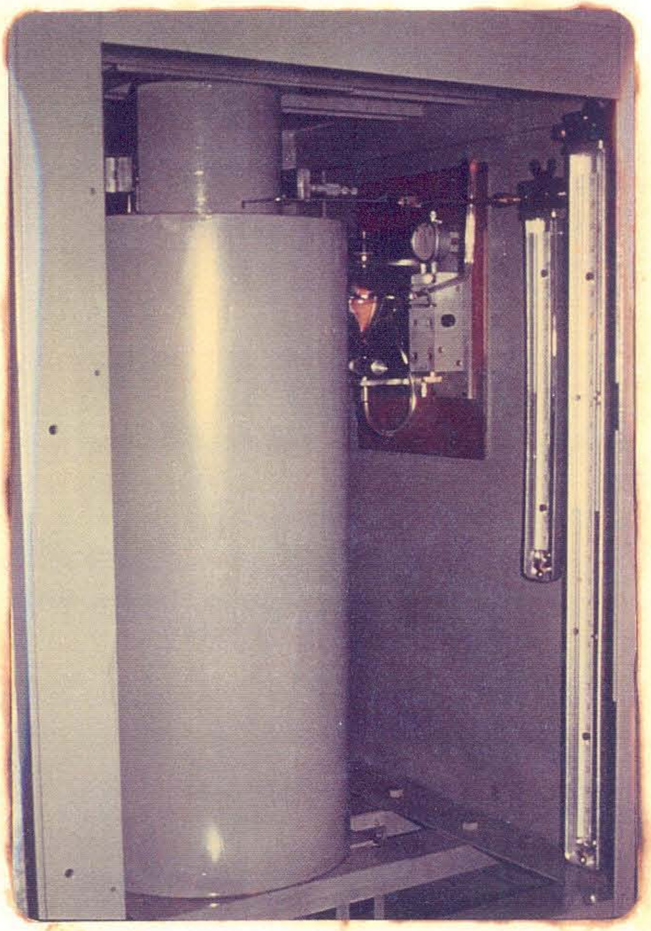


Figure 3. Right Front Angle View of Reactor Bay

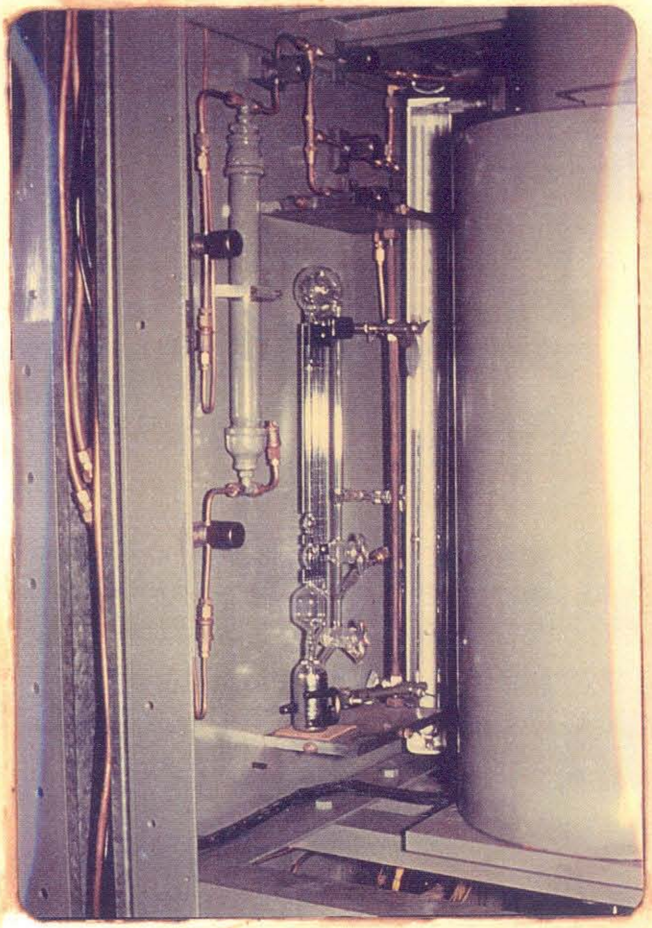


Figure 4. Left Front Angle View of Reactor Bay

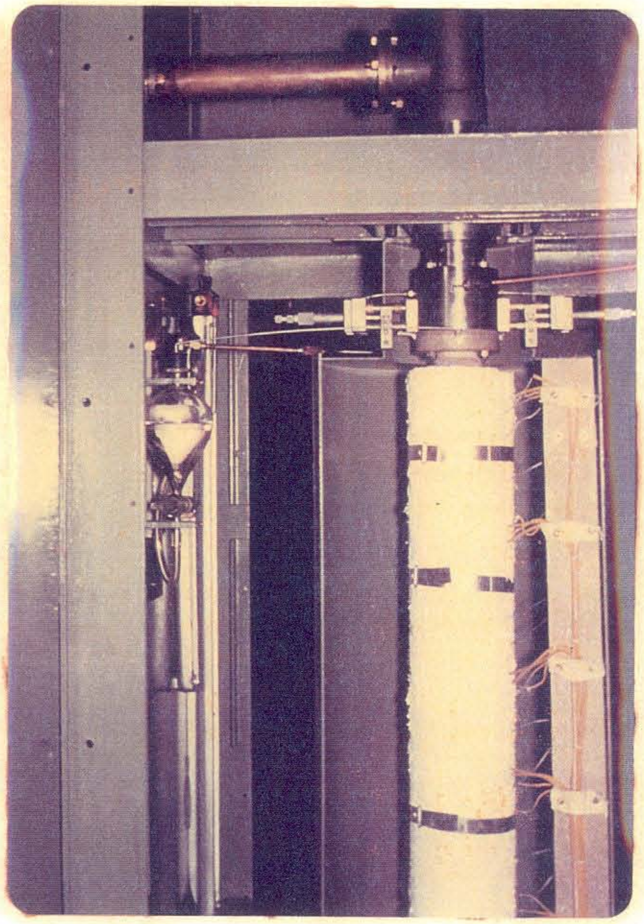


Figure 5. Rear View of Reactor Bay

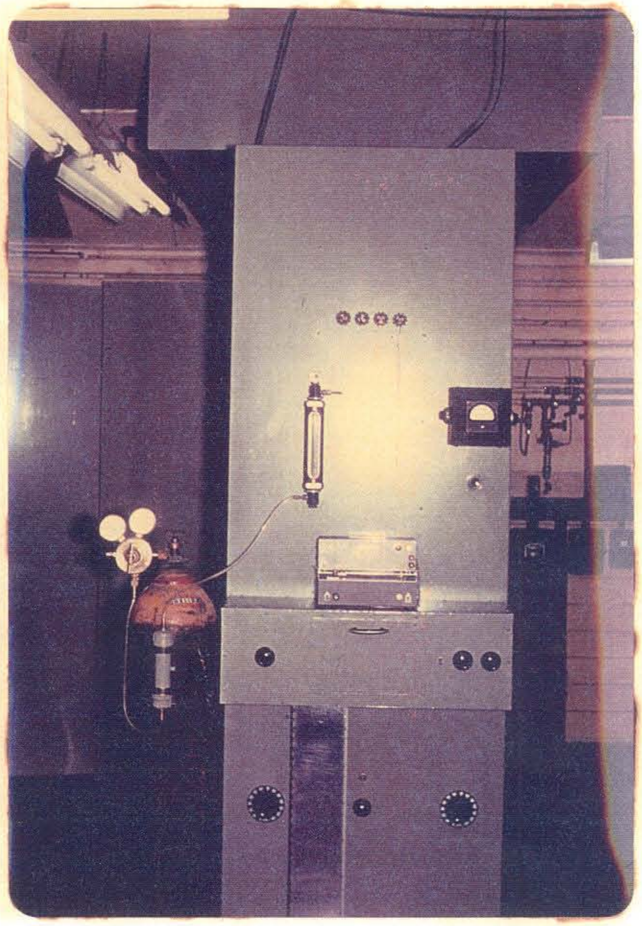


Figure 6. Chromatography Unit

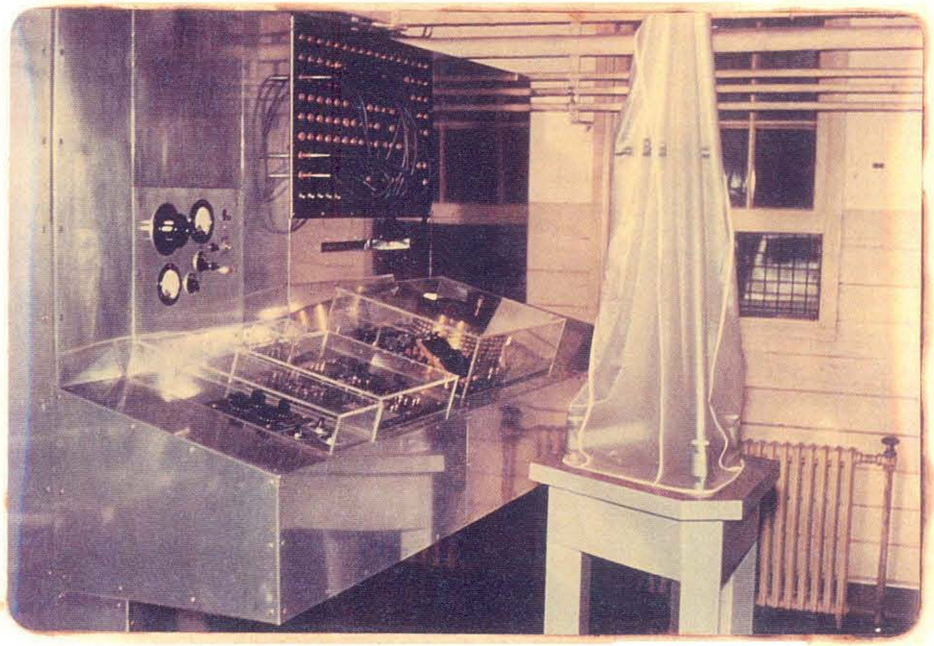


Figure 7. Temperature Bench

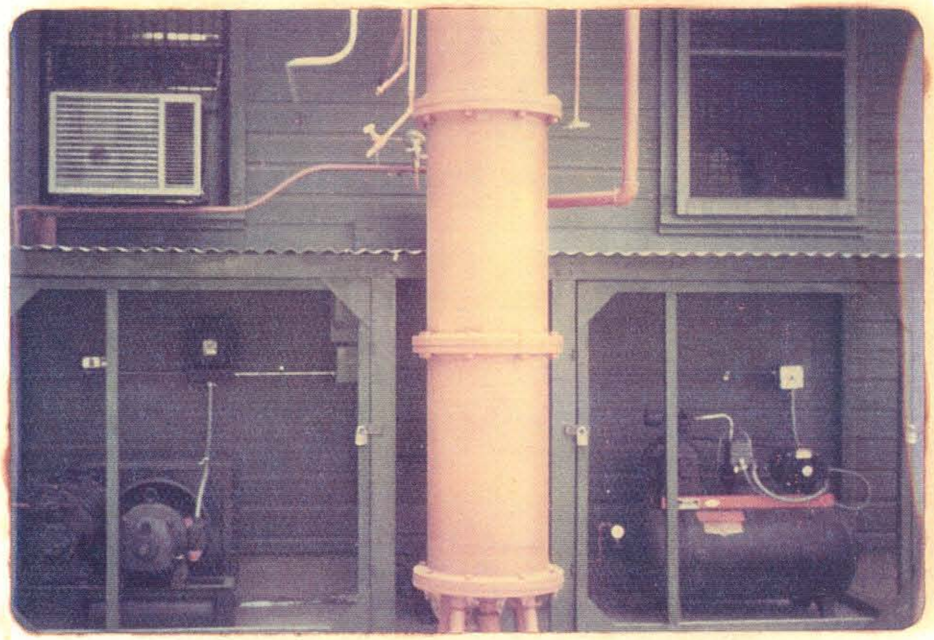


Figure 8. Equipment for Vacuum System

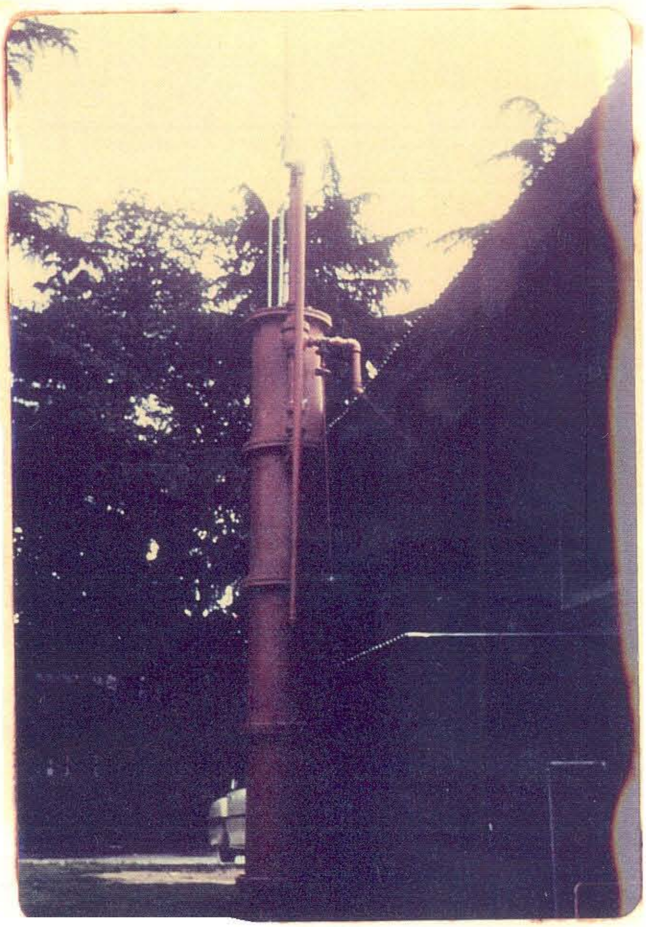


Figure 9. Stripping Column

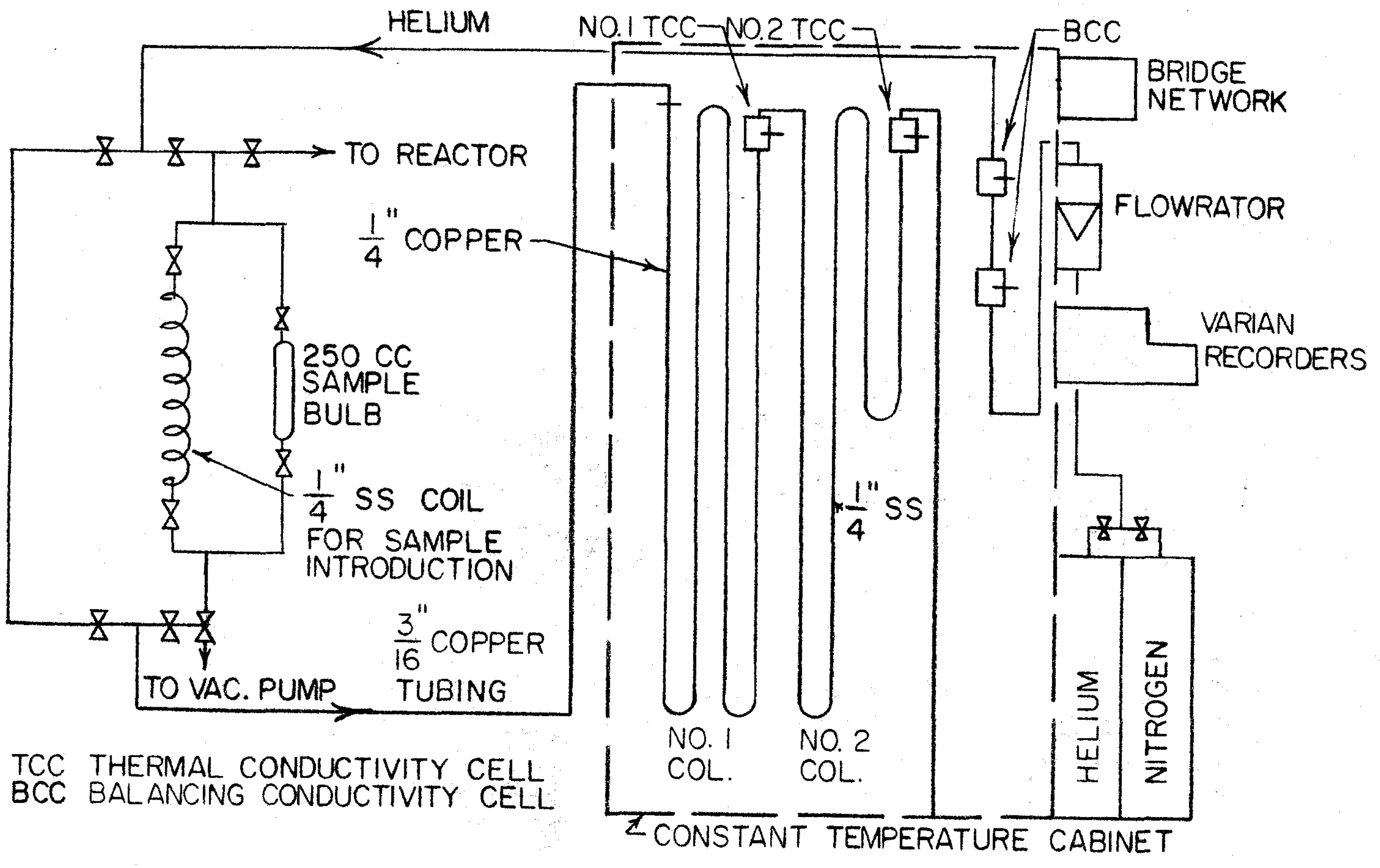
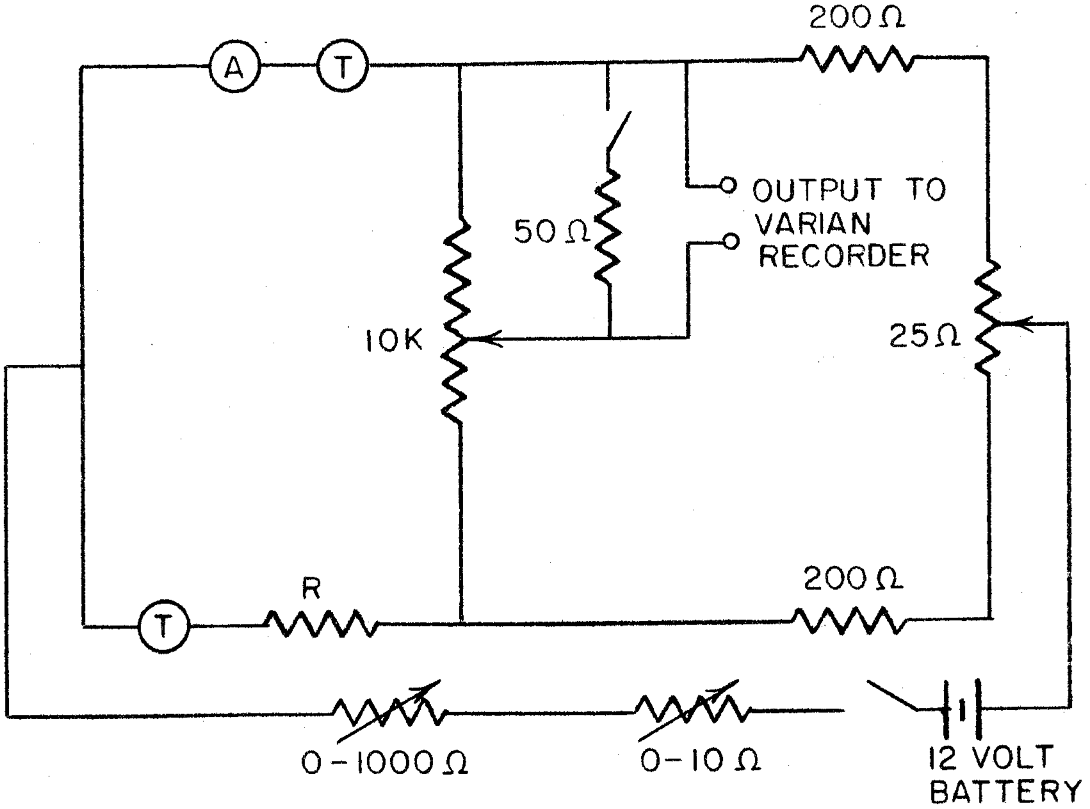


Fig. 10 FLOWSHEET OF GAS CHROMATOGRAPHY EQUIPMENT



A	AMMETER
T	THERMAL CONDUCTIVITY CELL
R	NO. 1 DET. CKT. = 30Ω NO. 2 DET. CKT. = 120Ω

Fig. 11 CIRCUIT DIAGRAM FOR GAS CHROMATOGRAPHY DETECTOR BRIDGE NETWORK

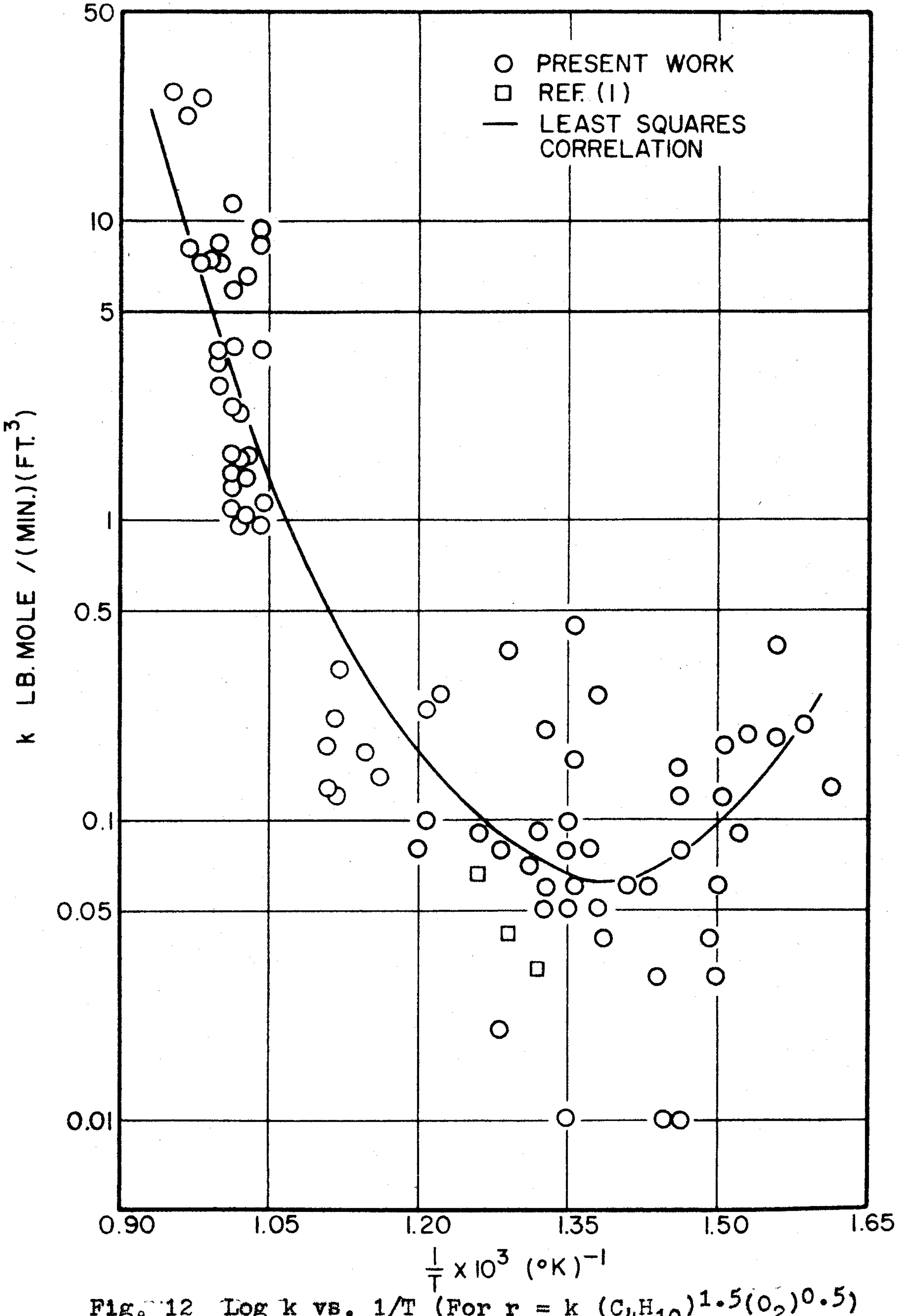


Fig. 12 Log k vs. 1/T (For $r = k\,(C_4H_{10})^{1.5}(O_2)^{0.5}$)
(Partial Oxidation of n-Butane)

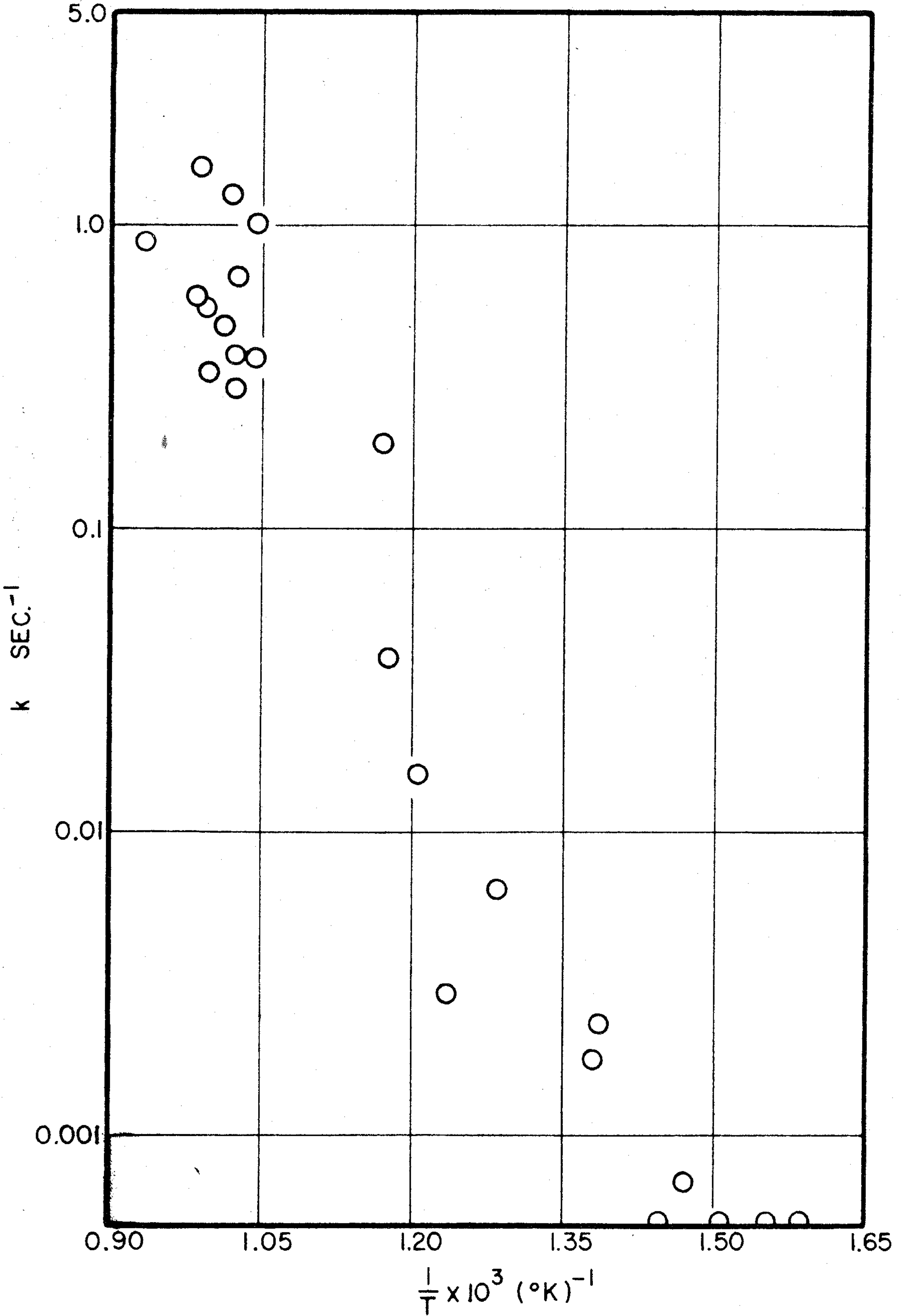


Fig. 13 Log k vs. 1/T (For $r = k\ C_4H_{10}^{\circ}$)
(Thermal Decomposition of n-Butane)

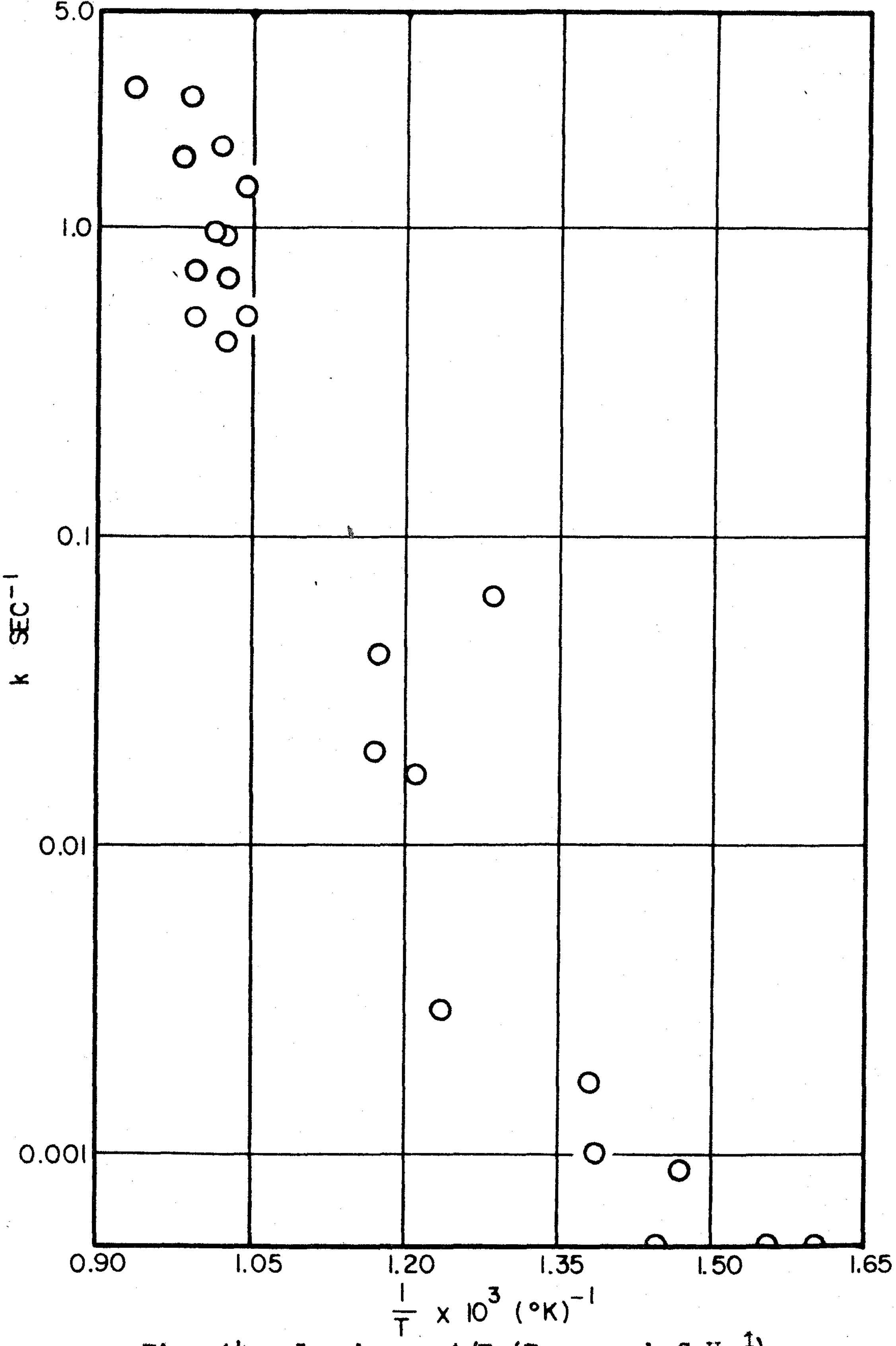


Fig. 14 Log k vs. 1/T (For $r = k\, C_4H_{10}^{1}$)
(Thermal Decomposition of n-Butane)

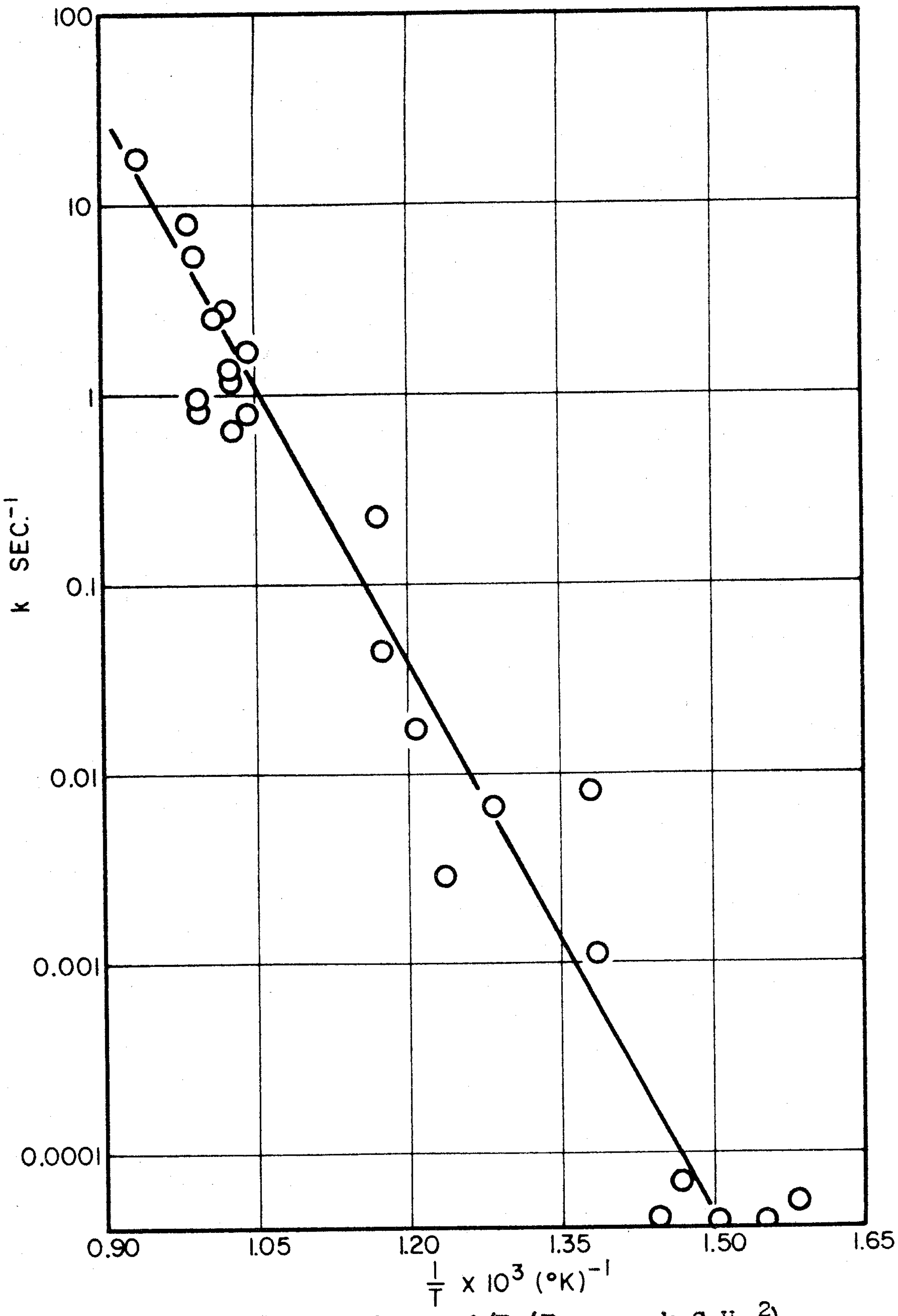


Fig. 15 Log k vs. 1/T (For $r = k\, C_4H_{10}^2$)
(Thermal Decomposition of n-Butane)

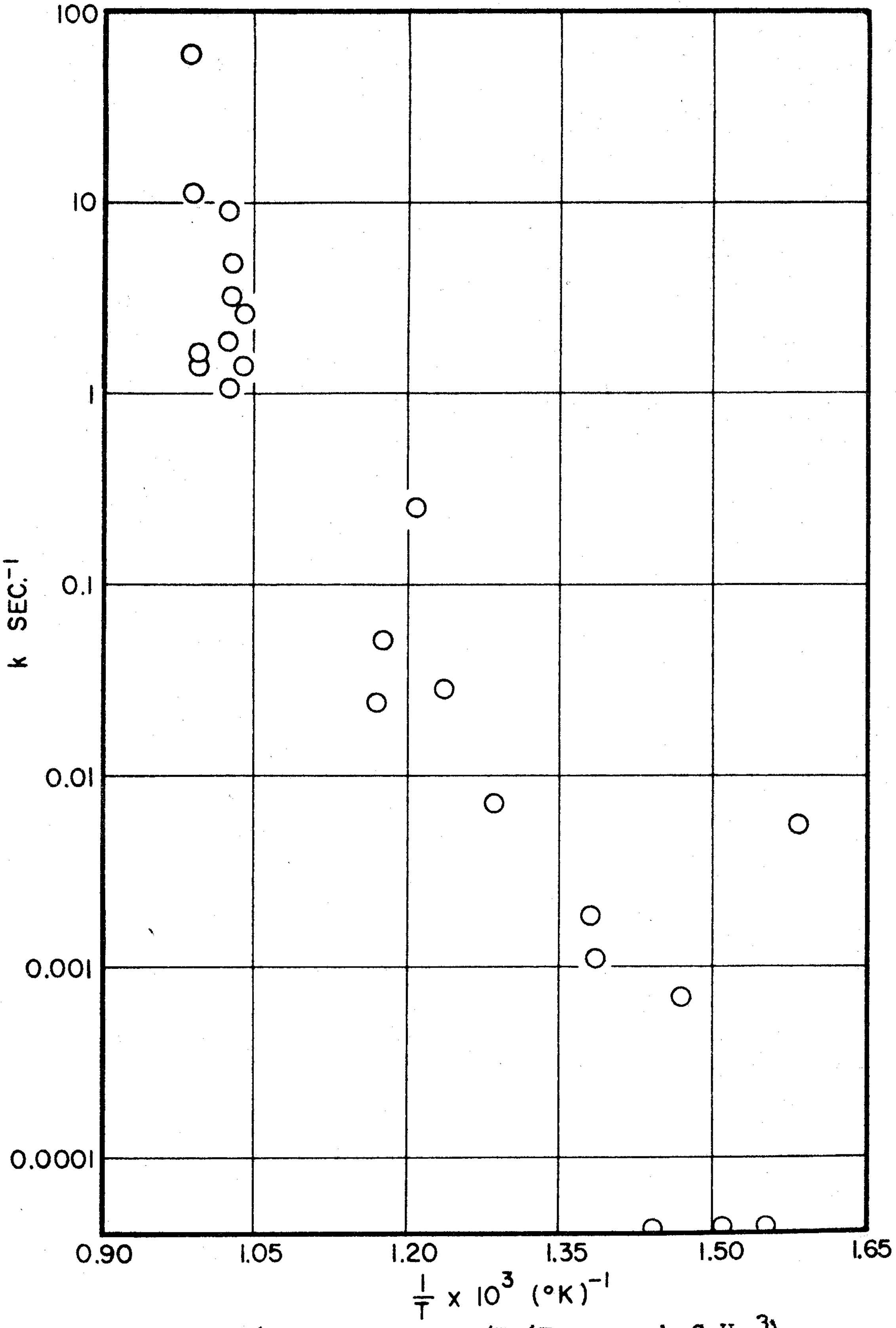


Fig. 16 Log k vs. 1/T (For $r = k\ C_4H_{10}^3$)
(Thermal Decomposition of n-Butane)

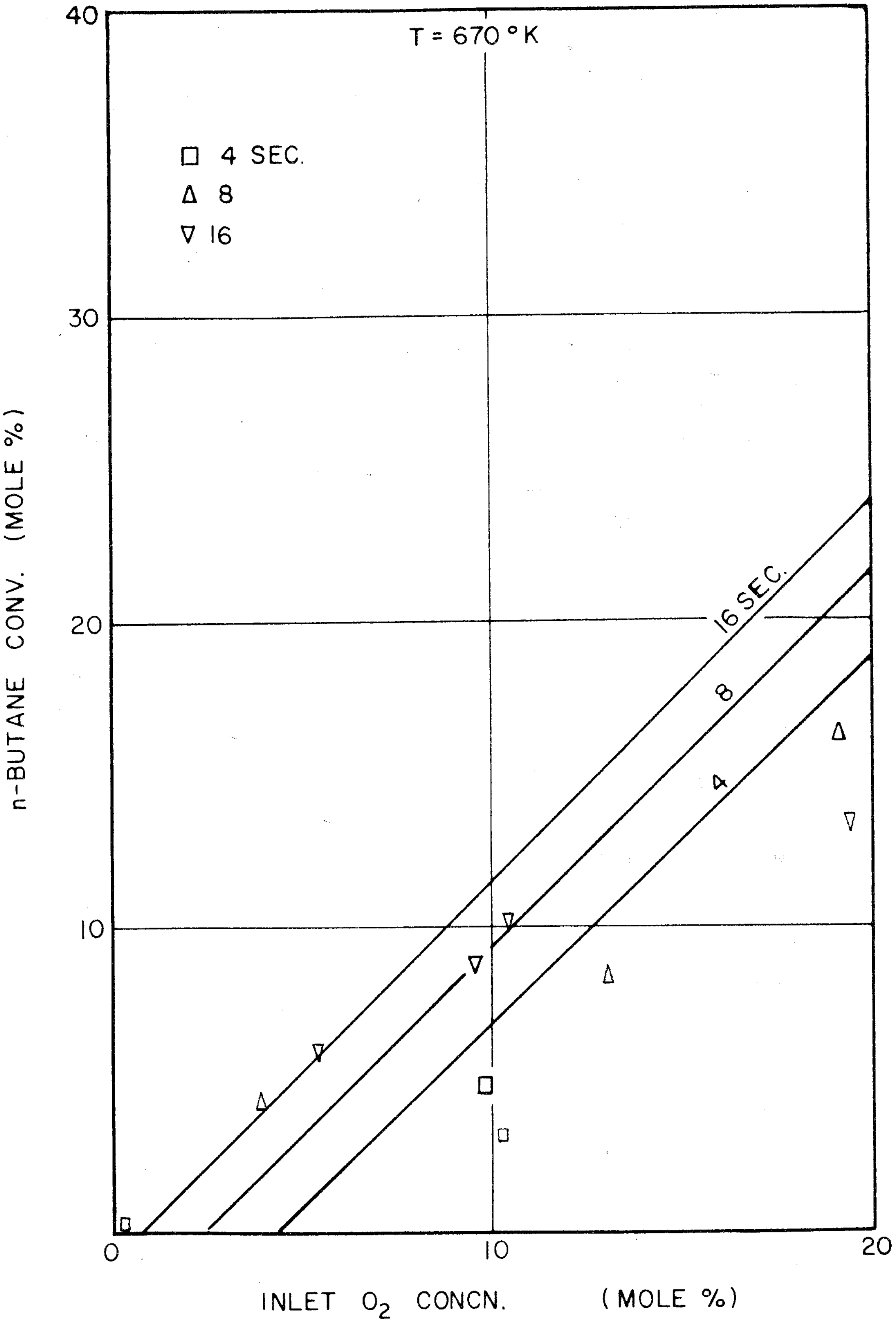


Fig. 17 n-Butane Conversion vs. Inlet O_2 Concn. (670°K., 4, 8, and 16 sec.)

