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**A PRELIMINARY INVESTIGATION OF NATURAL GAS COMBUSTION
AS APPLIED TO THERMAL RECOVERY OF PETROLEUM**

BY

ROGER J. SCHOEPEL

A

THESIS

**submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the**

Degree of

MASTER OF SCIENCE IN MINING ENGINEERING

PETROLEUM ENGINEERING OPTION

Rolla, Missouri

January, 1959

Approved _____

J. P. Givier
Advisor

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CONTENTS

	Page
Acknowledgment	ii
List of figures.	iv
List of tables	v
Abstract	vi
Purpose.	1
Introduction	1
Preliminary investigation.	3
Review of literature	6
[*] Flameless oxidation	7
Ignition temperature, induction period, and explosive limits	8
Chemical kinetics.	10
Chemical reactions.	10
Reaction equations in flow system	13
First-order reaction equations.	14
Second-order reaction equations	15
Experimental apparatus and procedure	18
Low pressure apparatus and procedure.	19
High pressure apparatus and procedure	23
Experimental results	26
Discussion of results.	35
Oxidation temperature	35
Preliminary kinetic application	38
Example calculations.	43
Qualitative interpretation.	44
Conclusions.	45
Appendix	49
Bibliography	51
Vita	53

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Schematic diagram of low pressure apparatus	20
2	Photograph of low pressure apparatus.	21
3	Temperature profile of low pressure apparatus	22
4	Schematic diagram of high pressure apparatus.	24
5	Effect of pressure in reduction of ignition temperature	30
6	Variation in oxygen content of effluent gases with tem- perature.	31
7	Results of high pressure hydrocarbon oxidation in porous medium.	32
8	Graph showing variation in calculated pseudo-reaction rate constant	41

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Experimental data obtained from linear-low pressure apparatus	27
II	Experimental data obtained from radial-high pressure experiments	28
III	Experimental data showing effect of flow rate on combustion of 8.6% O ₂ /32.6% N ₂ /58.8% natural gas mixture .	34
IV	Calculated reaction rate constants based on pseudo-order rate equations 8, 10, 13, and 15.	40

ABSTRACT

Present application of the subsurface combustion processes in the thermal recovery of petroleum afford favorable and opportune methods of providing greater recoveries from petroleum reservoirs. This study attempts to elucidate some of the parameters controlling the complex hydrocarbon oxidation for one such process. The experimental phase consisted of investigating the combustion behavior of eight nonexplosive and one explosive natural gas-air mixtures at low and intermediate pressures. The hydrocarbon was allowed to oxidize by self-ignition under controlled conditions within environments precluding a visible flame type reaction. Progress of the reaction was followed by measuring effluent oxygen content.

Experimental evidence indicate the combustion reactions were inhibited by packing and varying degrees of reaction completion could be obtained through variation of controlling parameters. Effects of increasing reactor pressure permitted a lower oxidation temperature. Initial oxidation temperatures were found to vary from 950 °F at atmospheric pressure to approximately 470 °F at 27.65 atmospheres absolute pressure.

Although data obtained experimentally are not sufficient to permit a rigorous interpretation, nevertheless a qualitative interpretation of parameters controlling natural gas combustion in a porous flow system has been presented.

PURPOSE

The purpose of this thesis was to analyze, through laboratory experiments, some of the more obvious parameters controlling natural gas combustion within a porous medium. As a practical aim, this study intended to roughly define the temperature necessary to initiate and propagate a subsurface combustion wave through a petroleum reservoir. Because of the experimental fuel selected, the study pertains directly to the patented Sinclair "heatwave" process (1)* used to increase the recovery of crude oil from natural reservoirs.

INTRODUCTION

Since the discovery in 1859 of the Drake well in Western Pennsylvania, the total United States production of crude oil to January 1, 1958, has been estimated by the Interstate Oil Compact Commission's Secondary Recovery and Pressure Maintenance Committee (2) to be approximately 57.8 billion barrels. Estimation of original content of reservoirs totaled 309.9 billion barrels of oil which 43.1 billion barrels were considered as still economically producible by existing primary and secondary production techniques. Based on these estimates, the ultimate recovery of crude oil will total 100.9 billion barrels or only 32.6 per cent of the original oil in place. Although this percentage recovery is much less than that obtained by certain other mineral industries, it represents a great improvement over the recovery that was obtained from oil fields a few decades ago. (3)

The application of thermal processes to oil field secondary recov-

* Numbers in parentheses indicate references in bibliography.

ery methods attempts to better the approximate one-third recovery estimated ultimately; however, engineering analyses of laboratory, pilot plant, and field trial data have been unable to determine the feasibility of combustion processes under varying reservoir conditions. Some thermal techniques appear to be particularly adaptable to petroleum reservoirs which contain a high viscosity oil and do not respond favorably to ordinary flooding with water. The primary idea in thermal recovery by this procedure is to increase productivity and recovery through effective utilization of heat in reducing oil viscosity and thus decreasing resistance to flow. The general thermal processes which have received considerable attention during the last few decades are as follows:

1. Electrical bottom hole heating.
2. Hot water injection.
3. Steam injection.
4. Hot flue gas injection.
5. Subsurface combustion.

Various combinations of these processes are possible. Two different subsurface combustion techniques have performed satisfactorily in pilot and field trials. Basically they are:

1. Subsurface combustion of residual-high molecular weight-hydrocarbon fuels in situ supported by continuous air injection. (4)
2. Subsurface combustion of injected-low molecular weight-hydrocarbon fuels supported by simultaneous air injection. (5)

An excellent comparison of the differences in the two processes has been presented by Breston. (6)

PRELIMINARY INVESTIGATION

A rapidly developing and promising method for increasing the recovery of crude oil from petroleum reservoirs utilizes a unique technique of applying heat to the subsurface formation. The method incorporates a slow exothermic hydrocarbon oxidation, either gaseous, liquid, or solid, which provides the necessary energy to increase petroleum recovery. The method is applied by introduction of a subsurface combustion zone in the three stage sequence: lighting, transferring, and propagating.

The initiation of a combustion process may be visualized by the following model: Four "producing" wells are drilled through a productive horizon, on any square pattern, with a fifth "injection" well being centrally located. The first or lighting stage is performed by maintaining a fire, through the use of a specially designed burner, opposite the injection well sand face with the hot combustion gases being carried off radially to the producing wells. The temperature of the formation in the immediate vicinity of the injection well bore subsequently increases through heat transfer by conduction, convection, radiation, and latent heat effects. When the formation temperature is sufficient to support combustion and the first stage complete, the injected gas is converted to pure air which ignites with carbonaceous residue material and proceeds to burn away from the well bore. The injected air picks up sensible heat in passing radially from the well bore thus cooling the burned-out formation behind a zone of combustion. This heat is transferred to cooler portions of the reservoir ahead of the combustion front by the migrating fluids. In this manner a combustion wave may be created moving radially through a formation leaving in its wake dry-

clean sand void of hydrocarbons or water.