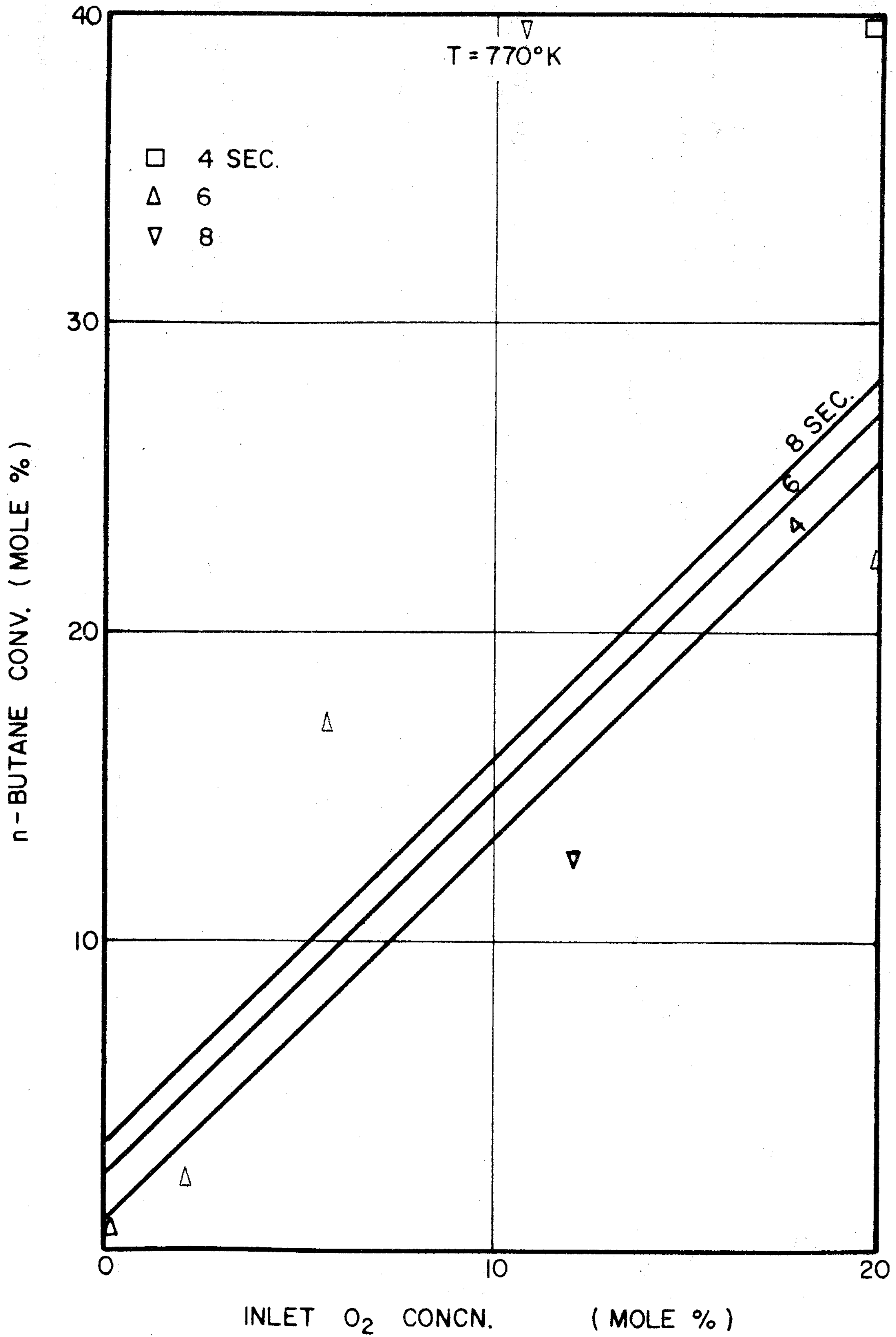


Fig. 18 n-Butane Conversion vs. Inlet O_2 Concn. (770°K., 4, 6, and 8 sec.)

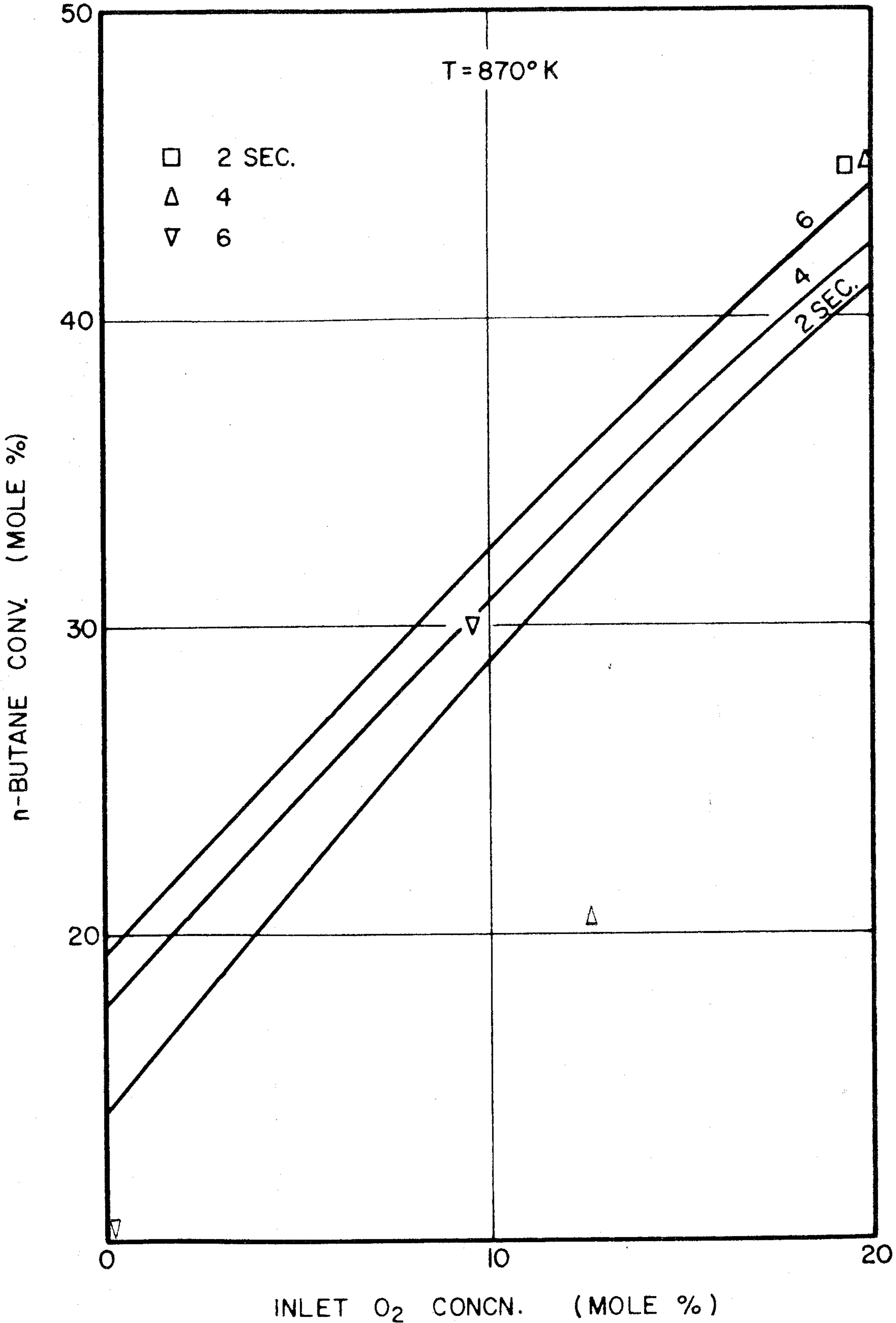


Fig. 19 n-Butane Conversion vs. Inlet O_2 Concn. (870°K., 2, 4, and 6 sec.)

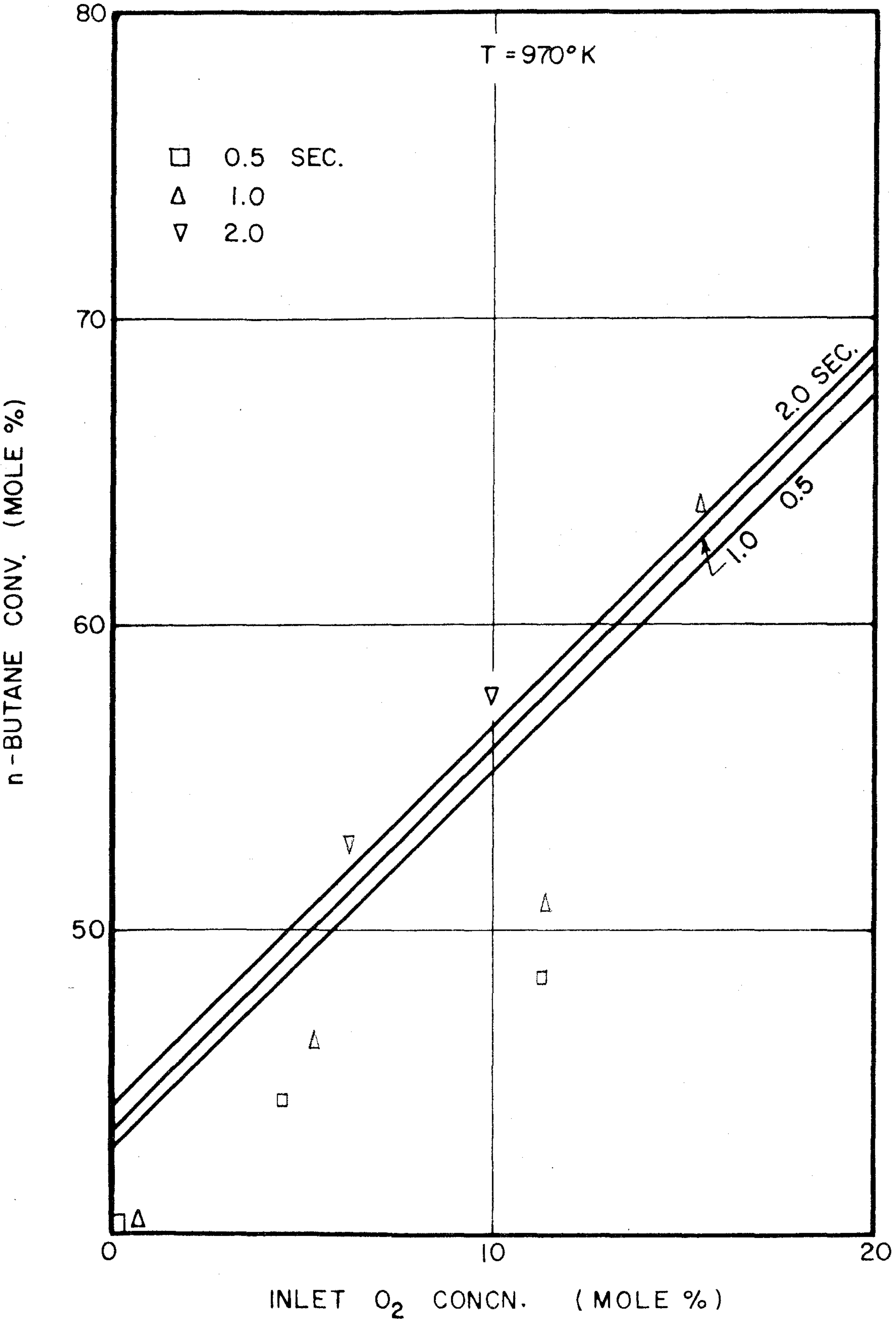


Fig. 20 n-Butane Conversion vs. Inlet O_2 Concn. (970°K., 0.5, 1.0, and 2.0 sec.)

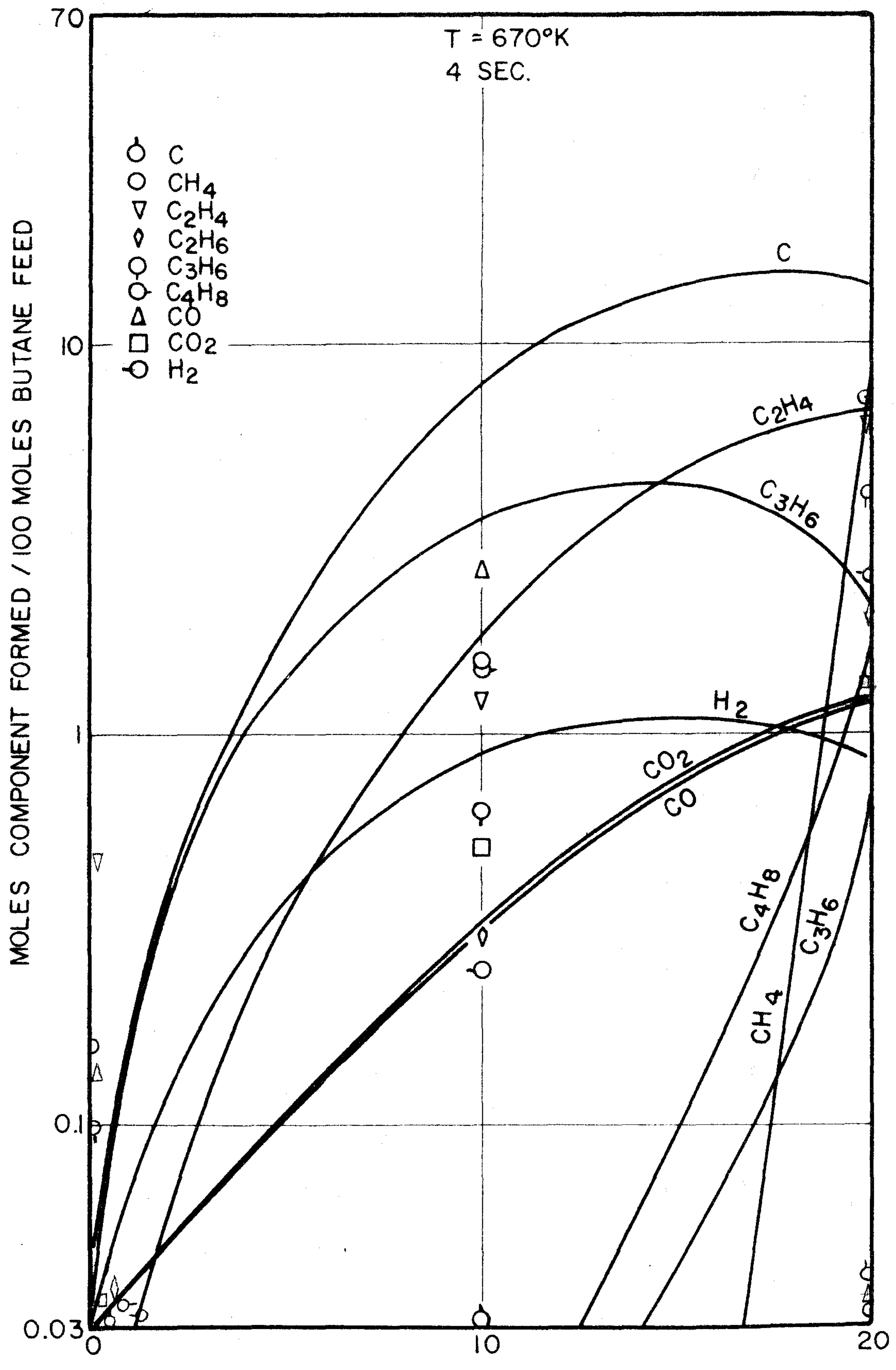


Fig. 21 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (670°K., 4 sec.)

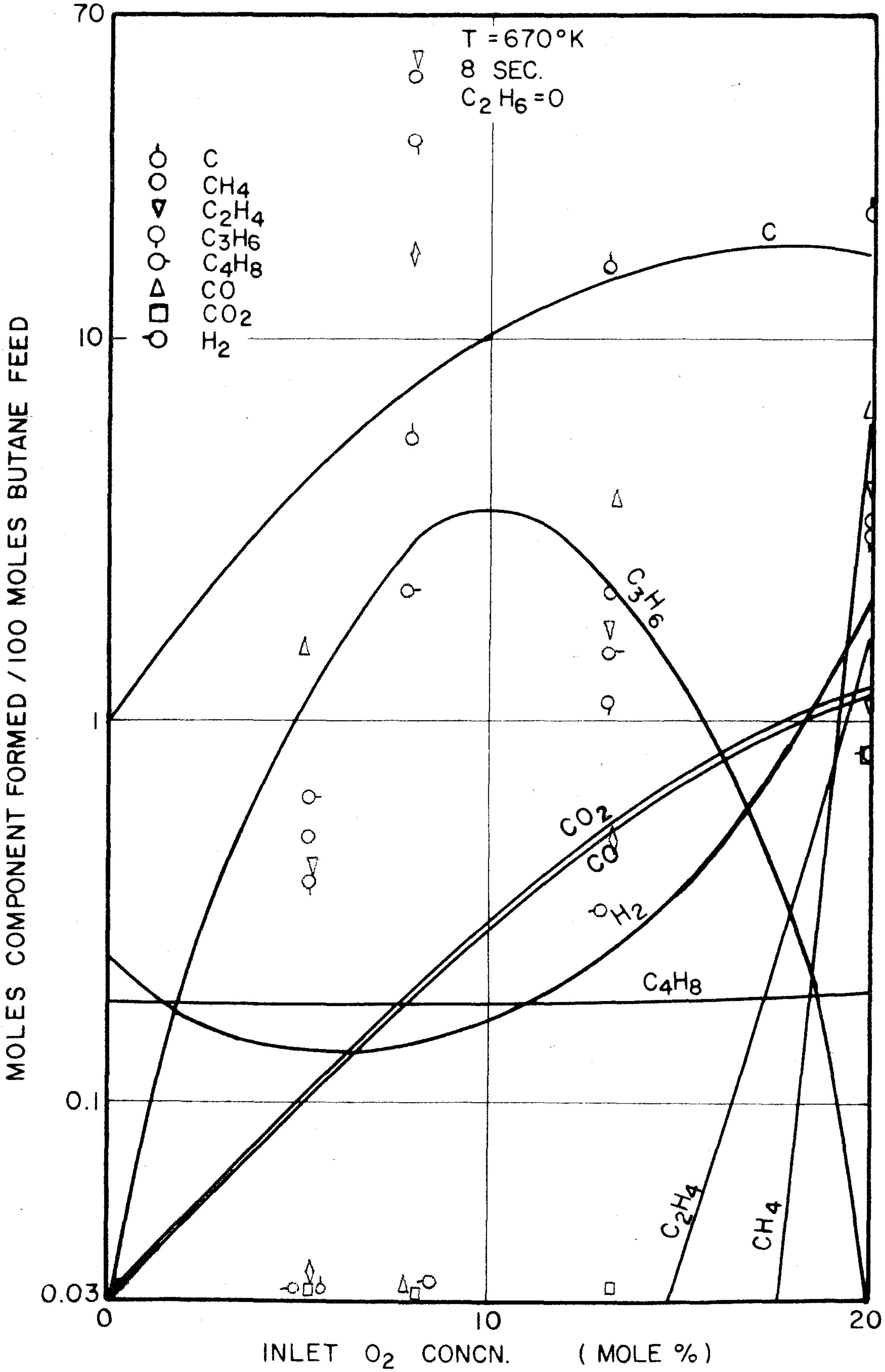


Fig. 22 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (670°K., 8 sec.)

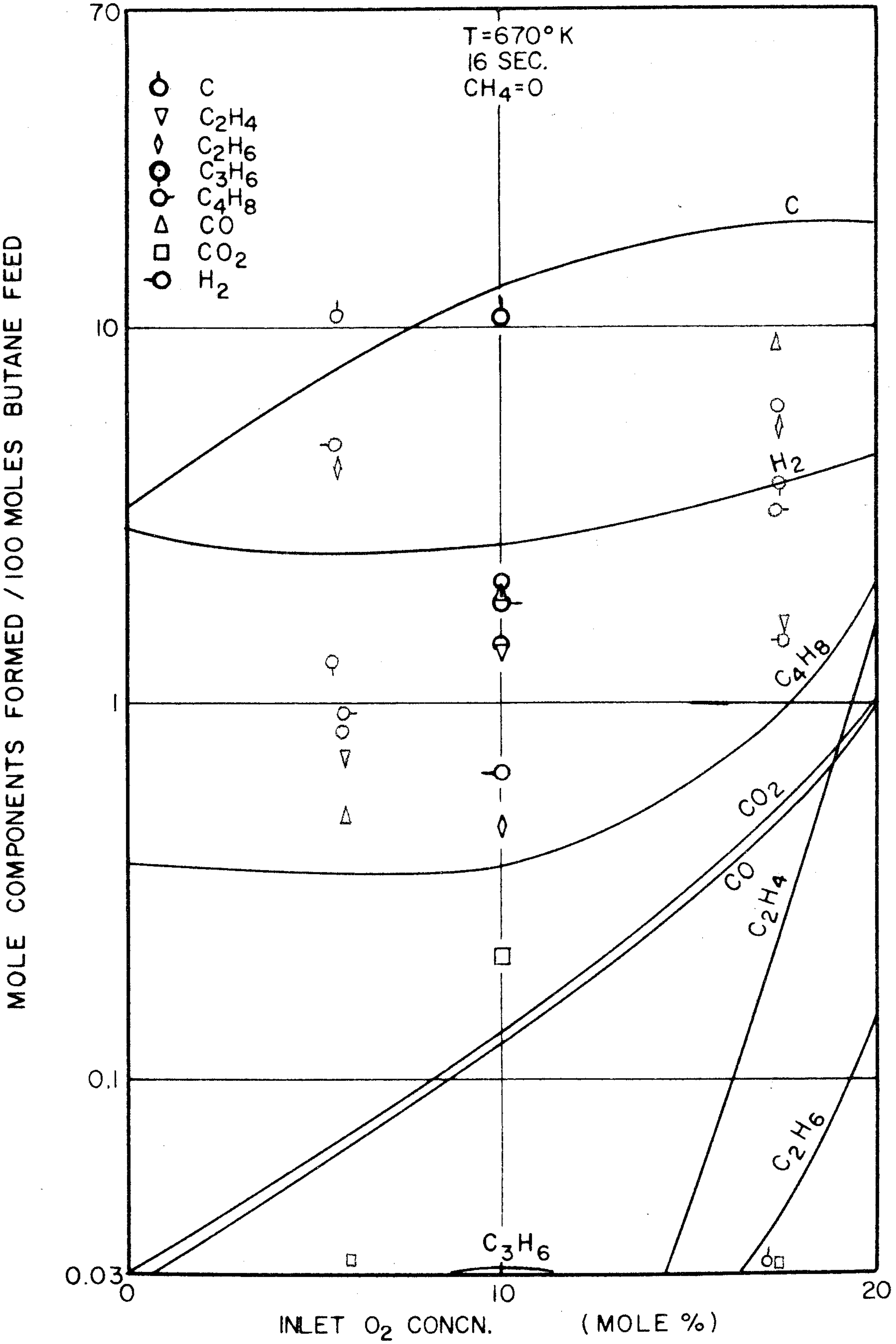


Fig. 23 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (670°K., 16 sec.)

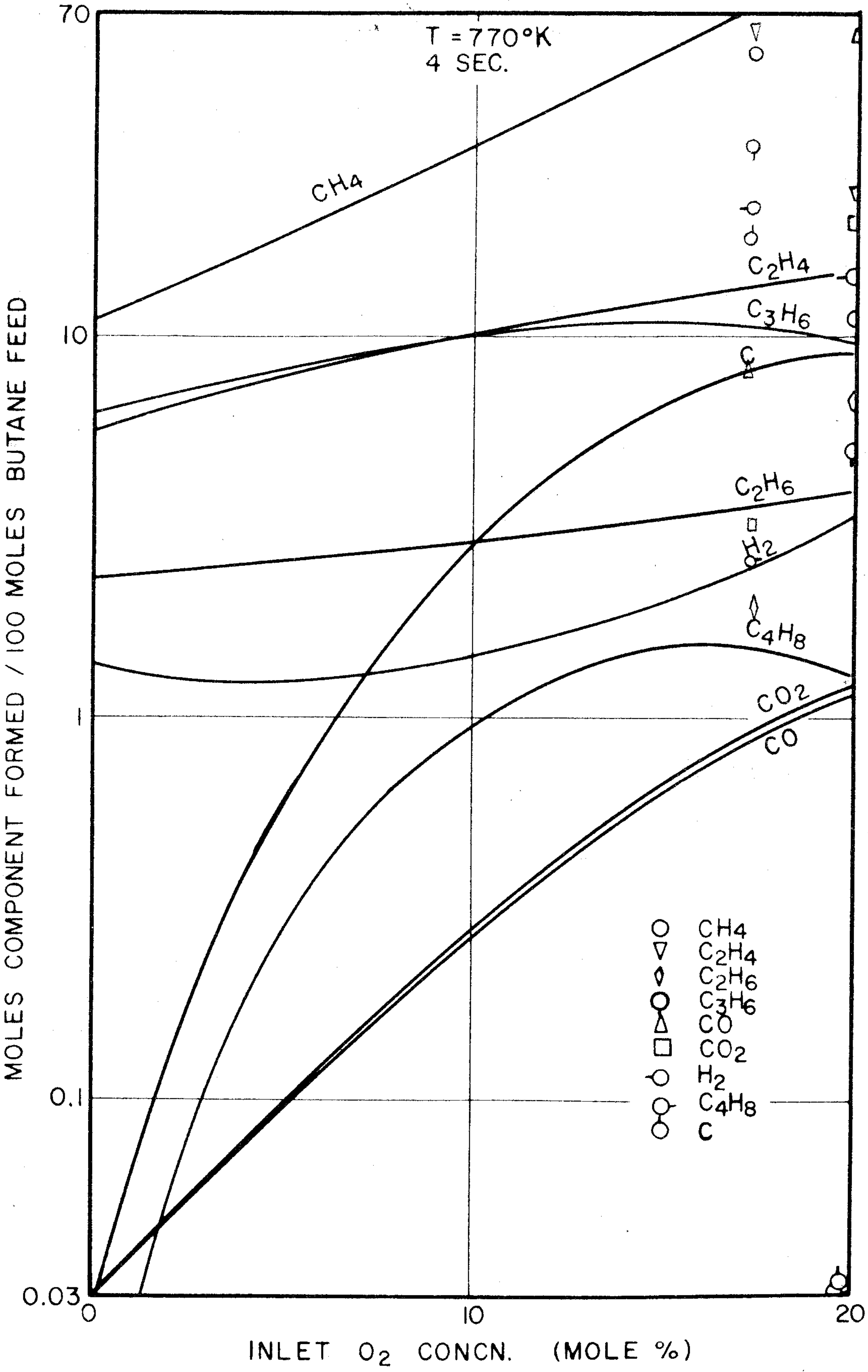


Fig. 24 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (770°K., 4. sec.)

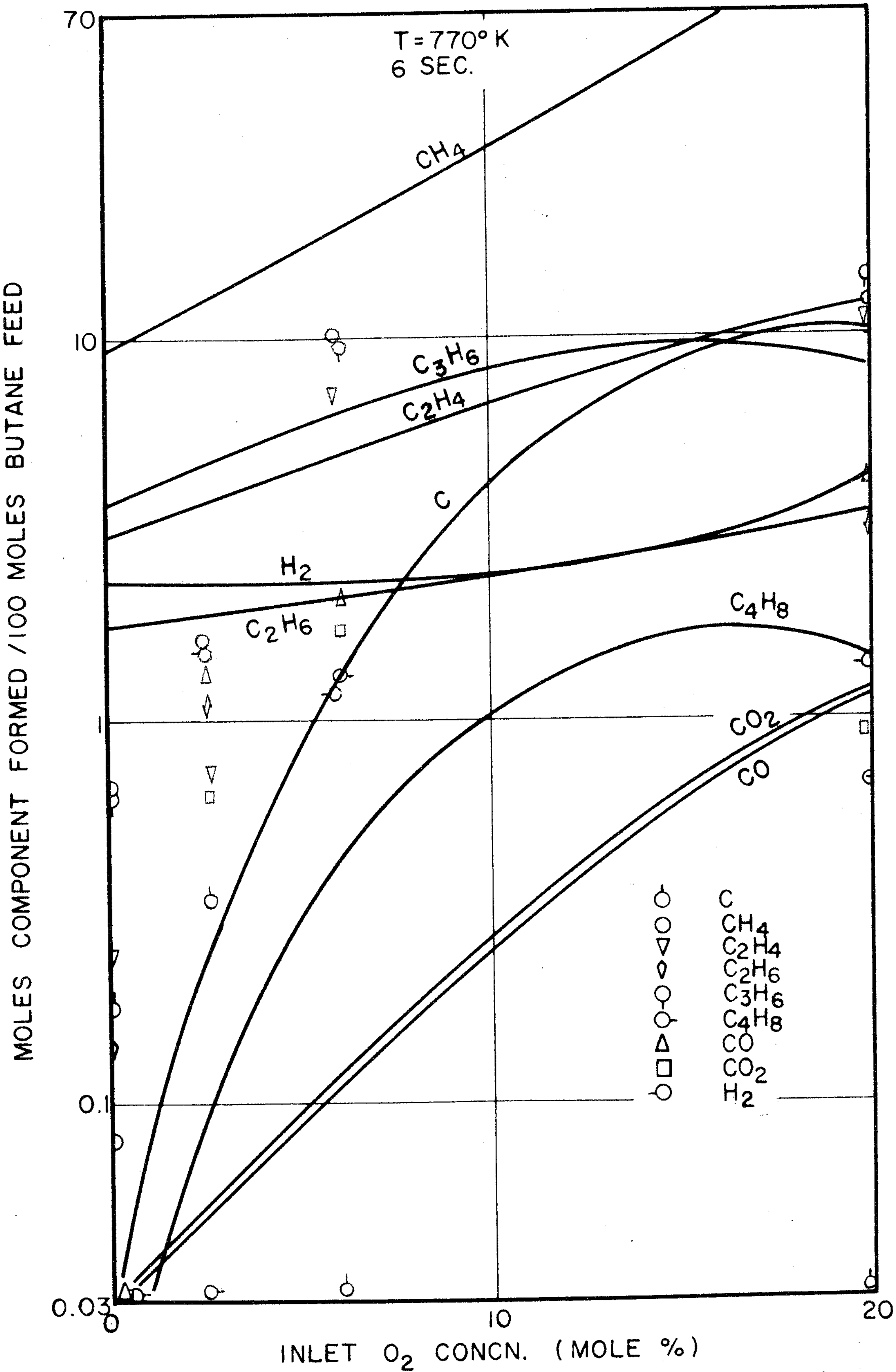


Fig. 25 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (770°K., 6 sec.)

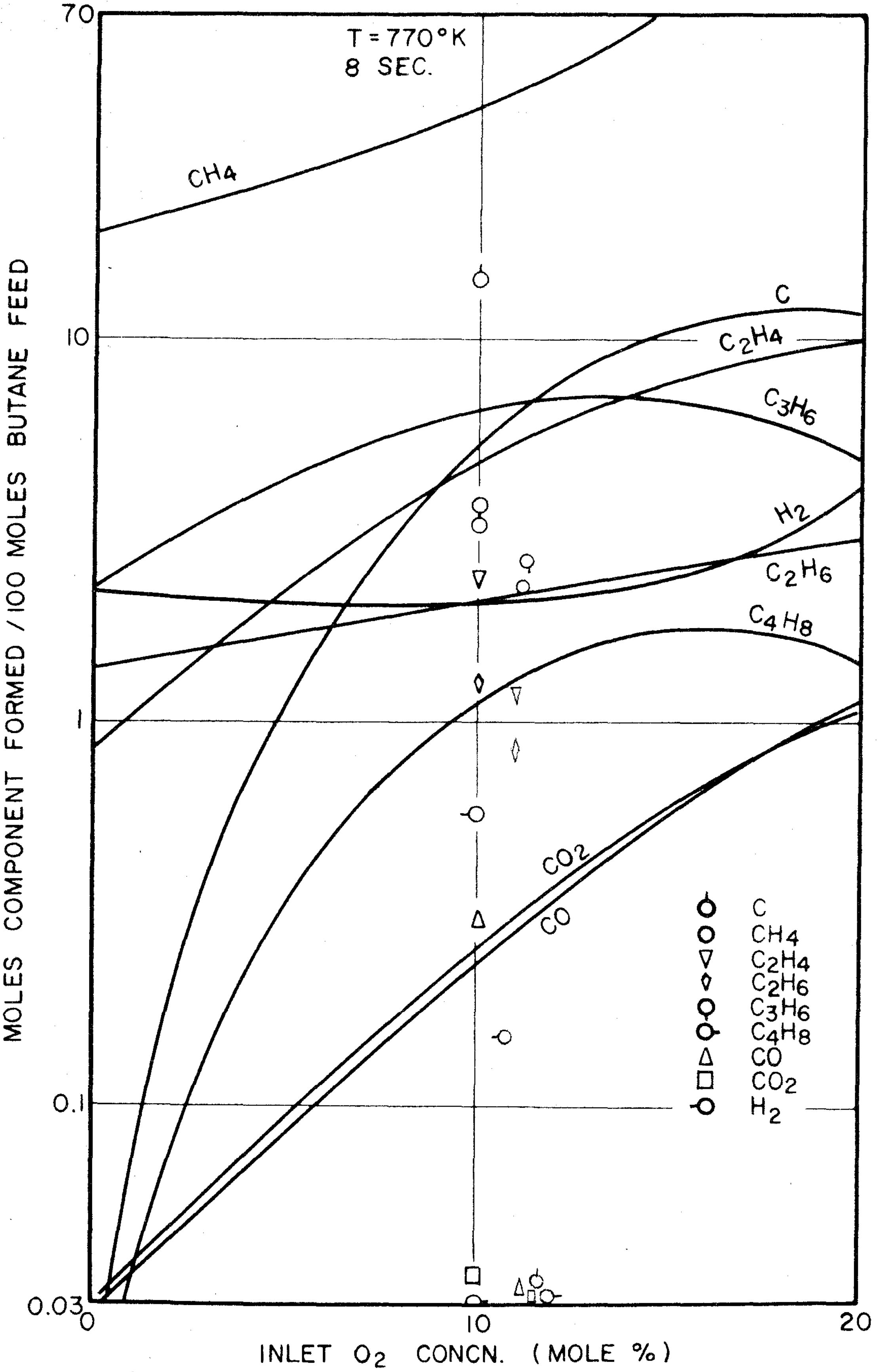


Fig. 26 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (770°K., 8 sec.)

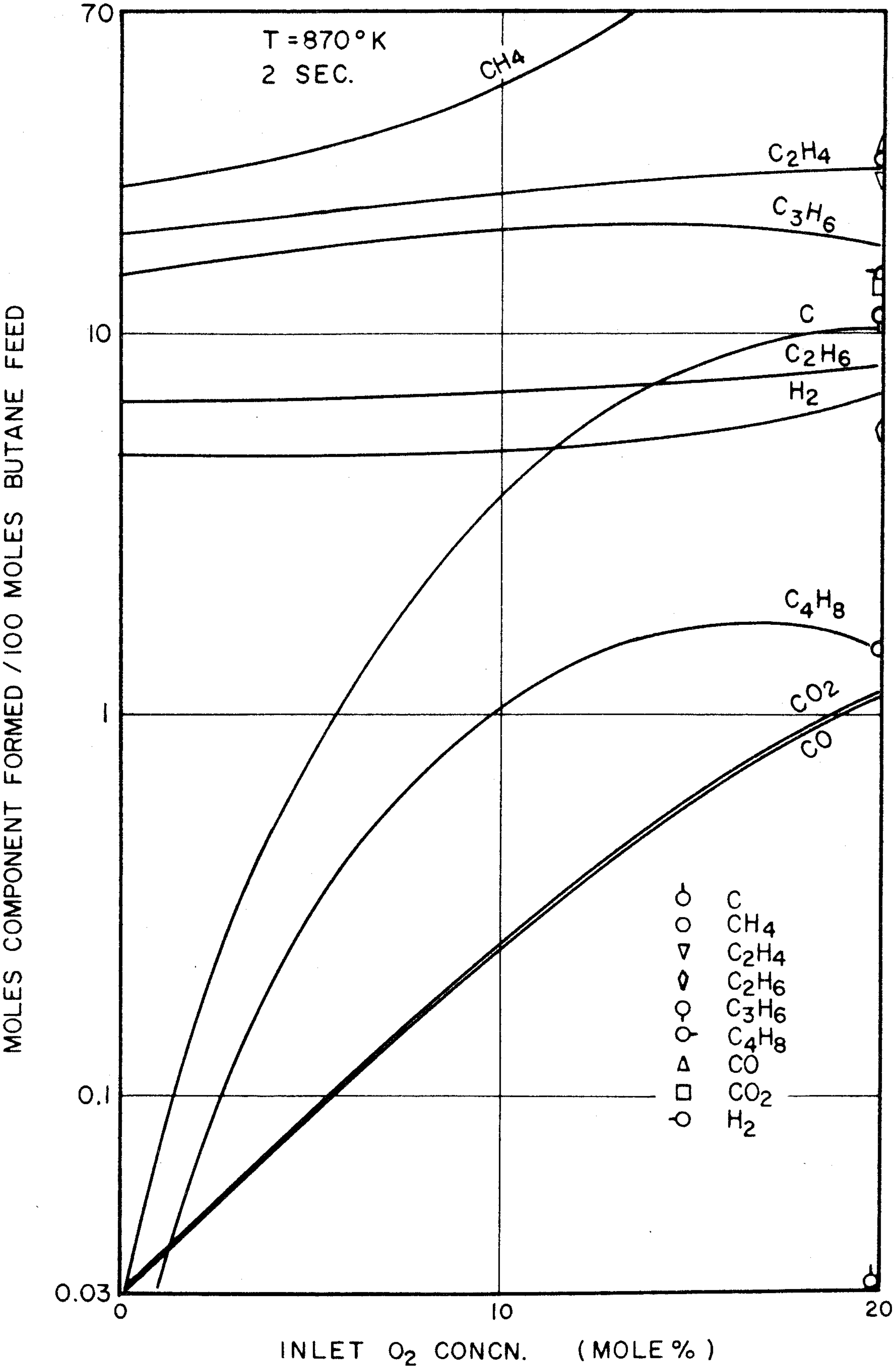


Fig. 27 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (870°K., 2 sec.)

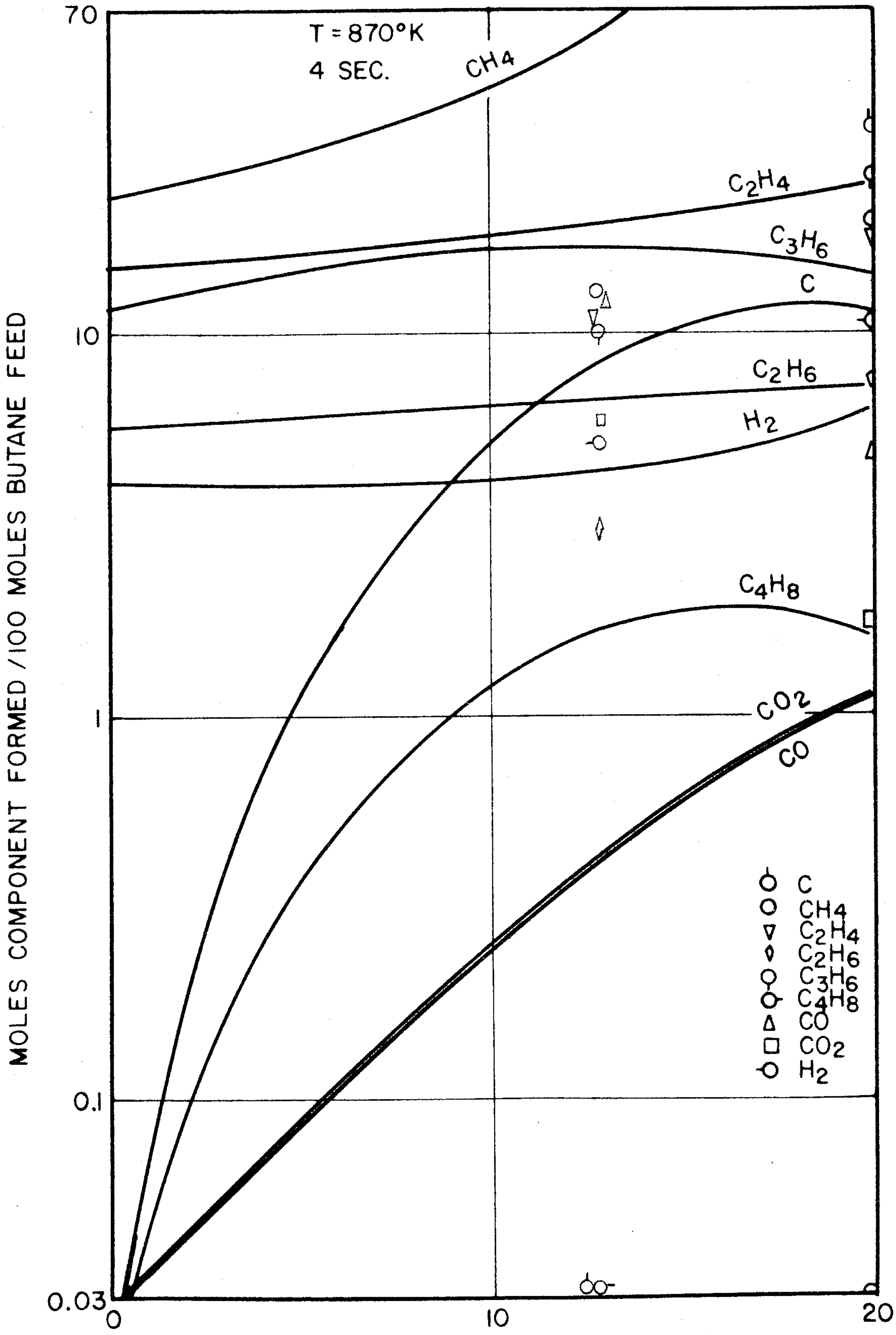


Fig. 28 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (870°K., 4 sec.)

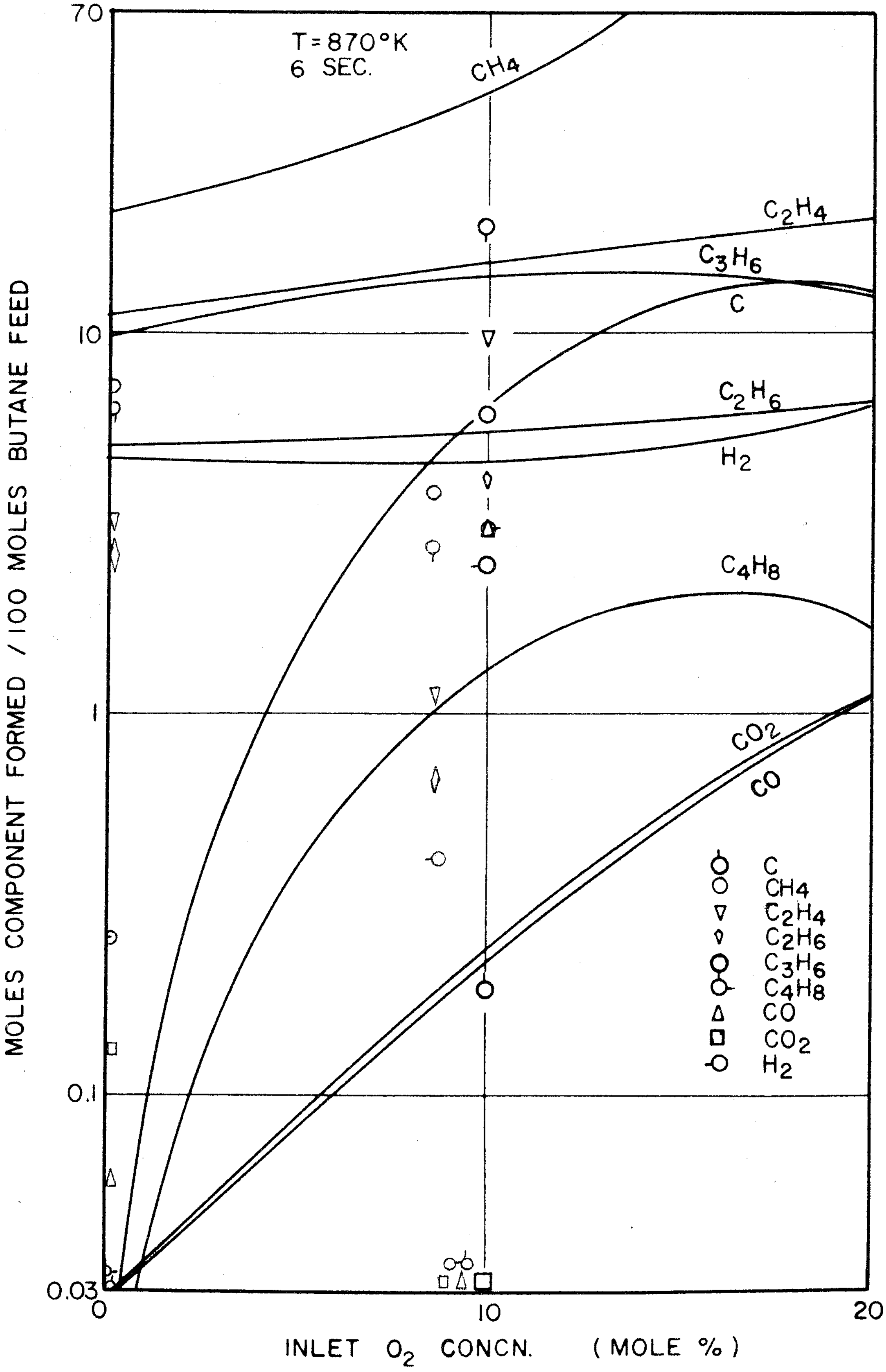


Fig. 29 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (870°K., 6 sec.)

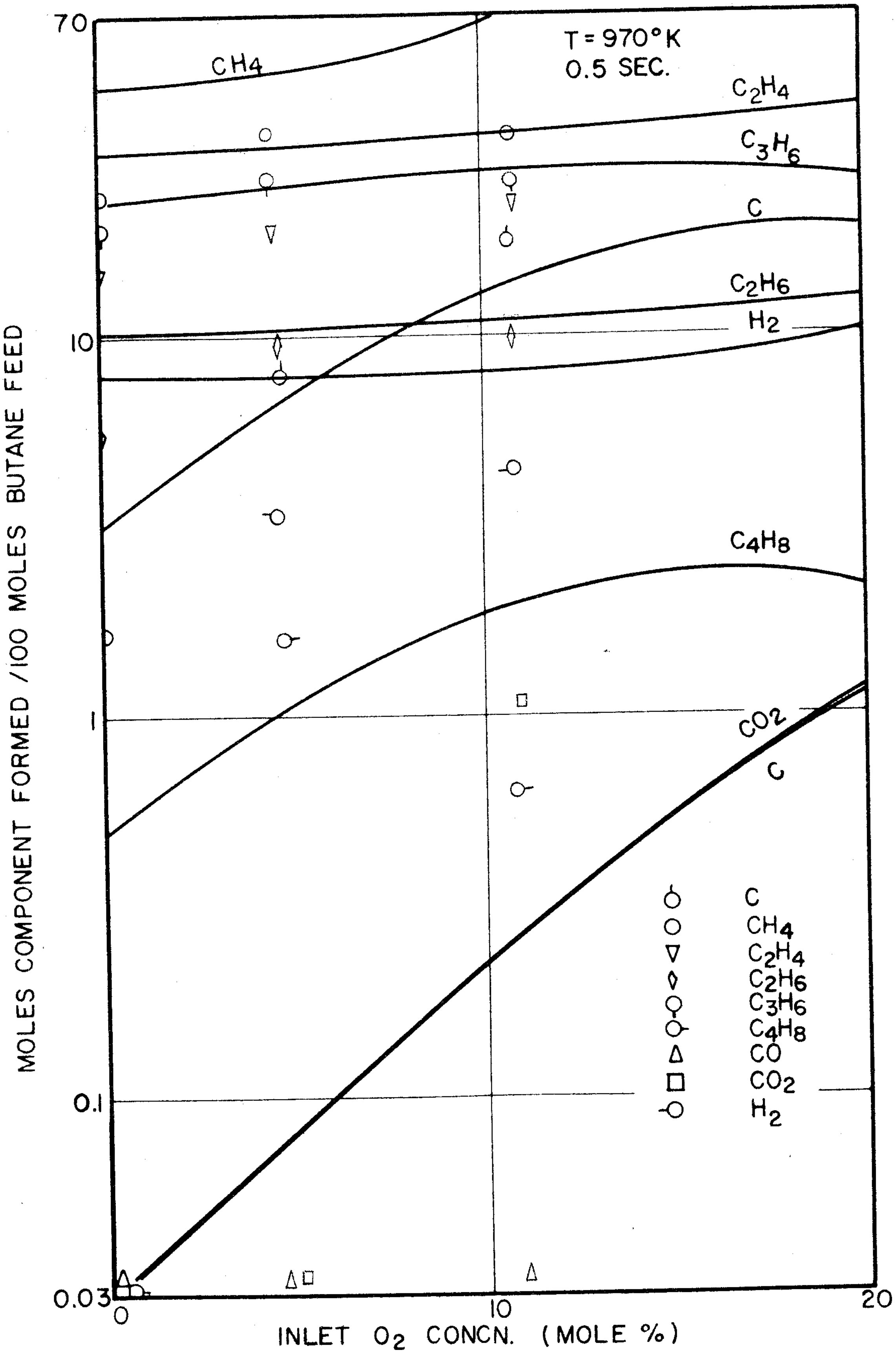


Fig. 30 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (970°K., 0.5 sec.)

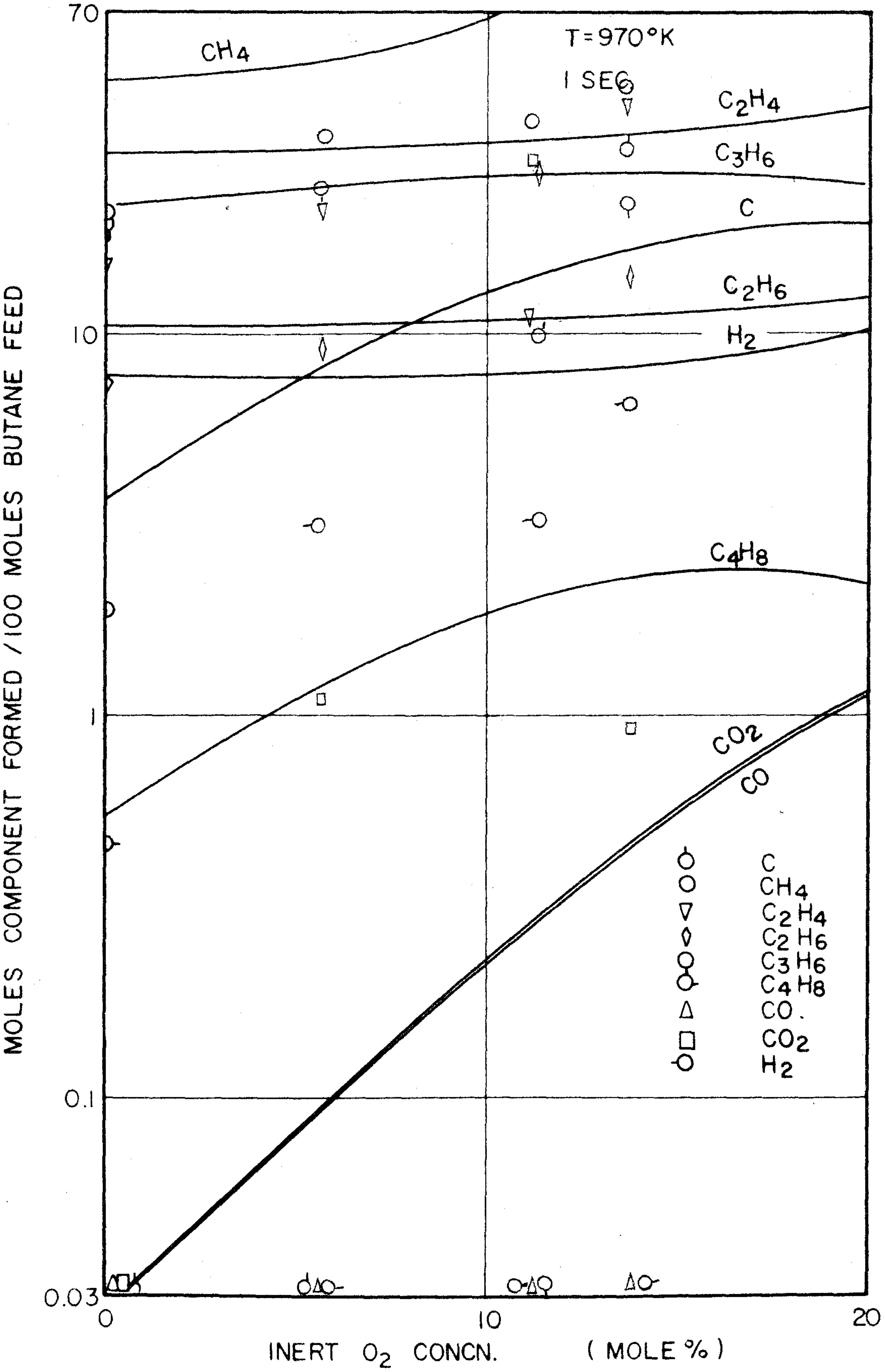


Fig. 31 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (970°K., 1 sec.)

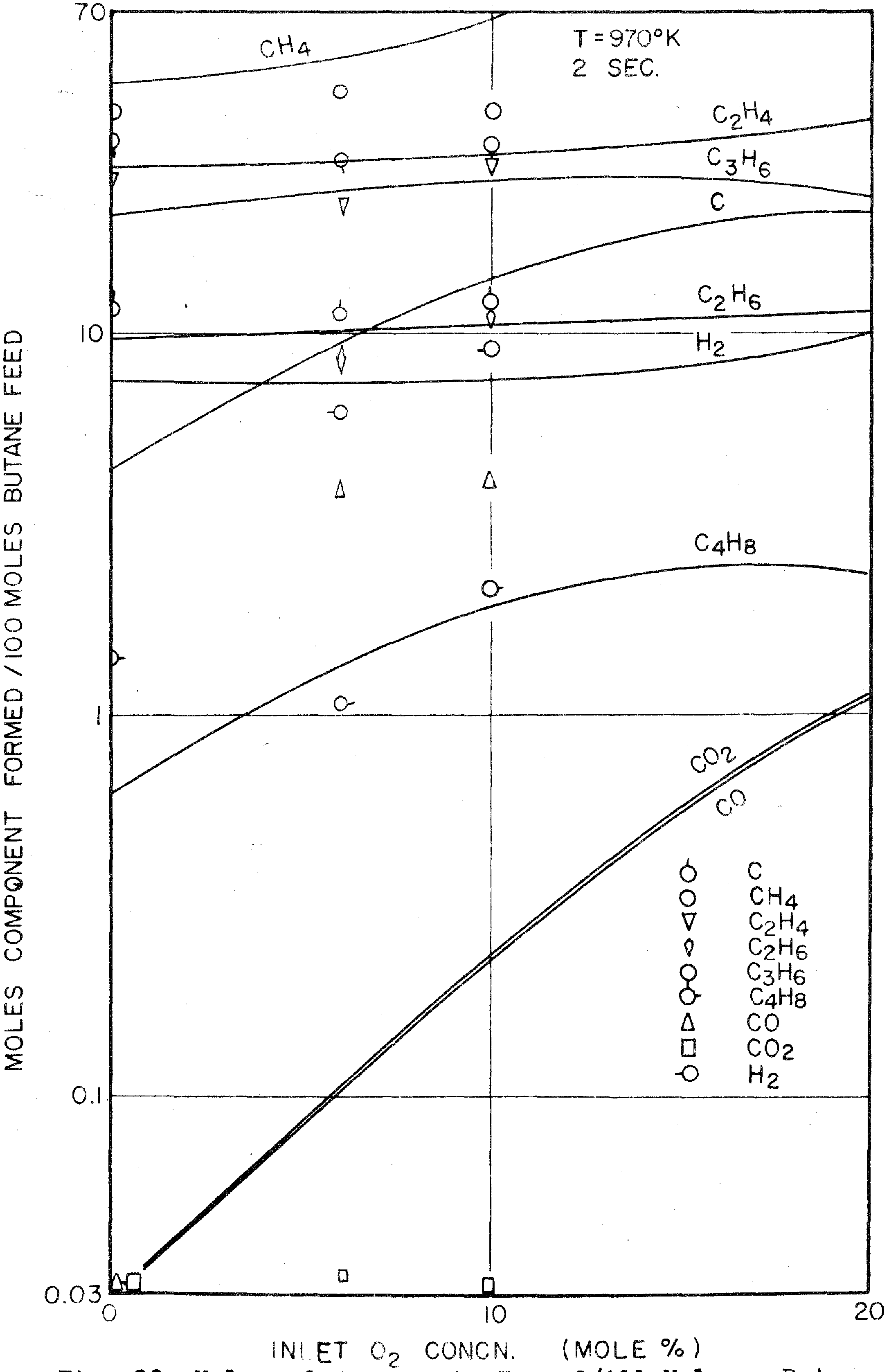


Fig. 32 Moles of Components Formed/100 Moles n-Butane Feed vs. Inlet O_2 Concn. (970°K., 2 sec.)

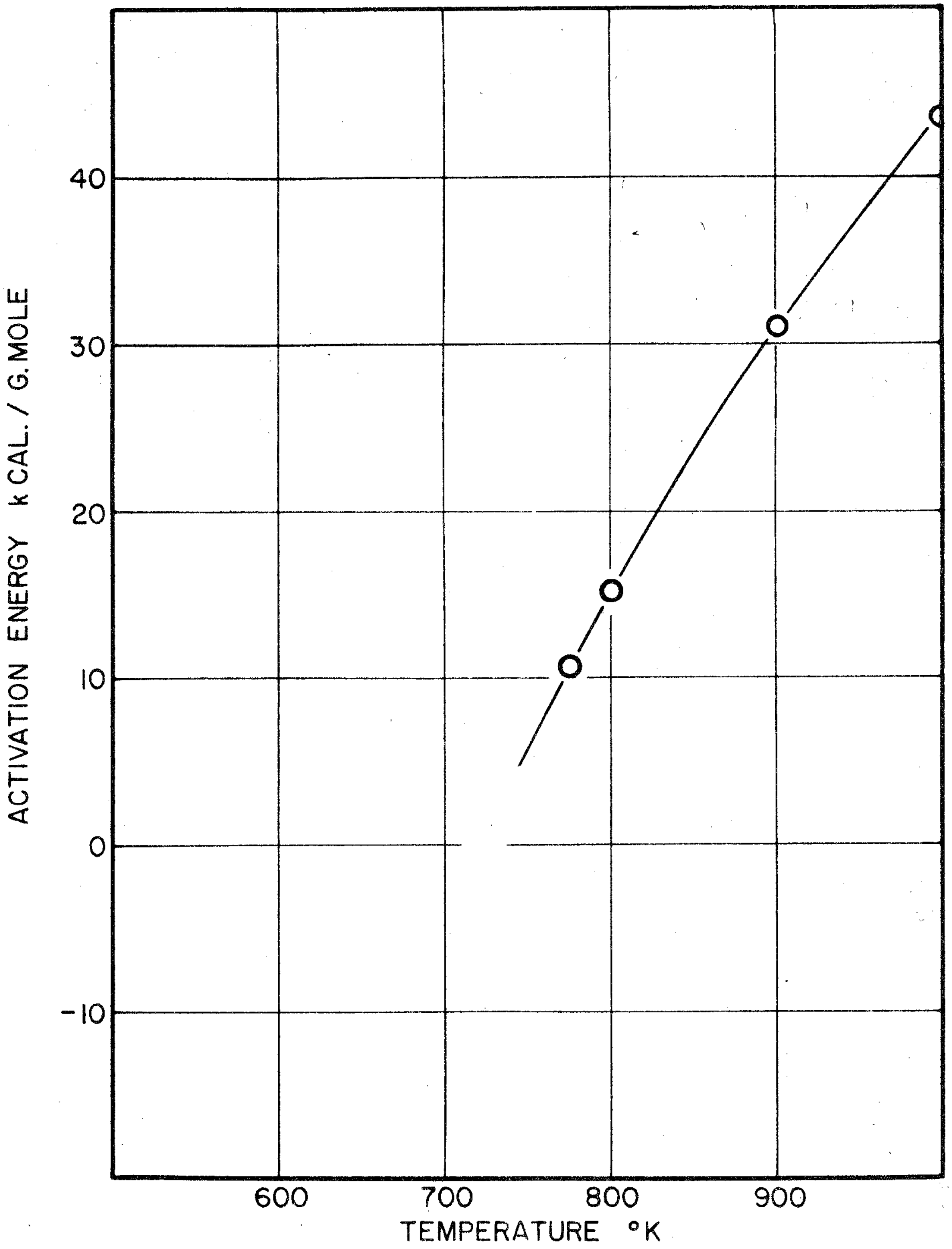


Fig. 33 Activation Energy for Oxidation of n-Butane vs. Temperature

LIST OF TABLES

LIST OF TABLES (Cont'd.)

TABLE I*

THE EFFECT OF TEMPERATURE AND OXYGEN CONCENTRATION ON THE PRODUCT COMPOSITION OF THE n-BUTANE-OXYGEN REACTION

Residence Time (sec.)	Temperature (^{o}C.)	n-Butane to Oxygen Mole Ratio	n-Butane Conversion (Mole %)	Oxygen Conversion (Mole %)	Product Composition (% Volume of Total)								
					H_2	CO	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	H_2O
0.9[b]	486	3.25	15.2	36.8	0.0	7.1	1.8	5.7	2.5	3.4	0.0	24.3	55.1
0.9	486	6.03	9.3	39.3	1.2	5.0	3.4	3.3	3.2	4.4	0.0	25.1	54.3
0.9[a]	486	10.8	7.2	45.1	2.7	2.6	7.2	5.3	2.3	6.5	0.0	24.2	49.1
0.9[a]	503	3.8	16.7	50.7	1.0	5.0	6.6	7.4	3.0	5.7	0.0	16.8	54.5
0.9	503	27.2	7.2	71.3	2.2	0.0	14.5	9.6	4.3	14.5	0.0	20.1	34.8
0.9	526	10.3	12.4	60.7	0.9	5.0	16.5	10.7	4.8	16.9	0.0	12.4	32.7

a = average of two runs

b = average of three runs

---

*Ref. 1

TABLE II*

THE EFFECT OF TEMPERATURE, n-BUTANE-OXYGEN RATIO AND SURFACE-VOLUME RATIO ON THE PRODUCT COMPOSITION OF THE n-BUTANE-OXYGEN REACTION

Residence Time (sec.)	Temperature (°C.)	Inlet O_2 Concn. (Mole %)	Reactor	Butane Conv. (Mole %)	Inlet O_2 Conv. (Mole %)	Product Composition (% Volume of Total)				
						Unsaturates	CH_4	H_2	CO	CO_2
13.0	350	25.0	LEC	64.00	93.0	28.0	24.30	5.50	33.60	8.40
12.6	400	75.0	LPC	15.00	18.7	33.0	12.10	12.10	21.20	21.20
12.6	400	25.0	LPC	00.00	00.0	00.0	00.00	00.00	00.00	00.00
12.6	450	75.0	LPC	46.00	46.5	19.4	00.00	3.88	44.60	32.00
12.6	450	25.0	LPC	11.65	58.0	54.0	14.30	1.59	6.35	23.80
13.0	450	25.0	LEC	30.30	96.0	43.5	23.70	3.96	2.20	6.76
1.6	450	25.0	SEC	16.35	70.0	53.9	5.13	2.56	21.80	16.60
12.6	500	75.0	LPC	63.00	61.0	19.5	5.03	4.40	50.30	20.80
12.6	500	25.0	LPC	28.30	88.0	53.5	15.10	4.10	15.75	11.65
1.6	500	25.0	SEC	25.00	70.0	61.3	9.00	3.60	74.40	11.70
1.6	550	25.0	SEC	41.30	93.0	55.3	22.55	3.40	13.60	5.10

Legend: L = Large (Vol. = 26.6 cc., i.d. = 1.65 cm., length = 11 cm.)
S = Small (Vol. = 2.6 cc., i.d. = 0.5 cm., length = 10 cm.)
P = Packed (Void volume = 15.8 cm. in large reactor)
E = Empty (No packing)
C = KCl coated walls and packing

Reactor: Pyrex glass reactors 1.65 cm. i.d. x 11 cm.
and 0.5 cm. i.d. by 10 cm.

---

* Ref. 2

TABLE III*

PRODUCT DISTRIBUTION IN THE PYROLYSIS OF n-BUTANE

Residence Time (sec.)	Temperature (°C.)	Butane Conversion (Mole %)	Product Composition (% Volume of Total)								
			H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	$n\text{-}C_4H_{10}$	C_5^+
13.5	600	21.8	1.8	9.5	5.9	5.4	6.6	1.3	3.6	65.4	0.5
33.0	600	28.4	2.2	11.4	7.6	6.0	11.9	1.8	2.3	56.6	0.2
48.0	600	38.9	2.1	16.7	6.7	4.7	16.5	4.6	2.6	45.5	0.6
99.0	600	53.2	2.5	23.3	12.2	8.0	16.6	2.0	4.5	30.6	0.3
1.4	650	10.8	0.5	2.3	1.5	1.5	3.0	2.8	2.6	84.7	1.1
11.0	650	46.2	3.0	18.8	11.5	9.0	13.7	4.9	2.4	36.7	0.0
21.0	650	59.7	3.9	22.9	16.7	6.9	15.0	2.9	4.8	25.4	1.5
36.0	650	82.0	5.8	33.5	21.0	8.9	15.3	2.0	3.5	9.3	0.7

Reactor: Electrically heated aluminium bronze blocks, containing a single hole 2.85 cm. in diameter and equipped with automatic temperature control. Reaction tubes were 18-8 chromium nickel steel treated by pickling with hot 17% HCl and treating with H_2S at 25°C. and 600°C. Reaction zone was 50.8 x 1.58 cm., volume = 95 cc.

---

* Ref. 6

TABLE IV

COMPARISON OF MASS SPECTROMETER AND GAS CHROMATOGRAPHY ANALYSES

RUN NO.	M.S. 166-1	G.C. 166-2	M.S. 166-4	G.C. 166-3	M.S. 167-5	G.C. 167-6
COMPONENTS						
Oxygen	3.34	5.08	4.04	7.04	0.27	0.00
Nitrogen	0.00	0.00	0.00	0.42	0.60	0.00
Hydrogen	11.91	11.81	13.85	12.22	9.10	10.08
Methane	27.66	32.25	28.66	30.40	22.92	26.18
Carbon Monoxide	0.75	1.63	1.48	0.37	3.28	3.87
Carbon Dioxide	1.68	0.49	1.17	0.52	2.21	2.69
Ethylene	32.14	32.97	33.00	29.74	25.56	28.61
Ethane	3.88	1.41	3.27	3.67	4.29	0.93
Propylene	11.05	9.78	8.08	9.00	14.13	14.49
Propane	0.29	0.00	0.44	0.00	0.81	0.00
Butene	0.84	1.18	0.46	1.12	1.80	1.33
Butane	4.43	1.37	1.36	1.31	12.46	9.25
Total	97.97	97.97	95.81	95.81	97.43	97.43
Acetylene	0.00		0.95		0.00	
Propadiene	0.00		0.29		0.00	
Vinylacetylene	0.00		0.03		0.00	
Acetone	0.10		0.07		0.48	
C4 Acetylenes and/or diolefins	0.81		1.14		0.35	
Pentenes	0.09		0.04		0.33	
C5 Acetylenes and/or diolefins	0.53		0.69		0.40	
Hexenes	0.08		0.00		0.07	
C6 Acetylenes and/or diolefins	0.37		0.11		0.09	
Benzene	0.05		0.77		0.07	
Toluene	0.00		0.08		0.01	
Styrene	0.00		0.01		0.00	
ylene	0.00		0.01		0.00	
elium	0.00		0.00		0.77	
otal	2.03		4.19		2.57	

Mass Spectrometer Analyses Reported by Consolidated Electrodynamics

TABLE V

COMPARISON OF TRAVERSE SAMPLE CONCENTRATIONS AT THE OUTLET OF THE n-BUTANE OXIDATION REACTOR

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (Sec.)	Traverse* Sampling Location	Sample Concentrations, Mole %											
					O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
62	765	12.59	8.71	0.1	0.00	0.00	0.53	2.63	2.34	0.27	1.79	0.80	2.89	1.66	68.20	19.42
65	753	12.59	8.77	0.1	0.00	0.00	0.56	2.94	2.56	0.00	2.42	0.94	3.14	2.10	65.95	19.13
63	754	12.59	8.81	0.3	0.24	0.00	0.55	2.88	2.23	0.29	2.11	1.12	2.92	1.92	67.08	18.65
66	754	12.59	8.81	0.3	0.37	0.00	0.40	3.76	3.13	0.34	2.42	0.75	3.04	2.03	66.35	17.42
64-1	752	12.59	8.86	0.5	0.00	0.00	0.53	3.31	2.62	0.32	2.35	0.87	3.70	1.50	69.63	15.04
67	756	12.59	8.92	0.5	0.00	0.00	0.46	3.99	3.14	0.30	2.64	1.11	3.97	1.77	67.72	18.77

---

*Inches from reactor wall.

Table VI

COMPARISON OF MEASURED TEMPERATURE INCREASE OF INLET GAS STREAM TO THAT EXPECTED ON THE BASIS OF CALCULATED HEAT TRANSFER

Run No.	Butane conc. (Mole%)	Inlet O_2 Conc. (Mole%)	Average Reactor Wall Temp. (°C.)	Inlet Gas Temp. (6" from reactor outlet, °C.)	Average Traverse Temp. (3" from reactor outlet, °C.)	Approx. Value* of Traverse (Temp. °C.)
122	39.67	0.00	724	545	711	650
123	44.31	4.22	706	456	688	606
124	48.39	11.31	716	466	690	606
125	68.51	20.43	732	508	716	636

---

* based on calculated heat transfer

$$h_{av.} = 1.34 \frac{\text{B.T.U.}}{(\text{hr.})(\text{ft.}^2)(^\circ\text{F.})}$$

TABLE VII

TRAVERSE TEMPERATURES AT THE OUTLET OF THE n-BUTANE OXIDATION REACTOR

Run	Reactor Length (inches)	Total Flow Rate (cu.ft./min)	Average Traverse Temp. °C.	Inlet Nozzle * (1/2 in. long)	Traverse Location (Inches from Wall) 0.2	0.3	0.4	0.5	0.6	0.7
					(Traverse Temperature (°C.) 0					
76	28.00	0.0960	709.70	Q	718.0	718.0	703.5	705	704.0	
79	28.00	0.1080	700.20	Q	704.0	703.5	699.0	699	698.0	
102	14.00	0.1004	735.50	Q	736.0	737.0	735.0	735	735.0	735.0
103	14.00	0.1150	723.17	Q	728.0	725.0	723.0	722	721.0	720.0
154	28.00	0.0130	421.50	Q_2	422.0	421.0	418.0	423.0	422.5	422.5
156	28.00	0.0160	438.80	Q_2	430.0	434.5	437.5	445.5	442.5	442.5
152	14.00	0.0160	417.50	Q_2	421.0	419.0	413.0	418.0	416.0	418.0
153	14.00	0.0170	428.00	Q_2	437.0	424.0	422.0	424.0	427.0	434.0
135	7.00	0.0100	411.25	Q_2	413.5	413.0	413.0	410.0	409.0	409.0
137	7.00	0.0120	413.25	Q_2	420.0	416.5	416.0	414.0	407.0	404.0
92	28.50	0.1070	750.00	None	750.0	751.0	751.0	750.0	750.0	
37	15.75	0.0290	541.50	None	546.0	542.0	542.0	541.0	538.0	538.0
24	28.00	0.0290	535.75	S.S.	534.0	540.0	740.0	540.0	534.0	529.0
29	14.00	0.0240	482.50	S.S.	482.5	487.5	488.0	481.0	478.0	478.0

---

* Q = Quartz (Nozzle made of fine quartz tubing; tubing less than 0.020 in. i.d.)

Q_2 = Quartz (Nozzle made of 1/4 in. o.d. tubes)

S.S. = Stainless Steel (Nozzle made of stainless steel hypodermic tubing,less than 0.020 in i.d.)

TABLE VIII

CHROMATOGRAPH ANALYSES OF PRODUCT SAMPLES IN THE PARTIAL OXIDATION OF n-BUTANE

Run Number	Chromatographic Analysis Mole %											Total ** Components Analyzed x 10^5 (gram moles)	Total * Sample x 10^5 (gram moles)
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}		
11	0.26	4.71	17.72	28.96	0.00	0.00	25.77	7.607	12.61	0.00	29.15	88.04	87.15
12	1.24	7.94	10.87	6.27	2.28	0.00	3.99	1.97	0.86	9.89	64.68	107.90	106.24
13	4.88	28.18	7.18	2.70	4.84	0.00	9.38	2.76	0.72	0.00	43.82	100.38	106.24
14-1	1.56	4.64	12.56	2.03	10.12	0.00	8.62	4.59	0.92	0.00	54.96	87.83	106.24
14-2	0.16	6.44	12.12	2.49	12.10	0.00	8.32	4.43	0.89	0.00	53.05	72.69	84.87
15	1.60	12.02	13.19	2.67	11.02	0.00	8.19	5.45	0.00	0.00	46.11	83.66	92.96
16	4.85	20.06	6.17	1.21	3.21	0.00	4.84	2.44	2.53	0.00	54.71	64.48	69.72
17	4.54	21.51	3.76	0.92	0.86	0.00	3.23	2.38	1.00	0.00	61.80	93.28	107.28
18	3.65	22.66	0.00	0.63	0.00	0.00	2.67	0.00	0.00	0.00	70.38	87.24	107.28
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	89.34	111.84
20-1	0.31	0.99	7.678	22.45	0.00	0.00	16.22	7.38	17.85	0.00	27.13	104.22	104.17
20-2	0.50	1.66	7.58	22.59	0.00	0.00	16.00	7.28	17.61	0.00	26.77	86.27	85.08
21	0.44	0.97	0.00	13.56	0.00	0.00	7.93	4.31	13.23	0.00	59.57	98.88	102.92
22	2.39	4.03	3.92	12.22	0.00	0.00	9.30	5.25	11.72	0.00	51.19	103.81	103.75
23	0.00	1.12	2.81	13.17	0.65	1.42	10.19	7.45	22.12	0.00	41.07	112.36	104.58
24	0.50	1.27	2.49	21.14	2.54	2.88	13.23	5.93	12.66	1.36	34.55	103.68	103.75
25	0.53	1.05	3.71	18.75	5.56	3.94	16.22	7.89	21.75	2.11	16.96	67.46	101.47
26	0.95	1.57	7.88	22.97	1.00	1.94	19.90	19.90	16.15	0.87	20.70	94.72	100.64
27	0.31	0.74	8.73	26.38	.26	0.00	23.42	7.23	17.75	1.24	13.95	92.46	101.05
28	0.00	0.52	19.05	25.20	0.00	0.00	19.03	6.08	16.81	1.35	11.96	115.15	103.75
29	0.00	0.00	11.40	25.14	0.00	0.00	25.89	6.96	18.25	0.57	12.70	107.18	106.66
30	0.37	1.01	10.59	25.50	0.93	0.00	18.45	6.72	17.53	0.69	18.20	96.84	107.28
31	0.00	0.41	12.79	21.30	3.02	1.06	20.40	6.25	16.36	0.00	18.41	95.30	107.69
32	0.00	0.98	4.98	23.82	7.36	1.97	24.54	5.93	17.51	0.00	12.92	79.86	105.41
33	0.00	0.48	0.00	0.53	0.00	0.00	0.00	0.00	1.01	0.00	97.98	88.22	103.75
34	0.00	0.75	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	98.86	101.80	106.66
35	0.16	1.23	0.23	3.62	0.00	0.00	1.87	1.32	4.00	0.00	87.62	101.86	107.07
36	0.44	1.08	1.13	10.10	3.41	0.71	8.75	2.73	10.29	0.54	60.82	92.86	102.92
37-1	0.00	0.53	1.36	12.89	2.66	0.65	9.91	4.50	12.32	0.64	54.19	93.87	104.58
37-2	1.66	4.09	1.23	12.76	1.60	1.43	9.81	3.82	14.00	0.00	49.59	71.27	71.38
38-1	0.00	0.71	0.38	3.43	0.00	0.00	1.08	0.63	2.47	0.00	91.30	101.07	105.41
38-2	5.53	14.11	0.30	2.33	0.00	0.00	1.36	1.24	2.12	0.00	73.01	104.63	86.32
39-1	0.07	0.96	0.21	2.10	0.00	0.00	1.14	1.25	2.71	0.00	91.56	103.33	102.92
39-2	8.14	21.65	0.21	1.16	1.11	0.00	1.26	0.80	1.47	0.00	64.20	100.46	95.87
40	0.31	2.59	0.10	1.58	0.00	0.00	0.73	0.71	1.74	0.00	89.46	106.62	105.20
41	0.00	0.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.33	90.32	103.75

---

* Total sample admitted to chromatography columns.

**Total sample size on basis of analysis.

TABLE VIII CONT'D.

CHROMATOGRAPH ANALYSES OF PRODUCT SAMPLES IN THE PARTIAL OXIDATION OF n-BUTANE

Run Number	Chromatographic Analysis Mole %											Total ** Components Analyzed x 10^5 (gram moles)	Total * Sample x 10^5 (gram moles)
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}		
42	0.00	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	98.57	108,70	105.41
43	0.00	1.09	0.22	2.72	0.45	0.30	1.60	0.68	1.88	0.79	90.26	107.19	105.41
44	0.00	1.09	0.54	6.36	2.94	0.00	5.05	1.69	6.29	2.15	73.89	106.47	105.20
45	0.00	0.96	7.49	18.58	3.57	1.24	12.78	5.26	14.20	0.00	39.49	107.55	104.58
46-1	0.00	1.79	0.08	0.24	0.00	0.00	0.25	0.13	0.64	0.00	96.86	101.77	108.11
46-2	0.00	2.03	0.08	0.67	0.00	0.00	0.23	0.13	0.59	0.00	96.25	82.19	86.74
47	0.00	2.05	1.08	8.51	1.73	1.47	6.04	1.97	8.37	1.12	67.67	98.84	108.11
48	0.00	4.28	0.37	5.75	0.50	0.84	3.28	1.31	5.86	0.65	76.96	108.65	108.32
49	0.00	7.35	1.34	1.43	1.16	0.57	0.62	0.27	1.02	0.00	86.24	101.44	106.03
50-1	0.29	2.19	0.23	6.02	0.00	0.00	2.83	2.04	5.65	0.00	80.75	106.36	25.50
50-2	0.40	1.96	0.18	5.08	0.04	0.10	2.34	1.48	4.73	0.00	65.70	84.40	84.25
51	0.56	1.53	1.87	6.35	5.73	4.35	4.83	1.45	2.38	0.00	70.94	106.48	109.15
52-1a	0.93	2.40	7.30	0.00	32.12	0.00	0.00	5.21	0.25	0.00	49.22	65.35	105.20
52-2	0.47	1.42	5.99	3.88	22.66	11.00	12.59	2.43	2.77	0.00	42.08	68.81	86.32
53	0.56	1.30	8.30	2.84	31.73	10.40	15.16	2.95	3.30	0.00	23.46	78.32	103.75
54	0.55	1.23	6.26	4.78	26.84	9.16	10.66	2.95	2.16	0.00	24.33	90.00	104.17
55	0.60	1.54	4.37	5.26	19.73	8.82	10.69	1.83	2.37	0.00	44.76	82.22	85.70
56-1	0.44	1.40	9.76	2.24	11.98	7.19	5.88	2.01	4.58	0.00	58.31	90.55	107.49
56-2	0.44	1.11	6.64	1.00	39.54	5.27	3.80	0.84	0.71	0.00	40.65	94.50	76.36
57	0.69	1.95	1.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	95.54	86.34	108.73
58	0.42	2.09	0.92	10.46	0.00	0.00	4.62	3.41	9.31	0.00	68.78	95.17	107.49
59	0.50	1.51	3.72	8.90	9.15	4.22	8.21	2.15	7.40	0.00	54.23	85.42	109.56
60	0.44	1.46	7.55	14.61	16.76	6.90	13.94	3.36	6.16	0.78	28.04	82.40	107.07
62-1	0.00	0.28	0.65	3.23	2.88	0.34	2.20	0.98	3.56	2.04	83.84	41.12	39.92
62-2	0.53	0.27	0.64	3.50	3.06	0.00	2.43	1.05	3.41	2.29	83.05	33.81	31.75
63	0.41	0.40	0.68	3.53	2.72	0.35	2.58	1.37	3.57	2.35	83.03	63.14	63.29
64-1	0.18	0.15	0.62	3.89	3.08	0.38	2.77	1.03	4.35	1.76	81.79	71.92	78.85
64-2	0.00	0.16	0.62	4.26	3.17	0.00	2.68	0.74	4.33	1.75	82.30	58.35	63.58
65	1.59	6.31	0.63	3.35	3.21	0.00	2.76	1.07	3.57	2.40	75.12	71.33	74.70
66	1.33	3.40	0.46	4.36	3.62	0.39	2.81	0.87	3.52	2.36	76.89	51.79	54.16
67	0.13	0.16	0.56	4.90	3.63	0.37	3.25	1.36	4.88	2.18	83.21	65.28	71.17
68-1	1.45	4.68	0.94	5.11	0.00	0.00	2.33	1.84	4.25	0.00	79.41	54.84	58.93
68-2	1.22	3.43	0.833	3.64	0.00	0.00	1.78	1.22	2.90	0.00	85.00		
69	6.12	19.18	1.97	0.93	1.91	0.00	6.66	3.90	10.57	0.93	47.83	73.86	81.34
70	7.02	21.97	1.41	8.84	1.67	0.00	5.62	2.44	10.89	1.68	38.47	71.08	72.00
71	6.73	20.41	1.07	8.25	1.31	0.00	5.23	3.24	8.10	1.05	44.61	71.35	67.44
72	5.14	15.82	5.51	13.62	0.00	0.00	9.91	4.51	11.89	1.17	32.45	89.74	110.81

---

* Total sample admitted to chromatography columns.

**Total sample size on basis of analysis.

a Propane = 0.25

TABLE VIII CONT'D.