The final stage in propagating the combustion zone through the reservoir may be performed by injecting gaseous hydrocarbon in air mixtures where the injected hydrocarbon, in conjunction with a residual material, provides the necessary fuel to sustain the formation temperature and thus insure continued combustion. Contained reservoir fluids in the immediate vicinity of the advancing thermal wave, which are not removed by the sweeping gas drive or a condensing hot water drive, are gradually reduced to a "coked" carbonaceous residue which remains on the sand grains due to distillation and pyrolysis of the crude oil originally present ahead of the combustion front. Subsequent oxidation of this residue depends upon the relative oxidation temperatures of the two fuels, their proportions present, the combustion zone temperature, and the presence of free oxygen.

Determination of the minimum temperature at which the injected gas initially reacts and the rate of reaction at other temperature levels is basic to understanding the propagation mechanisms which make the process possible. This situation is complicated by the possibility of quenching environments and by individual reaction mechanisms if a multi-component natural gas fuel is injected.

Another point of interest is the degree of oxygen conversion obtained as coinjected air traverses the combustion zone. If complete oxygen utilization is not realized, free oxygen will appear in the effluent gases provided it is not adsorbed physically or removed by chemisorption. Thus large concentrations of effluent oxygen, relative to injected nitrogen (in air), indicate either an insufficient quantity of fuel or a temperature below that necessary for effective burning.

Measuring exhaust gas composition in the produced fluids affords the only practical method of determining if the field applied underground fire is being propagated through effective heat release. The degree of oxygen utilization, in addition, gives some idea of reaction completeness.

An alternate method of determining if the combustion zone is sustained is by drilling observation wells in the path of the approaching heat wave. This procedure becomes quite expensive and must be repeated at different stages of propagation; therefore, the former procedure of analyzing produced gases is generally preferred even though the results are less quantitative than actual data obtained from drilled wells.

Gaseous reactions occurring in thermal recovery by combustion are influenced by a large number of variables, the more obvious of which are as follows: reaction vessel or chamber dimensions, catalytic surface and gas phase effects, physical and chemical adsorption, gas phase and surface reactions, pressure, temperature, degree of preheating, time in residence (space velocity), flux, fuel type and concentration, quenching, moisture content, energy of activation, burning velocity, presence of combustion products and inert gases, heats of combustion, ignition lag, and oxidation mechanisms. Many of these variables appear to be relatively unimportant to the basic process under study here while others are probably interdependent so that the overall effects are quite complex.

In recognition of the numerous parameters involved in analyzing combustion propagation mechanisms, this investigation was designed to study the effect of temperature in governing oxidation of "rich" (fuel content greater than stoichiometric proportions) samples of natural gas

in air when burned within a porous medium. Because of complexities involved in the reaction, this investigation is limited to analysis of the combustion behavior under different conditions of temperature, fuel/air ratio, pressure, and length of time within an atmosphere permitting reaction. The experimental approach utilizes natural gas, in the presence of air, flowing continuously through a dry simulated porous medium maintained at various temperature levels.

Effluent oxygen was selected as the "tag" constituent in following the oxidation reaction as all other components taking place in the reaction, for example in field combustion tests, are difficult to analyze in addition to being susceptible to dilution by natural gases common to the reservoir. This method, while controversial, is indicative of the conditions where utilization of free oxygen commences and ceases. In addition, it should lend some idea as to reaction completeness. Burke, Fryling, and Schumann, (7) using a similar approach in analyzing propane combustion at pressures up to 100 atmospheres, obtained excellent mathematical and experimental agreement. For a more complete investigation, the combustion mechanisms and stoichiometry of each simultaneous or consecutive reaction must be determined independently.

REVIEW OF LITERATURE

Use of thermal application to oil recovery dates from a patented process in 1923. (8) Combustion type experiments were first attempted by Russian technologists in 1933. (9) Conclusions from these experiments show that combustion can be maintained in the form of an advancing heat zone by continued air injection and that coinjection of a liquid crude oil restricted the burning to the vicinity of the well bore.

Revived interest in the subsurface combustion process is represented in recent literature by experimental studies such as by Kuhn and Koch, (4) Grant and Szasz, (5) Martin, Alexander, and Dew, (10) and Wilson and co-workers. (11) Varied concepts of combustion techniques are presented which agree favorably in observed thermodynamic and hydrodynamic mechanisms regarding propagation of a subsurface combustion wave.

Flameless Oxidation

Interpretation of theoretical and experimental analyses of combustion phenomena in thermal recovery processes indicate the oxidation reaction involved to be one of flameless nature. (12) This concept is based on the observation that the pore geometry and dimensions normally encountered in reservoir rock are of insufficient magnitude for visible chain reaction type combustion and that, therefore, flame quenching results. Such would be the case for oxidation of both flammable and nonflammable hydrocarbon-air combinations. Based on this interpretation, flammability or limits of explosivity appear significant only in instances where combustion occurs in a reaction chamber in which chain breaking actions at the chamber walls play a minor role.

The literature studied is practically devoid of experimental evidence of hydrocarbon oxidation under quenching environments. Jost (13) has described the minimum tube diameter for suppressing methane in air reactions as being of the order of magnitude of 1 mm, below which a flame does not propagate at all. This value apparently decreases as the temperature difference between tube wall and ignition temperature decreases.

Ignition Temperature, Induction Period, and Explosive Limits

Generally, the temperature where combustion is first detectable and proceeds with rapid oxidation is defined as the reaction ignition temperature. The necessary and sufficient condition for ignition to occur is that the rate of heat generation is at least equal to the rate of heat loss.

Variations in reported ignition temperature of natural gas, or methane, are quite numerous. This discrepancy in experimentally determined ignition temperature stems from significant differences in experimental procedure used by a particular investigator, (13) the main difference being the manner in which the ignition source is brought in contact with the flammable gas. In nearly all cases, the reaction chamber was large in comparison with exposed surface area.