CHROMATOGRAPH ANALYSES OF PRODUCT SAMPLES IN THE PARTIAL OXIDATION OF n-BUTANE

Run Number	Chromatographic Analysis Mole %										Total ** Components Analyzed x 10^5 (gram moles)	Total * Sample x 10^5 (gram moles)
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}		
73	6.97	22.94	3.48	13.81	0.23	0.00	10.39	5.01	11.74	0.00	25.44	110.93	110.39
74	6.17	20.01	3.89	16.22	0.75	0.00	12.70	4.28	13.79	0.00	22.21	72.79	74.91
75	6.31	19.31	4.29	17.42	1.60	0.00	13.32	4.52	13.32	1.55	18.37	72.60	73.25
76	7.91	29.10	0.80	9.77	0.00	0.00	9.59	4.29	11.03	0.00	27.50	97.83	107.07
77	7.68	35.31	0.26	5.86	0.00	0.00	8.66	3.68	11.32	0.00	27.01	96.66	111.64
78	8.20	36.38	2.91	9.58	0.18	0.00	10.04	3.77	10.01	0.00	18.93	95.75	110.39
79	8.56	32.95	4.52	10.97	0.88	0.00	11.98	4.29	11.31	0.36	14.93	98.25	112.88
80	0.00	0.00	4.97	17.03	0.00	0.00	12.48	6.45	17.92	0.00	41.15	100.25	106.03
81	0.00	0.00	5.46	23.28	2.45	0.00	16.96	6.68	18.84	1.30	25.04	95.71	104.79
82	0.00	0.00	3.75	27.41	2.38	0.00	13.06	5.80	17.81	0.66	29.13	107.53	105.41
83	0.00	7.50	3.71	19.41	0.46	0.00	11.43	5.36	16.50	0.00	35.63	108.22	105.83
84	0.71	24.07	8.34	0.00	0.00	0.00	19.92	7.26	18.18	0.78	13.74	112.07	108.94
85	0.00	0.00	10.32	27.18	1.48	0.00	20.79	0.00	17.41	0.84	14.51	107.70	109.35
86	0.00	0.00	11.58	20.61	3.11	0.64	19.13	7.11	16.18	0.80	20.86	87.31	86.74
87	0.00	0.00	7.37	22.54	0.00	0.00	15.87	7.53	19.10	0.83	26.76	104.68	107.49
88-1	0.00	0.00	2.57	34.85	0.00	0.00	28.27	8.55	19.13	0.92	5.70	115.34	106.45
88-2	0.00	0.18	2.88	33.15	0.00	0.00	29.26	10.25	15.77	1.17	7.34	84.87	87.77
89	0.00	0.00	5.98	52.60	3.27	0.00	6.53	11.63	15.86	1.31	3.40	69.35	109.15
90	0.00	0.00	5.82	37.57	0.92	0.00	32.69	10.50	11.84	1.08	1.58	100.21	108.73
91	1.23	3.50	4.56	54.75	0.24	0.00	6.03	8.66	16.74	1.66	2.64	73.92	107.07
92-1	0.00	0.85	4.34	37.87	0.00	0.00	30.15	6.91	14.00	1.28	4.60	86.77	104.17
92-2	0.00	3.27	4.79	39.16	0.00	0.00	28.40	5.92	12.95	1.18	4.32	82.04	84.04
93	0.00	2.43	5.26	38.45	0.00	0.00	30.18	7.95	12.40	0.00	3.33	91.64	103.13
94	0.00	0.00	6.22	40.65	0.00	0.00	31.24	7.63	10.70	1.24	2.33	94.98	103.13
95	0.16	3.85	5.15	41.92	0.00	0.00	33.14	8.21	6.41	1.15	0.28	93.41	103.54
96	0.00	0.22	2.88	25.14	0.00	0.00	41.77	6.28	13.90	1.46	8.35	124.80	105.83
97	0.00	0.37	3.79	29.58	0.00	0.00	30.78	9.54	15.99	1.75	8.20	102.96	106.66
98	0.00	0.41	4.32	34.56	0.00	0.00	30.15	13.00	8.01	1.82	4.36	99.66	105.41
99	0.00	0.00	2.00	18.90	0.00	0.00	16.26	3.88	37.10	4.69	17.18	154.71	84.66
100	0.00	1.08	0.31	15.57	0.00	0.00	10.59	4.41	14.19	0.23	53.93	120.24	108.73
101	0.00	0.00	0.00	21.94	0.00	0.79	16.03	6.80	16.69	0.00	37.74	94.84	107.49
102	0.00	0.00	2.91	23.23	0.00	0.70	23.72	6.51	17.60	1.06	24.27	118.60	107.69
103	0.51	0.93	4.45	25.91	0.00	2.47	25.27	7.90	0.00	0.57	16.14	108.13	105.20
104	0.39	1.11	3.85	23.24	0.00	2.75	18.58	6.28	14.06	0.69	26.98	116.13	107.07
105	0.00	0.00	2.74	20.35	0.00	1.26	16.40	5.83	15.85	0.70	36.93	119.47	105.62
106	0.00	0.39	3.20	19.97	0.00	1.13	20.28	7.01	15.22	0.90	31.91	122.05	105.41
107	0.00	0.00	2.51	16.80	0.00	0.81	17.45	6.40	18.36	1.79	35.88	119.14	107.82
108	0.00	0.00	1.82	16.78	0.00	0.00	12.12	7.83	14.99	0.00	46.45	97.95	107.49

---

* Total sample admitted to chromatography columns.

**Total sample size on basis of analysis.

TABLE VIII CONT'D.

CHROMATOGRAPH ANALYSES OF PRODUCT SAMPLES IN THE PARTIAL OXIDATION

OF n-BUTANE

Run Number	Chromatographic Analysis Mole %										Total ** Components Analyzed x 10^5 (gram moles)	Total * Sample x 10^5 (gram moles)
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}		
109	0.00	0.00	1.43	15.72	0.00	0.00	11.22	5.67	14.93	0.35	50.69	98.84	111.84
110-1	0.00	0.29	1.49	16.86	0.00	0.00	12.12	5.78	19.46	0.00	43.99	107.69	117.03
111	0.00	0.00	3.83	25.33	0.00	0.57	26.26	8.49	13.83	0.00	21.69	109.96	109.15
112	0.00	0.00	1.97	22.85	0.00	0.00	18.12	7.61	17.64	0.00	31.80	109.69	109.35
113-1	0.00	0.57	1.24	16.60	0.00	0.00	19.67	8.50	17.49	0.00	35.92	148.43	109.35
113-2	0.00	0.24	1.28	15.44	0.00	0.00	20.34	8.79	20.72	0.00	33.19	83.92	63.91
114	0.00	0.27	3.33	29.15	0.00	0.47	18.66	6.96	16.49	0.99	23.68	97.07	105.41
115	0.00	0.00	5.43	36.81	0.00	0.03	22.05	7.02	17.38	0.56	10.72	81.73	108.11
116	0.00	0.00	1.92	21.35	0.00	0.00	13.10	5.64	14.86	0.89	42.23	100.45	108.52
117	0.34	0.67	1.24	17.17	0.00	0.00	10.95	4.08	14.21	0.00	51.33	100.37	106.03
118	0.45	1.18	5.17	36.24	0.00	1.72	21.88	7.30	12.68	1.56	11.80	95.23	103.54
119	0.34	0.54	4.00	31.23	0.00	0.00	19.77	6.49	16.30	1.38	19.96	100.44	108.32
120	0.41	0.66	2.32	23.96	0.00	0.00	18.13	6.79	17.79	0.99	28.96	105.71	108.73
121	0.00	0.00	2.61	22.94	0.00	0.00	18.17	7.59	18.40	1.28	29.01	101.99	106.24
122	0.00	0.00	1.91	20.83	0.00	0.00	14.76	0.12	18.71	1.23	42.45	102.83	109.98
123	0.00	0.00	2.39	21.50	0.00	0.00	13.35	6.24	17.19	1.05	38.29	98.56	108.94
124	1.48	3.50	2.75	21.07	0.00	0.65	15.24	6.12	15.61	0.39	33.15	95.90	104.58
125	0.00	0.55	0.56	33.38	0.00	2.29	22.22	6.67	14.28	1.09	18.97	87.25	103.75
127	3.02	18.19	0.00	0.75	0.00	0.00	3.11	0.00	0.00	0.53	74.09	107.00	110.39
128	1.80	14.46	0.00	2.92	5.97	2.34	5.87	0.00	1.26	3.17	62.22	93.14	108.73
129	3.02	10.25	0.00	12.07	0.00	3.03	12.56	6.24	10.67	0.00	42.18	102.19	110.39
130	3.89	12.48	0.00	23.05	0.00	0.00	24.13	7.98	15.77	1.02	11.69	95.02	107.69
131-1	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.57	73.40	102.51
131-2	0.24	1.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	98.73	63.62	80.72
132	0.28	3.11	0.00	0.16	0.13	0.00	0.45	0.00	0.08	0.00	95.79	90.97	108.65
133-1	2.218	3.67	0.00	0.88	0.00	0.00	0.88	0.00	0.55	0.96	90.84	81.38	107.49
134	1.90	3.40	0.22	1.39	2.38	0.45	1.15	0.28	0.58	1.39	86.86	79.36	105.41
135	0.22	0.00	0.00	2.58	0.00	0.00	0.00	0.00	0.00	0.00	96.91	74.78	105.49
136	0.28	1.82	0.06	1.66	0.18	0.23	0.81	0.36	0.87	0.33	93.43	89.79	108.73
137-1	0.54	0.82	0.78	7.35	7.27	1.21	4.62	1.48	5.59	2.79	67.56	86.66	109.35
137-2	0.53	0.77	5.39	6.47	7.60	1.01	4.67	1.19	3.63	2.99	65.77	70.17	87.15
138	0.31	2.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	97.55	45.25	61.09
139	0.18	1.25	0.00	0.19	0.00	0.00	0.00	0.00	0.00	0.00	98.39	97.08	108.32
140	3.54	1.28	0.25	1.14	1.78	0.52	1.72	0.61	0.85	1.57	86.74	94.03	107.07
141-2	2.50	0.91	1.69	4.97	10.56	1.02	5.73	1.37	2.77	29.69	38.79	58.36	87.98
141-3	3.15	0.95	1.86	6.18	12.63	1.36	5.55	1.61	4.70	5.72	56.29	43.69	72.42

---

* Total sample admitted to chromatography columns.

**Total sample size on basis of analysis.

TABLE VIII CONT'D.

CHROMATOGRAPH ANALYSES OF PRODUCT SAMPLES IN THE PARTIAL OXIDATION OF n-BUTANE

Run Number	Chromatographic Analysis Mole %											Total ** Components Analyzed x 10^5 (gram moles)	Total * Sample x 10^5 (gram moles)
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}		
142	0.00	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.57	109.93	108.32
143-1	0.00	0.40	0.00	0.00	0.33	0.00	0.58	0.00	0.43	0.67	97.60	104.41	109.77
143-2	0.15	0.42	0.00	0.49	1.52	0.00	0.42	0.00	0.39	0.61	95.98	91.47	88.81
144	0.17	0.68	0.31	2.06	3.53	0.00	1.72	0.48	1.01	1.51	88.54	111.08	110.72
145 b	0.58	2.49	0.60	3.02	7.87	0.76	3.08	0.96	1.51	2.93	76.17	108.29	110.39
146	0.09	0.37	0.73	3.31	6.20	0.89	3.52	0.92	2.55	0.00	77.98	103.33	108.73
147-1	0.00	0.47	0.28	2.59	3.24	0.62	2.44	0.73	1.73	2.25	85.65	103.59	111.72
147-2	0.10	0.44	0.28	2.14	3.29	0.00	0.00	2.78	1.45	3.47	86.05	84.46	91.51
148	0.00	0.59	0.25	0.78	0.57	0.32	1.05	0.39	0.99	0.86	94.19	102.93	110.06
149	0.00	1.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	90.69	104.99	109.23
150	0.15	0.62	0.42	0.07	0.00	0.00	0.20	0.17	0.33	0.00	98.04	96.36	99.81
151	0.13	0.61	0.00	0.91	0.36	0.27	0.09	0.32	0.98	0.60	95.75	103.00	107.90
152	0.17	0.50	0.35	2.20	2.42	0.61	3.58	0.89	2.99	2.61	87.07	90.95	99.39
153	0.43	1.01	0.87	5.49	7.26	1.02	0.54	1.71	7.74	3.48	70.44	91.34	104.58
154-1	0.00	2.96	0.45	1.34	0.00	0.00	0.62	0.59	1.06	0.00	92.97	87.25	86.94
154-2	0.69	3.03	0.46	1.21	0.00	0.00	0.00	0.00	0.83	0.00	93.79	70.39	70.76
155-1	0.41	0.77	0.64	4.07	6.93	0.77	4.04	1.37	3.17	3.03	74.81	87.45	88.19
155-2	0.35	0.73	0.65	4.26	6.92	0.65	4.20	1.18	3.23	3.21	73.80	71.66	72.83
155-3	0.83	0.86	0.79	4.51	8.30	0.74	4.63	1.18	3.69	0.00	70.01	51.20	60.26
155-4	0.46	0.86	0.67	4.59	7.61	0.00	3.99	0.76	2.16	1.89	77.02	46.45	49.26
156	0.47	1.55	0.63	5.18	1.98	0.00	3.66	1.55	4.71	1.67	78.59	92.60	90.47
157	0.16	0.69	0.38	1.00	0.59	0.00	1.01	0.55	0.64	0.85	94.13	91.37	87.98
158	0.24	0.87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	98.89	91.63	88.19
159	0.20	0.70	0.63	1.42	1.89	0.21	1.45	0.46	2.06	1.26	89.72	91.44	88.60
160-2	0.15	0.70	4.47	0.80	0.46	0.00	0.71	0.24	1.21	0.82	90.43	75.19	72.92
161	0.21	0.39	0.75	3.20	6.21	0.75	3.73	1.05	2.91	2.93	77.86	81.92	87.77
162	1.66	6.90	0.00	0.43	0.00	0.00	0.27	0.32	0.31	0.00	90.11	69.41	94.41
163-1	0.12	0.58	0.63	2.37	1.62	0.48	2.78	1.07	3.15	1.69	85.50	92.51	88.81
163-2	0.13	0.66	0.62	2.31	1.41	0.00	2.16	0.84	2.31	2.12	87.44	77.13	72.63
164	0.11	0.61	0.16	1.62	0.49	0.00	1.42	0.74	1.67	2.55	90.63	68.16	69.72
165	0.14	0.20	1.29	5.03	7.40	0.00	1.28	4.63	3.13	2.83	74.06	66.04	71.80
166-2	5.19	0.00	12.06	32.90	1.66	0.51	33.64	1.44	9.98	1.21	1.41	90.47	89.85
166-3	7.55	0.46	13.08	32.54	0.41	0.56	31.84	3.93	9.63	1.43	1.08	104.05	112.05
167-6	0.00	0.34	10.45	27.18	4.00	1.40	29.68	0.94	15.05	1.35	9.61	101.29	107.69
167-7	0.00	0.00	9.82	30.87	5.39	1.56	27.64	1.51	14.25	1.06	7.90	111.18	110.81

---

*Total sample admitted to chromatography columns.
**Total sample size on basis of analysis.

b Propane = 0.13

TABLE IX

ANALYSIS OF CARBON DEPOSITED IN THE n-BUTANE OXIDATION

SAMPLE NO.	REPORTED* ANALYSES	ANALYSES ON C/H BASIS	C/H MOLE RATIO
1C	82.90 wt. % C 0.56 wt. % H_2 13.00 wt. % ash (as CaO) 94.46 wt. % Total	92.50 Mole % 7.50 Mole %	12.3
2C	78.35 wt. % C 0.78 wt. % H_2 14.50 wt. % ash (as CaO) 93.63 wt. % Total	89.32 Mole % 10.68 Mole %	8.36

Average C/H = 10 (used in carbon hydrogen balances)

---

* Elek Micro Analytical Laboratories

TABLE X

PRODUCT STREAM CONCENTRATIONS IN THE n-BUTANE OXIDATION REACTOR

Run No.	Temp. °K.	Inlet O_2 Conc. Mole %	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 1063-1022 °K.															
92-1	1063	0.00	1.16	0.00	0.83	4.26	37.18	0.00	0.00	29.60	6.79	13.75	0.00	4.52	3.11
92-2	1063	0.00	1.08	0.00	3.22	4.69	38.56	0.00	0.00	27.96	5.83	12.75	1.16	4.25	1.55
88	1025	0.00	1.58	0.00	0.17	2.84	32.64	0.00	0.00	28.82	10.44	15.53	1.15	7.23	1.53
91	1048	3.57	1.52	0.30	0.00	4.66	55.86	0.24	0.00	6.15	8.83	17.08	1.70	2.69	2.49
95	1038	5.40	1.17	0.15	3.67	4.90	39.95	0.00	0.00	31.59	7.83	5.86	1.10	0.26	4.70
90	1051	6.19	1.44	0.00	0.00	3.64	35.78	0.87	0.00	31.13	9.99	3.39	1.02	1.51	4.78
119	1022	11.31	0.34	0.30	0.47	3.49	27.27	0.00	0.00	17.27	5.67	14.23	1.21	17.43	12.66
118	1027	21.02	0.27	0.55	0.94	4.11	28.84	0.00	1.37	17.41	5.81	10.09	1.24	9.39	20.42
Temperature Range 1019-1000 °K.															
72	1005	0.00	1.76	1.18	0.00	6.97	17.23	0,00	0.00	12.54	5.69	15.04	1.48	41.05	0.00
100	1003	0.00	0.87	0.00	0.00	21.79	15.57	0.00	0.00	10.59	4.41	14.19	0.23	53.93	0.00
121	1010	0.00	0.46	0.00	0.00	2.61	22.94	0.00	0.00	18.17	7.59	18.40	1.28	29.01	0.00
73	1010	3.00	1.65	1.21	0.00	4.84	19.26	0.31	0.00	14.49	6.98	16.37	0.00	35.47	1.06
120	1001	4.74	0.45	0.41	0.66	2.32	23.96	0.00	0.00	18.13	6.79	17.79	0.99	28.96	0.00
94	1016	4.95	1.24	0.00	0.00	5.94	38.82	0.00	0.00	29.83	7.29	10.21	1.18	2.22	4.50
74	1014	4.99	1.57	1.05	0.00	5.04	21.00	0.97	0.00	16.44	5.54	17.86	1.66	28.76	3.30
85	1001	5.71	1.59	0.00	0.00	10.01	52.63	1.43	0.00	20.17	7.25	16.88	0.82	14.07	2.99
102	1003	7.37	0.69	0.00	0.00	2.69	21.44	0.00	0.65	21.90	6.01	16.25	0.98	22.41	7.68
93	1011	8.86	1.11	0.00	2.23	4.83	35.31	0.00	0.00	7.30	0.00	11.39	0.00	3.05	8.16
75	1019	9.05	1.44	0.00	0.00	5.33	21.66	1.99	0.00	16.57	5.62	16.56	1.93	22.86	6.01
115	1000	17.69	0.29	0.00	0.00	4.39	29.79	0.00	0.02	17.84	5.68	14.06	0.45	8,68	19.07
Temperature Range 999-982 °K.															
99	991	0.00	1.79	0.00	0.00	2.00	18.90	0.00	0.00	16.26	14.46	37.10	4.69	17.18	0.00
122	984	0.00	0.46	0.00	0.00	1.91	20.83	0.00	0.00	14.76	0.12	18.71	1.22	42.45	0.00
113-1	983	2.33	1.42	0.00	0.55	1.19	16.01	0.00	0.00	18.98	8.20	16.87	0.00	34.65	3.55
113-2	983	2.21	1.39	0.00	0.23	1.24	14.99	0.00	0.00	19.75	8.54	20.12	0.00	32.22	2.99
84	999	3.52	1.59	0.00	0.00	8.20	23.67	0.70	0.00	19.58	7.14	17.87	0.76	13.50	1.70
116	987	4.00	0.43	0.00	0.00	1.82	20.24	0.00	0.00	12.42	5.35	14.08	0.85	40.03	5.21
103	996	7.37	0.54	0.21	0.00	3.58	20.88	0.00	1.99	20.37	6.36	12.79	0.46	13.01	21.60

TABLE X CONT'D.

Run No.	Temp. °K.	Inlet O_2 Conc. Mole %	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 999-982 °K. (continued)															
98	987	8.95	1.23	0.00	0.37	3.95	31.57	0.00	0.00	27.55	11.88	7.15	1.67	3.98	8.53
79	991	9.13	1.41	0.00	0.00	7.00	17.01	1.36	0.00	18.57	6.66	17.54	0.56	22.01	9.29
86	992	10.10	1.62	0.00	0.00	11.11	19.77	2.98	0.61	18.35	6.83	15.52	0.76	20.01	8.07
112	987	11.00	1.28	0.00	0.00	1.83	21.24	0.00	0.00	16.85	7.07	16.40	0.00	29.56	7.05
114	990	12.87	0.40	0.00	0.23	2.84	24.87	0.00	0.40	15.92	5.94	14.07	0.85	20.21	14.68
111	989	14.63	1.01	0.00	0.00	3.20	21.18	0.00	0.47	21.96	7.10	11.56	0.00	18.13	16.39
107	982	8.00	0.61	0.00	0.00	2.28	15.23	0.00	0.73	15.82	5.79	16.65	1.62	32.54	9.31
106	994	16.56	0.53	0.00	0.31	2.57	16.04	0.00	0.90	16.29	5.63	12.23	0.72	25.62	19.69
125	989	20.43	0.27	0.00	0.43	0.44	26.36	0.00	1.81	17.54	5.27	11.28	0.86	14.97	21.04
Temperature Range 978-961 °K.															
87	973	0.00	1.94	0.00	0.00	7.37	22.54	0.00	0.00	15.87	7.53	19.10	0.83	26.76	0.00
76	972	0.00	1.93	0.27	0.00	1.27	15.50	0.00	0.00	15.22	6.80	17.52	0.00	43.66	0.00
109	969	0.00	0.74	0.00	0.00	1.42	15.72	0.00	0.00	11.22	5.67	14.93	0.35	50.69	0.00
110	968	0.00	1.52	0.00	0.29	1.49	16.86	0.00	0.00	12.12	5.78	19.46	0.00	43.99	0.00
117	963	0.00	0.49	0.34	0.67	1.24	17.17	0.00	0.00	10.95	4.08	14.21	0.00	51.31	0.00
96	965	2.79	1.38	0.00	0.22	2.80	24.44	0.00	0.00	40.62	6.10	13.51	1.42	8.12	2.76
108	976	4.07	0.67	0.00	0.00	1.72	15.81	0.00	0.00	11.42	7.38	14.13	0.00	43.78	5.76
123	961	4.22	0.43	0.00	0.00	2.25	20.27	0.00	0.00	12.59	5.88	16.21	0.99	35.77	5.72
101	978	4.91	0.82	0.00	0.00	2.88	20.80	0.00	0.75	15.20	6.45	15.82	0.00	35.78	0.00
97	975	5.05	1.47	0.00	0.35	3.58	27.89	0.00	0.00	29.03	9.00	15.08	1.65	7.74	5.69
78	977	5.18	1.68	0.00	0.00	4.91	16.18	0.31	0.00	16.96	6.37	16.92	0.00	31.98	6.37
83	962	5.71	1.65	0.00	6.94	3.43	17.96	0.00	0.43	10.58	4.96	15.26	0.00	32.96	7.48
82	964	5.76	1.76	0.00	0.00	3.56	26.06	2.27	0.00	12.42	5.51	16.93	0.63	27.70	4.91
81	976	9.41	1.62	0.00	0.00	4.96	21.13	2.22	0.00	15.40	6.07	17.10	1.18	22.73	9.21
124	963	11.31	0.34	1.31	3.09	2.43	18.62	0.00	0.58	13.47	5.45	13.80	0.34	29.31	11.60
Temperature Range 902-881 °K.															
70	899	9.50	6.04	1.47	0.00	1.76	11.09	2.09	0.00	7.05	3.06	13.66	2.10	48.26	9.45
71	902	9.50	6.04	1.57	0.00	1.29	9.97	1.58	0.00	6.33	3.92	9.78	1.27	53.91	10.38
69	901	10.04	6.18	1.19	0.00	2.30	1.08	2.23	0.00	7.78	4.56	12.34	1.08	55.85	11.59
59	882	12.93	4.00	0.49	1.48	3.65	8.73	8.98	4.14	24.16	2.11	0.00	0.00	53.20	1.90
60	881	19.12	3.40	0.44	1.46	7.55	14.61	16.76	6.90	13.94	3.35	0.00	0.00	28.04	0.00

TABLE X CONT'D.

Run No.	Temp. °K.	Inlet O_2 Conc. Mole %	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 868-843 °K.															
68-1	853	0.00	8.07	0.00	0.00	1.00	5.44	0.00	0.00	2.49	1.96	4.53	0.00	84.57	0.00
68-2	853	0.00	8.06	0.00	0.00	0.78	3.42	0.00	0.00	1.67	11.51	2.72	0.00	79.89	0.00
50-1	846	0.00	5.31	0.00	0.00	0.23	5.98	0.00	0.00	2.82	2.03	5.62	0.00	82.3	0.54
50-2	846	0.00	5.31	0.00	0.00	0.23	6.15	0.00	0.12	2.94	1.87	5.96	0.00	84.0	0.00
58	868	0.65	4.79	0.42	2.09	0.92	10.46	0.00	0.00	4.62	3.41	9.31	0.00	68.78	0.00
38-1	843	9.31	5.7	0.00	0.71	0.38	3.43	0.00	0.00	1.08	0.63	2.46	0.00	91.28	0.02
38-2	843	9.31	5.7	0.00	0.88	0.37	2.87	0.00	0.00	1.68	1.53	2.62	0.00	90.21	0.00
45	864	19.67	3.71	0.00	.74	5.79	14.37	2.76	0.96	9.88	4.06	10.98	0.00	30.53	22.69
Temperature Range 837-818 °K.															
40	825	0.00	6.83	0.31	5.09	0.19	3.17	0.00	0.00	0.73	0.71	1.74	0.00	89.46	0.00
39	837	4.27	5.86	0.07	0.96	0.22	4.21	0.00	0.00	1.14	1.25	2.71	0.00	91.56	0.00
61	833	12.11	4.59	0.53	1.44	1.74	5.96	0.00	4.08	4.53	1.35	2.23	0.00	66.49	6.26
37-1	827	19.32	4.81	0.00	0.88	1.36	12.89	2.66	0.65	9.91	4.50	12.32	0.64	54.19	0.00
37-2	827	19.32	4.81	0.00	0.88	1.29	13.42	1.68	1.51	10.32	4.02	14.73	0.00	52.15	0.00
52-1*	818	20.78	4.01	0.93	2.39	7.30	2.57	32.12	0.00	0.00	0.00	5.21	0.00	49.21	0.00
52-2	818	20.78	3.71	0.42	1.29	5.45	3.53	20.62	10.01	11.46	2.21	2.52	0.00	38.29	4.19
53	827	26.01	3.69	0.56	1.30	8.30	2.84	31.73	10.40	15.16	2.95	3.30	0.00	23.46	0.00
Temperature Range 814-773 °K.															
33	807	0.00	6.93	0.00	0.47	0.00	1.07	0.00	0.00	0.00	0.00	1.01	0.00	97.98	0.00
46-1	780	0.00	6.10	0.00	1.78	0.08	0.24	0.00	0.00	0.25	0.13	0.64	0.00	96.00	0.88
46-2	780	0.00	6.10	0.00	2.01	0.08	0.66	0.00	0.00	0.23	0.13	0.58	0.00	95.26	1.04
48	784	1.95	6.27	0.00	4.22	0.36	5.78	0.51	0.83	3.24	1.30	5.79	0.64	76.01	1.22
49	781	2.14	6.03	0.00	7.35	1.34	1.43	1.16	0.57	0.62	0.27	1.02	0.00	86.24	1.88
34	789	4.64	7.10	0.00	1.49	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	98.86	0.00
47	785	5.61	5.61	0.00	1.94	1.02	8.08	1.64	1.40	5.74	1.87	7.95	1.06	64.27	5.02
35	782	11.32	8.39	1.25	1.23	0.23	3.62	0.00	0.00	3.74	2.64	7.99	0.00	87.62	0.00
167-6	773	17.60	3.20	0.00	0.00	9.21	23.97	3.53	2.46	26.18	0.83	13.27	1.19	8.47	12.11
167-7	773	17.60	3.20	0.00	0.00	8.83	27.78	4.85	1.40	24.87	1.36	12.82	0.96	7.11	10.02
36	791	20.07	5.48	0.43	1.08	2.25	10.10	3.41	0.71	17.49	2.73	10.29	0.54	0.54	0.00
54	775	27.00	4.07	0.55	1.23	6.26	4.78	26.84	9.16	10.66	2.95	2.16	0.00	24.33	0.00

---

* Propane = 0.24

TABLE X CONT'D.

Run No.	Temp. °K.	Inlet O_2 Conc. Mole %	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 770-750 °K.															
62	765	12.59	8.71	0.00	0.00	0.53	2.63	2.34	0.27	1.79	0.80	2.89	1.66	68.20	19.42
67	756	12.59	8.92	0.00	0.00	0.46	3.99	3.14	0.30	2.64	1.11	3.97	1.77	67.72	18.77
66	754	12.59	8.81	0.37	0.00	0.40	3.76	3.13	0.34	2.42	0.75	3.04	2.03	66.35	17.42
63	754	12.59	8.81	0.24	0.00	0.55	2.88	2.23	0.29	2.11	1.12	2.92	1.92	67.08	18.65
65	753	12.59	8.77	0.00	0.00	0.56	2.94	2.56	0.00	2.42	0.94	3.14	2.10	65.95	19.13
64-1	752	12.59	8.80	0.00	0.00	0.53	3.31	2.62	0.32	2.35	0.87	3.70	1.50	69.63	15.04
64-2	752	12.59	8.80	0.00	0.00	0.50	3.44	2.56	0.00	2.16	0.60	3.49	1.41	66.44	19.39
Temperature Range 748-730 °K.															
41	744	0.14	7.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	96.68	2.67
57	736	0.53	6.38	0.68	1.95	1.82	0.00	0.00	0.00	0,00	0.00	0.00	0.00	95.54	0.00
42	738	4.93	6.71	0.00	1.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	89.13	9.58
157	743	5.08	18.79	0.00	0.00	0.35	0.92	0.54	0.00	0.93	0.51	0.58	0.78	86.28	9.11
43	742	10.54	5.89	0.00	1.77	0.18	2.20	0.37	0.24	1.29	0.55	1.52	0.63	73.04	19.08
136	738	10.58	2.85	0.00	1.36	0.04	1.24	0.13	0.17	0.60	0.26	0.64	0.25	69.75	25.34
56-1	733	14.72	5.03	0.44	1.40	9.76	2.24	11.98	7.19	5.88	2.01	0.79	0.00	58.31	0.00
56-2	733	14.72	5.03	0.44	1.11	6.85	1.00	39.54	5.27	3.80	0.84	0.71	0.00	40.64	0.00
44	748	19.03	4.76	0.00	0.77	0.38	4.50	2.08	0.00	3.57	1.19	4.44	1.51	52.20	29.36
153	734	19.07	6.36	0.13	0.00	0.67	4.21	5.56	0.79	0.41	1.31	0.61	2.67	53.98	24.34
Temperature Range 726-705 °K.															
154	725	0.00	22.82	0.00	0.00	0.47	1.26	0.00	0.00	0.00	0.00	0.85	0.00	97.40	0.00
150	720	0.00	9.65	0.00	0.00	0.42	0.07	0.00	0.00	0.20	0.17	0.33	0.00	98.81	0.00
135	720	0.67	4.79	0.20	2.27	0.00	0.25	0.00	0.00	0.00	0.00	0.00	0.00	85.54	11.74
151	705	5.40	8.89	0.00	0.00	0.00	0.83	0.32	0.24	0.08	0.29	0.89	0.55	87.25	9.54
156	721	11.11	16.72	0.03	0.00	0.53	4.36	1.67	0.00	3.08	1.31	3.96	1.40	66.16	17.47
152	726	11.39	7.63	0.03	0.00	0.29	1.99	2.01	0.50	0.00	0.74	2.48	2.16	72.24	17.55
155-1	710	17.65	14.00	0.21	0.00	0.46	2.93	4.99	0.55	2.91	0.98	2.28	2.18	67.51	28.72
155-2	710	17.65	14.00	0.11	0.00	0.46	3.05	4.96	0.47	3.01	0.85	2.31	2.30	53.51	29.00
155-3	710	17.65	14.00	0.16	0.00	0.58	3.32	6.11	0.54	3.41	0.87	2.71	3.60	51.53	27.19
155-4	710	17.65	14.00	0.16	0.00	0.48	3.27	5.43	0.00	2.85	0.54	1.54	1.35	54.92	29.47
137-1	725	19.40	3.00	0.41	0.63	0.60	5.63	5.57	0.92	3.53	1.13	4.28	2.14	51.74	23.42
137-1	725	19.40	3.00	0.47	0.59	4.16	4.99	5.87	0.78	3.60	0.92	2.81	2.31	50.81	22.74

TABLE X CONT'D.

Run No.	Temp. °K.	Inlet O_2 conc. Mole%	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 701-680 °K.															
149	695	0.00	9.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00
162	680	0.00	21.18	0.00	0.00	0.00	0.47	0.00	0.00	0.29	0.35	0.34	0.00	98.55	0.48
139	685	0.34	3.84	0.18	1.25	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	98.05	0.34
164	685	4.75	17.73	0.00	0.00	1.50	1.49	0.45	0.00	1.30	0.68	1.53	2.34	83.06	9.01
148	690	5.96	8.34	0.00	0.53	0.22	0.70	0.51	0.28	0.94	0.35	0.89	0.79	84.64	10.15
140	686	10.13	3.25	3.19	1.16	0.22	1.02	1.60	0.47	1.55	0.55	0.77	1.41	78.07	9.99
163-1	694	10.18	17.00	0.00	0.00	0.53	2.01	1.37	0.40	2.35	0.90	2.66	1.43	72.26	16.08
163-2	694	10.18	17.00	0.00	0.00	0.55	2.05	1.26	0.00	1.92	0.75	2.05	1.89	77.75	11.79
147-1	686	12.54	7.30	0.00	0.00	0.23	2.11	2.65	0.50	1.99	0.60	1.41	1.84	69.95	18.71
147-2	686	12.54	7.30	0.00	0.00	0.22	1.68	2.58	0.00	0.00	2.18	1.14	2.71	67.46	22.03
166-2	691	17.69	8.00	5.00	0.00	11.63	31.72	1.60	0.49	32.43	1.39	9.62	1.17	1.36	3.59
166-3	691	17.35	8.00	7.55	0.46	13.08	32.54	0.41	0.56	31.84	3.93	9.63	1.21	1.41	0.00
165	701	18.57	14.85	0.00	0.00	1.39	5.05	7.43	0.00	1.28	4.64	3.14	2.84	74.31	0.00
146	685	19.79	6.29	0.00	0.00	0.53	2.41	4.50	0.64	2.56	0.67	1.85	2.50	56.67	27.67
141-2	690	23.54	2.70	0.00	0.00	1.71	0.00	0.00	1.34	5.91	2.06	3.56	6.06	79.37	0.00
141-3	690	23.54	2.70	2.44	0.89	1.65	4.85	10.29	0.99	5.59	1.33	2.70	28.94	33.82	2.51
Temperature Range 673-653 °K.															
158	665	0.00	21.77	0.008	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00
132	673	0.81	5.33	0.28	3.08	0.00	0.15	0.13	0.00	0.45	0.00	0.08	0.00	94.99	0.84
143-1	673	4.49	7.80	0.00	0.37	0.00	0.00	0.30	0.00	0.53	0.00	0.39	0.61	89.78	8.38
143-2	673	4.49	8.04	0.042	0.00	0.00	0.47	1.48	0.00	0.41	0.00	0.38	0.60	93.09	6.86
160	657	5.06	19.48	0.00	0.00	4.08	0.73	0.42	0.00	0.65	0.22	1.10	0.75	82.59	9.45
130	659	8.04	8.97	0.62	0.00	0.00	25.25	0.00	0.00	26.43	8.74	17.27	1.12	12.80	7.77
159	661	9.64	18.04	0.01	0.00	0.54	1.21	1.62	0.18	1.24	0.39	1.77	1.08	76.78	15.18
134	665	9.90	4.61	1.73	3.10	0.20	1.27	2.17	0.41	1.05	0.26	0.53	1.26	79.22	8.79
144	660	12.50	8.21	0.00	0.00	0.25	1.67	2.86	0.00	1.39	0.39	0.82	1.23	71.78	19.62
161	668	19.35	7.26	0.08	0.00	0.55	2.35	4.55	0.55	2.73	0.77	2.13	2.15	57.09	27.05
145**	653	22.22	6.74	0.00	0.00	0.43	2.16	5.64	0.55	2.21	0.66	1.08	2.10	54.56	30.57

** Propane = 0.10

TABLE X CONT'D.

Run No.	Temp. °K.	Inlet O_2 conc. Mole%	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 646-621 °K.															
131-1	646	0.00	5.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00
131-2	646	0.00	5.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00
138	633	0.00	5.77	0.31	2.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	97.01	0.55
133-1	621	8.01	4.93	1.85	3.07	0.00	0.73	0.00	0.00	0.73	0.00	0.46	0.81	80.59	16.46
133-2	621	8.01	5.82	1.86	2.89	0.00	0.00	0.00	0.00	0.62	0.00	0.07	0.00	83.23	11.32
129	642	13.04	10.30	0.62	0.00	0.00	12.09	0.00	3.04	12.58	6.25	10.69	0.00	42.28	12.78
127	629	17.49	8.41	2.32	13.97	0.00	0.57	0.00	0.00	2.62	0.00	0.00	0.41	56.92	23.17
128	644	23.89	7.84	1.27	10.16	0.00	2.05	4.19	1.64	4.12	0.00	0.88	2.22	43.69	0.00

TABLE XI

SUMMARY OF REACTOR OPERATING CONDITIONS FOR THE n-BUTANE REACTIONS

Run Number	Reactor Temp. (°K.)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
Temperature Range 1063-1022 °K.												
92-1	1063	0.00	1.16	28.5	790.08	750.00	759.97	0.107	0.0000	0.0026	0.4	None
92-2	1063	0.00	1.08	28.5	790.08	750.00	759.97	0.107	0.0000	0.0149	0.4	None
88	1025	0.00	1.58	28.0	779.12	749.00	745.17	0.081	0.0000	0.0061	0.5	Q
91	1048	3.57	1.52	28.0	804.72	781.00	736.03	0.081	0.0030	0.0000	0.5	Q
95	1038	5.40	1.17	28.5	785.48	762.20	764.57	0.093	0.0030	0.0120	0.4	None
90	1051	6.19	1.44	28.0	805.48	779.38	771.13	0.081	0.0054	0.0000	0.5	Q
119	1022	11.31	0.34	7.0	768.70	749.33	736.40	0.065	0.0082	0.0008	0.5	Q_L
118	1027	21.02	0.27	7.0	768.25	754.33		0.065	0.0178	0.0021	0.5	Q_L
Temperature Range 1019-1000 °K.												
72	1005	0.00	1.76	28.0	698.10	715.00	598.57	0.099	0.0000	0.0000	0.5	Q
100	1003	0.00	0.87	14.0	764.70	720.80	708.95	0.096	0.0000	0.0000	0.5	Q
121	1010	0.00	0.46	7.0	757.60	737.00	723.20	0.062	0.0000	0.0000	0.5	Q_L
73	1010	3.00	1.65	28.0	669.56	730.00	613.70	0.099	0.0030	0.0000	0.5	Q
120	1001	4.74	0.45	7.0	753.55	728.08	716.10	0.063	0.0030	0.0008	0.5	Q_L
94	1016	4.95	1.24	28.5	767.75	737.20	743.47	0.099	0.0052	0.0000	0.4	None
74	1014	4.99	1.57	28.0	677.42	725.50	622.77	0.099	0.0052	0.0000	0.5	Q
85	1001	5.71	1.59	28.0	763.72	714.00	727.90	0.085	0.0052	0.0000	0.5	Q
102	1003	7.37	0.69	14.0	798.17	735.50	729.35	0.093	0.0074	0.0000	0.5	Q
93	1011	8.86	1.11	28.5	756.60	730.80	738.40	0.099	0.0093	0.0074	0.4	None
75	1019	9.05	1.44	28.0	689.94	733.60	635.17	0.098	0.0097	0.0000	0.5	Q
115	1000	17.69	0.29	7.0	744.40	727.00		0.067	0.0142	0.0000	0.5	Q_L

---

* Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

** Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i.d. section.)

TABLE XI CONT'D.

Run Number	Reactor Temp. (°K.)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
Temperature Range 999-982 °K.												
99	991	0.00	1.79	28.5	736.60	709.80	718.23	0.098	0.0000	0.0000	0.4	None
112	984	0.00	0.46	7.0	721.20	711.00	545.50	0.068	0.0000	0.0000	0.5	Q_L
113-1	983	2.33	1.42	14.0	724.60	709.83		0.055	0.0012	0.0006	0.5	Q_L
113-2	983	2.21	1.39	14.0	724.60	709.83		0.055	0.0012	0.0002	0.5	QL
84	999	3.52	1.59	28.0	757.82	726.50	717.13	0.085	0.0031	0.0000	0.5	Q
116	987	4.00	0.43	7.0	734.85	713.50		0.068	0.0030	0.0000	0.5	Q_L
103	996	7.37	0.54	14.0	757.67	723.17	722.70	0.090	0.0220	0.0000	0.5	Q
98	987	8.95	1.23	28.5	736.60	709.80	718.23	0.098	0.0095	0.0014	0.4	None
79	991	9.13	1.41	28.0	735.00	700.60	663.30	0.098	0.0099	0.0000	0.5	Q
86	992	10.10	1.62	28.0	719.50	705.17	741.42	0.085	0.0096	0.0000	0.5	Q
112	987	11.00	1.28	14.0	735.77	714.00		0.055	0.0032	0.0000	0.5	Q_L
114	990	12.87	0.40	7.0	735.40	717.00		0.058	0.0078	0.0003	0.2	QL
111	989	14.63	1.01	14.0	749.17	716.17		0.056	0.0096	0.0000	0.5	QL
107	982	16.56	0.61	14.0	769.80	723.17	709.50	0.115	0.0100	0.0000	0.5	Q
106	994	16.56	0.53	14.0	774.76	743.67	721.15	0.107	0.0212	0.0008	0.5	Q
125	989	20.43	0.27	7.0	727.75	716.00	508.20	0.074	0.0190	0.0009	0.5	Q_L
Temperature Range 978-961 °K.												
87	973	0.00	1.94	28.0	729.84	698.17	699.93	0.085	0.0000	0.0000	0.5	Q
76	972	0.00	1.93	28.0	716.30	709.70	639.67	0.096	0.0000	0.0000	0.0	Q
109	969	0.00	0.74	14.0	769.43	699.33	696.40	0.115	0.0000	0.0000	0.5	Q
110	968	0.00	1.52	14.0	728.27	695.00		0.055	0.0000	0.0003	0.5	Q_L
117	963	0.00	0.49	7.0	715.10	689.67		0.068	0.0000	0.0004	0.5	QL
96	965	2.79	1.38	28.5	697.40	672.00	692.50	0.105	0.0029	0.0006	0.4	None
108	976	4.07	0.67	14.0	771.47	703.50	702.90	0.115	0.0048	0.0000	0.5	Q
123	961	4.22	0.43	7.0	703.95	688.33	456.10	0.068	0.0030	0.0000	0.5	Q_L
101	978	4.91	0.82	14.0	735.00	715.67	705.50	0.093	0.0048	0.0000	0.5	Q
97	975	5.05	1.47	28.5	706.75	678.80	701.60	0.100	0.0050	0.0010	0.4	Q
78	977	5.18	1.68	28.0	719.20	700.20	656.23	0.098	0.0054	0.0000	0.5	Q
83	962	5.71	1.65	28.0	705.58	684.17	662.87	0.090	0.0032	0.0139	0.5	Q
82	964	5.76	1.76	28.0	711.72	698.00	670.97	0.090	0.0055	0.0000	0.5	Q
81	976	9.41	1.62	28.0	720.56	699.50	685.10	0.089	0.0093	0.0000	0.5	Q
124	963	11.31	0.34	7.0	710.10	690.33	466.10	0.074	0.0088	0.0058	0.5	Q_L

---

* Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
** QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

** Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i.d. section.)

TABLE XI CONT'D.