The predominant method found for measuring ignition temperature of flammable mixtures followed pressure changes in a "batch" type reactor in which the volume is constant. By noting pressure changes after exposure to the ignition source, repeated at consecutive increasing or decreasing temperature levels with various ignition devices, the temperature is found which barely permits the pressure to rise rapidly, indicating ignition. Initiating reactions, particularly among hydrocarbons, are frequently preceded by an induction period between exposure to the excitation source and subsequent rapid pressure rise. (13) Delays of up to a few minutes have been observed before the reaction proceeds with any rapidity. Methane oxidation, which is inhibited by packing the reaction vessel, is reported to have such an induction period. (13)(14)(15)

Upper and lower explosive limits for natural gas combustion in air are given as approximately 15 per cent and 4 per cent of the combustible, respectively, at atmospheric pressure. (16) An increase in pressure produces an increasing difference between the limiting concentrations, with the predominant change occurring in the upper limit. (17) Minimum ignition temperature for explosive mixtures of the primary natural gas components, in air and observed with various experimental procedures, are listed by Lewis (18) as:

<u>Component</u>	<u>Minimum Ignition Temperature, °F</u>
Methane	1168
Ethane	880
Propane	918
Butane	767
Pentane	552

The oxidation reaction of methane and other low molecular weight paraffinic hydrocarbons has been found to take place at lower temperatures than the decomposition or "cracking" reactions of these hydrocarbons; however, some of the combustion products, such as water, carbon dioxide, carbon monoxide, alcohols, aldehydes, etc., are partly due to such decomposition reactions assisted by the oxidation mechanisms. (19) As seen by the above listing, ignition temperatures of the less volatile paraffin hydrocarbons lie at lower values than that of methane, the temperature generally decreasing as the number of carbon atoms increase. Unsaturated hydrocarbons are known to have lower ignition temperatures than their paraffin counterpart.

CHEMICAL KINETICS

One of the objectives of reaction kinetic studies is to determine relationships which characterize a particular reaction without attempting to describe the mechanism by which the reaction occurs. The analysis here is primarily concerned with this objective in order to provide a clearer understanding of natural gas combustion occurring within petroleum reservoirs. Before proceeding with the basic development of chemical kinetic equations to be used in this study, it should be mentioned that ordinarily-in work of this nature-the final equations are applied irrespective of the basic derivation. This type of analysis attempts to find the theoretical relation which best describes the experimental data.*

A limited number of elementary chemical reactions are found to follow simple quantitative relationships based on the concentration of reactants remaining at any time during the reaction. Complex chemical reactions, such as hydrocarbon combustion where consecutive and side reactions are frequently observed, cannot be expected to obey these laws and only approximations are possible through their use.

Chemical Reactions

Chemical reactions are classified kinetically by either 1) molecularity, such as bimolecular, where the minimum number of combining molecules is indicated, or 2) the order of reaction, where the concentration of the reacting molecules limits the reaction velocity of the chemical transformation. This distinction is frequently necessary as

* The examples of Chapter VI in Smith's book *Chemical Engineering Kinetics* (reference 26) are primarily devoted to this procedure.

the two are identical only in the simplest cases.

Reactions involving a number of reactants may be expressed in the stoichiometric form



where a moles of reactant A combine with b moles of reactant B and c moles of reactant C . The kinetic expression relating the unreacted concentration C_A of A in terms of the reactants and time t is

$$r = -\frac{dC_A}{dt} = k C_A^a C_B^b C_C^c \quad \text{Equation 2}$$

where r and k represent the rate of reaction and the reaction rate constant, respectively. Reaction rate constants are temperature sensitive and therefore subject to Arrhenius's equation. The summation $a + b + c$ determines the true order of reaction; however, the order of a reaction cannot ordinarily be predicted from the stoichiometric proportions and must be obtained by experiment. The values a , b , and c , therefore, may just as well be other unknown values m , n , and p .

Application of kinetic theory to natural gas combustion is complicated because of the multi-component reactants and products involved. Norrish (20) has aptly summarized the situation:

"It is not legitimate to compare the rates of oxidation of hydrocarbons by pressure changes in view of the great variability of end products. The only certain way is to measure the rate of disappearance of hydrocarbon by analytic technique. This has not yet been done."

An attempt to resolve the problem of describing combustion reactions by approximate methods using a limiting reactant, in this case oxygen, offers a measure of reaction completion and a means of approximating the rate of reaction for specific test conditions. The approach follows a procedure devised by Ostwald (21) and involves the following considerations: Equation 2 is rewritten in terms of pseudo- (22) or apparent-velocity constants

$$r = -dC_A/dt = (k_A C_A^m)(k_B k_C)(C_B^n C_C^p) \quad \text{Equation 3}$$

where k_A is the pseudo-reaction constant common to A and m is the pseudo-order of reaction, also with respect to component A , etc.. Variations in the total value of the multiplied terms

$$(k_B k_C)(C_B^n C_C^p) \quad \text{Equation 4}$$

will be considered negligible as a first approximation. This situation is nearly correct if reactants B and C are in sufficient excess. The approximation should also hold if A utilization is large in relation to the utilization of other reactants so that the variation in concentration of B and C during the reaction is approximately constant. Simplification of an otherwise complex reaction equation into such an expression relating the rate of reaction to the limiting reactant can only be rigorously attested after verification by experiment.

Experimental analysis applying equation 3, based on the decrease in concentration of one reactant C_A , may result in an overall pseudo-reaction rate constant k' if the term shown as equation 4 remains

reasonably constant. In this case, the k' value obtained would include concentration effects of other reactants that apparently are of minor consequence in the overall reaction. The net result of these considerations is shown by the reduced reaction equation

$$r = -\frac{dC_A}{dt} = k' C_1^m \quad \text{Equation 5}$$

where:

$$k' = k_A (k_B k_C) \left(\frac{C_B^n}{C_B} \frac{C_C^p}{C_C} \right)$$

Reaction Equations in Flow System

Chemical kinetic equations for homogeneous first- and second-order irreversible gaseous reactions occurring under flow conditions at constant pressure and temperature have been developed by Hougen and Watson. (22) Their derivation was obtained by applying a general rate equation to the concentration of unconverted reactant. A similar approach, designed to show the relation between "batch" and "flow" type systems, is append d. The expressions derived by Hougen and Watson have been reduced to a simplified form by use of the following notation:

x = moles reactant utilized per mole feed.

y = moles reactant remaining in effluent per mole effluent.

y_i = moles reactant injected per mole feed.

k_1 = reaction rate constant for first-order reaction.

k_2 = reaction rate constant for second-order reaction.

F = feed rate, total moles injected per unit time.

P = total pressure of system.

V = volume of reactor occupied by reacting fluids.

First-Order Reaction Equations

First-order reactions, of the above type, may be represented by unimolecular chemical disintegrations as



where one molecule of reactant dissociates to form n molecules of product. Resulting kinetic expressions must account for reactant dilution during the process being dependent on the molecules of product formed. The variable n may be either integral or fractional, but cannot be zero, in agreement with the law of conservation of matter.

The simplest approach relating first-order reaction variables is by considering one molecule of product formation from the unimolecular reaction:



Here, the rate of product formation is identical to that of reactant consumption and the kinetic equation resulting from simplification of the Hougen and Watson expression is, as shown in the appendix,

$$k_1 = (F/V) \left[\ln (y_1/y) \right] \quad \text{Equation 8}$$

where symbols are as previously defined. The variable F/V , when multiplied by the standard molar volume, is frequently termed "space velocity" having dimensions of time^{-1} . The reciprocal expression represents the period reacting fluids are contained within the reactor and

is termed "residence time." Unit residence time indicates that the volume rate of flow numerically equals the reactor volume.

The influence of residence time in equation 8 may be seen by considering a specific reaction wherein a certain flow rate (F times normal molar volume) limits the extent of reaction, variables other than y remaining constant. A decrease in flow rate then permits an increasing time of residence, allowing the reaction to proceed further toward completion. On the other hand, an increase in flow rate decreases residence time, further restricting the reaction.

The next simplest approach relating variables of first-order reactions is by considering the reaction:



Equation 9

Here, the products form at a rate equal to twice that of reactant conversion. This means that, for a specific injected flow rate, the effluent flow rate will have increased in proportion to the reactant consumed. The simplified kinetic equation expressing the reaction velocity in terms of the variables used in equation 8 is:

$$k_1 = (F/VP) \left[(y_1 + y)/(1 + y) + (1 + y_1) \ln (y_1 y + y_1)/(y_1 y + y) \right]$$

Equation 10

Second-Order Reaction Equations

Second-order reactions differ from first-order by their second power dependence on chemical concentration. The general bimolecular chemical formula



demands that two molecules of reactant form n molecules of product upon reaction. The simplest kinetic expression for this type reaction is when two molecules of product are formed by the reaction:



The kinetics are then represented by the simplified formula

$$k_2 = (F/VP^2) \left[(y_i - y)/y_i y \right] \quad \text{Equation 13}$$

Another second-order rate expression is obtained when only one molecule of product forms as indicated by:



The relationship between the variables defining the flow system may then be expressed by:

$$k_2 = (F/VP^2) \left[(y_i - y)/(4 - 4y) + (1 - y_i/2)^2 (y_i - y)/(y_i y - yy_i^2) \right. \\ \left. + (1 - y_i/2)(y_i - y_i y)/(y - y_i y) \right] \quad \text{Equation 15}$$

Analysis of laboratory data obtained from flow reactors where concentration of only one reactant is followed may be seen to depend on

measurement of composition as a function of feed rate for a constant volume reactor operated under constant pressure, temperature, and inlet concentration. The value of k calculated, when only the flow rate is varied, will remain constant if the actual chemical reaction agrees with the assumed conditions forming the basis of calculation. Calculated values of k are often difficult to interpret because of the scattered and erratic data which are typical of kinetic measurements. Continually increasing or decreasing values of k indicate the reaction does not follow the assumed rate equation. A scattering of calculated values, about a specific k level, indicate inadequate experimental techniques.

EXPERIMENTAL APPARATUS AND PROCEDURE

Two different but similar procedures were used in performing the experimental analysis. This involved 1) determining the effects of concentration, flow rate, and temperature on natural gas combustion within a simulated porous medium, and 2) a similar study of concentration and temperature variation at a higher pressure. The two investigations were conducted with the aid of devised linear and radial flow systems, respectively, for varying compositions of natural gas in air.

In all experiments the composition of refined commercial grade natural gas was :

<u>Component</u>	<u>Volume Per Cent</u>
Methane	91.4
Ethane	4.2
Propane	1.7
Butenes	0.3
Butanes	0.8
Pentenes	0.1
Pentanes	0.5
Nitrogen	0.2
Carbon dioxide	<u>0.8</u>
	100.0

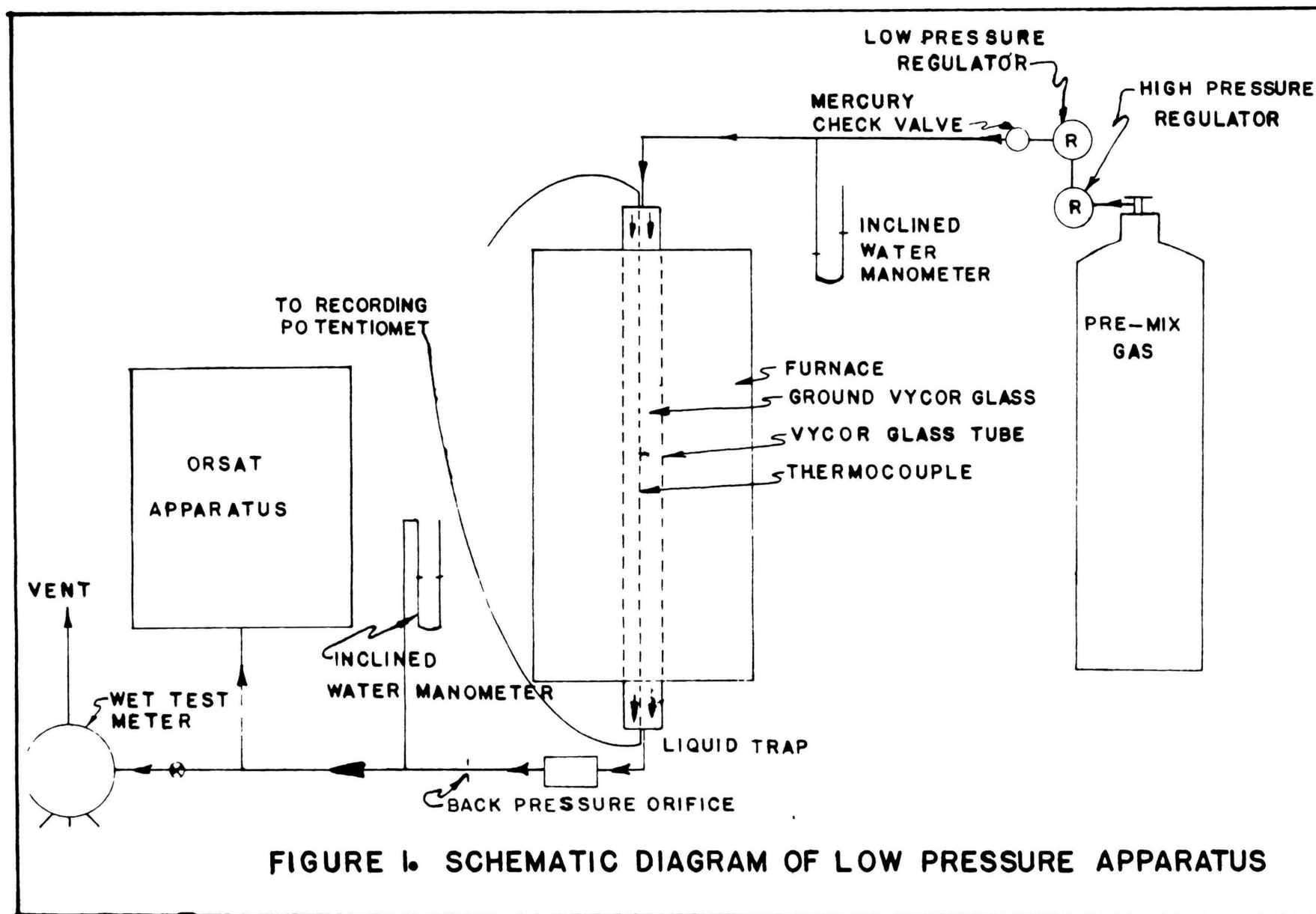
The purity is as specified from the supplier, Phillips Petroleum Company. No further purification was attempted. Varying proportions of natural gas in air were mixed to form the sample gas. These sample concentrations, as well as experimental gas analyses, were obtained with an Orsat Gas Analyzer.