Run Number	Reactor Temp. ($^oK.$)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. ($^oK.$)	Average Traverse Temp. ($^oK.$)	Average Gas Temp. ($^oK.$)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
Temperature Range 902-881 $^oK.$												
70	899	9.50	6.04	28.00	607.33	575.70	626.10	0.030	0.0032	0.0000	0.1	Q
71	902	9.50	6.04	28.00	615.40	577.50	628.65	0.030	0.0032	0.0000	0.3	Q
69	901	10.04	6.18	28.00	601.30	565.40	628.20	0.030	0.0034	0.0000	0.5	Q
59	882	12.93	4.00	13.25	609.30	582.92	602.90	0.025	0.0070	0.0007	0.0	Q
60	881	19.12	3.40	13.25	621.40	589.58	629.20	0.025	0.0060	0.0009	0.0	Q
Temperature Range 868-843 $^oK.$												
68-1	853	0.00	8.07	28.00	579.43	550.40	607.00	0.030	0.0000	0.0000	0.5	Q
68-2	853	0.00	8.06	28.00	579.43	550.40	607.00	0.030	0.0000	0.0000	0.5	Q
50-1	846	0.00	5.31	13.25	572.70	556.00	549.50	0.024	0.0000	0.0007	0.0	Q
50-2	846	0.00	5.37	13.25	572.70	556.00	549.50	0.024	0.0000	0.0008	0.0	Q
58	848	0.65	4.79	13.25	595.50	549.75	576.70	0.025	0.0000	0.0258	0.0	Q
38-1	843	9.31	5.85	15.75	561.27	555.17	552.50	0.024	0.0027	0.0000	0.0	None
38-2	843	9.31	5.61	15.75	561.27	555.17	552.50	0.024	0.0027	0.0000	0.0	None
45	864	19.67	3.71	15.75	590.50	582.00	602.90	0.025	0.0060	0.3100	0.0	None
Temperature Range 837-818 $^oK.$												
40	825	0.00	6.83	15.75	551.87	539.00	536.40	0.023	0.0000	0.0000	0.0	None
39	837	4.27	5.86	15.75	559.23	547.17	543.40	0.026	0.0000	0.0000	0.0	None
51	833	12.11	4.59	13.25	578.40	524.33	591.80	0.024	0.0030	0.0006	0.0	Q
37-1	827	19.32	4.89	15.75	550.87	541.50	562.60	0.024	0.0060	0.0000	0.0	None
37-2	827	19.32	4.81	15.75	550.87	541.50	562.60	0.024	0.0060	0.0000	0.0	None
52-1	818	20.78	4.01	13.25	550.50	517.08	557.20	0.024	0.0060	0.0012	0.0	Q
52-2	818	20.79	3.71	13.25	550.50	517.08	557.20	0.024	0.0060	0.0007	0.0	Q
53	827	26.01	3.69	13.25	564.97	540.67	571.70	0.024	0.0080	0.0002	0.0	Q
Temperature Range 814-773 $^oK.$												
33	807	0.00	6.93	15.75	538.43	515.00	522.30	0.024	0.0000	0.0000	0.0	None
46-1	780	0.00	6.15	13.25	506.93	476.66	505.2	0.024	0.0000	0.0005	0.0	Q
46-2	780	0.00	6.01	13.25	506.93	476.66	505.2	0.024	0.0000	0.0006	0.0	Q
48	784	1.95	6.27	13.25	516.63	473.92	522.3	0.022	0.0004	0.0001	0.0	Q
49	781	2.14	6.03	13.25	507.57	471.10	511.3	0.022	0.0004	0.0023	0.0	Q

---

* Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

** Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i.d. section.)

TABLE XI CONT'D.

Run Number	Reactor Temp. (°K.)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
Temperature Range 814-773 °K. (cont'd)												
34	789	4.64	7.10	15.75	520.00	505.17	502.17	0.022	0.0013	0.0000	0.0	None
47	785	5.61	5.61	13.25	512.30	475.17	539.40	0.022	0.0012	0.0007	0.0	Q
35	782	11.32	8.39	15.75	516.57	491.50	497.20	0.022	0.0030	0.0000	0.0	None
167-6	773	17.66	3.20	28.00	511.24	505.30	499.97	0.045	0.0010	0.0000	0.5	Q_L
167-7	773	17.58	3.20	28.00	511.24	505.30	499.97	0.045	0.0010	0.0000	0.5	Q_L
36	791	20.07	5.48	15. 5	524.33	507.17	523.30	0.022	0.0059	0.0000	0.0	None
54	775	27.00	4.07	13.25	525.07	462.08	554.50	0.024	0.0090	0.0009	0.0	Q
Temperature Range 770-750 °K.												
62	765	12.59	8.71	28.00	492.03	480.30	523.20	0.025	0.0036	0.0000	0.1	Q
67	756	12.59	8.92	28.00	482.53	492.00	524.20	0.025	0.0036	0.0000	0.5	Q
66	754	12.59	8.81	28.00	481.00	495.25	521.20	0.025	0.0036	0.0000	0.3	Q
63	754	12.59	8.81	28.00	481.17	383.88	518.20	0.025	0.0036	0.0000	0.3	Q
65	753	12.59	8.77	28.00	479.47	488.10	521.20	0.025	0.0036	0.0000	0.1	Q
64-1	752	12.59	8.86	28.00	478.63	488.20	519.20	0.025	0.0036	0.0000	0.5	Q
64-2	752	12.59	8.76	28.00	478.63	488.20	519.20	0.025	0.0036	0.0000	0.5	Q
Temperature Range 748-730 °K.												
41	744	0.14	7.41	15.75	470.80	449.33	463.10	0.024	0.0000	0.0002	0.0	None
57	736	0.53	6.38	13.25	463.43	440.67	440.00	0.024	0.0000	0.0006	0.0	Q
42	738	4.93	6.71	15.75	465.10	450.33	463.10	0.025	0.0012	0.0005	0.0	None
157	743	5.08	18.79	28.00	425.52	466.50	427.90	0.014	0.0008	0.0000	0.5	Q
43	742	10.54	5.89	15.75	469.10	452.83	470.10	0.025	0.0029	0.0004	0.0	None
136	738	10.85	2.85	7.00	426.45	459.33	465.10	0.010	0.0007	0.0050	0.5	Q_L
56-1	733	14.73	5.03	13.25	459.60	437.58	453.10	0.024	0.0041	0.0006	0.0	Q
56-2	733	14.72	5.07	13.25	459.60	437.58	453.10	0.024	0.0041	0.0007	0.0	None
44	748	19.03	4.76	15.75	475.50	470.17	491.20	0.025	0.0058	0.0004	0.0	None
153	734	19.07	6.36	14.00	420.60	428.00	461.10	0.014	0.0033	0.0000	0.5	Q_L
55	742	20.80	4.56	13.25	489.87	445.25	520.30	0.024	0.0063	0.0008	0.0	Q

---

* Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

** Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i .d. section.)

TABLE XI CONT'D.

Run umber	Reactor Temp (°K.)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
emperature Range 726-705 °K.												
54	725	0.00	22.82	28.00	445.46	421.50	451.73	0.013	0.0000	0.0000	0.5	QL
50	720	0.00	9.65	14.00	423.63	408.33	447.05	0.014	0.0000	0.0000	0.5	QL
35	720	0.63	4.79	7.00	413.35	411.25	447.10	0.010	0.0000	0.0003	0.5	QL
51	705	5.40	8.89	14.00	406.20	395.83	431.95	0.014	0.0008	0.0000	0.5	QL
56	721	11.11	16.72	28.00	440.80	438.75	448.07	0.014	0.0018	0.0000	0.5	QL
52	726	11.39	7.63	14.00	420.23	417.50	453.10	0.014	0.0018	0.0000	0.5	QL
55-1	710	17.65	14.02	28.00	426.44	409.83	437.33	0.014	0.0038	0.0000	0.5	QL
55-2	710	17.65	14.00	28.00	426.44	409.83	437.33	0.014	0.0038	0.0000	0.5	QL
55-3	710	17.65	14.00	28.00	426.44	409.83	437.33	0.014	0.0038	0.0000	0.5	QL
55-4	710	17.65	14.00	28.00	426.44	409.83	437.33	0.014	0.0038	0.0000	0.5	QL
37-1	725	19.37	2.73	7.00	382.15	413.25	452.10	0.010	0.0024	0.0001	0.5	QL
37-2	725	19.41	3.36	7.00	382.15	413.25	452.10	0.010	0.0024	0.0001	0.5	QL
mperature Range 701-680 °K.												
9	695	0.00	9.33	14.00	400.47	400.67	421.95	0.015	0.0000	0.0000	0.5	QL
2	680	0.00	21.18	28.00	405.62	386.67	407.35	0.015	0.0000	0.0000	0.5	QL
9	685	0.34	3.84	7.00	415.95	391.50	437.00	0.014	0.0000	0.0002	0.5	QL
4	685	4.75	17.73	28.00	410.70	408.17	412.40	0.016	0.0090	0.0000	0.5	QL
8	690	5.96	8.34	14.00	396.43	392.17	417.40	0.015	0.0010	0.0000	0.5	QL
0	686	10.13	3.25	7.00	399.35	385.67	412.90	0.014	0.0016	0.0002	0.5	QL
3-1	694	10.18	16.82	28.00	407.86	403.58	420.90	0.015	0.0017	0.0000	0.5	QL
3-2	694	10.18	17.25	28.00	407.86	403.58	420.90	0.015	0.0017	0.0000	0.5	QL
7-1	686	12.54	7.35	14.00	388.40	388.33	412.85	0.015	0.0022	0.0000	0.5	QL
7-2	686	12.54	7.26	14.00	388.40	388.33	412.85	0.015	0.0022	0.0000	0.5	QL
6-2	691	17.69	7.88	28.00	410.30	418.67	417.93	0.020	0.0005	0.0000	0.5	QL
6-3	691	17.35	8.29	28.00	410.30	418.67	417.93	0.020	0.0005	0.0000	0.5	QL
5	701	18.57	14.85	28.00	405.66	416.58	428.00	0.01	0.0039	0.0000	0.5	QL
6	685	19.79	6.29	14.00	392.97	402.67	412.10	0.015	0.0037	0.0000	0.5	QL
1-2	690	42.07	2.65	7.00	363.55	398.17	428.00	0.012	0.0037	0.0002	0.5	QL
1-3	690	109.10	2.77	7.00	363.55	398.17	428.00	0.012	0.0037	0.0002	0.5	QL

Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i.d. section.)

TABLE XI CONT'D.

Run Number	Reactor Temp. (°K.)	Inlet O_2 Concn. Mole %	Retention Time (sec.)	Reactor Length (in.)	Average Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)	Sampling** Location	Reactor* Nozzle
Temperature Range 673-653 °K.												
158	665	0.00	21.77	28.00	389.14	372.67	392.30	0.015	0.0000	0.0000	0.5	QL
132	673	0.81	5.33	7.00	386.75	371.67	399.80	0.010	0.0000	0.0004	0.5	QL
143-1	673	4.49	7.80	14.00	384.43	354.33	400.30	0.017	0.0008	0.0000	0.5	QL
143-2	673	4.49	8.04	14.00	384.43	354.33	400.30	0.017	0.0008	0.0000	0.5	QL
160	657	5.06	19.48	28.00	383.74	378.83	377.15	0.015	0.0008	0.0000	0.5	QL
130	659	8.04	8.97	7.00	389.75	355.50		0.004	0.0004	0.0000	0.5	QL
159	661	9.64	18.04	28.00	389.34	378.17	387.75	0.015	0.0016	0.0000	0.5	QL
134	665	9.90	4.61	7.00	371.15	370.67	391.80	0.010	0.0011	0.0005	0.5	QL
144	660	12.50	8.21	14.00	361.20	368.00	386.75	0.014	0.0020	0.0000	0.5	QL
161	668	19.35	7.26	28.00	386.32	382.17	394.80	0.015	0.0036	0.0000	0.5	QL
145	653	22.22	6.74	14.00	380.80	360.33	379.70	0.014	0.0040	0.0000	0.5	QL
Temperature Range 646-621 °K.												
131-1	646	0.00	5.81	7.00	344.95	353.33	372.70	0.010	0.0000	0.0000	0.5	QL
131-2	646	0.00	5.81	7.00	344.95	353.33	372.70	0.010	0.0000	0.0000	0.5	QL
138	633	0.00	5.77	7.00	355.05	354.17	360.60	0.010	0.0000	0.0003	0.5	QL
133-1	621	8.01	4.93	7.00	342.95	347.67	342.40	0.010	0.0008	0.0005	0.5	QL
133-2	621	8.01	5.82	7.00	342.95	347.67	342.40	0.010	0.0008	0.0004	0.5	QL
129	642	13.04	10.30	7.00	393.25	338.17		0.004	0.0006	0.0000	0.5	QL
127	629	17.49	8.41	7.00	374.15	330.00		0.005	0.0011	0.0002	0.5	QL
128	644	23.89	7.84	7.00	381.75	331.83		0.004	0.0013	0.0010	0.5	QL

* Q quartz nozzle (tubing diameter making up nozzle, less than 0.020 in. i.d.)
QL quartz nozzle (tubing diameter making up nozzle, 1/4 in. o.d.)

** Sampling location (numbers indicate the location of sampling tube in the reactor, inches from the wall. Blank indicates that sampling was obtained down stream of the reactor outlet where the gases were flowing through a 1/8 i.d. section.)

TABLE XII

MOLES OF COMPONENTS PRESENT IN THE EXIT STREAM OF THE n-BUTANE REACTOR

PER 100 MOLES OF n-BUTANE FEED

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 1063-1022 °K.														
92-1	1063	0.00	1.16	89.71	0.00	84.80	0.00	0.00	67.51	15.49	31.40	2.87	2.42	9.71
92-2	1063	0.00	1.08	89.76	0.00	92.87	0.00	0.00	67.35	14.05	30.71	2.80	0.00	11.36
88	1025	0.00	1.58	85.06	0.00	67.52	0.00	0.00	59.60	20.87	32.13	2.38	5.83	5.87
91	1048	3.57	1.52	94.03	81.78	123.95	0.54	0.00	13.64	19.59	37.90	3.76	56.40	10.33
95	1038	5.40	1.17	99.35	93.97	100.57	0.00	0.00	79.52	19.71	14.74	2.77	43.03	12.35
90	1051	6.19	1.44	96.49	100.00	83.57	2.04	0.00	72.72	23.34	26.34	2.39	19.61	8.50
119	1022	11.31	0.34	51.70	95.54	53.01	0.00	0.00	33.56	11.02	27.66	2.35	29.89	6.79
118	1027	21.02	0.27	78.42	96.98	66.29	0.00	3.15	40.03	13.36	23.20	2.86	56.41	9.45
Temperature Range 1019-1000 °K.														
72	1005	0.00	1.76	39.79	0.00	25.27	0.00	0.00	9.81	8.35	22.07	2.17	5.54	10.22
100	1003	0.00	0.87	29.24	0.00	20.44	0.00	0.00	13.90	5.79	18.62	0.30	0.00	28.60
121	1010	0.00	0.46	53.75	0.00	36.59	0.00	0.00	28.98	12.10	29.34	2.04	0.00	4.16
73	1010	3.00	1.65	44.04	36.38	30.39	0.50	0.00	22.80	11.01	25.83	0.00	0.00	7.63
120	1001	4.74	0.45	55.55	0.00	36.78	0.00	0.00	27.83	10.42	27.32	1.52	0.00	3.56
94	1016	4.95	1.24	94.88	100.00	89.66	0.00	0.00	69.91	0.00	28.73	3.87	17.28	13.72
74	1014	4.99	1.57	52.60	66.12	34.62	1.60	0.00	27.10	9.13	29.44	0.00	2.46	8.31
85	1001	5.71	1.59	70.88	100.00	2.62	0.00	0.00	41.73	14.99	34.93	1.69	0.98	20.71
102	1003	7.37	0.69	59.92	100.00	38.37	0.00	1.16	39.19	10.75	29.07	1.75	5.98	4.81
93	1011	8.86	1.11	92.30	100.00	89.06	0.00	0.00	69.91	0.00	28.73	3.87	17.28	0.00
75	1019	9.05	1.44	58.61	73.23	39.24	3.61	0.00	30.02	10.18	30.00	3.50	7.17	9.65
115	1000	17.69	0.29	80.62	100.00	66.51	0.00	0.05	39.83	12.68	31.40	1.01	52.65	9.81
Temperature Range 999-982 °K.														
99	991	0.00	1.79	74.05	0.00	28.55	0.00	0.00	24.56	5.86	56.04	7.08	0.00	3.02
122	984	0.00	0.46	39.67	0.00	29.61	0.00	0.00	20.98	0.18	26.59	1.73	0.00	2.72
113-1	983	2.33	1.42	49.39	100.00	23.40	0.00	0.00	27.73	27.73	24.66	0.00	19.38	1.74
113-2	983	2.21	1.39	50.59	100.00	23.00	0.00	0.00	30.29	30.29	30.86	0.00	0.00	1.90
84	999	3.52	1.59	71.35	100.00	0.00	0.00	0.00	41.55	15.15	37.93	1.62	0.00	17.40
116	987	4.00	0.43	40.06	100.00	30.31	0.00	0.00	18.60	8.01	21.09	1.27	8.28	2.73
103	996	7.37	0.54	72.02	98.09	44.91	0.00	4.28	43.81	13.69	27.49	0.99	37.44	7.71

TABLE XII CONT'D.

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (Sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 999-982 °K. (Continued)														
107	982	8.00	0.61	47.49	100.00	24.59	0.00	1.18	25.54	9.37	26.88	2.62	3.23	3.68
98	987	8.95	1.23	90.73	100.00	73.52	0.00	0.00	64.16	27.66	17.04	3.88	40.22	9.20
79	991	9.13	1.41	58.45	100.00	32.11	2.57	0.00	35.06	12.57	33.12	1.05	0.27	13.22
86	992	10.10	1.62	60.65	100.00	38.88	5.86	1.20	36.09	13.42	30.53	1.50	0.00	21.85
112	987	11.00	1.28	51.21	100.00	35.05	0.00	27.81	11.67	27.07	0.00	0.00	9.63	3.03
114	990	12.87	0.40	61.72	100.00	47.13	0.00	0.76	30.16	11.26	26.66	1.61	29.68	5.38
111	989	14.63	1.01	64.17	100.00	41.87	0.00	0.94	43.41	14.03	22.86	0.00	30.34	6.33
106	994	16.56	0.53	52.38	100.00	29.81	0.00	1.68	30.26	10.47	22.72	1.34	23.05	4.78
125	989	20.43	0.27	68.51	100.00	55.42	0.00	3.81	36.89	11.08	23.71	1.80	40.50	0.93
Temperature Range 978-961 °K.														
87	973	0.00	1.94	54.84	0.00	38.04	0.00	0.00	26.78	12.71	32.24	1.41	0.00	12.45
76	972	0.00	1.93	39.10	0.00	21.63	0.00	0.00	21.24	9.49	24.43	0.00	0.00	1.77
109	969	0.00	0.74	32.08	0.00	21.07	0.00	0.00	15.04	7.60	20.01	0.47	0.00	1.91
110	968	0.00	1.52	38.70	0.00	23.50	0.00	0.00	16.89	8.06	27.13	0.00	0.00	2.07
117	963	0.00	0.49	30.46	0.00	23.26	0.00	0.00	14.83	5.53	19.26	0.00	0.00	1.69
96	965	2.79	1.38	83.49	100.00	49.73	0.00	0.00	82.64	12.42	27.50	5.79	0.00	5.70
108	976	4.07	0.67	36.56	100.00	22.92	0.00	0.00	16.56	10.70	20.48	0.00	7.32	2.49
123	961	4.22	0.43	44.31	100.00	31.27	0.00	0.00	19.42	9.07	25.00	1.52	7.79	3.47
101	978	4.91	0.82	46.67	100.00	31.01	0.00	1.12	22.66	9.61	23.58	0.00	0.00	3.15
97	975	5.05	1.47	85.43	100.00	52.54	0.00	0.00	54.66	16.94	28.40	3.10	48.37	6.74
78	977	5.18	1.68	50.55	100.00	25.01	0.48	0.00	26.22	9.85	26.15	0.00	0.00	7.59
83	962	5.71	1.65	43.12	100.00	31.00	0.73	0.00	18.25	8.56	26.34	0.00	8.08	5.92
82	964	5.76	1.76	52.82	100.00	44.39	3.86	0.00	21.15	9.39	28.84	1.07	11.14	6.07
81	976	9.41	1.62	58.67	100.00	38.42	4.04	0.00	28.00	11.03	31.11	2.15	12.20	9.02
124	963	11.31	0.34	48.39	82.98	32.80	0.00	1.02	23.73	9.59	24.30	0.60	17.68	4.28
Temperature Range 902-881 °K.														
70	899	9.50	6.04	30.06	79.67	16.07	3.03	0.00	10.22	4.44	19.80	3.05	0.19	2.55
71	902	9.50	6.04	25.05	79.22	13.87	2.20	0.00	8.80	5.45	13.60	1.77	7.74	1.79
69	901	10.04	6.18	23.69	85.35	1.48	3.05	0.00	10.63	6.23	16.86	1.48	0.00	3.14
59	882	12.93	4.00	23.11	95.12	12.62	12.98	5.98	11.64	3.05	10.50	0.00	0.00	5.28
60	881	19.12	3.40	45.72	97.21	28.29	32.45	13.36	26.98	6.50	11.93	1.52	0.00	14.61

TABLE XII CONT'D.

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (Sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 868-843 °K.														
68-1	853	0.00	8.07	7.56	0.00	5.94	0.00	0.00	2.72	2.14	4.95	0.00	0.49	1.09
68-2	853	0.00	8.06	12.50	0.00	3.74	0.00	0.00	1.83	12.60	2.97	0.00	17.47	0.86
50-1	846	0.00	5.31	9.21	0.00	6.77	0.00	0.00	3.18	2.30	6.35	0.00	0.00	0.26
50-2	846	0.00	5.31	9.33	0.00	7.07	0.06	0.13	3.25	2.06	6.59	0.00	0.00	0.26
58	868	0.65	4.79	16.62	0.00	12.68	0.00	0.00	5.60	4.13	11.29	0.00	0.39	1.11
38-1	843	9.31	5.70	96.24	0.00	3.62	0.00	0.00	1.14	0.67	2.60	0.00	0.00	0.40
38-2	843	9.31	5.70	87.07	0.00	2.83	0.00	0.00	1.66	1.51	2.58	0.00	28.61	0.36
45	864	19.67	3.71	45.21	100.00	25.78	4.95	1.72	17.73	7.29	19.71	0.00	34.36	10.39
Temperature Range 837-818 °K.														
40	825	0.00	6.83	2.64	0.00	1.72	0.00	0.00	0.79	0.77	1.89	0.00	0.00	0.10
39	837	4.27	5.86	3.89	0.00	2.21	0.00	0.00	1.19	1.31	2.85	0.00	11.60	0.23
51	833	12.11	4.59	11.30	94.93	7.94	7.30	5.44	6.04	1.81	2.98	0.00	0.00	2.33
37-1	827	19.32	4.81	28.07	100.00	17.11	3.53	0.87	13.16	5.97	16.36	0.84	0.00	1.81
37-2	827	19.32	4.81	30.37	57.35	17.92	2.24	0.20	13.78	5.37	19.67	0.00	0.00	1.72
52-1*	818	20.78	3.90	20.67	94.46	4.15	51.77	0.00	0.00	0.00	8.40	0.00	0.00	11.77
52-2	818	20.78	3.90	28.80	46.67	6.36	37.12	18.01	20.62	3.98	4.54	0.00	0.00	9.82
53	827	26.01	3.69	49.26	97.91	6.14	68.48	22.50	32.79	6.38	7.14	0.00	0.00	17.96
Temperature Range 814-773 °K.														
33	807	0.00	6.93	0.92	0.00	5.39	0.00	0.00	0.00	0.00	10.23	0.00	0.00	0.00
46-1	780	0.00	6.10	4.11	0.00	0.24	0.00	0.00	0.25	0.13	0.64	0.00	0.00	0.08
46-2	780	0.00	6.10	0.87	0.00	0.69	0.00	0.00	0.24	0.14	0.61	0.00	0.18	0.08
48	784	1.95	6.27	10.59	100.00	6.69	0.58	0.98	3.81	1.53	6.81	0.75	0.00	0.43
49	781	2.14	6.03	2.36	100.00	1.62	1.31	0.65	0.71	0.30	1.16	0.00	0.32	1.52
34	789	4.64	7.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	785	5.61	5.61	17.48	100.00	10.38	2.10	1.79	7.37	2.40	10.21	1.36	0.00	1.32
35	782	11.32	8.39	43.36	0.00	2.34	0.00	0.00	1.21	0.85	2.58	0.00	0.00	0.15
167-6	773	17.60	3.20	79.93	100.00	56.79	8.36	2.92	62.01	1.96	31.43	2.83	18.06	21.83
167-7	773	17.60	3.20	82.75	100.00	67.40	11.77	3.40	60.33	3.29	31.11	2.32	18.51	21.43
36	791	20.07	5.48	22.40	84.72	12.89	4.36	0.91	11.16	3.49	13.13	0.69	0.00	1.44
54	775	27.00	4.07	43.36	97.63	11.12	62.49	21.33	24.82	6.86	5.04	0.00	0.00	14.58

---

* Propane = 0.40

TABLE XII CONT'D.

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (Sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 770-750 °K.														
62	765	12.59	8.71	12.76	100.00	3.39	3.03	0.35	2.31	1.03	3.73	0.00	14.63	0.58
67	756	12.59	8.92	13.89	99.39	5.07	4.00	0.38	3.36	1.41	5.05	2.26	12.36	0.58
66	754	12.59	8.81	12.96	96.67	4.93	4.10	0.44	3.18	0.98	3.98	2.67	11.43	0.52
63	754	12.59	8.81	12.68	97.81	3.75	2.90	0.37	2.75	1.46	3.80	2.50	10.19	0.72
65	753	12.59	8.77	13.47	100.00	3.86	3.70	0.00	3.18	1.23	4.11	2.76	14.13	0.73
64-1	752	12.59	8.80	9.77	98.72	4.29	3.40	0.41	3.01	1.13	4.80	1.94	0.00	0.68
64-2	752	12.59	8.80	12.83	100.00	4.51	3.35	0.00	2.84	0.79	4.59	1.86	15.03	0.65
Temperature Range 748-730 °K.														
41	744	0.14	7.41	0.39	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.49	0.00
57	736	0.53	6.38	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.78	1.90
42	738	4.93	6.71	2.02	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.99	0.00
157	743	5.08	18.79	4.23	100.00	1.02	0.60	0.00	1.03	0.56	0.65	0.86	6.66	0.39
43	742	10.54	5.89	8.77	100.00	2.75	0.46	0.30	0.16	0.69	1.91	0.79	17.97	0.22
136	738	10.85	2.85	8.68	100.00	1.62	0.17	0.22	0.79	0.35	0.84	0.32	26.57	0.06
56-1	733	14.72	5.03	14.51	96.80	3.28	17.57	10.54	8.63	2.95	1.16	0.00	0.00	14.30
56-2	733	14.72	5.03	26.05	46.53	1.81	7.19	9.60	6.92	1.53	1.30	0.00	0.00	12.09
44	748	19.03	4.76	20.99	100.00	6.81	3.14	0.00	5.40	1.81	6.72	2.29	30.15	0.58
153	734	19.07	6.36	19.80	99.20	6.25	8.26	1.17	0.62	1.95	8.81	3.97	16.03	0.99
55	742	20.80	4.56	26.93	96.89	8.59	32.24	14.40	17.45	2.98	3.87	0.00	0.00	7.14
Temperature Range 726-705 °K.														
154	725	0.00	22.82	0.98	0.00	1.28	0.00	0.00	0.00	0.00	0.88	0.00	0.00	0.48
150	720	0.00	9.65	1.19	0.00	0.07	0.00	0.00	0.20	0.17	0.33	0.00	0.00	0.42
135	720	0.67	4.79	2.70	96.75	0.29	0.00	0.00	0.00	0.00	0.00	0.00	10.52	0.00
151	705	5.40	8.89	3.68	100.00	0.91	0.36	0.27	0.08	0.32	0.98	0.61	6.88	0.00
156	721	11.11	16.72	14.08	99.45	5.66	2.17	0.00	4.00	0.17	5.15	1.82	14.30	0.69
152	726	11.39	7.63	9.94	99.68	2.48	2.50	0.63	0.00	0.92	3.10	2.70	12.25	0.36
155-1	710	17.65	14.00	80.44	99.16	4.47	7.61	0.84	4.44	1.50	3.48	3.32	22.73	0.70
155-2	710	17.65	14.00	19.20	99.36	4.66	7.58	0.71	4.60	1.29	3.53	3.51	23.71	0.71
155-3	710	17.65	14.00	20.64	99.05	5.12	9.42	0.84	57.13	1.33	4.19	5.50	18.56	0.90
155-4	710	17.65	14.00	16.46	99.08	49.78	82.55	43.30	8.20	8.20	23.40	20.48	27.10	0.73
137-1	725	19.40	3.00	21.91	97.40	8.59	8.49	1.41	5.39	1.72	6.53	3.26	15.57	0.91
137-2	725	19.40	3.00	20.28	97.37	7.84	9.21	1.22	5.65	1.44	4.40	3.63	20.92	6.53

TABLE XII CONT'D.

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (Sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 701-680 °K.														
149	695	0.00	9.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
162	680	0.00	21.18	0.71	0.00	0.47	0.00	0.00	0.29	0.35	0.34	0.00	0.00	0.00
139	685	0.34	3.84	0.05	48.51	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
164	685	4.75	17.73	6.75	100.00	1.67	0.51	0.00	1.46	0.76	1.71	2.62	4.74	0.17
148	690	5.96	8.34	4.53	100.00	0.79	0.58	0.32	1.06	0.39	1.01	0.89	6.86	0.25
140	686	10.13	3.25	5.63	66.28	0.00	0.00	0.57	1.87	0.66	0.92	1.71	4.01	0.27
163-1	694	10.18	17.00	10.31	100.00	2.49	1.70	0.50	2.92	1.12	3.30	1.77	11.38	0.66
163-2	694	10.18	17.00	12.17	100.00	2.42	1.48	0.00	2.26	0.88	2.41	2.22	7.36	0.65
147-1	686	12.54	7.30	10.33	100.00	2.70	3.39	0.64	2.55	0.76	1.81	2.35	0.00	13.10
147-2	686	12.54	7.30	12.13	100.00	2.18	3.36	0.00	0.00	2.84	1.48	3.54	0.00	20.84
166-2	691	17.69	8.00	96.40	38.23	84.41	4.26	1.31	86.31	31.39	25.61	3.11	26.87	30.91
166-3	691	17.35	8.00	97.21	9.38	83.93	1.06	1.45	82.12	10.12	24.83	3.70	28.57	33.75
165	701	18.57	14.85	13.18	100.00	5.90	8.68	0.00	1.50	5.43	3.67	3.32	0.00	1.51
146	685	19.79	6.29	16.46	100.00	3.55	6.64	0.95	3.77	0.99	2.73	3.68	0.00	22.29
141-2	690	23.54	2.70	55.67	75.18	0.00	0.00	1.45	6.39	2.22	3.85	6.55	0.00	2.64
141-3	690	23.54	2.70	24.82	86.85	6.35	0.00	1.30	7.32	1.74	3.54	37.94	0.00	1.52
Temperature Range 673-653 °K.														
158	665	0.00	21.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	673	0.81	5.33	0.39	63.49	0.16	0.13	0.00	0.47	0.00	0.09	0.00	0.00	0.00
143-1	673	4.49	7.80	2.70	100.00	0.00	0.33	0.00	0.57	0.00	0.42	0.66	5.38	0.00
143-2	673	4.49	8.04	3.88	99.08	0.49	1.52	0.00	0.42	0.00	0.39	0.61	0.00	0.00
160	657	5.06	19.48	5.27	100.00	0.84	0.49	0.00	0.74	4.37	1.26	0.86	10.46	4.68
130	659	8.04	8.97	75.13	86.23	49.07	0.00	0.00	51.36	16.98	33.56	2.18	5.34	0.00
159	661	9.64	18.04	7.50	99.89	1.46	1.95	0.21	1.49	0.47	2.13	1.29	10.83	0.65
134	665	9.90	4.61	3.97	77.28	1.54	2.63	0.50	1.27	0.31	0.64	1.53	0.00	0.25
144	660	12.50	8.21	8.76	100.00	2.12	3.63	0.00	1.77	0.49	1.04	1.56	15.37	0.32
161	668	19.35	7.26	16.21	99.53	3.45	6.68	0.80	4.01	1.13	3.13	3.16	21.57	0.81
145**	653	22.22	6.74	16.45	100.00	3.31	8.64	0.83	3.38	1.00	1.66	3.21	26.13	0.66

** Propane = 0.15

TABLE XII CONT'D.

Run Number	Temp. ($^oK.$)	Inlet O_2 Concn. Mole %	Time (Sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Components/100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 646-621 $^oK.$														
131-1	646	0.00	5.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131-2	646	0.00	5.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	633	0.00	5.77	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.73	0.00
133-1	621	8.01	4.93	6.56	81.62	0.91	0.00	0.00	0.91	0.00	0.57	1.00	15.23	0.00
133-2	621	8.01	5.82	6.56	75.28	0.00	0.00	0.00	0.55	0.00	0.55	0.01	0.00	0.00
129	642	13.04	10.30	34.77	97.00	17.06	0.00	4.29	17.75	8.82	15.08	0.00	8.05	0.00
127	629	17.49	8.41	9.99	83.30	0.00	0.00	0.00	4.14	0.00	0.00	0.65	29.09	0.00
128	644	23.89	7.84	19.81	93.64	3.76	7.69	3.01	7.57	0.00	1.62	4.08	28.43	0.00

TABLE XIII

SUMMARY OF REACTION VARIABLES AND REACTION RATE CONSTANTS OBTAINED FOR THE N-BUTANE OXIDATION RATE EQUATION ($r = k\, C_4H_{10}{}^{1.5} O_2{}^{0.5}$)

Run Number	Temp. (^{o}K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ (^{o}K.)$^{-1}$	$\left(\frac{Vr}{F}\right)$ $\left(\frac{ft.^3 (min.)}{lb.Mole}\right)$	$\left(k \frac{Vr}{F}\right)$	k $\frac{lb.Moles}{(ft.^3)(min.)}$
Temperature Range 1063-1022 ^{o}K.							
90	1051	6.19	1.44	0.95	47.10	1275.86	27.09
119	1022	11.31	0.34	0.98	9.54	70.04	7.34
118	1027	21.02	0.27	0.97	8.35	189.47	22.69
Temperature Range 1019-1000 ^{o}K.							
94	1016	4.95	1.24	0.98	39.32	1029.82	26.19
74	1014	4.99	1.57	0.99	39.00	278.53	7.14
85	1001	5.71	1.59	1.00	45.02	153.50	3.41
102	1000	7.37	0.69	1.00	18.12	64.62	3.57
75	1019	9.05	1.44	0.98	37.79	309.05	8.18
115	1000	17.69	0.29	1.00	8.72	74.51	8.54

TABLE XIII (CONT'D)

Run Number	Temp. (°K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ $(^{\circ}K.)^{-1}$	$\frac{(Vr)}{(F)}$ $\left(\frac{ft.^3 (min.)}{lb.Mole}\right)$	$(k \frac{Vr}{F})$	k $\frac{lb.Moles}{(ft.^3)(min.)}$
Temperature Range	999-982 °K.						
113-1	983	2.33	1.42	1.02	32.26	31.16	0.97
84	999	3.52	1.59	1.00	46.21	132.88	2.88
116	987	4.00	0.43	1.00	9.99	72.05	7.21
103	996	7.37	0.54	1.01	15.82	21.01	1.33
98	987	8.95	1.23	1.01	37.64	423.16	11.24
79	991	9.13	1.41	1.01	37.68	65.09	1.73
86	992	10.10	1.62	1.01	43.11	62.86	1.46
112	987	11.00	1.28	1.01	31.52	35.69	1.13
114	990	12.87	0.40	1.01	10.69	63.53	5.94
111	989	14.63	1.01	1.01	27.93	69.02	2.47
107	982	16.56	0.61	1.02	14.55	33.40	2.30
106	994	16.56	0.53	1.01	14.10	43.36	3.08

TABLE XIII (CONT'D)

Run Number	Temp. (^{o}K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ (^{o}K.)$^{-1}$	$\left(\frac{Vr}{F}\right)$ $\left(\frac{ft.^3(min.)}{lb.Mole}\right)$	$(k \frac{Vr}{F})$	k $\frac{lb.Moles}{(ft.^3)(min.)}$
Temperature Range 978-961 ^{o}K.							
96	965	2.79	1.38	1.04	37.76	351.97	9.32
108	976	4.07	0.67	1.03	15.20	24.65	1.62
123	961	4.22	0.43	1.04	9.94	37.09	3.73
101	978	4.91	0.82	1.02	18.61	31.52	1.69
97	975	5.05	1.47	1.03	38.58	256.05	6.64
78	977	5.18	1.68	1.03	39.37	42.90	1.09
83	962	5.71	1.65	1.04	37.91	36.50	0.96
82	964	5.76	1.76	1.04	42.52	49.53	1.17
81	976	9.41	1.62	1.03	41.37	58.34	1.41
124	963	11.31	0.34	1.04	7.97	67.03	8.41

TABLE XIII (CONT'D)

Run Number	Temp. (^{o}K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ (^{o}K.)$^{-1}$	$\left(\frac{Vr}{F}\right)$ $\left(\frac{ft.^3 (min.)}{lb.Mole}\right)$	$\left(k \frac{Vr}{F}\right)$	k $\frac{lb.Moles}{(ft.^3)(min.)}$
Temperature Range 902-881 ^{o}K.							
70	899	9.50	6.04	1.12	122.45	27.08	0.22
71	902	9.50	6.04	1.11	122.45	21.78	0.18
69	901	10.04	6.18	1.11	121.84	15.24	0.13
59	882	12.93	4.00	1.14	74.88	8.78	0.12
60	881	19.12	3.40	1.14	69.09	22.04	0.32
Temperature Range 868-843 ^{o}K.							
58	868	0.65	4.79	1.15	85.10	14.84	0.17
45	864	19.67	3.71	1.16	81.17	11.71	0.14
Temperature Range 837-818 ^{o}K.							
51	833	12.11	4.59	1.20	78.81	6.11	0.08
37-1	827	19.32	4.89	1.21	86.36	8.60	0.10
52-2	818	20.79	3.71	1.22	70.79	18.65	0.26
53	827	26.01	3.69	1.21	67.20	16.20	0.24

TABLE XIII (CONT'D)

Run Number	Temp. ($^oK.$)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T x 10^3$ $(^oK.)^{-1}$	$\frac{(Vr)}{(F)}$ $(\frac{ft.^3 (min.)}{lb.Mole})$	$(k \frac{Vr}{F})$	k $\frac{lb.Moles}{(ft.^3)(min.)}$
Temperature Range	814-773 $^oK.$						
48	784	1.95	6.27	1.28	97.38	4.28	0.04
49	781	2.14	6.03	1.28	90.08	1.96	0.02
47	785	5.61	5.61	1.28	91.83	7.51	0.08
167-6	773	17.66	3.20	1.30	74.72	148.37	1.99
167-7	773	17.58	3.20	1.30	74.72	139.44	1.87
36	791	20.07	5.48	1.26	90.06	8.37	0.09
54	775	27.00	4.07	1.29	64.82	23.86	0.37
Temperature Range	770-750 $^oK.$						
62	765	12.59	8.71	1.31	142.38	9.40	0.07
67	756	12.59	8.92	1.32	142.38	12.63	0.09
66	754	12.59	8.81	1.33	142.38	7.58	0.05
63	754	12.59	8.81	1.33	142.38	21.42	0.15

TABLE XIII (CONT'D)

Run Number	Temp. (°K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ $(^oK.)^{-1}$	$\frac{(V_r)}{(F)}$ $\left(\frac{ft.^3 (min.)}{lb. Mole}\right)$	$\left(\frac{k V_r}{F}\right)$	k $\frac{lb. Moles}{(ft.^3)(min.)}$
Temperature Range 770 - 750 °K. (cont'd)							
65	753	12.59	8.77	1.33	142.38	8.30	0.06
64-1	752	12.59	8.76	1.33	142.38	8.47	0.06
64-2	752	12.59	8.76	1.33	142.38	8.47	0.06
Temperature Range 748 - 730 °K.							
41	744	0.14	7.41	1.35	104.06	5.21	0.05
42	738	4.93	6.71	1.36	96.25	5.40	0.06
157	743	5.08	18.79	1.35	276.86	3.17	0.01
43	743	10.54	5.89	1.35	90.60	7.50	0.08
136	738	10.85	2.85	1.36	45.09	20.13	0.45
56-2	733	14.72	5.07	1.37	76.44	5.96	0.08
153	734	19.07	6.36	1.36	106.08	17.31	0.16
55	742	20.80	4.56	1.35	70.64	7.36	0.10

TABLE XIII (CONT'D)

Run Number	Temp. ($^oK.$)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ $(^oK.)^{-1}$	$\left(\frac{V_r}{\bar{F}}\right)$ $\frac{(ft.^3)(min.)}{lb. Mole}$	$\left(k \frac{V_r}{\bar{F}}\right)$	k $\frac{lb. Moles}{(ft.^3)(min.)}$
Temperature Range 726 - 705 °K.							
151	705	5.40	8.89	1.42	123.96	2.96	0.24
156	721	11.11	16.72	1.39	259.33	9.27	0.04
152	726	11.39	7.63	1.38	116.13	6.35	0.05
155-2	710	17.65	14.00	1.41	230.19	13.88	0.06
137-1	725	19.37	2.73	1.38	56.45	14.51	0.26
Temperature Range 701 - 680 °K							
139	685	0.34	3.84	1.46	49.60	4.08	0.08
164	685	4.75	17.73	1.46	242.45	3.28	0.01
148	690	5.96	8.34	1.45	114.92	0.75	0.01
140	686	10.13	3.25	1.46	44.80	6.75	0.15
163-1	694	10.18	16.82	1.44	244.37	6.50	0.03
147-2	686	12.54	7.26	1.46	106.90	8.53	0.08
165	701	18.57	14.85	1.43	207.63	13.01	0.06
146	685	19.79	6.29	1.46	97.80	11.46	0.12
141-3	690	109.10	2.77	1.45	44.52	52.82	1.19

TABLE XIII (CONT'D)

Run Number	Temp. (^{o}K.)	Inlet O_2 Concn. (Mole %)	Time (sec.)	$1/T \times 10^{3}$ (^{o}K.)$^{-1}$	$(\frac{V_r}{F})$ $\frac{(ft.^{3})(min.)}{lb. Mole}$	$(k \frac{V_r}{F})$	k $\frac{lb. Moles.}{(ft.^{3})(min.)}$
Temperature Range 673 - 653 ^{o}K.							
132	673	0.81	5.33	1.49	67.99	2.61	0.04
160	657	5.06	19.84	1.50	258.78	7.15	0.03
159	661	9.64	18.04	1.51	245.89	43.22	0.18
134	665	9.60	4.61	1.51	61.33	7.17	0.12
144	660	12.50	8.21	1.52	114.44	10.48	0.09
161	668	19.35	7.26	1.50	219.50	13.85	0.06
145	653	22.22	6.74	1.53	101.77	19.03	0.19
Temperature Range 646 - 621 ^{o}K.							
133-1	621	8.01	4.93	1.61	62.59	8.05	0.13
129	642	13.04	10.30	1.56	153.65	58.93	0.38
127	629	17.49	8.41	1.59	112.59	23.38	0.21
128	644	23.89	7.84	1.56	115.65	21.79	0.19

TABLE XIV

SUMMARY OF REACTION RATE CONSTANTS OBTAINED FOR ZERO, FIRST, SECOND, AND THIRD ORDER RATE EQUATIONS FOR THE THERMAL DECOMPOSITION OF N-BUTANE.