Low Pressure Apparatus and Procedure

The primary element of the low pressure apparatus consisted of an externally heated 25 mm ID x 750 mm "vycor" glass tube packed with ground vycor glass of U.S. standard mesh 20-70 screen size. Initial attempts to use well sorted glass beads for the synthetic medium were unsuccessful because of their low melting point. Finest quality (Berkeley No. 1-dry, 99.9% SiO_2) natural sand proved unadaptable to experimentation because of polymorphic inversion of quartz near 1050 °F. Ottawa sand was unsatisfactory for the same reason. The substitute for native material was manufactured from waste vycor tubing which was ground to the desired size.

Equipment supplementing the primary element is as shown in the schematic drawing of figure 1 and the photograph of figure 2. The essential instruments and devices are a gas container and pressure regulating valve, combustion furnace, continuous recording potentiometer, gas analyzer, and wet test flow meter. Inclined manometers, exaggerating the reading by a factor of ten, aided in calibrating flow at extremely low feed rates. A chromel-alumel thermocouple, located in the center of the packed tube at the midpoint of the temperature profile of figure 2, provided continuous temperature recordings with time. The accuracy of the flow meter was ascertained by calibration with a Bureau of Standards one-tenth cubic foot bottle and the potentiometer was found to read accurately at room temperature and 212 °F.

The exploratory investigation indicated oxygen content in effluent products to be highly sensitive to variation in flow rate, other conditions held constant. Experimental procedure used in evaluating this effect was as follows: The furnace temperature, controlled by a vari-



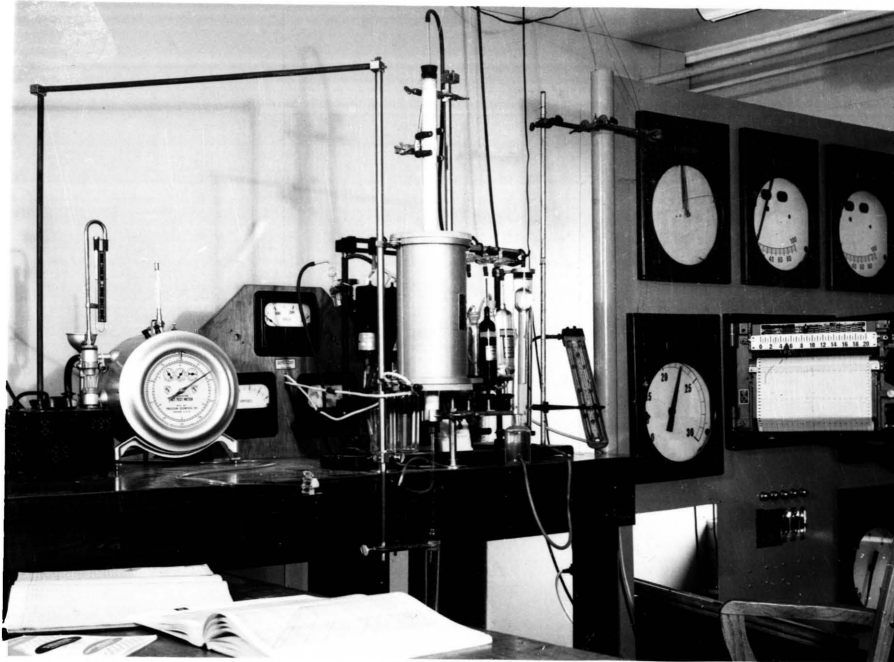


Figure 2

Photograph of Low Pressure Apparatus

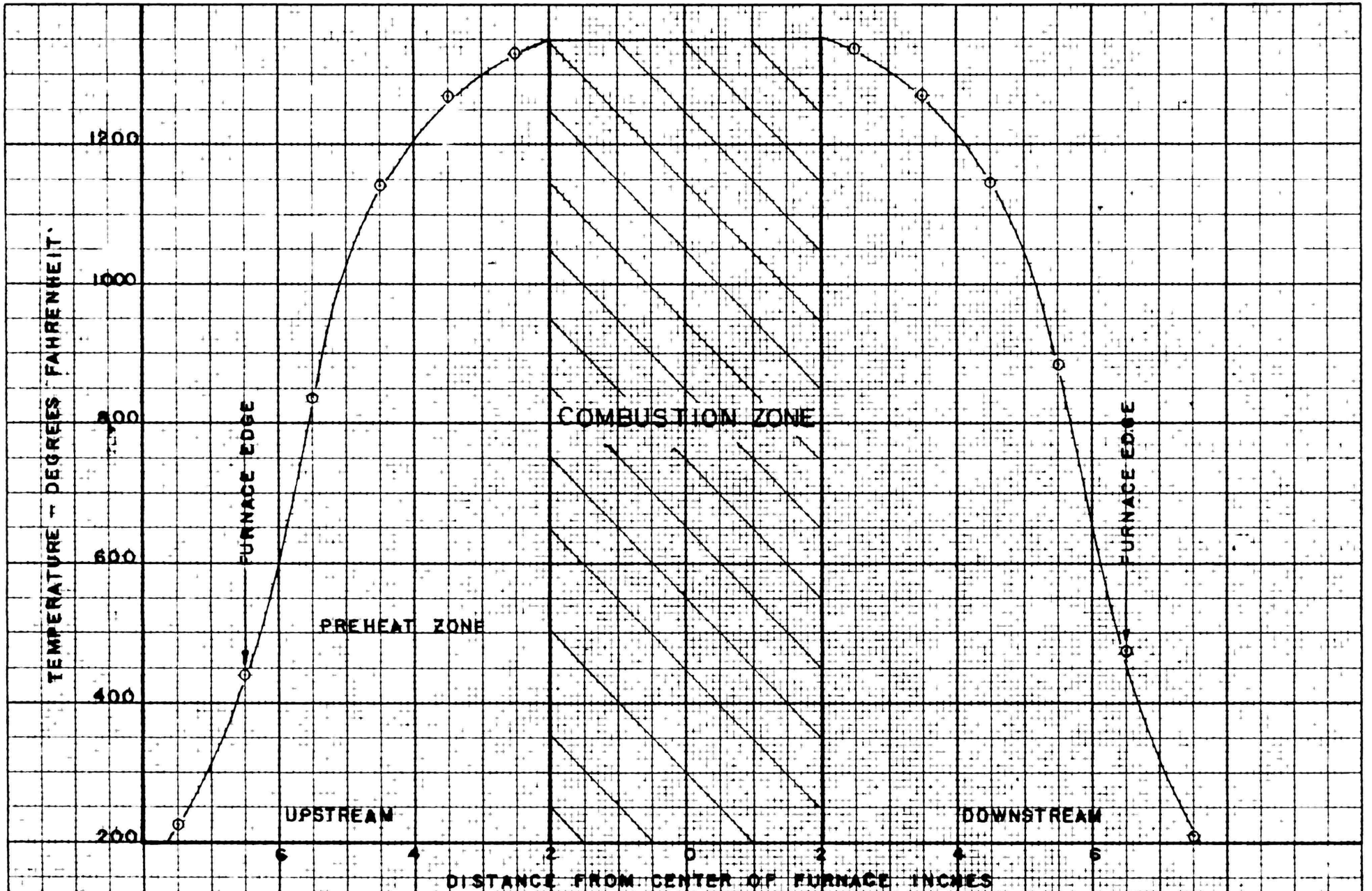


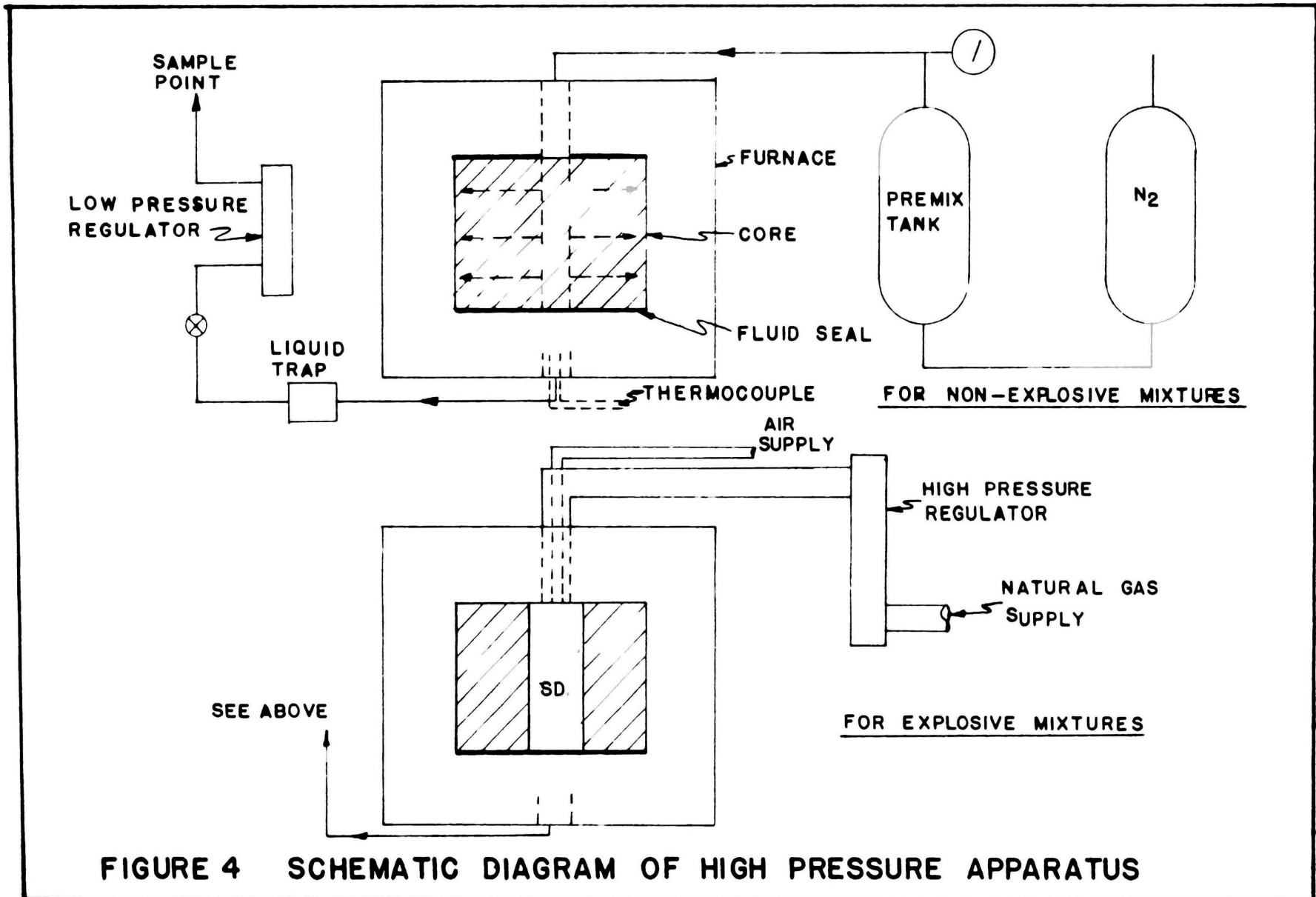
FIGURE 3 TEMPERATURE PROFILE OF LOW PRESSURE APPARATUS

able power supply, was allowed to reach a specific temperature where combustion occurred. The exhaust flow rate, of a specific sample gas, was adjusted by a stepwise procedure through a range of values allowing sufficient time for oxidation to barely proceed, on one extreme, to near complete oxygen utilization on the other. Measurements of effluent carbon dioxide and oxygen contents were made at each step while keeping the flow rate and temperature constant. Free oxygen remaining in the exhaust gases indicated the degree of reaction progression. Variations in power supply voltage and sensitivity of the apparatus to drafts, etc., caused the reactor temperature to fluctuate slightly so that the investigation was conducted within a narrow temperature range rather than at a specific temperature.