Run Number	Temp. (°K.)	Time (sec.)	$1/T \times 10^3$ (°K.)$^{-1}$	Butane concn. at Outlet (Mole %)	Rate Constants (k, sec.$^{-1}$)			
					Zero order	1st order	2nd order	3rd order
Temperature Range 1063 - 1022 °K.								
92-1	1063	1.16	0.94	0.045	0.870	2.820	19.293	224.46
88	1025	1.58	0.98	0.025	0.587	1.660	8.121	60.22
Temperature Range 1019 - 1000 °K.								
72	1005	1.76	1.00	0.410	0.334	0.507	0.816	1.40
100	1003	0.87	1.00	0.540	0.533	0.710	0.985	1.40
121	1010	0.46	0.99	0.290	1.538	2.670	5.300	11.78
Temperature Range 999 - 982 °K.								
99	991	1.79	1.01	0.170	0.462	0.984	2.690	9.18
122	984	0.46	1.02	0.420	1.245	1.845	2.930	4.92
Temperature Range 978 - 961 °K.								
87	973	1.94	1.03	0.270	0.378	0.680	1.141	3.34
76	972	1.93	1.03	0.440	0.292	0.430	0.670	1.10
109	969	0.74	1.03	0.510	0.667	0.916	1.310	1.95
110	968	1.52	1.04	0.450	0.361	0.524	0.800	1.29
117	963	0.49	1.04	0.510	0.100	1.368	1.940	2.87

TABLE XIV (Cont'd)

Run Number	Temp. (°K.)	Time (sec.)	1/T x 10^3 (°K.) $^{-1}$	Butane concn. at Outlet (Mole %)	Rate Constants (k, sec. $^{-1}$) Zero order	1st order	2nd order	3rd order
Temperature Range 868 - 843 °K.								
68-1	853	8.07	1.17	0.85	0.0190	0.020	0.23000	0.0250
50-1	846	5.31	1.18	0.80	0.0370	0.042	0.04600	0.0520
Temperature Range 837 - 818 °K.								
40	825	6.83	1.21	0.90	0.0153	0.017	0.01710	0.2660
Temperature Range 814 - 773 °K.								
33	807	6.93	1.24	0.98	0.0029	0.0029	0.00290	0.0290
46-1	780	6.15	1.28	0.96	0.0065	0.0640	0.00690	0.0070
Temperature Range 726 - 705 °K.								
154	725	22.82	1.38	0.96	0.0018	0.0017	0.00180	0.0019
150	720	9.65	1.39	0.99	0.0023	0.0010	0.00124	0.0012
Temperature Range 701 - 680 °K.								
149	695	9.33	1.44	1.00	0.0000	0.0000	0.00000	0.0000
162	680	21.18	1.47	0.99	0.0007	0.0009	0.00070	0.0007
Temperature Range 673 - 653 °K.								
158	665	21.77	1.51	1.00	0.0000	0.0000	0.00000	0.0000
Temperature Range 646 - 621 °K.								
131-1	646	5.81	1.55	1.00	0.0000	0.0000	0.00000	0.0000
138	633	5.77	1.58	0.97	0.0052	0.0051	0.00540	0.0055

TABLE XV

EQUATIONS OBTAINED FOR THE CORRELATION OF PRODUCT COMPOSITION AND BUTANE CONVERSION DATA WITH REACTOR OPERATING CONDITIONS

A Least Squares Program for the Datatron 205 (2:30:030) written by Darwin W. Smith and the Linear Regression Code written by Jack Warga and George Gerson were both used to obtain second order least squares fit of the composition and conversion data with respect to the operating variables of time, inlet O_2 concentration and temperature. In the case of CO and CO_2, oxygen was introduced also as a cross-multiplier of the equation to satisfy the condition of zero CO and CO_2 at zero O_2. In the case of CH_4 and H_2, cross product terms were introduced and a third order of T in order to get a better correlation of the data.

The equations were used to obtain Figures 17-32 by substituting back into the equations the variables time, temperature, and O_2 concentration, where:

T = temperature (°K.)

O_2 = oxygen concentration (Mole %)

θ = time (sec.)

The equations that were obtained are:

$$\frac{\text{Moles } CO_2}{100\,M\,C_4H_{10}} = (2.1513 \times 10^{-2} - 1.3535 \times 10^{-3} T + 6.251855 \times 10^{-7} T^2 + 7.375 \times 10^{-2}\, O_2 - 6.82 \times 10^{-5}\, O_2^2 + 7.444 \times 10^{-3}\, \theta - 1.2 \times 10^{-3}\, \theta^2)\ O_2$$

TABLE XV (Cont'd.)

$$\begin{aligned}\frac{\text{Moles } H_2}{100 \text{ M}C_4H_{10}} = & -5.312 \times 10^{-2}\, T + 1.031 \times 10^{-4}\, T^2 - 8.211 \times 10^{-2}\, O_2 + 2.176 \times 10^{-2}\, O_2^2 + 1.351\, \theta \\ & - 9.5897 \times 10^{-3}\, \theta^2 - 4.108 \times 10^{-8}\, T^3 - 1.483 \times 10^{-3}\, \theta\, T - 2.6917 \times 10^{-3}\, O_2\, \theta \\ & - 1.22773 \times 10^{-2}\, T\, O_2\end{aligned}$$

$$\begin{aligned}\frac{\text{Moles } CH_4}{100 \text{ M}C_4H_{10}} = & \; 0.2543\, T \times 10^{-1} - 6.994 \times 10^{-4}\, T^2 - 5.482 \times 10^{-1}\, O_2 - 1.25 \times 10^{1}\, O_2^2 - 1.056\, \theta + \\ & \; 1.787 \times 10^{-2}\, \theta^2 + 4.9854 \times 10^{-6}\, T^3 + 2.76 \times 10^{-4}\, \theta T - 5.2 \times 10^{-5}\, O_2\, \theta \\ & - 1.8669 \times 10^{-1}\, T\, O_2\end{aligned}$$

$$\begin{aligned}\frac{\text{Moles } CO}{100 \text{ M}C_4H_{10}} = & \; (+1.987323 \times 10^{-2} - 1.2180623 \times 10^{-3}\, T + 5.09945 \times 10^{-7}\, T^2 + 7.358803 \times 10^{-2}\, O_2 \\ & - 7.939 \times 10^{-5}\, O_2^2 - 3.439132 \times 10^{-7}\, \theta - 8.4151 \times 10^{-4}\, \theta^2)\, O_2\end{aligned}$$

$$\begin{aligned}\frac{\text{Moles } C_2H_6}{100 \text{ Moles } C_4H_{10} \text{ Feed}} = & \; 2.767927 \times 10^{-2}\, T + 3.59729 \times 10^{-6}\, T^2 + 4.10161 \times 10^{-2}\, O_2 + 1.991635 \times 10^{-3}\, O_2^2 \\ & - 5.37961 \times 10^{-1}\, \theta + 2.46092 \times 10^{-2}\, \theta^2 - 1.931287 \times 10^{1}\end{aligned}$$

$$\begin{aligned}\frac{\text{Moles } C_4H_{10}}{100 \text{ Moles } C_4H_{10} \text{ Feed}} = & - 4.654482 \times 10^{-2}\, T + 2.990918 \times 10^{-5}\, T^2 + 1.7719225 \times 10^{-1}\, O_2 - 4.499243 \times 10 \\ & \; O_2^2 + 7.889 \times 10^{-2}\, \theta - 2.3161 \times 10^{-3}\, \theta^2 + 1.746444 \times 10^{1}\end{aligned}$$

TABLE XV (CONT'D)

$$\frac{\text{Moles } C_3H_6}{100 \text{ Moles } C_4H_{10} \text{ Feed}} = 5.667392 \times 10^{-2}\, T + 3.94631 \times 10^{-6}\, T^2 + 7.268214 \times 10^{-1}\, O_2 - 2.918254 \times 10^{-2} O_2^2$$
$$- 1.599817\theta + 6.47024 \times 10^{-2} \theta^2 - 3.505881 \times 10^{1}$$

$$\frac{\text{Moles } C_2H_4}{100 \text{ Moles } C_4H_{10} \text{ Feed}} = 5.9021202 \times 10^{-2}\, T + 1.505834 \times 10^{-5}\, T^2 + 2.952729 \times 10^{-1}\, O_2 +$$
$$7.92568 \times 10^{-3}\, O_2^2 - 2.650317\theta + 1.7471 \times 10^{-2} \theta^2 - 3.931207 \times 10^{1}$$

$$\frac{\text{Moles Carbon}}{100 \text{ Moles } C_4H_{10} \text{ Feed}} = -5.867292 \times 10^{-1}\, T + 3.7234197 \times 10^{-4}\, T^2 + 1.04512\, O_2 - 1.2163153 \times 10^{-2}\, O_2^2$$
$$+ 8.15362 \times 10^{-1}\, \theta - 2.11155 \times 10^{-2} \theta^2 + 2.2171358 \times 10^{2}$$

$$C_4H_{10} \text{ Conv. (Mole \%)} = 7.043799 \times 10^{-1}\, T + 5.35814 \times 10^{-4}\, T^2 + 1.2934688\, O_2 - 2.61882 \times 10^{-3}\, O_2^2 +$$
$$1.09430 - 3.43173 \times 10^{-2} \theta^2 + 2.220114 \times 10^{2}$$

TABLE XVI

SUMMARY OF DATA ON n-BUTANE CONVERSION AND MOLES OF COMPONENTS IN EXIT STREAM PER 100 MOLES OF COMPONENTS

PLOTTED ON FIGURES 17-32

Run Number	Temp. (^oK)	Inlet O_2 conc. (Mole%)	Time (sec.)	Butane Conversion (Mole%)	O_2 Conversion (Mole%)	Mole Components/ 100 Moles Butane Feed								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
134	665	9.90	4.61	3.97	77.28	1.54	2.63	0.50	1.27	0.31	0.64	1.53	0.00	0.25
159	661	9.64	18.04	7.50	99.89	1.46	1.95	0.21	1.49	0.47	2.13	1.29	10.83	0.65
161	668	19.35	7.26	16.21	99.53	3.45	6.68	0.80	4.01	1.13	3.13	3.16	21.57	0.81
54	775	27.00	4.07	43.36	97.63	11.12	62.49	21.33	24.82	6.86	5.04	0.00	0.00	14.58
46-2	780	0.00	6.10	0.87	0.00	0.69	0.00	0.00	0.24	0.14	0.61	0.00	0.18	0.08
62	765	12.59	8.71	12.76	100.00	3.39	3.03	0.35	2.31	1.03	3.73	0.00	14.63	0.58
60	881	19.12	3.40	45.72	97.21	28.29	32.45	13.36	26.98	6.50	11.93	1.52	0.00	14.61
45	864	19.67	3.71	45.21	100.00	25.78	4.95	1.72	17.73	7.29	19.71	0.00	34.36	10.39
70	899	9.50	6.04	30.06	79.67	16.07	3.03	0.00	10.22	4.44	19.80	3.05	0.19	2.55
117	963	0.00	0.49	30.46	0.00	23.26	0.00	0.00	14.83	5.53	19.26	0.00	0.00	1.69
109	969	0.00	0.79	32.08	0.00	21.07	0.00	0.00	15.04	7.60	20.01	0.47	0.00	1.91
87	973	0.00	1.94	54.84	0.00	38.04	0.00	0.00	26.78	12.71	32.24	1.41	0.00	12.45
81	976	9.41	1.62	58.67	100.00	38.42	4.04	0.00	28.00	11.03	31.11	2.15	12.20	9.02

TABLE XVII

SUMMARY OF REACTOR OPERATING CONDITIONS FOR RUNS WITH A STAINLESS STEEL INLET GAS NOZZLE IN THE n-BUTANE REACTION

Run Number	Reactor Temp. (°K.)	Inlet O_2 Concn. (Mole %)	Retention Time (sec.)	Reactor Length (in.)	Av. Reactor Wall Temp. (°K.)	Average Traverse Temp. (°K.)	Average Gas Temp. (°K.)	Butane Flow Rate (s.c.f.m.)	Oxygen Flow Rate (s.c.f.m.)	Air Flow Rate (s.c.f.m.)
Temperature Range 902-881 °K.										
20	888	0.00	6.00	28.00	591.86	614.67	441.00	0.033	0.000	0.0000
Temperature Range 864-843 °K.										
21	857	0.00	9.66	28.00	583.56	545.83	539.40	0.024	0.000	0.0000
22	843	3.97	10.00	28.00	569.86	528.50	580.8	0.023	0.001	0.0000
23	843	10.35	8.43	28.00	575.50	530.42	548.50	0.023	0.003	0.0005
24	846	19.27	7.19	28.00	572.88	535.75	499.70	0.023	0.006	0.0000
Temperature Range 814-773 °K.										
28	786	0.00	8.95	28.00	513.38	510.50	521.30	0.022	0.000	0.0000
29	789	0.00	4.46	14.00	516.27	482.50	498.20	0.024	0.000	0.0000
9	799	0.00	0.00	24.63	526.08	513.00	525.40	0.012	0.000	0.0000
8	808	0.00	0.00	24.63	535.20	525.00	495.20	0.006	0.000	0.0000
10	814	7.00	0.00	24.63	540.90	517.89	535.40	0.012	0.001	0.0000
7	805	14.73	0.00	24.63	532.78	519.08	484.20	0.006	0.001	0.0012
5	803	15.90	0.00	25.00	530.84	502.93	494.20	0.006	0.001	0.0000
25	795	20.43	7.64	28.00	521.92	492.42	630.20	0.022	0.006	0.0000
Temperature Range 770-750 °K.										
30	758	5.15	3.63	14.00	485.16	438.58	482.20	0.023	0.001	0.0000
27	770	5.26	8.74	28.00	497.30	489.50	514.30	0.023	0.001	0.0000
31	762	8.75	4.38	14.00	488.87	440.91	490.20	0.024	0.002	0.0000
26	769	10.54	8.64	28.00	495.72	480.00	485.20	0.023	0.003	0.0000
32	764	16.70	4.01	14.00	518.37	469.58	518.30	0.023	0.005	0.0000
15	750	28.65	10.25	16.75	477.30	435.42	558.60	0.010	0.004	0.0003
Temperature Range 748-730 °K.										
19	742	0.00	1.58	7.00	459.10	413.00	460.10	0.059	0.000	0.0000
11	733	0.00	26.97	24.63	459.00	441.83	455.60	0.012	0.000	0.0000
13	730	2.00	19.18	24.63	465.92	420.85	498.2	0.010	0.002	0.0000
18	738	5.98	11.54	16.75	464.77	452.42	463.10	0.012	0.000	0.0048
17	736	6.25	14.19	16.75	463.43	439.00	482.20	0.012	0.001	0.0000
12	731	7.35	11.86	24.63	457.82	405.33	477.60	0.012	0.0001	0.0000
16	744	15.06	12.69	16.75	471.63	426.20	558.60	0.011	0.002	0.0000
14-1	734	28.50	15.28	24.63	461.58	433.75	513.30	0.010	0.004	0.0011
14-2	734	27.00	14.50	24.63	461.58	433.75	513.30	0.010	0.004	0.0011

TABLE XVIII

SUMMARY OF n-BUTANE REACTOR EXIT STREAM CONCENTRATIONS USING A STAINLESS STEEL INLET GAS NOZZLE

Run Number	Temp. (°K.)	Inlet O_2 Conc. (Mole %)	Time (Sec.)	Exit Stream Concentrations (Mole %)											
				O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
Temperature Range 902-881 °K.															
20	888	0.00	6.00	0.0005	0.000	0.078	0.228	0.000	0.000	0.165	0.075	0.181	0.000	0.276	0.000
Temperature Range 864-843 °K.															
21	851	0.00	9.66	0.002	0.000	0.000	0.138	0.000	0.000	0.081	0.088	0.269	0.000	0.608	0.000
22	843	3.97	10.00	0.133	0.000	0.000	0.124	0.000	0.000	0.094	0.053	0.119	0.000	0.519	0.038
23	843	10.35	8.43	0.000	0.010	0.025	0.116	0.006	0.013	0.090	0.066	0.195	0.000	0.363	0.116
24	846	19.27	7.19	0.001	0.000	0.020	0.172	0.021	0.023	0.108	0.048	0.120	0.011	0.282	0.197
Temperature Range 814-773 °K.															
28	786	0.00	8.95	0.000	0.005	0.190	0.252	0.000	0.000	0.190	0.061	0.168	0.014	0.120	0.000
29	789	0.00	4.46	0.000	0.000	0.114	0.503	0.000	0.000	0.259	0.061	0.182	0.006	0.127	0.000
25	795	20.43	7.64	0.002	0.000	0.033	0.167	0.050	0.035	0.144	0.070	0.194	0.019	0.151	0.122
Temperature Range 770-750 °K.															
30	758	5.15	3.63	0.001	0.000	0.102	0.247	0.009	0.000	0.178	0.058	0.170	0.007	0.176	0.045
27	770	5.26	8.74	0.001	0.000	0.836	0.253	0.002	0.000	0.224	0.069	0.170	0.012	0.134	0.051
31	762	8.75	4.38	0.000	0.004	0.127	0.212	0.030	0.011	0.203	0.062	0.163	0.000	0.183	0.004
26	769	10.54	8.64	0.005	0.000	0.075	0.219	0.010	0.018	0.190	0.058	0.308	0.008	0.198	0.064
32	764	16.70	4.01	0.000	0.009	0.046	0.440	0.068	0.018	0.227	0.055	0.162	0.000	0.119	0.076
15	750	28.65	10.25	0.012	0.087	0.095	0.019	0.079	0.000	0.059	0.039	0.000	0.000	0.332	0.279
Temperature Range 748-730 °K.															
19	742	0.00	1.58	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000
11	733	0.00	26.97	0.000	0.000	0.179	0.293	0.000	0.000	0.261	0.077	0.128	0.000	0.062	0.000
13	730	2.00	19.18	0.000	0.000	0.079	0.030	0.054	0.000	0.104	0.031	0.008	0.000	0.485	0.210
18	738	5.98	11.54	0.035	0.216	0.000	0.006	0.000	0.000	0.026	0.000	0.000	0.000	0.672	0.046
17	736	6.25	14.19	0.000	0.000	0.046	0.011	0.011	0.000	0.001	0.029	0.012	0.000	0.752	0.099
12	731	7.35	11.86	0.000	0.000	0.009	0.062	0.002	0.000	0.039	0.019	0.008	0.097	0.639	0.103
16	744	15.06	12.69	0.000	0.000	0.061	0.024	0.032	0.000	0.048	0.024	0.025	0.000	0.539	0.260
14-1	734	28.50	15.28	0.011	0.033	0.089	0.015	0.073	0.000	0.062	0.033	0.007	0.000	0.394	0.284
14-2	734	27.00	14.50	0.011	0.044	0.083	0.034	0.083	0.000	0.057	0.030	0.006	0.000	0.364	0.313

TABLE XIX

MOLES OF COMPONENTS PRESENT IN EXIT STREAM OF THE n-BUTANE REACTOR PER 100 MOLES OF FEED FOR RUNS WITH A STAINLESS STEEL GAS INLET NOZZLE

Run Number	Temp. (°K.)	Inlet O_2 Concn. Mole %	Time (sec.)	Butane Conversion Mole %	O_2 Conversion Mole %	Mole Component/100 Mole n-Butane								
						CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C	H_2
Temperature Range 902-881 °K.														
20	888	0.00	6.00		0.00	38.75	0.00	0.00	27.99	12.73	30.81	0.00	0.00	10.82
Temperature Range 864-843 °K.														
21	857	0.00	9.66	15.73	0.00	19.18	0.00	0.00	11.22	6.09	0.00	0.00	9.05	0.00
22	843	3.97	10.00	28.34	55.44	17.11	0.00	0.00	13.02	7.35	16.41	0.00	6.23	5.48
23	843	10.35	8.43	42.36	100.00	18.49	0.92	2.00	14.30	10.45	31.04	0.00	5.42	3.94
24	846	19.27	7.19	48.27	98.03	31.65	3.80	4.31	19.80	8.88	4.09	2.03	24.45	3.74
Temperature Range 814-773 °K.														
28	786	0.00	8.95	75.26	0.00	52.15	0.00	0.00	39.38	12.59	34.79	2.80	29.39	39.42
29	789	0.00	4.46	75.07	0.00	49.36	0.00	0.00	50.83	11.89	35.83	1.12	9.89	22.39
9	779	0.00			0.00	4.97	0.00	1.12	2.63	2.04	6.02	0.00	42.69	27.36
8	808	0.00			0.00	1.03	0.00	0.00	0.75	0.56	1.91	0.00	0.00	0.00
10	814	7.00			42.85	16.39	4.99	5.89	12.55	6.79	20.54	0.25	20.43	18.58
7	805	14.73			0.00	16.80	0.71	1.52	11.38	3.60	19.14	0.00	36.36	23.95
5	803	15.90			98.72	17.04	1.88	1.56	14.59	6.31	21.46	0.00	20.44	4.30
25	795	20.43	7.64	68.89	98.16	34.41	10.21	7.23	29.77	14.47	39.91	3.87	0.00	6.80
Temperature Range 770-750 °K.														
30	758	5.15	3.63	65.36	96.51	48.53	1.77	0.00	35.12	12.79	33.37	1.32	12.65	20.16
27	770	5.26	8.74	26.49	96.08	50.11	0.49	0.00	44.47	13.73	33.72	2.35	10.19	16.59
31	762	8.75	4.38	64.04	100.00	41.60	5.90	2.08	39.84	12.21	31.95	0.00	6.63	24.98
26	769	10.54	8.64	61.56	91.64	42.65	1.85	3.60	36.95	10.45	29.98	1.62	5.27	14.63
32	764	16.70	4.01	73.94	100.00	48.05	14.85	3.98	49.50	11.96	35.31	0.00	0.00	10.05
15	750	28.65	10.25	28.34	93.95	4.16	17.13	0.00	12.74	8.48	0.00	0.00	49.59	20.50
Temperature Range 748-730 °K.														
19	742	0.00	1.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	733	0.00	26.97	99.23	0.00	66.17	0.00	0.00	58.88	17.38	28.81	0.00	39.02	40.50
13	730	2.00	19.18	24.39	100.00	4.65	8.35	0.00	16.18	4.77	1.25	0.00	38.93	12.39
18	738	5.98	11.54	2.99	39.83	0.87	0.00	0.00	3.68	0.00	0.00	0.00	3.71	0.00
17	736	6.25	14.19	8.90	100.00	1.35	1.27	0.00	4.76	3.51	1.48	0.00	12.06	5.54
12	731	7.35	11.86	18.51	100.00	8.13	2.96	0.00	5.18	2.56	1.11	12.83	0.00	1.13
16	744	15.06	12.69	18.01	100.00	1.81	4.81	0.00	7.26	3.66	3.80	0.00	32.18	9.25
14-1	734	28.50	15.28	24.86	94.09	2.78	13.84	0.00	11.78	6.27	1.26	0.00	42.93	17.17
14-2	734	27.00	14.50	24.86	99.44	3.46	16.80	0.00	11.54	6.14	1.24	0.00	46.04	16.83

TABLE XX

SUMMARY OF REACTION VARIABLES AND REACTION RATE CONSTANTS

(WITH A STAINLESS STEEL GAS INLET NOZZLE) FOR THE OXIDATION RATE EQUATION

$(r = k \; C_4H_{10}^{1.5} \; O_2^{0.5})$

Run Number	Temp. (°K.)	Inlet O_2 Conc. (Mole %)	Time (sec.)	$1/T \times 10^3$ $(°K.)^{-1}$	$(\frac{V_r}{F})$ $\frac{(ft.^3)(min.)}{lb.\ mole}$	$(k\frac{V_r}{F})$	k $\frac{(lb.\ moles)}{(ft.^3)(min.)}$
Temperature Range 864 - 843 °K.							
24	846	19.27	7.19	1.18	155.73	32.85	0.21
Temperature Range 814 - 773 °K.							
10	814	7.00		1.23			
7	805	14.73		1.24			
5	803	15.90		1.25			
25	795	20.43	7.64	1.26	161.33	72.70	0.45
Temperature Range 770 - 750 °K.							
30	758	5.15	3.63	1.32	97.05	322.85	3.33
27	770	5.26	8.74	1.30	188.18	65.69	0.35
31	762	8.75	4.38	1.31	89.46	32.54	0.36
26	769	10.54	8.64	1.30	177.74	102.88	0.58
32	764	16.70	4.01	1.31	85.16	77.10	0.91
15	750	28.65	10.25	1.33	193.17	30.51	0.16

TABLE XX (CONT'D)

Run Number	Temp. ($^oK.$)	Concn. (Mole %)	Time (sec.)	$1/T \times 10^3$ $(^oK.)^{-1}$	$(\frac{V_r}{F})$ $\frac{(ft.^3)(min.)}{lb.\ mole}$	$(k\frac{V_r}{F})$	k $\frac{(lb.\ moles)}{(ft.^3)\ (min.)}$
Temperature Range 748 - 730 $^oK.$							
13	730	2.00	19.18		329.97	4.15	0.01
18	738	5.98	11.54	1.35	165.57	13.10	0.08
17	736	6.25	14.19	1.36	216.75	6.08	0.03
12	731	7.35	11.86		306.28		
16	744	15.06	12.69	1.35	214.52	18.15	0.08
14-1	734	28.50	15.28	1.36	282.39	11.47	0.04

TABLE XXI

SUMMARY OF REACTION RATE CONSTANTS OBTAINED FOR ZERO, FIRST, SECOND, AND THIRD ORDER RATE EQUATIONS FOR THE THERMAL DECOMPOSITION OF n-BUTANE, USING A STAINLESS STEEL GAS INLET NOZZLE.

Number	Temp. (°K)	Time (sec.)	$1/T \times 10^3$	Butane Concn. at Outlet	Rate Constants (k, sec.$^{-1}$)			
					Zero order	1st order	2nd order	3rd order
Temperature Range 902 - 881 °K.								
20	888	6.00	1.128	0.275	0.121	0.215	0.439	1.020
Temperature Range 864 - 843 °K.								
21	857	9.66	1.165	0.606	0.041	0.052	0.067	0.089
Temperature Range 814 - 773 °K.								
28	786	8.95	1.270	0.120	0.098	0.237	0.822	3.900
29	789	4.46	1.270	0.127	0.196	0.338	1.541	6.840
Temperature Range 748 - 730 °K.								
19	742	1.58	1.350	1.000	0.000	0.000	0.000	0.000
11	733	26.97	1.365	0.062	0.347	0.103	0.561	4.800

TABLE XXII

COMPARISON OF DUPLICATE CHROMATOGRAPHIC ANALYSES

Run Number	Sample Composition (Mole%)										
	O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}
46-1	0.00	1.79	0.08	0.24	0.00	0.00	0.25	0.13	0.64	0.00	96.86
46-2	0.00	2.03	0.08	0.67	0.00	0.00	0.23	0.13	0.59	0.00	96.25
64-1	0.18	0.15	0.62	3.89	3.08	0.38	2.77	1.03	4.35	1.76	81.79
64-2	0.00	0.16	0.62	4.26	3.17	0.00	2.68	0.74	4.33	1.75	82.30
113-1	0.00	0.57	1.24	16.60	0.00	0.00	19.67	8.50	17.49	0.00	35.92*
113-2	0.00	0.24	1.28	15.44	0.00	0.00	20.34	8.79	20.72	0.00	33.19*
155-1	0.41	0.77	0.64	4.07	6.93	0.77	4.04	1.37	3.17	3.03	74.81*
155-2	0.35	0.73	0.65	4.26	6.92	0.65	4.20	1.18	3.23	3.21	73.80*
155-3	0.83	0.86	0.79	4.51	6.30	0.74	4.63	1.18	3.69	0.00	70.01
155-4	0.46	0.86	0.67	4.59	7.61	0.00	3.99	0.76	2.16	1.89	77.02

---

*Butane Value obtained from second analysis since butane peak on the analysis went off scale

TABLE XXIII

EFFECT OF STORAGE TIME ON SAMPLE COMPOSITION

Run Number	Temp. ($^oK.$)	Inlet O_2 Concn. Mole %	Retention Time sec.	Date of Analysis	Sample Composition (Mole %)											
					O_2	N_2	H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	C_4H_{10}	H_2O
37-1	827	19.32	4.89	9-27-58	0.00	0.88	1.36	12.89	2.66	0.65	9.91	4.50	12.32	0.64	54.19	0.00
37-2	827	19.32	4.81	10-27-58	0.00	0.88	1.29	13.42	1.68	1.51	10.32	4.02	14.73	0.00	52.15	0.00
38-1	843	9.31	5.85	9-27-58	0.00	0.71	0.38	3.43	0.00	0.00	1.08	0.63	2.46	0.00	91.28	0.02
38-2	843	9.31	5.61	10-27-58	0.00	0.88	0.37	2.87	0.00	0.00	1.68	1.53	2.62	0.00	90.21	0.00
39-1	837	4.27	5.86	9-27-58	0.07	0.96	0.22	4.21	0.00	0.00	1.14	1.25	2.71	0.00	91.56	0.00
39-2	837	4.27	5.86	10-27-58	0.07	0.96	0.29	1.64	1.55	0.00	1.76	1.13	2.06	0.00	89.87	0.00

TABLE XXIV

OBSERVATION OF CARBON DEPOSITED IN REACTOR COMPARED TO CALCULATED VALUE OF CARBON

Date	Observation	Runs Made Prior to Observation	Average Calculated Values of Carbon (C/100 Moles Butane Feed)
(9-1-58	Carbon deposit on nozzle	11-18	29.386
9-23-58	Heavy carbon deposit	29-32	7.292
11-24-58	Heavy carbon deposit on nozzle	80-87	4.146
12-2-58	Heavy carbon deposit	88-91	34.871
12-4-58	Carbon deposit	92-99	23.496
12-18-58	Heavy carbon deposit	100-109	14.111
1-7-59	Heavy carbon deposit	111-113	19.783
10-7-58	No carbon deposits	46-49	0.126
11-4-58	No carbon deposit	62-67	12.960
11-12-58	No carbon deposit	72-75	3.792

LIST OF APPENDICES

APPENDIX A

CALIBRATION OF PEAK AREA RELATIVE TO THAT OF AIR FOR COMPONENTS ANALYZED IN CHROMATOGRAPHY UNIT

Component	Calibration Factor* (relative to air)
Air	1.00
Carbon Monoxide	0.95
Carbon Dioxide	0.84
Methane	1.13
Ethane	0.77
Ethylene	0.78
Propane	0.64
Propylene	0.74
Butane	0.52
Butene	0.59
Isobutane	0.57
Butadiene	0.78
Cis - 2 - Butene	0.66
Trans - 2 - Butene	0.56

---

* The calibration factor is equal to the peak area of air relative to that of the given component for a constant sample volume.

APPENDIX B

ELUTION TIMES OF COMPONENTS FROM CHROMATOGRAPHY UNIT

Components	Elution Time First Detector (min.)	Elution Time Second Detector (min.)
Oxygen	7.62	10.75
Nitrogen	7.62	11.25
Carbon Monoxide	7.80	12.90
Acetone	7.80	---
Methane	8.00	14.75
Acetylene	8.55	---
Carbon Dioxide	8.87	---
Ethylene	9.20	---
Ethane	10.00	---
Propylene	13.75	---
Propane	15.30	---
Acetaldehyde	24.00	---
Isobutane	25.80	---
Butadiene	30.00	---
1-Butene	30.70	---
Ethylene Oxide	31.50	---
Butane	35.30	---
Methanol	36.50	---
Formic Acid	36.60	---
Trans-2-Butene	38.10	---
Cis-2-Butene	41.40	---
Propylene Oxide	65.20	---

Chromatographic Operating Conditions:

Helium Flow Rate	60 std. cc./min.
Inlet Pressure	40 lbs./sq.in.gage
Varian Recorder Speed	48 in./hr.
Thermistor Operating Current	8 milliamperes
Number One Column:	30 ft. x ¼ in. Copper Tubing, packed with 35-48 mesh Sil-O-Cel coated with Tetraisobutylene
Number Two Column:	20 ft. x ¼ in. Stainless Steel Tubing packed with 35-48 mesh Molecular Sieves
Cabinet Temperature	30°C.

APPENDIX C

DETERMINATION OF REACTION TEMPERATURES AND CALCULATION OF RETENTION TIME FOR THE REACTION OF n-BUTANE

1. Reaction Temperature Determination

In many cases the traverse temperature, reaction gas temperature and wall temperature were not identical. In this case, a decision was made as to the most representative temperature to assume for the reaction conditions and calculation of retention time. For the first 61 runs, the inlet gas temperature was measured at the preheater. Here conduction problems from the preheater to the thermocouple caused this temperature to be a relatively unreliable measure of the inlet gas temperature. Also, it was found that at low flow rates the traverse temperature was low by about 20-30°C. Therefore, for the first 61 runs, the average reactor wall temperature was used as the reaction temperature except when the traverse temperature was higher. Then the average traverse temperature was used. For runs 62-167, thermocouples were located inside the reactor at 6 inches, 13 inches and 27 inches from the reactor outlet. These thermocouples were a fairly reliable measure of the gas temperature. The reaction temperature was taken as the average of the three. When the inlet gas came into the reactor substantially below the reaction temperature, the average of the other two thermocouple readings was taken for the reaction temperature. The justification is that the inlet gas reaches reaction temperature during flow through only a short length of reactor, as shown in Table XV.

2. Total Moles of Gas in the Reactor

From the sample analysis the ratio of the sum of the components in the sample (including water) to that of the components based on $(\frac{\Sigma C + C}{4} + \Sigma O_2 + N_2)$ was obtained. The second term is equivalent to the butane, oxygen and air coming into the reactor, while the first term is equivalent to the product stream. Since both are on the same basis, the ratio yields the number of moles at the outlet of the reactor to that at the inlet. The arithmetic average is used for the computation of residence time.

3. Reactor Volume

The reactor volume included consisted of the volume of the porcelain reactor up to the sample section plus the volume of the mixing chamber and inlet nozzle. The volume of the downstream nozzle was also included for the first 61 runs, since the sampling was downstream of the nozzle.

4. Retention Time

The equation used for calculating the retention time was:

$$\theta = \frac{(V \times L + C)\ 35.280}{\left[\left(\frac{\Sigma \text{Components}}{(\frac{\Sigma C + C}{4}) + \Sigma O_2 + N_2}\right) + 1\right] (\text{Total Flow})(T)}$$

APPENDIX C (Cont'd.)

Where: V = reactor volume ($ft.^3$/1 in. length)

L = length of reactor (in.)

C = volume of mixing chamber and inlet nozzle ($ft.^3$)(runs 1-61 include downstream nozzle volume)

T = reaction temperature (°K.)

Total Flow Rate = $ft.^3$/min. (70°F., 760 mm.Hg.)

θ = reaction time (sec.)

APPENDIX D

AIR SAMPLE CALIBRATION OF THE CHROMATOGRAPHY UNIT FOR THE ANALYSES OF n-BUTANE REACTION PRODUCTS

Date	Detector	Air Calibration Prior to Sample Analysis $(\frac{\text{Std. cc.}}{\text{1 gm. area}})$	Air Calibration After Sample Analysis $(\frac{\text{Std. cc.}}{\text{1 gm. area}})$	Average Calibration Value $(\frac{\text{Std. cc.}}{\text{1 gm. area}})$
8-22-58	2	53.79	48.52	
9-1-58	2	59.84	59.79	59.82
9-2-58	1	53.65	57.20	55.43
9-2-58	2	51.69	55.45	53.57
9-20-58	1	64.65	70.33	67.49
9-20-58	2	62.30	66.78	64.54
9-27-58	1	65.85	69.39	67.62
9-27-58	2	61.82	52.85	57.33
10-28-58	1	71.25	71.25	71.25
10-28-58	2	58.47	59.86	59.16
11-4-58	1	96.19	84.48	90.33
11-4-58	2	65.37	60.77	63.07
11-11-58	1	65.93	67.47	66.70
11-11-58	2	56.30	55.81	56.05
11-22-58	1	70.21	75.13	72.67
11-22-58	2	57.67	64.73	61.20
12-2-58	1	69.57	67.95	68.76
12-2-58	2	44.72	51.43	48.08
12-26-58	1	72.24	76.49	74.37
12-26-58	2	57.16	52.55	54.85
1-10-59	1	67.54	70.73	69.13
1-10-59	2	53.13	57.88	55.50
1-20-59	1	57.87	68.61	63.24
1-20-59	2	59.13	60.39	59.75
1-22-59	2	67.03	58.49	62.76
1-24-59	1	87.74	89.44	88.59
1-24-59	2	62.72	57.42	60.07
1-31-59	2	69.19	60.36	64.78

APPENDIX D (Cont'd.)

Chromatographic Operating Conditions:

Helium Flow Rate	60 Std. cc./min.
Inert Pressure	40-42 lbs./sq. in. gage
Varian Recorder Speed	48 in./hr.
Thermistor Operating Current	8 milliamperes
Number One Column	30 ft. x $\frac{1}{4}$ in. Copper Tubing packed with 35-48 mesh Sil-O-Cel coated with Tetraisobutylene
Number Two Column	20 ft. x $\frac{1}{4}$ in. Stainless Steel Tubing packed with 35-48 mesh Molecular Sieves

APPENDIX E

SAMPLE CALIBRATION OF THE CHROMATOGRAPHY UNIT FOR THE ANALYSES OF HYDROGEN

Date	Detector	Hydrogen Calibration Prior to Sample Analyses (Std.cc./gm.area)	Hydrogen Calibration After Sample Analyses (Std.cc./gm.area)	Average
9-28-58	2	61.70	50.69	56.19
10-29-58	2	21.20	17.87	19.54
11-5-58	2	17.08	16.95	17.02
11-12-58	2	14.86	18.95	16.91
11-23-58	2	23.75	22.15	22.95
12-2-58	2	22.24	27.17	24.71
12-5-58	2	19.12	25.17	22.14
12-27- 8	2	15.49	16.06	15.78
1-11-59	2	18.74	18.98	18.56
1-25-59	2	21.46	21.37	21.42

Chromatographic Operating Conditions:

Nitrogen Flow Rate	Std. cc./min.
Inert Pressure	30-35 lbs./sq. in. gage
Varian Recorder Speed	48 in./hr.
Thermistor Operating Current	8 milliamperes
Number One Column	30 ft. x $\frac{1}{4}$ in. Copper Tubing packed with 35-48 mesh Sil-O-Cel coated with Tetraisobutylene
Number Two Column	20 ft. x $\frac{1}{4}$ in. Stainless Steel Tubing packed with 35-48 mesh Molecular Sieves

APPENDIX F

METHOD OF OBTAINING SAMPLE CONCENTRATIONS FROM GAS CHROMATOGRAPHY DATA

1. Known volume of component (volume reduced to basis of 70°F., 760 mm. Hg.) admitted to chromatography unit.

2. Value of the recorded area for the component was obtained by cutting out the area under the response curve and weighing.

3. Ratio of volume of component ($cm.^3$) to area under curve (grams) is obtained.

4. During this same period, a known volume of air is admitted to the chromatography unit and the ratio of $cm.^3$ air/area in grams obtained.

5. The relative ratio of

   $$\left(\frac{\text{component sample, cm.}^3}{\text{peak area, grams}}\right)/\left(\frac{\text{air sample, cm.}^3}{\text{peak area, grams}}\right)$$

   is obtained and recorded for the various components in Table X, as Calibration Factors.

6. During the period when reactor gas samples are analyzed, air samples are admitted prior to and at the termination of the period of analyses to determine the response of the air peak on the recorder as a means of calibrating the chromatography unit for the given period of operation.

7. The area for each component is obtained by cutting and weighing to give the area in grams.

8. $$\text{Component, cm.}^3 = (\text{Component area, grams}) \times (CF) \times \left(\frac{\text{air, cm.}^3}{\text{area, grams}}\right)$$

   Where: CF = Calibration Factors, as shown in No. 5, above.

9. $$\text{Component concentration} = \frac{\text{component, cm.}^3}{{}^{*}\,\Sigma\ \text{components, cm.}^3}$$

---

* Since the thermal conductivity of hydrogen is close to that of helium, the hydrogen peak does not occur unless hydrogen is in very large concentrations. Consequently, hydrogen was analyzed separately using a nitrogen carrier gas. The concentration in the gas samples was obtained by dividing the volume of hydrogen found in the sample (by use of calibration) by the volume of sample admitted to the chromatography unit. This volume of hydrogen in the sample analyzed for the remaining components can be obtained by multiplying the size sample by the hydrogen concentration to get a hydrogen volume which can then be included in the summation of component volumes.

APPENDIX G

SUMMARY OF RUNS AND SAMPLE ANALYSES CORRECTED FOR AIR CONTAMINATION

Run Number	O_2 Concn. in Sample (based on N_2 and O_2 only) (Mole %)	Assumed Source of Contamination*
11-2	21.29	Ais
12	13.52	Ais
13	18.71	Ais
14-1	25.16	Inl
14-2	1.32	Inl
15	11.77	Inl
16-1	---	No
16-2	19.47	Ais
17	17.41	Ais
18	13.90	Inl
19-1	---	No
19-2	---	No
20-1	23.83	Ais
20-2	23.09	Ais
21	31.00	Ais
22	37.21	Ais
23	0.00	Inl
24	27.99	Ais
25	33.74	Ais
26	37.66	Ais
27	29.67	Ais
28	0.00	No
29	---	No
30	26.83	Ais
31	---	No
32	---	No
33	---	No
34	29.60	Inl
35	9.26	Inl
36	28.70	Inl
37-1	0.00	Inl
37-2	28.86	Inl
38-1	0.00	Inl
38-2	28.16	Inl
39-1	6.41	Inl
39-2	27.33	Inl
40	---	No
41	---	Inl
42	0.00	Inl

* Ais = Air leakage into Sampler
Inl = Air leakage at Reactor Inlet
No = No leakage

APPENDIX G (Cont'd.)

Run Number	O_2 Concn. in Sample (based on N_2 and O_2 only) (Mole %)	Assumed Source of Contamination*
43	0.00	Inl
44	0.00	Inl
45	0.00	Inl
46-1	0.00	Inl
46-2	0.00	Inl
47	0.00	Inl
48	---	Inl
49	---	Inl
50-1	11.56	Inl
50-2	17.13	Inl
51	26.86	Inl
52-1	27.99	Inl
52-2	24.75	Inl
53	30.12	Inl
54	30.82	Inl
55	27.99	Inl
56-1	23.72	Inl
56-2	28.57	Inl
57	26.01	Inl
58	16.79	Inl
59	24.86	Inl
60	23.10	Inl
61	20.80	Inl
62-1	0.00	Ais
62-2	52.79	Ais
63	---	Ais
64-1	53.97	Ais
64-2	---	Ais
65	20.13	Ais
66	28.09	Ais
67	44.47	Ais
68-1	23.60	Ais
68-2	26.20	Ais
69	24.18	Ais
70	24.21	Ais
71	---	Ais
72-1	24.54	Ais
72-2	---	Ais
73	23.30	Ais
74	23.56	Ais
75	0.00	Ais
76	21.38	Ais
77	17.76	Ais

* Ais = Air leakage into Sampler
Inl = Air leakage at Reactor Inlet
No = No leakage

APPENDIX G (Cont'd.)