The second phase of the low pressure investigation concerned the effect of temperature on combustion of different natural gas concentrations. The analyses were made by maintaining a near constant exhaust flow while measuring the effluence concentration at various temperature levels. An arbitrarily selected flow range of 16.5 to 17.5 cc/min was maintained because of flux sensitivity. This was near the practical lower limit of measurement with the particular apparatus used.

High Pressure Apparatus and Procedure (23)(24)

Experimental apparatus used in the high pressure investigation is shown in schematic form of figure 4. The reaction system consisted of a furnace which applied external heat to a 3 inch OD x 4 inch "Bartlesville" sandstone core contained within a thick walled steel pressure "bomb." The bomb was fabricated to contain the core in a manner allowing injected gas to pass radially from a small hole drilled in the core



center. Copper end gaskets were used to effect the pressure seal on the core ends. A special temperature resistant compound was used to facilitate the bomb pressure sealing at elevated temperatures.

Supplementary equipment differed slightly depending on whether non-explosive or explosive gas samples were being investigated. Nonexplosive mixtures were premixed and forced through the system by a high pressure nitrogen supply using water to displace the experimental gas. Because of flashback possibilities, in mixing explosive gas, the alternate procedure consisted of mixing natural gas and air prior to entering the reactor.

The experiments were conducted at an arbitrarily selected pressure of 400 psig which was controlled by regulating the upstream pressure on the reactor. A preselected flow rate of 1000 cc/min was maintained relatively constant through manipulation of a back-pressure valve. Differential pressures across the reactor were negligible.

Reactor temperatures were measured by a chromel-alumel thermocouple located within the pressure bomb in the zone immediately downstream from the point at which effluent gases leave the core. Electric potentials were measured with a portable potentiometer and converted to temperatures by available conversion charts.

Experimental procedure consisted of passing a specific natural gas/air sample to be investigated through the reactor at a constant rate while continually decreasing the temperature and following the reaction by oxygen analyses as previously explained. The technique used involved decreasing the reactor temperature from a level above complete oxygen utilization to the point of initial oxidation. Possible hysteresis effects, resulting from measurements while increasing reactor temper-

ature, were not considered. Orsat analysis of produced gases provided carbon dioxide, oxygen, and carbon monoxide contents.

EXPERIMENTAL RESULTS

Numerical results obtained from the experimental investigation represent 1) effluent oxygen and carbon dioxide analyses as a function of temperature for four natural gas/air ratios in the low pressure experiments, 2) effluent oxygen, carbon dioxide, and carbon monoxide analyses as functions of temperature for five gas-air combinations in the high pressure experiments, and 3) effluent oxygen and carbon dioxide analyses as a function of flow rate for one of the low pressure concentrations. Results of gas analysis for components other than oxygen are included to show the relative occurrence of the more easily measurable components of combustion. Carbon dioxide concentrations given are exclusive of initial amounts common to the natural gas used.

The four sample gases studied in the low pressure experiments, as described by their initial volumetric analysis for oxygen, are: 8.6% O_2 ; 11.6% O_2 ; 13.6% O_2 ; 16.3% O_2 . These concentrations are readily transferred to another basis by considering air as 20.9% oxygen. Thus the 8.6% oxygen mixture contains $0.086 \times 100/0.209$ or approximately 41.1% air. The remaining amount, 58.9%, is the initial natural gas concentration.

Results obtained in the low pressure investigation are presented in tabular form by table I. A graphical representation of recorded effluent oxygen content, as a function of temperature, is shown by figure 6. Table II and figure 7 contain similar data obtained for the high pressure investigation. Initial concentrations for the five

TABLE I

Experimental Data Obtained From Linear-Low Pressure Apparatus

<u>Input, % Oxygen</u>	<u>Temp, °F</u>	<u>Flow Rate, cc/min</u>	<u>Effluent Analysis</u>	
			<u>% Oxygen</u>	<u>% Carbon Dioxide</u>
8.6	943	17.3	8.5	none
	1072	16.5	7.5	0.1
	1136	17.0	7.2	0.2
	1168	16.5	6.5	0.3
	1174	16.8	6.0	0.7
	1173	17.4	5.9	1.1
	1183	16.7	5.9	0.9
	1207	16.5	5.2	1.0
	1220	16.5	4.3	1.2
	1238	16.5	2.4	1.6
	1354	16.6	0.5	1.8
	1432	16.9	none	1.8
	11.6	998	16.7	11.6
1119		16.9	10.7	0.2
1189		16.7	8.5	0.9
1243		17.0	5.8	1.0
1300		16.9	2.0	1.4
1362		16.7	0.9	1.8
1398		17.1	0.2	2.3
1414		16.8	none	2.7
13.6		1043	17.5	13.1
	1121	17.0	12.2	0.8
	1230	17.1	9.2	1.4
	1288	17.2	6.5	1.8
	1360	16.6	3.0	2.0
	1412	17.0	0.7	2.6
16.3	1021	17.1	15.7	0.2
	1113	16.7	14.8	0.6
	1204	16.5	13.4	1.2
	1284	17.0	10.5	1.8
	1359	16.7	7.0	2.5
	1432	16.7	2.5	3.5
	1482	16.8	0.5	3.5
	1510	16.9	0.2	3.3
	1542	16.9	none	3.6