Run Number	O_2 Concn. in Sample (based on N_2 and O_2 only) (Mole %)	Assumed Source of Contamination*
78	18.86	Ais
79	20.62	Ais
80	---	No
81	---	No
82	---	No
83	0.00	Inl
84	---	No
85	---	No
86	---	No
87	---	No
88-1	---	No
88-2	---	Inl
89	---	No
90	---	No
91	26.00	Ais
92	0.00	Inl
93	0.00	Inl
94	---	No
95	3.95	Inl
96	0.00	Inl
97	0.00	Inl
98	0.00	Inl
99	---	No
100	---	No
101	---	No
102	---	No
103	35.32	Ais
104	26.26	Ais
105	---	No
106	0.00	Inl
107	---	No
108	---	No
109	---	No
110	0.00	Inl
111	---	No
112	---	No
113-1	0.00	Inl
113-2	0.00	Inl
114	0.00	Inl
115	---	No
116	---	No
117	33.59	Inl
118	27.73	Inl

* Ais = Air leakage into Sampler
Inl = Air leakage at Reactor Inlet
No = No leakage

APPENDIX G (Cont'd.)

Run Number	O_2 Concn. in Sample (based on N_2 and O_2 only) (Mole %)	Assumed Source of Contamination*
119	38.55	Inl
120	38.41	Inl
121	---	No
122	---	No
123	---	No
124	29.73	Inl
125	0.00	Inl
126	21.07	Ais
127	14.25	Inl
128	11.08	Inl
129	22.74	Ais
130	23.74	Ais
131-2	18.48	Ais
132	8.28	Inl
133-1	37.65	Inl
133-2	39.12	Inl
134	35.81	Inl
135	7.98	Inl
136	13.13	Inl
137-1	39.75	Inl
137-2	40.76	Inl
138	12.67	Inl
139	12.64	Inl
140	73.39	Inl
141-1	---	---
141-2	73.31	Inl
141-3	76.86	Inl
142	0.00	Inl
143-1	0.00	Ais
143-2	26.94	Ais
144	19.74	Ais
145	18.87	Ais
146	20.26	Ais
147-1	0.00	Ais
147-2	19.21	Ais
148	---	No
149	0.00	Ais
150	19.78	Ais
151	17.42	Ais
152	25.77	Ais
153	60.19	Ais
154-1	---	Ais
154-2	18.45	Ais

---

* Ais = Air leakage into Sampler
Inl = Air leakage at Reactor Inlet
No = No leakage

APPENDIX G (Cont'd.)

Run Number	O_2 Concn. in Sample (based on N_2 and O_2 only) (Mole %)	Assumed Source of Contamination*
155-1	34.76	Ais
155-2	32.49	Ais
155-3	18.45	Ais
155-4	34.69	Ais
156	23.45	Ais
157	18.53	Ais
158	21.60	Ais
159	22.00	Ais
160-1	---	No
160-2	17.79	Ais
161	34.85	Ais
162	19.44	Ais
162-1	---	No
162-2	19.56	Ais
163-1	17.66	Ais
163-2	16.26	Ais
163-3	24.05	Ais
164-1	0.00	Ais
164-2	15.14	Ais
165-1	---	Ais
165-2	40.52	Ais

---

* Ais = Air leakage into Sampler
Inl = Air leakage at Reactor Inlet
No = No leakage

APPENDIX H

METHOD USED TO CALCULATE AIR LEAKAGE INTO REACTOR

The method of calculating air leakage into the reactor is based on obtaining the ratio of nitrogen to equivalent butane present in the gas sample and multiplying the ratio by the butane flow rate. This will give the nitrogen flow rate into the reactor. Dividing the nitrogen flow rate by 0.79 will give the air flow rate.

The calculation is indicated by the following three steps:

(1) From sample analysis, obtain value of nitrogen present in gas sample.

(2) Obtain the volume of $(\frac{\Sigma \text{ Carbon}}{4})$ (equivalent C_4H_{10}) present in the sample.

Then:

(3) $$\text{Air Flow (ft}^3\text{/min.)} = \frac{\text{Butane Flow rate (ft}^3\text{/min.)}}{(\frac{\Sigma \text{ Carbon}}{4})} \times \frac{\text{Nitrogen}}{0.79}$$

APPENDIX I

EQUATIONS FOR CALCULATING WATER AND CARBON FROM MATERIAL BALANCES

(All ratios are on mole basis)

(1) Obtain C/O_2 from butane and oxygen flowrates (including air flowrate whenever present).

(2) $$Y = C/O_2$$ Let

(2) From C_4H_{10}, $C/H = 0.4$

(3) From analyses for deposited carbon, $C/H \simeq 10$, as shown in Table IX (this value of C/H taken for all carbon obtained by difference).

(4) Using as a basis the sample volume of gases (analyzed for), - sum the carbon containing compounds on the basis of C to give ΣC, and sum the hydrogen compounds on the basis of H to give ΣH (for example, 5cc. C_2H_4 in the sample would give values of $\Sigma C = 10$ and $\Sigma H = 20$).

Let $\underline{C}$ = unaccounted carbon

$.1\ \underline{C} = H_2$ associated with $\underline{C}$.

(5) $$\frac{\Sigma C + \underline{C}}{\Sigma H + .1\ \underline{C} + 2\ H_2O} = 0.4$$

Multiplying and collecting terms:

(6) $$\underline{C} = 0.416\Sigma H + 0.833H_2O - 1.043\Sigma C$$

Also:

(7) $$\frac{\Sigma C + \underline{C}}{\Sigma O_2 + 1/2\ H_2O} = Y$$

Multiplying and collecting terms:

$$\underline{C} = Y\Sigma O_2 + 0.5\,Y\,H_2O - \Sigma C$$

Equating (6) and (7):

(8) $$Y\Sigma O_2 + 0.5\,Y\,H_2O - \Sigma C = 0.416\Sigma H + 0.833\,H_2O - 1.042\,\Sigma C.$$

From (8), we obtain:

(9) $$H_2O = \frac{0.416\,\Sigma H - 0.042\,\Sigma C - Y\Sigma O_2}{(0.5\,Y - 0.833)}$$

From Gas Sample Volumes and C/O_2 and C/H ratios, H_2O is obtained. It can then be substituted back into equation (6) to obtain $\underline{C}$.

APPENDIX J

DERIVATION OF THE INTEGRATED FORM OF THE DESIGN EQUATION ($rdV_r = Fdx_A$) FOR THE OXIDATION OF n-BUTANE

With the equation indicated in Hougen and Watson, which relates reaction rate and conversion to reactor volume and feed rate, we have:

$$(1) \qquad rdV_r = Fdx_A$$

Where:
r = rate of reaction, moles of A converted per unit volume of reacting system per unit time.

V_r = reactor volume occupied by reacting system.

F = reactor feed rate, mass per unit time.

x_A = moles of A converted per unit mass of reactor feed.

By integrating (1) for a constant feed rate:

$$(2) \qquad \frac{V_r}{F} = \int_0^{x_A} \frac{dx_A}{r}$$

For 1 atmosphere, the reaction rate equation for the oxidation of butane to the 1.5 order of butane and 0.5 order of oxygen can be written as:

$$(3) \qquad r = \frac{k(n_{oA} - x_A)^{3/2}(n_{oC} - Zx_{C_4H_{10}})^{1/2}}{n_t^2}$$

Letting:
n_{oA} = initial moles of n-butane per unit mass of feed.

n_{oC} = initial moles of oxygen per unit mass of feed.

n_t = total moles of reacting system per unit mass in the section dV.

k = reaction velocity constant.

Z = stoichiometric ratio of oxygen to butane in the equation $C_4H_{10} + Z\ O_2 \rightarrow$ products.

Expressing n_t in terms of x_A,

(4) $$n_t = n_o(1 + \frac{\delta x_A}{n_o}) = n_o(1 + \omega x_A)$$

Where: n_o = total moles of initial feed per unit mass.

δ = increase in the number of moles of the system per mole of A converted.

$\omega = \delta/n_o$

Combining equations (2), (3) and (4):

(5) $$\frac{V_r}{F} = \int_0^{x_A} \frac{(1 + \omega x_A)^2 \, n_o^2 \, dx_A}{k \, (n_{oA} - x_A)^{3/2} (n_{oC} - Zx_A)^{1/2}}$$

Let: $n_{oA} - x_A = Y^2$

then: $x_A = n_{oA} - Y^2$

Also: $$(1 + \omega x_A)^2 = 1 + 2\omega x_A + \omega^2 x_A^2$$

$$(1 + \omega x_A)^2 = 1 + 2\omega(n_{oA} - Y^2)$$
$$+ \omega^2(n_{oA}^2 - 2n_{oA} Y^2 + Y^4)$$

$$(1 + \omega x_A)^2 = (1 + 2\omega n_{oA} + \omega^2 n_{oA}^2) - (2\omega + 2\omega^2 n_{oA}^2) Y^2 + \omega^2 Y^4$$

$$(1 + \omega x_A)^2 = a + bY^2 + cY^4$$

Where: $a = 1 + 2\omega n_{oA} + \omega^2 n_{oA}^2 = (1 + \omega n_{oA})^2$

$b = -2\omega(1 + \omega n_{oA})$

$c = \omega^2$

Also: $n_{oC} - Zx_A = n_{oC} - Zn_{oA} + ZY^2$

and: $dx_A = -2 Y d Y$

So:

(6) $$\frac{V_r}{F} = -\frac{2}{k}\int_{Y_o}^{Y} \frac{aY + bY^3 + cY^5}{Y^3\sqrt{n_{oC} - Zn_{oA} + ZY^2}} \, dy$$

APPENDIX J (Cont'd.)

Dividing through by Y^3 and extracting the $\sqrt{Z}$ from the denominator:

$$(7) \qquad \frac{V_r}{F} = -\frac{2}{k\sqrt{Z}} \int_{Y_o}^{Y} \frac{\frac{a}{Y^2} + b + cY^2}{\left[Y^2 + \left(\frac{n_{oC}}{Z} - n_{oA}\right)\right]^{1/2}} \, dY$$

Let: $\frac{n_{oC}}{Z} - n_{oA} = -\eta^2$

Then:

$$(8) \qquad \frac{V_r}{F} = \frac{-2}{k\sqrt{Z}} \int_{Y_o}^{Y} \frac{\frac{a}{Y^2} + b + cY^2}{(Y^2 - \eta^2)^{1/2}} \, dY$$

From Dwight "Tables of Integrals" we have:

$$(9) \qquad \int \frac{1}{Y^2 (Y^2 - \eta^2)^{1/2}} \, dY = \frac{(Y^2 - \eta^2)^{1/2}}{\eta^2 Y}$$

$$(10) \qquad \int \frac{1}{(Y^2 - \eta^1)^{1/2}} \, dY = \ln \left(Y + \sqrt{Y^2 - \eta^2}\right.$$

$$(11) \int \frac{Y^2}{(Y^2 - \eta^2)} \, dY = \frac{Y}{2} (Y^2 - \eta^2)^{1/2} + \frac{\eta^2}{2} \ln - \left[Y + (Y^2 - \eta^2)^{1/2}\right]$$

Combining (8), (9), (10) and (11), we have:

$$(12) \quad \frac{V_r}{F} = \frac{-2}{k\sqrt{Z}} \left[\frac{a\sqrt{y^2 - \eta^2}}{\eta^2 Y} + b \ln (Y + \sqrt{Y^2 - \eta^2}) + \frac{cY}{2}\sqrt{Y^2 - \eta^2} + \frac{c\eta^2}{2} \ln (Y + \sqrt{Y^2 - \eta^2} \right]_{Y_o}^{Y}$$

Substituting in the boundary conditions, Y and Y_o:

$$(13) \quad \frac{V_r}{F} = \frac{-2}{k\sqrt{Z}} \left[\left(\frac{a}{\eta^2 Y_o} + \frac{cY_o}{2}\right)\sqrt{Y_o^2 - \eta^2} + \left(b + \frac{c\eta^2}{2}\right) \ln(Y_o + \sqrt{Y_o^2 - \eta^2}) - \left(\frac{a}{\eta^2 Y} + \frac{cY}{2}\right)\sqrt{Y^2 - \eta^2} + \left(b + \frac{c\eta^2}{2}\right) \right] \ln (Y + \sqrt{Y^2 - \eta^2})$$

Where:

$a = (1 + \omega n_{oA})^2$
$b = -2\omega (1 + \omega n_{oA})$
$c = \omega^2$
$\eta = (n_{oA} - \frac{n_{oC}}{Z})^{1/2}$
$Y = (n_{oA} - x_A)^{1/2}$
$Y_o = n_{oA}^{1/2}$

APPENDIX K

VALUES OBTAINED FOR THE STOICHIOMETRIC RATIO OF O_2 TO C_4H_{10}, AND THE TOTAL MOLES OF PRODUCT FORMED PER MOLES C_4H_{10} REACTED

Run Number	Z*	ω*	Number	Z*	ω*
12	0.43	1.51	46-1	0.11	2.38
13	0.08	2.08	46-2	0.62	2.38
14-1	1.52	3.03	47	0.34	1.36
14-2	1.52	3.03	48	0.19	1.01
15	1.37	3.36	49	1.00	1.55
16	0.98	3.17	50-1	0.03	1.12
17	0.75	2.44	50-2	0.02	0.75
18	1.23	2.80	51	1.18	2.00
19	0.00	0.00	52-1	0.83	1.45
20-1	0.00	1.32	52-2	0.84	1.99
20-2	0.00	1.32	53	0.70	0.95
21	0.00	2.49	54	0.86	1.77
22	0.08	1.30	55	0.97	1.05
23	0.27	1.46	56-1	1.17	1.66
24	0.49	1.87	56-2	0.64	1.02
25	0.37	1.51	57	0.00	8.56
26	0.18	1.53	58	0.00	1.10
27	0.20	3.88	59	0.62	1.29
28	0.00	1.42	60	0.52	1.26
29	0.00	1.28	62-1	0.00	2.39
30	0.08	2.83	62-2	1.13	2.39
31	0.15	1.46	63	1.10	2.25
32	0.27	1.42	64-1	1.45	3.11
33	0.00	1.24	64-2	1.11	2.57
34	0.00	0.00	65	1.06	2.43
35	0.00	0.93	66	1.07	2.40
36	0.96	1.31	67	1.03	1.97
37-1	0.86	1.31	68-1	0.00	1.23
37-2	0.46	1.37	68-2	0.00	0.75
38-1	0.00	0.62	69	0.40	1.52
38-2	0.00	0.18	70	0.28	1.46
39-1	0.00	0.00	71	0.33	1.72
39-2	0.07	1.33	72	0.00	0.47
40	0.00	3.21	73	0.03	1.28
41	0.36	6.64	74	0.07	1.21
42	2.60	4.45	75	0.12	1.38
43	1.36	2.95	76	0.00	1.01
44	1.13	2.82	77	0.08	1.04
45	0.55	2.01	78	0.11	1.14

* Z = Stoichiometric Ratio of oxygen to butane
ω = Number of moles formed/mole of butane reacted

APPENDIX K (Cont'd.)

Run Number	Z*	ω*	Run Number	Z*	ω*
79	0.17	1.63	120	0.00	0.97
80	0.00	1.17	121	0.00	1.11
81	0.18	1.47	122	0.00	1.06
82	0.12	1.35	123	0.10	1.28
83	0.16	1.48	124	0.23	1.53
84	0.05	1.13	125	0.38	1.87
85	0.09	1.51	127	1.84	3.24
86	0.19	1.53	128	1.72	3.36
87	0.00	1.25	129	0.42	1.55
88-1	0.02	1.22	130	0.10	1.33
88-2	0.02	1.25	131-1	0.00	0.00
89	0.13	1.51	131-2	0.00	0.00
90	0.07	1.45	132	1.37	3.33
91	0.03	1.34	133-1	1.13	2.90
92-1	0.006	1.38	133-2	0.26	2.00
92-2	0.02	1.38	136	2.22	3.65
93	0.10	1.75	135	2.48	5.92
94	0.05	1.45	136	1.95	5.09
95	0.06	1.52	137-1	1.08	2.42
96	0.03	1.27	137-2	1.17	2.85
97	0.06	1.08	138	1.40	--
98	0.11	1.45	139	--	9.75
99	0.00	1.24	140	1.34	2.65
100	0.00	1.07	141-1	0.42	0.62
101	1.11	1.07	141-2	0.42	0.39
102	0.13	1.39	141-3	1.090	1.38
103	0.32	1.96	142	0.00	0.00
104	0.42	1.86	143-1	0.05	3.18
105	0.47	1.97	143-2	0.05	0.57
106	0.38	1.88	144	1.63	3.24
107	0.18	1.36	145	1.74	0.00
108	0.12	1.28	146	1.50	3.14
109	0.00	1.06	147-1	0.16	2.79
110-1	0.00	1.01	147-2	1.18	2.64
110-2	--	1.01	148	1.40	2.85
111	0.27	1.75	149	0.00	0.00
112	0.24	1.43	150	0.00	0.01
113-1	0.05	0.94	151	1.55	2.85
113-2	0.04	1.07	152	1.29	2.53
114	0.24	1.61	153	1.18	2.55
115	0.27	1.86	154-1	0.00	1.70
116	0.10	1.30	154-2	0.00	1.70
117	0.00	1.11	155-1	0.26	0.69
118	0.34	1.94	155-2	1.11	2.90
119	0.24	2.02	155-3	1.03	2.70
			155-4	1.29	3.37

* Z = Stoichiometric Ratio of oxygen to butane

ω = Number of moles formed/mole of butane reacted

APPENDIX K (Cont'd.)

Number	Z*	ω*
156	0.88	2.27
157	1.26	2.66
158	0.00	0.00
159	1.41	2.81
160-2	1.02	2.91
161	1.47	3.13
162	0.00	1.08
163-1	1.10	2.43
163-2	0.13	1.55
164	0.74	1.86
165	1.73	1.12
166-2	0.08	1.61
166-3	0.02	1.39
167-6	0.27	1.84
167-7	0.26	1.48

---

* Z = Stoichiometric Ratio of Oxygen to Butane
ω = Number of moles formed/mole of butane reacted

APPENDIX L

THERMOCOUPLE CALIBRATION BY THE NATIONAL BUREAU OF STANDARDS

Platinum vs. Platinum-Rhodium Thermocouple
(Test No. 146382b)

(Electromotive Force vs. Temperature of Measuring Junction-
Reference junctions at 0°C.)

Absolute Millivolts	Degrees C	Absolute Millivolts	Degrees C
0.000	0	5.228	600
0.643	100	6.266	700
1.437	200	7.336	800
2.318	300	8.439	900
3.254	400	9.575	1000
4.224	500	10.743	1100

Chromel-Alumel Thermocouple
(Test No. 146382c)

(Electromotive Force vs. Temperature of Measuring Junction-
Reference junctions at 0°C.)

Absolute Millivolts	Degrees C	Absolute Millivolts	Degrees C
0.00	0	24.52	600
3.99	100	28.72	700
7.90	200	32.85	800
11.92	300	36.84	900
16.06	400	40.70	1000
20.29	500	44.45	1100

APPENDIX M

BIBLIOGRAPHY

At the initiation of the work on the partial oxidation of n-butane, an extensive Bibliography was compiled.

The Bibliography is arranged in alphabetical order according to author. An index as to the specific subject matter covered in each reference is provided to a degree by the inclusion of the titles.

1. Alden, R. C., The Relation of the Liquified Petroleum Gas Industry to the Oil Industry, Am. Petroleum Inst. Bull. 10, No. 2, Sect. II, 86-90 (1929)(C.A. 24, 1728^{3} (1930)).

2. Anderson, John Ernest, Evaluation of Catalysts for Hydrocarbons Oxidation, Iowa State Coll. J. Sci. 29, 364 (1955)(C.A. 49, 9910a (1955)).

3. Andreev, E. A., Two Stage Process of Thermal Ignition of a (Equimolecular) Mixture of Butane and Oxygen, Acts. Physicochim U.S.S.R. 6, 57-64 (1936)(C.A. 31, 7728^{9}(1937)).

4. Andrianova, T. I. and Rozinskii, S. Z., Reasons Which Prevent the Preparation of Aldehydes and Carboxylic Acids by Catalytic Oxidation of Unsaturated Hydrocarbons, Zhur Obshchei Khim 24, 605-10 (1954)(C.A. 49, 5421f (1955)).

5. Anon., Refrigerants Tested for Toxicity, Ind. Eng. Chem., New Ed. 10, 3-4 (1932)(C.A. 26, 1660^{6}(1932)).

6. Anon., N.O.A.A. Standard Tables of Physical Constants for Paraffin Hydrocarbons, Oil Gas J. 44, No. 23, 115-16 (1945)(C.A. 40, 782^{8} (1946)).

7. Appleby, W. G.; Avery, W. H.; Meerbott, W. K.; and Sartor, A. F.; The Decomposition of Butane in the Presence of Oxygen, J. Am. Chem. Soc. 75, 1809-14 (1953)(C.A. 47, 9121g (1953)).

8. Aston, John G.; Isserow, Saul; Szasz, George J.; and Kennedy, Robert M., An Empirical Correlation and Method of Calculation of Barriers Hindering Internal Rotation, J. Chem. Phys. 12, 336-44 (1944)(C.A. 38, 5441^{9} (1944)).

9. Aston, J. G. and Messerly, G. H., The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of n-Butane, J. Am. Chem. Soc. 62, 1917-23 (1940)(C.A. 34, 6515^2(1940)).

10. Avramenko, L. I. and Kolesnikova, R. V., Elementary Reaction of Atomic Oxygen with Ethane, Doklady Akad. Nauk U.S.S.R. 89, 1037-40 (1953)(C.A. 49, 6701g (1955)).

11. Avramenko, L. I. and Kolesnikova, R. V., The Experimental Determination of the Sequence for the Elementary Reactions of Atoms and Radicals, Doklady Akad. Nauk S.S.R. 92, 349-52 (1953)(C.A. 49, 6701d (1955)).

12. Badin, Elmer J., Hydrocarbon Oxidation Initiated by Atomic Hydrogen, J. Am. Chem. Soc. 70, 3965-6 (1948) (C.A. 43, 1309c (1949)).

13. Balliet, L., A Study on Oil Deposits, Oil Age 20, No. 4, 10-12 (1923)(C.A. 18, 211^9(1924)).

14. Badami, G. N.; and Egerton, Alfred, The Determination of Burning Velocities of Slow Flames, Proc. Roy. Soc. A 228 297-322 (1955)(C.A. 49, 7836f (1955)).

15. Barr, John, Diffusion Flames, 4th Symposium on Combustion 1952, 765-71, (C.A. 49, 9901e (1955)).

16. Barrow, Gordon M., Vapor Heat Capacities Determined by the Use of Vapor-Pressure Equations, J. Chem. Phys. 21, 1912-13 (1953)(C.A. 48, 1751i (1954)).

17. Bartlett, Paul Doughty, Polymerization Kinetics, Agnew. Chem. 67, 45-52 (1955)(C.A. 49, 5940a (1955)).

18. Beattie, James A.; Simard, Gerald L.; and Su, Goug-Jen, Vapor Pressure and Critical Constants of Normal Butane, J. Am. Chem. Soc. 61, 24-6 (1939)(C.A. 33, 1562^4(1939)).

19. Beattie, James A.; Simard, Gerald L.; and Su, Goug-Jen, The Compressibility of an Equation of State for Gaseous Normal Butane, J. Am. Chem. Soc. 61, 26-7 (1939)(C.A. 33 1562^5(1939)).

20. Beckers, Marcel, The State Equations of Easily Liquifiable Hydrocarbons. II. New Determination of the Weight of the Liter of Normal Butane, Bull Soc. Chem. Belg. 36, 559-90 (1927)(C.A. 22, 1066^3(1928)).

21. Beckers, Marcel, State Equation of Easily Liquifiable Hydrocarbons. IV. Weight of the Liter and Compressibility Coefficient of Normal Butane, Bull. Soc. Chem. Belg. 39, 470-95 (1930)(C.A. 25, 2613^2(1931)).

22. Beebe, R. A.; Kington, G. L.; Polley, M. H.; and Smith, W. R., Heats of Adsorption and Molecular Configuration. The Pentanes on Carbon Black, J. Am. Chem. Soc. 72, 40-2 (1950)(C.A. 44, 4748i (1950)).

23. Beeck, Otto, The Exchange of Energy between Organic Molecules and Solid Surfaces. I. Accommodation Coefficients and Specific Heats of Hydrocarbon Molecules, J. Chem. Phys. 4, 680-9 (1936)(C.A. 30, 7937^4(1936)).

24. Behrens, H., Flame Instabilities and Combustion Mechanisms, 4th Symposium on Combustion 1952, 538-45 (C.A. 49, 6700i (1955)).

25. Belles, Frank E. and Bulad, A. L., Chain Breaking and Branching in the Active-Particle Diffusion Concept of Flame Quenching, NACA TN 3407 (1955)(C.A. 49, 9364c (1955)).

26. Benedict, Manson; Webb, Geo. B.; and Rubin, Louis C., An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures, Constants for Twelve Hydrocarbons, Chem. Eng. Progress 47 419-22 (1951)(C.A. 45, 8321c (1951)).

27. Benedict, Manson; Webb, Geo. B.; and Rubin, Louis C., An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures. Fugacities and Liquid Vapor Equilibria, Chem. Eng. Progress 47, 449-54 (1951)(C.A. 45, 10024b (1951)).

28. Benedict, Manson; Webb, Geo. B.; Rubin, Louis C.; and Friend, Leo., An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures. Reduction of Equations to Charts for Prediction of Liquid-Vapor Equilibria, Chem. Eng. Progress 47, 571-8, 609-20 (1951)(C.A. 46, 1340a (1952)).

29. Benz, G. R. and Howick, E. G., Butane and its Combustion, Heat Treating and Forging, Furnaces (Supplement) 16, 371-4 (1930)(C.A. 24, 4376^7(1930)).

30. Black, Cline; Joris, George G.; and Taylor, Hugh S., The Solubility of Water in Hydrocarbons, J. Chem. Phys. 16, 537-43 (1948)(C.A. 42, 4819h (1948)).

31. Bogaert, L. van, Researches on the State Equation of Easily Liquifiable Hydrocarbons. 1. The Weight of the Liter of Normal Butane, Bull. Soc. Chem. Belg. 36, 384-94 (1927)(C.A. 21, 2825^9(1927)).

32. Boie, Werner, General Diagrams for Fuels, Die Technik 8, 305-9 (1953)(C.A. 48, 3661a (1954)).

33. Bonino, G. B., Calculation of Molar Entropies of Paraffins in Normal and Branched Chain Molecules, Boll. sci. facolta, chim ind. Bologna 3, 191-200 (1942)(C.A. 38, 5119^2(1944)(Chem. Zeutra 1943II, 712).

34. Brescia, Frank, Liquid Association and Critical Temperature, J. Chem. Phys. 14, 501-2 (1946)(C.A. 40, 6312^9 (1946)).

35. Breton, Jean and Laffitte, Paul, Detonation Limits and Velocities of Gaseous Mixtures, Compt. rend. 202, 316-18 (1936)(C.A. 30, 2003^6(1936)).

36. Bretton, R. H.; Wan, Shen-Wu; and Dodge, B. F., Catalytic Vapor-phase Oxidation of Some Four-Carbon Hydrocarbons, Ind. Eng. Chem. 44, 594-603 (1952)(C.A. 46, 10093c(1952)).

37. Briner, E. and Carceller, J., Ozone as an Oxidation Catalyst. VIII. Ozonization of Propane and Butane, Helv. Chem. Acta 18, 973-81 (1935)(C.A. 29, 61304 (1935)).

38. Brinkley, Stuart R. Jr. and Richardson, John M., The Structure of Plane-Detonation Waves with Finite Reaction Velocity, 4th Symposium of Combustion 1952, 450-7 (C.A. 49, 6608b (1955)).

39. Brooks, Benj. T.; Boord, Cecil E.; Kurtz, Stewart S. Jr.; and Schnerling, Louis, The Chemistry of Petroleum Hydrocarbons, Reinhold Publishing Corp., N.Y., N.Y. Vol. 2, 448 pp. (1955)(C.A. 49, 9911b (1955)).

40. Brown, Geo. G., Compressibility of Gasses. VI. Calculations Involved in the Design of Fractionating Columns, Petroleum Engr. 11, No. 9, 55-8, 60 (1940)(C.A. 34, 6856^6 (1940)).

41. Bruckner, H. and Schoneberger, R., Ignition Temperatures of Hydrocarbons, Brennctoff-Chem. 16, 290-2 (1935)(C.A. 30, 2003^9(1936)).

42. Burgoyne, J. H. and Hirsh, H., The Combustion of Methane at High Temperatures, Proc. Roy. Soc. (London) A 227, 73-93 (1954)(C.A. 49, 5085b (1955)).

43. Burgoyne, J. H. and Weinberg, F., A Method of Analysis of a Plane Combustion Wave, 4th Symposium on Combustion 1952, 294-302 (C.A. 49, 9251e (1955)).

44. Burrell, G. A. and Robertson, I. W., Vapor Pressures of Propane, Propylene and Normal Butane at Low Temperatures, J. Am. Chem. Soc. 37, 2188-93 (1915)(C.A. 9, 2614^8).

45. Butler, J. A. V., The Energy and Entropy of Hydration of Organic Compounds, Trans Faraday Soc. 33, 229-36 (1937) (C.A. 31, 2906^1(1937)).

46. Byrne, John T., The Influence of Atmospheric Oxygen on Bunsen Flames, 4th Symposium on Combustion 1952, 345-8 (C.A. 49, 9252a (1955)).

47. Bywater, S. and Steacie, E. W. R., Mercury (3P$_1$)-sensitized Decomposition of Butane and Isobutane at High Temperature, J. Chem. Soc. 19, 172-5 (1951)(C.A. 45, 6496j (1951)).

48. Cambron, Adrien and Bayley, Colin H., Pyrolysis of the Lower Paraffins. II. The Preparation of Olefins in Baffled Quartz Tubes, Can. J. Research 9, 175-96 (1953) (C.A. 27, 5172^7(1933)).

49. Chertkov, Ya B. and Zrelov, V. N., Autoxidation of Hydrocarbon Fuels, J. Appl. Chem. U.S.S.R. 26, 963-8 (1953)(C.A. 49, 4977d (1955)).

50. Cheruzak, N. Ya; Antonovkii, V. L.; Revzin, A. F.; and Shtern, V. Ya., Mechanism of the Oxidation of Hydrocarbons in the Gas Phase. IX. The High and Low Temperature Oxidation of Propane, Zhur. Fiz. Khim 28, 240-53 (1954)(C.A. 49, 6698i (1955)).

51. Chukhonov, Z. F., Basic Theories of Thermal Conversion of Fuels, Izvest. Akad. Nauk S.S.S.R. Otdel Tekh Nauk 1954, No. 8,7-22 (C.A. 49, 5808i (1955)).

52. Clingman, Wm. H. Jr.; Brokaw, Richard, and Pease, Robert N., Burning Velocities of Butane with Nitrogen-Oxygen, Argon-Oxygen and Helium-Oxygen Mixtures, 4th Symposium on Combustion 1952, 310-13 (C.A. 49, 9251e (1955)).

53. Coats, Hal B. and Brown, George G., A Vapor-Pressure Chart for Hydrocarbons, Univ. Mich. Dept. Eng. Research, Cir. Series No. 2, 17 pp. (1928)(C.A. 23, 3610^5(1929)).

54. Codegone, Cesare, Dynamic Viscosity of Gases and Vapors, Atti. accad. sci. Torino Classe sci. fis. mat. e nat. 86 126-8 (1951-2)(C.A. 48, 8606g (1954)).

55. Codegone, Cesare, Thermal Conductivity and Thermodynamic Properties of Gases and Vapors, Thermotecnics (Milan) 6, 507-11 (1952)(C.A. 48, 8637h (1954)).

56. Coffin, C. C. and Maass, O., Preparation and Physical Properties of , , and -Butylene and normal and isobutane, J. Am. Chem. Soc. 50, 1427-37 (1928)(C.A. 22, 2140^1(1928)).

57. Conant, J. B., The Heat of Dissociation of the Carbon-Carbon Linkage, J. Chem. Physics 1, 427-31 (1933)(C.A. 27, 4474^3(1933)).

58. Copson, R. L. and Frolich, Per K, Vapor-Pressure Chart for Lower Aliphatic Hydrocarbons, Ind. Eng. Chem. 21, 1116-7(1929)(C.A. 24, 2652^5(1930)).

59. Corsiglia, John, New Method for Determining Ignition Velocity of Air and Gas Mixtures, Am. Gas. Assoc. Monthly 13, 437-42 (1931)(C.A. 26, 1752^6(1932)).

60. Courtney-Pratt, J. S., New Methods of Fast Photography and Their Application to Combustion Processes, 4th Symposium on Combustion 1952, 508=26 (C.A. 49, 6700j (1955)).

61. Crawford, V. A. and Steacis, E. W. R., Thermal Decomposition of n-Butane, Can. J-Chem. 31, 937-48 (1953)(C.A. 48, 1781a (1954)).

62. Crutchfield, John W. and Pruett, Horton T., Engineering Developments in Southwest Texas, Petroleum Engr. 13, 208-10 (1946)(C.A. 41, 261f (1947)).

63. Cullis, C. F. and Hinskelwood, C. N., Labile Molecules in the Kinetics of Hydrocarbon Reactions Part III. Low Temperature Oxidation of Higher Paraffins in Relation to Structure, Discussions Faraday Soc. 1947 No. 2, 117-28 (C.A. 43, 5269e (1949)).

64. Cullis, C. F. and Mulcahy, F. R., Slow Oxidation of Hydrocarbons, Rev. inst. franc petrole 4, 283-7 (1949) (in French)(C.A. 44, 6805a (1950)).

65. Delmei, Cisole; Delbourgo, Ralph; and Lafitte, Paul, Influence of Tube Diameter on the Flammability Limits of Mixtures of n-Butane and Air., Compt rend. 240, 192-4 (1955)(C.A. 49, 7837i (1955)).

66. Dana, L. I.; Jenkins, A. C. ; Burdick, J. N., and Timm, R. C., Thermodynamic Properties of Butane, Isobutane, and Propane, Refrigerating Eng. 12, 387-405 (1926)(C.A. 21, 2826^1(1927)).

67. David, W. T. and Mann, J., Influence of Water Vapor on the Combustion of Hydrocarbon Mixtures, Nature 151, 392 (1943)(C.A. 37, 4606^4(1943)).

68. Deymar, Julide, The Slow Movement of the Flame in Limit Mixtures of the Saturated Hydrocarbons with Air, Rev. faculte sci. univ. Istanbul 17, 19-38 (1952)(in English) (C.A. 47, 2022i (1953)).

69. Dixon-Lewis, G., Temperature Distribution in Flame Reaction Zones, 4th Symposium on Combustion 1952, 263-7 (C.A. 49, 9249i (1955)).

70. Dabrinokaya, A., and Neiman, M. B., Ignition of Gaseous Mixtures, XXII. Effect of the Addition of Ethyl Peroxide and Acetaldehyde on the Kinetics of the Cold Flame Oxidation of Butane. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1953, 559-63 (C.A. 49, 5085e (1955)).

71. Dugger, Gordon L., and Groab, Dorothy D., Flame Velocities of Hydrocarbons-Oxygen-Nitrogen Mixtures, 4th Symposium on Combustion 1952, 302-10 (C.A. 49, 9251d (1955)).

72. Dugger, Gordon L. and Simon, Dorothy M., Prediction of Flame Velocities of Hydrocarbon Flames, 4th Symposium on Combustion 1952, 336-45 (C.A. 49, 9251i (1955)).

73. Dugger, Gordon L., Flame Stability of Preheated Propane-Air Mixtures, Ind. Eng. Chem. 47, 109-14 (1955)(C.A. 49, 3509a (1955)).

74. Dugger, Gordon L.; Weast, R. C.; Heimel, Sheldon, Flame Velocity and Preflame Reaction in Heated Propane Air Mixtures, Ind. Eng. Chem. 47, 114-16 (1953)(C.A. 49, 3508i (1955)).

75. Dunstan, A.E.; Hague, E. N. and Wheeler, R. V., Thermal Treatment of Gaseous Hydrocarbons I. Laboratory-Scale Operation, Ind. Eng. Chem. 26, 307-14 (1934)(C.A. 28, 2499^1(1934)).

76. Dunstan, A. E.; Hague, E. N.; and Wheeler, R. V., The Thermal Treatment of Gaseous Hydrocarbons, Chaleur. E. ind. 15, No. 167, 402-13 (1934)(C.A. 28, 6557^2(1934)).

77. Echols, Leonard S. Jr., The Thermal Decomposition of n-Butane, Univ. Microfilms Pub. No. 2941, 105pp. (C.A. 47, 2121c (1953)).

78. Edmister, Wayne C., Application of Thermodynamics to Hydrocarbon Processing. XXII. Convergence Correction to Vapor-Liquid Equilibrium Ratios, Petroleum Refiner 28, No. 9, 95-102 (1949)(C.A. 44, 312b (1950)).

79. Edmister, Wayne,C., Applications of Thermodynamics to Hydrocarbon Processing. XIII: Heat Capacities, Petroleum Refiner 27, No. 11, 609-15 (1948)(C.A. 43, 2758f (1949)).

80. Edmister, Wayne C., Applications of Thermodynamics to Hydrocarbon Processing. XVI. Effects of Pressure on Enthalpy and Entropy, Petroleum Refiner 28, No. 2, 137-48 (1949)(C.A. 43, 5576 b.c. (1949)).

81. Egerton, Alfred C., Limits of Inflammability, 4th Symposium on Combustion 1952, 4-13 (C.A. 49, 5805d (1955)).

82. Egerton, A. C.; Everett, A. J.; and Minkoff, B. J., High Speed (3000 frames/sec.) Photography of Low Pressure, Spark-Ignited Explosions of Methane, and of Hydrogen in Oxygen, 4th Symposium on Combustion 1952, 392-5 (C.A. 49, 9364g (1955)).

83. Egerton, Alfred C. and Sen, D., Flame Propagation: The Influence of Pressure on the Burning Velocity of Flat Flames, 4th Symposium on Combustion 1952, 321-8 (C.A. 49, 9251g (1955)).

84. Egloff, Gustav; Thomas, Charles L.; and Linn, Carl B., Pyrolysis of Propane and the Butane-Olefins Concentrations, Yields and Related Factors, Ind. Eng. Chem. 28, 1283-94 (1936)(C.A. 30, 7988^7(1936)).

85. Farrar, Gerald L., High Acetic Acid Yield Obtained by Celanese at Pampa Plant, Oil Gas J. 52, No. 14, 119-22 (1953)(C.A. 47, 11700h (1953)).

86. Fernandez, J. Carceller, Catalytic Action of O_3 in the Slow Combustion of Paraffins. Ozonization of the Terminal Groups of the Saturated Hydrocarbons of the Aliphatic Series, Anal. fis. quin (Spain) 36, 235-40 (1940) (in Spanish)(C.A. 39, 2023^8(1945)).

87. Fleming, Sydney W.; Detection of Free Radicals from the Heterogeneous Decomposition of Butane by a Tracer Technique, Univ. Microfilms Publ. No. 7787 (C.A. 49, 5259f (1955)).

88. Francis, Alfred W., Relations Between Physical Properties of Paraffin Hydrocarbons, Ind. Eng. Chem. 33, 554-60 (1941)(C.A. 35, 3499 (1941)).

89. Friedman, Raymond, Measurement of the Temperature Profile in a Laminar Flame, 4th Symposium on Combustion 1952, 259-63 (C.A. 49, 9249h (1955)).

90. Frey, F. E. and Hepp, H. J., Thermal Decomposition of Simple Paraffins, Ind. Eng. Chem. 25, 441-9 (1933)(C.A. 27, 2670^1(1933)).

91. Frost, Arthur A. and Kalkwarf, Donald R., A Semi-empirical Equation for the Vapor Pressure of Liquids as a Function of Temperature, J. Chem. Phys. 21, 264-7 (1953)(C.A. 47, 4157b (1953)).

92. Garner, F. H.; Long, R.; and Temple, R. G., Oxidation of Hydrocarbons. II. Examination of the Products of the Vapor Phase Oxidation of n-Heptane and of Methylcyclohexane, Trans. Faraday Soc. 49, 1193-7 (1953)(C.A. 49, 1597c (1955)).

93. Garrside, J. E. and Jackson, B., The Formation and some Properties of Polyhedral Burner Flames, 4th Symposium on Combustion 1952, 545-52 (C.A. 49, 6701a (1955)).

94. Garvin, David; Guium, Vincent P.; and Kistiakowsky, G. B., The Temperature Pattern Method in the Study of Fast Reactions, Discussions Faraday Soc. No. 17, 32-9 (1954)(C.A. 49, 10022i (1955)).

95. Gerber, M. I. and Neiman, M. B., The Conditions of Ignition of Gaseous Mixtures, Zhur. Fiz. Khim. 27, 1572-9 (1953)(C.A. 49, 12158e-2160d (1955)).

96. Gerstein, Melvin, The Structure of Laminar Flames, 4th Symposium on Combustion 1952, 35-43 (C.A. 49, 5905f (1955)).

97. Gilbert, Mitchell and Lobdell, John H., Resistance-Thermometer Measurements in a Low Pressure Flame, 4th Symposium on Combustion 1952, 285-94 (C.A. 49, 9364i (1955)).

98. Gonikberg, M. G. and Voevodskii, V. V., The Effect of Pressure on the Thermal Cracking of Paraffin Hydrocarbons, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.1954 305-9 (C.A. 49, 9913a (1955)).

99. Grosse, Aristid V., Refractive Indices at Low Temperatures, J. Am. Chem. Soc. 59, 2739-41 (1937)(C.A. 32, 909^{6}(1938)).

100. Griffin, J. Dennis, Catalytic Oxidation of Propane, Iowa State College, J. Sci. 29, 418 (1955)(C.A. 49, 9910h (1955)).

101. Gross, Robert A., Boundary Layer Flame Stabilization, Jet Propulsion 25, 288-90, 293 (1955)(C.A. 49, 9907c (1955)).

102. Grove, J. R. and Welsh, A. D., The Propagation of Cool Flames, 4th Symposium on Combustion 1952, 429-39 (C.A. 49, 9253b (1955)).

103. Grunberg, L. and Nissan, H. H., Critical Temperature and Molecular Weight of n-Paraffins, Nature 161, 170-1 (1948)(C.A. 42, 2830e (1948)).

104. Guenode, H. and Joury, M., Changes in the Shape of Flames Propagating in Tubes, 4th Symposium on Combustion 1952, 403-7 (C.A. 49, 9364h (1955)).

105. Gyani, B. P. and Dee, S. N., Free Volumes and Internal Pressures of Liquids and Their Entropies of Evaporization, J. Indian Chem. Soc. 29, 858-64 (1952)(C.A. 47, 7275h (1953)).

106. Hachmuth, K. H. and Brennan, O. L., Dew Points of Commercial Butane and Butane-Air Mixtures, Am. Gas J. 135, 44-7 (1931)(C.A. 25, 5004^6(1931)).

107. Haehmuth, Karl; Hanson, George H.; and Smith, Mary L., Vapor Pressures of Twelve Four-Carbon-Atom Hydrocarbons, Trans. Am. Inst. Chem. Engrs. 42, 975-82 (1946)(C.A. 41, 635a (1947)).

108. Hague, Ernest Noel and Wheeler, Richard Vernon, Mechanism of the Thermal Decomposition of the Normal Paraffins J. Chem. Soc. 1929, 378-93 (C.A. 23, 2928^1(1929)).

109. Hanson, George H., Thermodynamic Properties of Saturated Propylene, Propane, Isobutane, Isobutylene and normal Butane, Trans. Am. Inst. Chem. Engr. 42, 959-73 (1946) (C.A. 41, 635c (1947)).

110. Heiningen, J. van, Explosion Limits. I. Influence of Argon, Nitrogen, Helium and Carbon Dioxide on the Explosion Limits of Hydrogen, Carbon Monoxide, Methane, and Butane in Air, Rec. trav. chim. 55, 65-75 (1936)(C.A. 30, 3237^8(1936)).

111. Heitler, W., Binding Energies of Hydrocarbons, Helv. Chim. Acta 38, 5-15 (1955)(in German)(English Summary) (C.A. 49, 6671f (1955)).

112. Helt, J. H. and Gilstein, J. B., Indicated Instantaneous Temperature of Liquid Rocket Exhausts and Combustion Chambers, Jet Propulsion 25, 19-27 (1955)(C.A. 49, 7250a (1955)).

113. Hepp, H. J. and Frey, F. E., Pyrolysis of Propane and Butane at Elevated Pressure, Ind. Eng. Chem. 45, 410-15 (1953)(C.A. 47, 4588e (1953)).

114. Heuse, W., Molecular Volumes of Hydrocarbons and Other Compounds at Low Temperatures, p. physik. chem., Abt.A. 147, 266-74 (1930)(C.A. 24, 4200^8(1930)).

115. Higuchi, Izumi and Utsugi, Hiroshi, The Differential Molar Entropy of Adsorbate and the Mobility of Molecules Adsorbed on a Solid Surface, Science Depts. Tohoku Univ. 36, 37-9 (1952)(C.A. 47, 5760c (1953)).

116. Hildebrand, J. H., Solubility of Water in Hydrocarbons, J. Chem. Phys. 17, 1346-7 (1949)(C.A. 44, 4754d (1950)).

117. Hirsch, M., Pressure-Temperature Chart for Vapors, Ind. Eng. Chem. 34, 174-82 (1942)(C.A. 36, 1533^7(1942)).

118. Hoare, M. F. and Linnett, J. W., Effect of Solid Surfaces on the Propagation of Flame Through Ethylene-Air Mixtures, J. Chem. Soc. 1955, 195-202 (C.A. 49, 6571h (1955)).

119. Holcomb, Dysart E., Thermodynamic Properties of Light Hydrocarbons, Ind. Eng. Chem. 36, 384 (1944)(C.A. 38, 2262^{5}(1944)).

120. Hooper, J. D. H. et al., The Testing of Liquified Petroleum Gas and Similar Hydrocarbon Gases. Some Notes on Procedures Currently Used in the United Kingdom. Report of the Petroleum Gases Panel of the Institute of Petroleum, J. Inst. Petroleum 41, 54-62 (1955)(C.A. 49, 5811c (1955)).

121. Hottel, H. C. and Person, R. A., Heterogeneous Combustion of Gases in a Vortex System, 4th Symposium on Combustion 1952, 781-8 (C.A. 49, 9904h (1955)).

122. Howland, A. H. and Simmonds, W. A., Combustion Inside Refractory Tubes, 4th Symposium on Combustion 1952, 592-600 (C.A. 49, 6701d (1955)).

123. Hsick, M. S. and Townsend, D. T. A., An Examination of the Mechanism by which "Cool" Flames May Give Rise to "Normal "Flames. II. The Inflammable Ranges of Higher Paraffin Hydrocarbons in Air. The Establishment of "Cool" Flame Ranges at Ordinary Temperature and High Pressure, J. Chem. Soc. 1939, 337-40, 341-5 (C.A. 33, 40384 (1939)).

124. Hurd, Charles D. and Spence, L. U., Pyrolysis of Hydrocarbons: Butane and Isobutane, J. Am. Chem. Soc. 51, 3353-62 (1929)(C.A. 24, 53^{2}(1930)).

125. Hurd, Charles and Pilgrim, Forrest D., Pyrolysis of Hydrocarbons. Further Studies on the Butanes. J. Am. Chem. Soc. 55, 4902-7 (1933)(C.A. 28, 737^{3}(1934)).

126. Hybl, Jaroslaw, The Heat of Vaporization of Liquids, Ges. Kalti-Ind. 37, 85-6 (1930)(C.A. 24, 4678^{1}(1930)).

127. Inoue, Euchi, Synthesis of Some Organic Compounds in the Electric Discharge I. Slow Oxidation of Hydrocarbons by Silent Discharge, J. Soc. Org. Synthetic Chem. (Japan) 11, 256-9 (1953)(C.A. 47, 12048 (1953)).

128. Ingersoll, L. R. and Liebenberg, D. H., The Faraday Effect in Gases and Vapors, J. Opt. Soc. Amer. 44, 566-71 (1954)(C.A. 48, 10423f (1954)).

129. Ingold, K. U.; Stubbs, F. J.; and Hinshelwood, Cycil, The Kinetics of the Thermal Decomposition of Normal Paraffin Hydrocarbons. III. Activation Energies and Possible Mechanisms of Molecular Reactions, Proc.Roy. Soc. (London) A 203, 486-501 (1950)(C.A. 45, 6024d (1951)).

130. Ito, Kazuo, Heats of Formation and Potential Barriers for Internal Rotation in Hydrocarbon Molecules, J. Am. Chem. Soc. 75, 2430-5 (1953)).

131. Jack, J.; Stubbs, F. J.; and Hinshelwood, Cycil, The Effect of Various Inhibitors on the Thermal Decomposition of Paraffins, Proc. Roy. Soc. (London) A 224, 283-6 (1954)(C.A. 49, 42h (1955)).

132. Jessen, F. W. and Lightfoot, J. H., Compressibility of Butane-Air Mixtures below One Atmosphere, Ind. Eng. Chem. 28, 870-1 (1936)(C.A. 30, 5848^9(1936)).

133. Jones, Elwyn, Flammable Inhibitors can Prevent Explosions in Chemical Plants, Chem. Eng. 59, No. 6, 185-8 (1952)(C.A. 46, 8374h (1952)).

134. Kane, G. P., The Effect of Nitrogen Peroxide on the Two-Stage Ignition of Hydrocarbons, Proc. Roy. Soc. (London) A 171, 251-69 (1939)(C.A. 33, 6575^5(1939)).

135. Kay, W. B., Pressure-Volume-Temperature Relations for Butane, Ind. Eng. Chem. 32, 358-60 (1940)(C.A. 34, 2238^5(1940)).

136. Kennedy, B. H.; Sage, B. H.; and Lacey, W. N., Joule-Thomson Coefficients of Butane and Pentane, Ind. Eng. Chem. 28, 718-20 (1936)(C.A. 30, 4747^1(1936)).

137. Kilpatrick, M. O.; Dean, L. F.; Hall, D. S.; and Speed, K. W., Use of Moving Bed Technique in the Pyrolytic Production of Olefins from Gaseous Paraffin Hydrocarbons, Riv. combustibili 8, 513-25 (1954)(C.A. 49, 5822^c (1955)).

138. Kinbara, Toshiro and Nakamura, Junji, Ions in Diffusion Flames, Sci. Papers Coll. Gen. Educ., Univ. Tokyo 4, 9-19 (1954)(C.A. 49, 7936B (1955)).

139. King, J. G. and Edgcomb, L. J., Oxidation of Hydrogen, Carbon Monoxide and the Paraffin Hydrocarbons by Copper Oxide, Dept. Sci. Ind. Research, Fuel Research Tech. Paper No. 33, 28 pp. (1931)(C.A.26, 4160^4(1932)).

140. Kintz, G. M., Prevention of Fires, Explosions, and Accidents from Inflammable Fluids, Petroleum Eng. 13, No. 9, 77, 80, 82, 84, No. 11, 75, 76, 78 (1942)(C.A. 36, 5351^4(1942)).

141. Kireev, V. A., Chemical Reactivity and Thermodynamic Properties of Some Hydrocarbons, Reactions of Isomerization and Thermal Decomposition, Uspekli Khim. 23, 921-42 (1944)(C.A. 49, 6697i (1955)).

142. Kobe, K. A. and Rosenberg, H. E., The Wohl Equation of State Applied to Light Hydrocarbons, Petroleum Engr. 23, No. 11, C 35-8 (1951)(C.A. 46, 795e (1952)).

143. Knox, J. H. and Norrish, R. G. W., Cool Flame Phenomena in the Oxidation of Ethane, Trans. Faraday Soc. 50, 928-33 (1954)(C.A. 49, 4386a (1955)).

144. Kretschme,, Carl B. and Wiebe, Richard, Solubility of Gaseous Paraffins in Methanol and Isopropyl Alcohol, J. Am. Chem. Soc. 74, 1276-7 (1952)(C.A. 46, 6467i (1952)).

145. Krowskoy, Ned C.; Piccher, Geoffrey; and Streiff, Anton J., Purity of Butane, Isobutane, Isobutene and Octane from Freezing Points, Anal. Chem. 27, 107-8 (1955)(C.A. 49, 5079f (1955)).

146. Kuenen, J. P. and Visser, S.W., Viscosity of Normal Butane Vapor, Verslag. Akad. Wetenschappen 22, 336-43 (1913)(C.A. 9, 989^5)).

147. Kurz. Philip F., Flame Stability Studies on an Inverted Bunsen Burner, Ind. Eng. Chem. 47, 121-7 (1955) (C.A. 49, 3509a (1955)).

148. Kurz, Philip F., Influence of Group VI Hydrides on Hydrocarbon Flame Speeds, Ind. Eng. Chem. 47, 197-302 (1955)(C.A. 49, 6572i (1955)).

149. Laffitte, G. and Delbourgo, R., Ignition Condenser Sparks, Region of Flammability of Ethane, Propane, Butane and Pentane, 4th Symposium on Combustion 1952, 114-20 (C.A. 49, 5806d (1955)).

150. Laporte, Marcel, Moving-Picture Films in the Study of the Kinetics of Brief Chemical Reactions, Mikrochim. Acta 1955, 155-69 (in French)(C.A. 49, 9367b (1955)).

151. Larnaudie, Marcel, Molecular Vibration and Force Constants, J. phys. radium 15, 365-74 (1954)(C.A. 48, 13424h (1954)).

152. Lee, D. H.; Martin, D. G.; and Moore, N. P. W., Combustion Within Heated Tubes, Fuel 34, S107=S18 (1955) (April)(C.A. 49, 7217b (1955)).

153. Lewis, W. K. and McAdams, W. H., Calculating the Specific Heats of Hydrocarbon Vapors, Chem. Met. Eng. 36, 336 (1929)(C.A. 23, 4400^7(1929)).

154. Linnelt, J. W., Methods of Measuring Burning Velocities, 4th Symposium on Combustion 1952, 2035 (C.A. 49, 5805c (1955)).

155. Ludwig, E. H. B., Propane, Butane, and Pentane, the "Liquid Gases", Z. Osterr, Ner. Gas-Wasserfach 74, 121-9, 132-5 (1934)(C.A. 29, 1230^6(1935)).

156. Lyuberskii, G. D.; Morilyainen, S. K.; and Ya, S., Kinetics of Dehydrogenation of Butane, Zhur. Ziz. Khim. 28, 1272-9 (1954)(C.A. 49, 7937f (1955)).

157. Maizus, Z. K.; Markovich, V. G.; and Neiman, M. B., Effect of an Additive of Oxygen on the Thermal Decomposition of Butane, Doklady Akad. Nauk. S.S.S.R. 66, 1121-4 (1949)(C.A. 43, 7309f (1949)).

158. Manton, John; Von Elbe, Guenther; and Lewis, Bernard, Burning Velocity Measurement in a Spherical Vessel with Central Ignition, 4th Symposium on Combustion, 1952, 358-63 (C.A. 49, 9252a (1955)).

159. Mapstone, George E., Equilibrium Constants of Gas Reactions, Petroleum Engr. 27, No. 1, C34 (1955)(C.A. 49, 2789a (1955)).

160. Margolis, L. Ya. and Plyshevskaya, E. G., Catalytic Oxidation of Simplest Unsaturated Hydrocarbons by Heavy Oxygen, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 1953, 625-30 (C.A. 49, 4494c (1955)).

161. McDonald, G. E. and Schalla, R. L., Effect of Free Methyl Radicals on Slow-Oxidation of Propane and Ethane, NACA RM-E52G17, 21 pp. (1952)(C.A. 49, 9904f (1955)).

162. Miller, C. O. and Barley, R. C., Correlation of Vapor-Liquid Equilibria Data for Hydrocarbons, Ind. Eng. Chem. 36, 1018-21 (1944)(C.A. 39, 234^8(1945)).

163. Mukherjee, Asoka K., Relationship between Viscosity and Vapor Pressure of Liquids, J. Indian Chem. Soc. 30, 725-7 (1953)(C.A. 48, 6765b (1954)).

164. Mulcaky, M. F. R., Oxidation of Hydrocarbons. Some Observations on the Induction Period. Trans. Faraday Soc. 45, 575-84 (1949)(C.A. 43, 7798g (1949)).

165. Newsocki, P. J.; Raley, J. H.; Rust, F. F.; and Vaughan, W. E., Oxidation of Hydrocarbons Catalyzed by Hydrogen Bromide. Oxidation of Stright-Chain Compounds, Ind. Eng. Chem. 41, 2604-8 (1949)(C.A. 44, 1887e (1950)).

166. Naylor, C. A. and Wheeler, R. V., The Ignition of Gases. VIII. Ignition by a Heated Surface (a) Mixtures of Ethane, Propane, or Butane with Air, J. Chem. Soc. 1933, 1240-7 (C.A. 28, 327^5(1934)).

167. Neiman, M. B. and Feklisov, G. I., The Oxidation of Butane-1-C^{14} and the Theory of Destructive Oxidation, Doklady Akad. Nauk. S.S.S.R. 91, 827-80 (1953)(C.A. 49, 12263i (1955)).

168. Nelson, L. C. and Obert, E. F., Generalized PVT Properties of Gases, Trans. Am. Soc. Mech. Engrs. 76, 1057-66 (1954)(C.A. 48, 13307a (1954)).

169. Neuhaus, Max and Marek, L. R., Thermal Decomposition of Butane into Primary Products, Ind. Eng. Chem. 24, 400-2 (1932)(C.A. 26, 2696^6(1932)).

170. Niclause, Michel, Mechanism of the Slow Reaction Between Oxygen and a Gaseous Organic Substance, Pubs. sci. et. tech. ministera air (France) No. 292, 121 ppg. (1954)(C.A. 49, 10022d (1955)).

171. O'Hara, J. B. and Fahien, R. W., Latent Heats of Vaporization of Some Organic Compounds, Ind. Eng. Chem. 43, 2924-5 (1951); Am. Doc. Inst., Doc. 3327 (C.A. 46, 2361g (1952)).

172. Opfell, J. B.; Schlinger, W. G.; and Sage, B. H., Benedict Equation of State--Application to Methane, Ethane, n-Butane and n-Pentane, Ind. Eng. Chem. 46, 1286-91 (1954)(C.A. 48, 11168b (1954)).

173. Orlicek, A. F. and Voetter, H., Graphic Conversion Pictures (Nomograms) Mitt. chem. Forsch-Insts. Wirtach Osterr. 6, 601 (1952)(C.A. 46, 9363d (1952)).

174. Parks, Geo. S.; Shomate, C. Howard; Kennedy, W. D.; and Crawford, Bryce L. Jr., The Entropies of Butane and Isobutane with Some Heat Capacity Data for Isobutane, J. Chem. Phys. 5, 359-63 (1937)(C.A. 31, 4580^6(1937)).

175. Partington, R. G., Labile Molecules in the Kinetics of Hydrocarbon Reactions II. Rates of Thermal Decomposition of Saturated Hydrocarbons, Discussions Faraday Soc. 1947, No. 2, 114-16 (C.A. 43, 5269d (1949)).

176. Paul, R. E. and Marek, L. R., Primary Thermal Dissociation Velocity Constants for Propane, Butane, and Isobutane, Ind. Eng. Chem. 26, 454-7 (1934)(C.A. 28, 3973^8(1934)).

177. Peard, M. G.; Stubbs, F. J.; and Hinshelwood, C., Activation Energies and Frequencies Factors in the Thermal Decomposition of Paraffin Hydrocarbons, Proc. Roy. Soc. (London) A 214, 471-81 (1952)(C.A. 46, 10835e (1952)).

178. Pease, Robert N., Characteristics of the Non-Explosive Oxidation of Propane and the Butanes, J. Am. Chem. Soc. 51, 1839-56 (1929)(C.A. 23, 3436^3(1929)).

179. Pease, Robert N., and Durgan, Elford S., Kinetics of the Thermal Dissociation of Propane and the Butanes, J. Am. Chem. Soc. 52, 1262-7 (1930)(C.A. 24, 1840^1 (1930)).

180. Pease, R. N., The Thermal Dissociation of Ethane, Propane, Butane, and Isobutane, Preliminary Study, J. Am. Chem. Soc. 50, 1779-85 (1928)(C.A. 22, 2362^2(1928)).

181. Perry, R. E. and Thodos, George, Vapor Pressures of the Light Normal Saturated Hydrocarbons. Ind. Eng. Chem. 44 1649-53 (1952)(C.A. 46, 9364e (1952)).

182. Person, Willis B. and Pimentel, George C., Thermodynamic Properties and the Characteristic CH_2 Frequencies of n-Paraffins, J. Am. Chem. Soc. 75, 532-8 (1953)(C.A. 47 5237e (1953)).

183. Pickering, S. F., A Review of the Critical Constants of Various Gases, J. Phys. Chem. 28, 97-124 (1924)(C.A. 18 1409^2(1924)).

184. Pickering, S. F., A Review of the Literature Relating to the Critical Constants of Various Gases, Bur. Standards, Sci. Papers No. 541, 597-629 (1926)(C.A. 21, 1036^3(1927)).

185. Pitzer, Kenneth S., Thermodynamics of Gaseous Hydrocarbons; Ethane, Ethylene, Propane, Propylene, Butane, Isobutane, 1-Butene, cis-and trans-2-Butenes, Isobutene and Neopentane (Tetramethylmethane) J. Chem. Phys. 5, 473-9 (1937)(C.A. 31, 4863^9(1937)).

186. Poitorek, V. A. and Voevodskii, V. V., A Single Chain Mechanism for the Thermal Decomposition of Hydrocarbon, Doklady Akad. Nauk. S.S.S.R. 91, 589-91 (1953)(C.A. 49, 11265g (1955)).

187. Polyakov, M. V. and Shoikhet, P. A., The Influence of V_2O_5 and SnO_2 Catalyst on the Reaction Kinetics and the Composition of the Products from the Incomplete Oxidation of Propane-Butane, Doklady Akad. Nauk. S.S.S.R. 89 1057-60 (1953)(C.A. 49, 9372g (1955)).

188. Porter, George, Mechanism of Carbon Formation, Agard (Advisory Group Aeronaut. Research and Development) AGB M9, 16 pp. (1954)(C.A. 49, 3627d (1955)).

189. Porter, George, Carbon Formation in the Combustion Wave, 4th Symposium on Combustion 1952, 248-52 (C.A. 49, 6523a (1955)).

190. Prengle, H. Wm. Jr.; Greenhaus, L. R.; and York, Robert Jr., Thermodynamic Properties of Butane, Chem. Eng. Progress 44, 863-8 (1948)(C.A. 43, 476d (1949)).

191. Prosen, Edward J.; Pitzer, Kenneth S.; and Rossini, Frederick, Heat and Free Energies of Formation of the Paraffin Hydrocarbons in the Gaseous State to 1500°K, J. Research Natl. Bur. Standards 34, 403-11 (1945) (C.A. 39, 4290^{2}(1945)).

192. Prosen, Edward and Rossini, Frederick D., Heats of Combustion and Formation of the Paraffin Hydrocarbons at 25°C., J. Research Natl. Bur. Standards 34, 263-69 (1945)(C.A. 39, 2924^{7}(1945)).

193. Quon, D.; Dalla Lana, I.; and Govier, G. K., The Vapor-Phase Partial Oxidation of Butane. Effect of Pressure, Reaction Time and Inlet Gas Composition, Can. J. Chem. 32, 880-95 (1954)(C.A. 49, 6578a(1955)).

194. Revzin, A. F.; Sergoev, G. B.; and Shtern, V. Ya., Mechanism of Oxidation of Hydrocarbons in the Gas Phase. VII. Influence of Homogeneous Addition (Nitrogen Dioxide, Bromine) on the Oxidation of Propane, Zhur. Ziz. Khim. 28, 985-96 (1954)(C.A. 49, 7351b (1955)).

195. Ribaud, G., Thermodynamic Constants of Gases at High Temperatures, Publ. sci. et. tech. ministere air (France) 1952, No. 266, 169 pp. (C.A. 47, 6722c (1953)).

196. Rice, F. O., Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. I. Saturated Hydrocarbons, J. Am. Chem. Soc. 53, 1959-72 (1931)(C.A. 25, 2967^{6}(1931)).

197. Rice, F. O. and Evering, B. L., Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IX. The Combination of Methyl Groups with Metallic Mercury., J. Am. Chem. Soc. 56, 2105-7 (1934) (C.A. 29, 447^{5}(1935)).

198. Rice, F. O. and Glasebrook, A. L., Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. X. The Identification of Methyl Groups as Dimethyl Ditelluride, J. Am. Chem. Soc. 56, 2472 (1934)(C.A. 29, 723^{4}(1935)).

199. Rogener, H., The Ignition of Hydrocarbon-Air Mixtures Through Adiabatic Compression, Elecktrochem. 53, 389-97 (1949)(C.A. 44, 4227b (1950)).

200. Rossini, Frederick D., Calorimetric Determination of the Heats of Combustion of Ethane, Propane, Butane, and Pentane, Bur. Standards J. Research 12, 735-50 (1934)(C.A. 28, 4974^1(1934)).

201. Sage, B. H., Status of Thermodynamics in the Petroleum Industry, Ind. Eng. Chem. 42, 631-9 (1950)(C.A. 44, 5083a (1950)).

202. Sage, B. H. and Lacey, W. N., Phase Equilibria in Hydrocarbon Systems. IX. Specific Heat of Butane and Propane, Ind. Eng. Chem. 27, 1484-8 (1935)(C.A. 30, 946^6(1936)).

203. Sage, B. H., Olds, R. H., and Lacey, W. N., Tentative Partial Enthalpies of the Lighter Hydrocarbons, Calif. Oil World 39, No. 22, 29-46 (1946)(C.A. 41, 1541h (1947)).

204. Sage, B. H.; Webster, D. C.; and Lacey, W. N., Phase Equilibria in Hydrocarbon Systems. XIX. Thermodynamic Properties of n-Butane, Ind. Eng. Chem. 29, 1188-94 (1937)(C.A. 31, 8344^2(1937)).

205. Sage, B. H.; Webster, D. C.; and Lacey, W. N., Phase Equilibria in Hydrocarbon Systems. XX. Isobaric Heat Capacity of Gaseous Propane, Butane, Isobutane and Pentane, Ind. Eng. Chem. 29, 1309-14 (1937)(C.A. 32, 345^5(1938)).

206. Satterfield, Charles N. and Reid, Robert C., Kinetics of the Reactions of the Propyl Radical with Oxygen, J. Phys. Chem. 59, 283-5 (1955)(C.A. 49, 7936g (1955)).

207. Sax, N. Irving, Handbook of Dangerous Materials, Reinhold Publishing Corp. 1951, p. 60

208. Scheibel, Edward G. and Jenny, Frank J., Nomographs for Enthalpies of Pure Hydrocarbons and Their Mixtures Ind. Eng. Chem. 37, 990-5 (1945)(C.A. 39, 5164^2(1945)).

209. Schenk, Paul and Osterlok, Karl, The Catalytic-Thermal Reforming of Gaseous and Liquid Hydrocarbons, Gas-u. Wasserfach 96, 1-8 (1955)(C.A. 49, 6577i (1955)).

210. Schuit, G. C. A., Oxidation of Normal Butane, I. Experimental Part , Rec. trav. chim. 60, 29-49 (1941) (in English)(C.A. 35, 6177^5(1941)).

211. Serber, Robert, Energies of Hydrocarbon Molecules, J. Chem. Physics 3, 81-6 (1935)(C.A. 29, 2037^3(1935)).

212. Selchkin, Nicholas P., Self-Ignition Temperature of Combustible Liquids, J. Research Nat'l. Bur. Standards 53, 49-65 (1954)(C.A. 49, 585h (1955)).

213. Small, N. J. H. and Vbbelohde, A. R., Influence of Molecular Structure on the Oxidation of Aliphatic Hydrocarbons, J. Appl. Chem. (London) 3, 193-8 (1953) (C.A. 49, 5259d (1955)).

214. Smith, K. A. and Smith, R. B., Vaporization Equilibrium Constants and Activity Coefficient Charts, Petroleum Processing 4, 1355-60 (1949)(C.A. 44, 3758c (1950)).

215. Smith, M. L. and Hanson, O. H., Physical Properties of Light Hydrocarbons, Oil Gas J. 44, No. 10, 119-21 (1945)(C.A. 39, 3783^2(1945)).

216. Sorokin, A. F., The Toxicity and Explosion Hazards of Refinery Gases, Neft 4, No. 1, 23-4 (1933)(C.A. 29, 2713^8(1935)).

217. Spencer, Hugh M, Empirical Heat-Capacity Equations of Various Gases, J. Am. Chem. Soc. 67, 1859-60 (1945)(C.A. 40, 783^5(1946)).

218. Spencer, Hugh M. and Flannagan, Gordon M., Empirical Heat-Capacity Equations of Gases, J. Am. Chem. Soc. 64, 2511-13 (1942)(C.A. 37, 10^3(1943)).

219. Srikantiah, G. and Ramachandran, A., Temperature Measurements in Low Velocity High Temperature Gas Streams, J. Indian Inst. Sci. 37B, 41-57 (1955)(C.A. 49, 7297a (1945)).

220. Steacie, E. W. R. and Fockins, H. C., The Kinetics of the Decomposition Reactions of the Lower Paraffins. IV. The Role of Free Radicals in the Decomposition of Butane, Can. J. Research 17B, 105-20 (1939)(C.A. 33, 4855^9(1939)).

221. Stepukhovich, A. D., The Kinetics of the Stepwise Decomposition of Paraffin Hydrocarbons, Doklady Akad. Nauk. S.S.S.R. 92, 373-6 (1953)(C.A. 49, 5938g(1955)).

222. Stepukhovich, A. D., and Vorobeva, G. P. IV, Kinetics and Mechanism of Decomposition of Isobutane in the Presence of Isobutylene and Propylene as Inhibitors, Zhur. Fiz. Khim. 28, 1361-70 (1954)(C.A. 49, 7937b (1955)).

223. Stepukhovich, A. D. and Derevenskikh, Kinetics and Mechanism of the Decomposition of Hydrocarbons. II. Kinetics and Mechanisms of the Decomposition of Ethane at Low Pressures with Traces of Isobutylene, Zhar. Fiz. Khim. 28, 199-203 (1954)(C.A. 49, 5938b (1955)).

224. Stepukhovich, A. D. and Chaikin, A. M., Kinetics and Mechanism of the Decomposition of Hydrocarbons. III. Kinetics and Mechanism of the Decomposition of Butane at Low Pressure in the Presence of Isobutene and Proene as Inhibitors, Zhur. Fiz. Khim. 27, 1737-47 (1953) (C.A. 48, 12524h (1954)).

225. Stepukhovich, A. D., The Kinetics of the Stepwise Decomposition of Paraffin Hydrocarbons in the Presence of Inhibitors, Doklady Akad. Nauk. S.S.S.R. 89, 889-92 (1953)(C.A. 49, 5938h (1955)).

226. Stepukhovich, A. D., The Kinetics and the Mechanism of the Decomposition of Paraffin Hydrocarbons in the Presence of Inhibitors, Doklady Akad. Nauk. S.S.S.R. 90, 213-16 (1953)(C.A. 49, 5938i (1955)).

227. Stepukhovich, A. D. and Kats, G. I., Kinetics and Mechanism of Decomposition of Hydrocarbons. III. Kinetics and Mechanism of the Thermal Decomposition of Bivinyl at Low Pressures, Zhur. Fiz. Khim. 28, 1174-85 (1954)(C.A. 49, 7936h (1955)).

228. Stevens, F. W., Gaseous Explosive Reaction: Effect of Pressure on the Rate of Propagation of the Reaction Zone and on the Rate of Molecular Transformation, NACA R 372, 3-19 (1930)(C.A. 25, 2293^{8}(1931)).

229. Stevenson, D. P., The Strength of Carbon-Hydrogen and Carbon-Carbon Bonds, J. Chem. Phys. 10, 291-4 (1942) (C.A. 36, 3713 (1942)).

230. Stoughton, Roger W. and Samson, Paul D., The Relative Anesthetic Activity of the Butanes and Pentanes, J. Pharmacol 58, 74-8 (1936)(C.A. 31, 465^{9}(1937)).

231. Stubbs, F. J. and Hinshelwood, Cycil N., The Kinetics of the Thermal Decomposition of Normal Paraffin Hydrocarbons. I. The Inhibition of Chains and the Nature of the Residual Reaction, Proc. Roy. Soc. (London) A 200, 458-73 (1950)(C.A. 44, 7629c-h(1950)).

232. Stull, Daniel R., Heat Capacities of Hydrocarbon Gases Ind. Eng. Chem. 35, 1303-4 (1943)(C.A. 38, 677^{9}(1944)).

233. Sviridov, Yu. B., The Nature of Turbulent Combustion, Izvest. Akad. Nauk. S.S.S.R. Otdel. Tekh. Nauk. 1953, 1577-97 (C.A. 49, 7339g (1955)).

234. Tcherkezoff, N., Thermodynamic Properties of Hydrocarbons. II. The Application of Data in Numerical Examples, Rev. inst. frac. petrole et Ann. combustibles liquides 1, 50-8 (1946)(C.A. 42, 2825c(1948)).

235. Thacker, C. M.; Falkins, H. O.; and Miller, E. L., Free Energies of Formation of Gaseous Hydrocarbons and Related Substances, Ind. Eng. Chem. 33, 584-90 (1941)(C.A. 35, 3888^{2}(1941)).

236. Townsend, Donald T. A. and Mandlekar, M. R., The Influence of Pressure on the Spontaneous Ignition of Inflammable Gas-Air Mixture. I. Butane-Air Mixtures, Proc. Roy. Soc. (London) A 141, 484-93 (1933)(C.A. 27, 5189^{7}(1933)).

237. Trautz, Max, Probable Values of Cv for Water Vapor, Ammonia, Methane, and Higher Paraffins, Ann. Physik 9, 465-85 (1931)(C.A. 25, 4453^{5}(1931)).

238. Tropsch, Hans; Thomas, Charles L.; and Egloff, Gustav, Pressure Pyrolysis of Gaseous Paraffin Hydrocarbons, Ind. Eng. Chem. 28, 324-32 (1936)(C.A. 36, 3212^{9}(1936)).

239. Van Artsdalen, E. R., The Carbon-Carbon Bond Strengths in Ethane, Propane and n-Butane, J. Chem. Phys. 10, 653 (1942)(C.A. 36, 6849^{6}(1942)).

240. Vandaveer, F. E. and Segeler, C. George, Partial Combustion of Gas with a Deficiency of Air, Ind. Eng. Chem. 37, 816-20 (1945)(C.A. 39, 5069^{6}(1945)).

241. Vanpee, M., A Calorimetric Method for Measuring Reaction Rates in the Gas Phase, Bull. soc. chim. Belges. 62, 468-87 (1953)(in French)(C.A. 48, 4294i(1954)).

242. Varshni, Vatendra Pal, Relation Between Critical Temperature and Pressure of Normal Paraffins, J. Chem. Phys. 21, 1400 (1953)(C.A. 47, 1093i (1953)).

243. Varshni, Vatendra Pal and Srivastava, Surendra Nath, Additive Function of Critical Pressures, Science and Culture (India) 19, 308 (1953)(C.A. 48, 6763d(1954)).

244. Vichnievsky, B. Sak and Marcadet, J., Combustion Temperature and Gas Composition, Jet Propulsion 25, 105-18 (1955)(C.A. 49, 7224h (1955)).

245. Voevodskii, V. V., Empirical Equations for the Calculation of the Dissociation Energies of C-H and C-C bonds in the Molecules of Saturated Hydrocarbons and Free Aliphatic Radicals, Doklady Akad. Nauk. S.S.S.R. 79, 455-8 (1951)(C.A. 45, 9940b (1951)).

246. Wackher, Richard C.; Linn, Carl B. and Groose, Aristid V., Physical Properties of Butanes and Butenes, Ind. Eng. Chem. 37, 464-8 (1945)(C.A. 39, 2681^8(1945)).

247. Wiezerich, Peter J. and Frolish, Perk, Direct Oxidation of Saturated Hydrocarbons at High Pressures, Ind. Eng. Chem. 26, 267-76 (1934)(C.A. 28, 2249 (1934)).

248. Wohl, Kurt and Shore, Leon, Burning Velocity of Unconfined Turbulent Flames. Experiments with Butane-Air and Methane-Air Flames, Ind. Eng. Chem. 47, 828-34 (1955)(C.A. 49, 8581e (1955)).

249. York, Robert and Weber, Harold C., Isothermal Changes in Enthalpy for Some Gases, Ind. Eng. Chem. 32, 388-92 (1940)(C.A. 34, 2663 (1940)).

250. Zehnle, P., Utilization of Hydrocarbons for Production of Energy, Ann. combustible liquids 14, 25-91 (1939) (C.A. 33, 8451^3(1939)).

251. U.S. 2,049,239, Wilcox, Francis W. (Padhill-Wade Inc.) Apparatus for Dispersing and Metering Volatile Liquids Such as Butane or Propane (C.A. 30, 6243^9(1936)).

252. U.S. 2,287,125, Owen, John H. and Parker, Paul T. (Standard Oil Development Co.) Oxidation of Hydrocarbons of Low Molecular Weight in the Liquid State, with Use of a Catalyst (C.A. 37, 137^5(1943)).

253. U.S. 2,299,790, Bludworth, Joseph E. (Celanese Corp. of America) Vapor-Phase Oxidation of Hydrocarbons Such as in the Production of Various Products from Butane, Air and Steam (C.A. 37, 1721^3(1943)).

254. U.S. 2,492,985 Grosse, Aristid V. and Snyder, John C. (Houdry Process Corp.) Oxidation of Hydrocarbons (C.A. 44, 3002a (1950)).

255. U.S. 2,533,581, Harris, Charles R. (E. I. duPont de Nemours and Co.) Hydrogen Peroxide by the Partial Oxidation of Hydrocarbons (C.A. 45, 2640c (1951)).

256. U.S. 2,683,158, Brown, James W. and Burnside, Harvey E. W. (Standard Oil Development Co.) Hydrocarbons (C.A. 49, 594e (1955)).

257. U.S. 2,698,349, Bills, John L. (Union Oil Co. of Calif.) Acetylene Manufacture by the Partial Oxidation of Saturated Hydrocarbons in the Presence of Hydrogen (C.A. 49, 5728i (1955)).

258. U.S. 2,706,210, Harris, Ford W. (Wulff Process Co.) Conversion of Saturated Hydrocarbon Gases to Olefinic Hydrocarbons (C.A. 49, 9840h (1955)).

259. US. 2,706,740, Barusch; Maurida; Payne, Jack; and Neu, John T., (California Research Corp.) Unsaturated Hydrocarbons and Oxygen Compounds by Oxidation of Hydrocarbon Gases (C.A. 49, 9906i (1955)).

260. Brit. 597,029, Rust, Frederick F. and Vaughan, Wm., (Shell Development Co.) Controlled Oxidation of Paraffinic Hydrocarbons and Partially Halogenated Derivatives Therof (C.A. 42, 4602B (1948)).

261. Brit. 721,915, (Celanese Corp. of America) Oxidation of Aliphatic Hydrocarbons (C.A. 49, 7587e (1955)).

262. Japan 3847 ('54), Okada, Koe Chi and Miyamoto, Yoshimotsu, An Apparatus for a Continuous and Automatic Average Sampling of Gas (C.A. 49, 7899a(1955)).

263. "Physical Measurements in Gas Dynamics and Combustion" Vol. IX. Editors, R. N. Ledenburg, B. Lewis, R. N. Pease, H. B. Taylor.

264. Steacie, E. W. R., Atomic and Free Radical Reactions, The Kinetics of Gas-Phase Reactions Involving Atoms and Organic Radicals, Reinhold Publishing Corp., N.Y. p. 106 (1946).

265. "Combustion Processes," Vol. II. High Speed Aerodynamics and Jet Propulsion, Editors B. Lewis, R. N. Pease, and H. B. Taylor, Princeton University Press, Princeton N. J. (1956). Section E. Kinetics of Several Oxidation Reactions, R. N. Pease, p. 160.

266. Podbielniak Inc., Apparatus for Analysis by Vapor Phase Chromatography (Price List, Order Form, and Specifications-Podbielniak Chromanette Series 9495), A-17-D-857 (1956).

267. Johns, Theron, Beckman, Gas Chromatography Manual, Beckman Instruments Inc.

PROPOSITIONS

1. A negative temperature coefficient occurs in the partial oxidation of hydrocarbons (1, 2). It is proposed that the negative temperature coefficient can be explained on the basis of a change in the reaction mechanism with the temperature.

   The postulated mechanism in the low temperature region involves the fate of an energy-rich peroxide radical. The postulated reactions are:

   $$R\cdot + O_2 \longrightarrow RO_2$$

   $$RO_2\cdot + RH \longrightarrow R\cdot + ROOH$$

   As the temperature of reaction increases, the importance of the reaction attributed to the energy-rich peroxide radical decreases, perhaps as a result of the instability of the peroxide radical at elevated temperatures. It is postulated that as the temperature increases another free radical mechanism governs the reaction. The following equations are illustrative:

   $$RH + O_2 \longrightarrow R\cdot + HO_2$$

   $$R\cdot + O_2 \longrightarrow R' + HO_2$$

   $$R\cdot \longrightarrow R''\cdot + R'''$$

   It is postulated that the decrease in the peroxide reaction is not compensated by at least a proportional increase in the free radical reaction and a negative reaction temperature coefficient results for a short temperature region.

2. It is proposed that unfavorable thermodynamic equilibrium conditions may be controlling in many catalytic reactions. This may be indicated by calculating the thermodynamic equilibrium of all the individual reaction steps involving the catalyst at the reaction conditions. Such a prior calculation might prove to be an effective screening process for proposed new catalysts as well as indicating the governing factors in the catalytic reaction.

3. The flotation process for the concentration of minerals from their ores involves the attachment of the mineral particle to the bubble. Heretofore, a general explanation for this attachment has been provided by suggest-

ing that surface tension forces are responsible for the attachment. A more specific explanation for the attachment is found in "Micro-Dimensional Film Bonding". It has been observed that films less than 0.25 microns in thickness will exert a definite bonding force to any surface in contact with the film (3, 4). In addition, the strength of the bond is inversely proportional to the film thickness. It is proposed that the bond between the bubble and the particles is a manifestation of micro-dimensional film bonding.

Calculations indicate that a bubble with a wall thickness of 0.12 microns would have a bonding force of approximately 7.5 lb./sq. in. (4). Gaudin (5) indicates that the maximum size of galena particle that can be floated is 0.2 mm. diameter. To support the particle to the bubble, less than 10% of the particle surface needs to be in contact with the bubble surface.

Additional data to support the above proposition is found in the work of Evans (6) who measured the rupture thickness (film thickness at time of adhesion) of bubbles. He has reported rupture thickness of the order of 0.15 microns.

4. It is proposed that, when the response (peak areas) of the thermal conductivity cell are corrected for differences in thermal conductivity between components, the sample composition is more accurately represented on a weight percent basis. In order to represent the composition on a volume percent basis, an additional correction should be introduced for the difference in molecular weights.

5. It is proposed that batch liquid phase processes such as mixed acid nitrations with high exothermic heats of reaction and rapid reaction rates be conducted in a "pipeline" reactor. The reaction mixture could be pumped through the reactor at a sufficiently rapid flowrate to provide sufficient heat transfer surface per unit reaction to permit good control of the reaction temperature while maintaining high reaction rates.

6. It is proposed that the use of an ammonium chloride catalyst for the condensation reaction of aniline to diphenylamine should result in a greater product yield than using an aluminum chloride or ferric chloride catalyst. It is considered that both aluminum chloride and ferric chloride catalysts are more versatile and would thus catalyze more side reactionsthan ammonium chloride.

7. It is proposed that in attempting to correlate data by means of a least squares fit of an assumed equation to the data, it might be desirable to divide the data into smaller groups with respect to the predominant variable.. This would simplify the form of equation required for the correlation of data in each group and thus permit a better preliminary correlation of data.

8. It is suggested that a program be written for the Datatron for the correlation of kinetics data which would be of general applicability in the determination of reaction orders. If the program were sufficiently general, it could provide the basis for correlating the data for a wide variety of reactions.

9. It is proposed for nitration processes using mixed acids, nitric and sulfuric, a more economical process might be obtained by combining the absorption of nitrogen dioxide gases obtained from an ammonia oxidation unit directly with a column reactor.

10. It is proposed that terrestrial time does not always provide an adequate basis for considerations in the field of astronautics and that in its place a time base related to the system under consideration be used.

References

1. Cullis, C. F. and Hinshelwood, C. N., Labile Molecules in the Kinetics of Hydrocarbon Reaction Part III. Low Temperature Oxidation of Higher Paraffins in Relation to Structure, Discussions Faraday Soc. 1947, No. 2, 117-28 (C.A. 43, 5269e (1949)).

2. Knox, J. H. and Norrish, R. G. W., Cool Flame Phenomenon in the Oxidation of Ethane, Trans. Faraday Soc. 50, 928-33 (1954)(C.A. 49, 4386a (1955)).

3. Byrne, Joseph "Bonding Properties of Micro-Dimensional Films" Sc.D. Thesis, Chem. Eng. Dept. M.I.T. (1950).

4. Kalvinskas, John "Micro-Dimensional Film Bonding in Liquids" S.M. Thesis, Chem. Eng. Dept. M.I.T. (1952).

5. Gaudin, A. M. "Flotation" McGraw-Hill Book Co., Inc. New York, 1932.

6. Evans, L. F. "Bubble-Mineral Attachment in Flotation" Ind. Eng. Chem. 46, 2420-24 (1954).