TABLE II

Experimental Data Obtained From Radial-High Pressure Experiments

Input, % Oxygen	Temp, °F	Effluent Analysis			
		% Oxygen	% Carbon Dioxide	% Carbon Monoxide	
3.0	575	none	0.9	1.3	
	565	0.2	0.9	0.9	
	555	0.3	0.9	0.8	
	545	0.5	0.9	0.6	
	534	0.8	0.9	0.5	
	525	1.2	0.9	0.3	
	515	1.5	0.7	0.3	
	505	1.8	0.6	0.2	
	494	2.1	0.4	0.2	
	480	2.4	0.3	0.2	
	460	2.7	0.1	0.2	
	450	2.7	0.1	0.1	
	400	3.0	none	none	
	6.3	600	none	1.5	3.1
585		0.2	1.6	2.8	
570		2.3	1.4	0.9	
555		2.7	1.5	0.5	
545		3.5	1.3	0.3	
530		4.4	0.9	0.2	
515		5.1	0.7	0.2	
500		5.6	0.4	0.1	
485		6.0	0.2	0.1	
460		6.2	0.1	0.1	
425		6.3	none	0.1	
12.0		715	none	4.6	3.3
		685	0.1	4.3	3.5
		660	0.1	4.3	3.4
	635	0.8	4.1	3.0	
	610	2.2	3.7	2.3	
	590	4.6	3.2	1.3	
	570	6.8	2.3	0.6	
	550	8.9	1.4	0.2	
	535	9.7	0.9	0.2	
	520	10.2	0.5	0.2	

TABLE II (continued)

<u>Input, % Oxygen</u>	<u>Temp, °F</u>	<u>Effluent Analysis</u>			
		<u>% Oxygen</u>	<u>% Carbon Dioxide</u>	<u>% Carbon Monoxide</u>	
14.3	735	none	6.5	3.8	
	710	0.4	6.3	3.2	
	695	1.0	6.1	2.4	
	620	5.8	4.5	1.2	
	600	8.1	3.4	0.9	
	580	10.1	2.4	0.5	
	560	11.8	1.5	0.3	
	540	12.7	1.1	0.1	
	520	13.4	0.6	0.1	
	500	13.8	0.4	0.1	
	480	14.1	0.1	0.1	
	460	14.2	none	0.1	
	410	14.3	none	none	
	19.5	900	none	11.5	0.9
		865	0.3	11.2	0.8
850		0.5	11.0	0.9	
830		0.8	10.7	0.9	
815		1.3	10.4	0.8	
790		2.5	9.7	0.8	
775		3.7	9.1	0.8	
760		4.3	8.7	0.8	
745		4.6	8.4	0.9	
735		4.8	8.2	0.9	
725		5.2	8.0	0.9	
705		5.5	7.7	0.9	
610		16.8	1.0	0.3	
600		17.5	0.7	0.2	
590		18.0	0.6	0.2	
580		18.4	0.4	0.1	
570		18.7	0.3	none	
560		18.7	0.3	none	
550		18.7	0.3	none	
540		18.7	0.3	none	
530		18.8	0.2	none	
520		19.3	0.2	none	
510	19.4	0.2	none		
500	19.5	0.1	none		

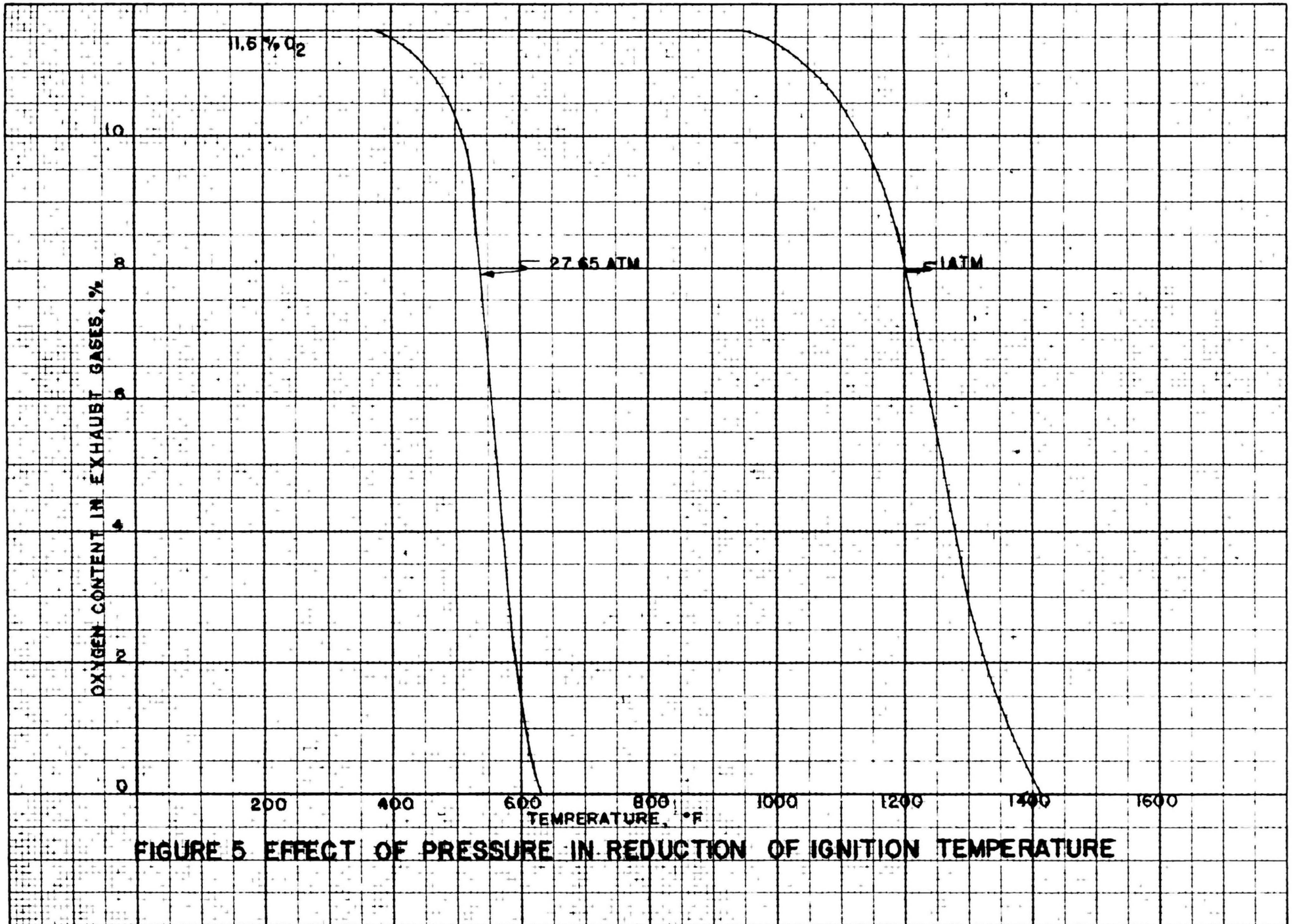


FIGURE 5 EFFECT OF PRESSURE IN REDUCTION OF IGNITION TEMPERATURE

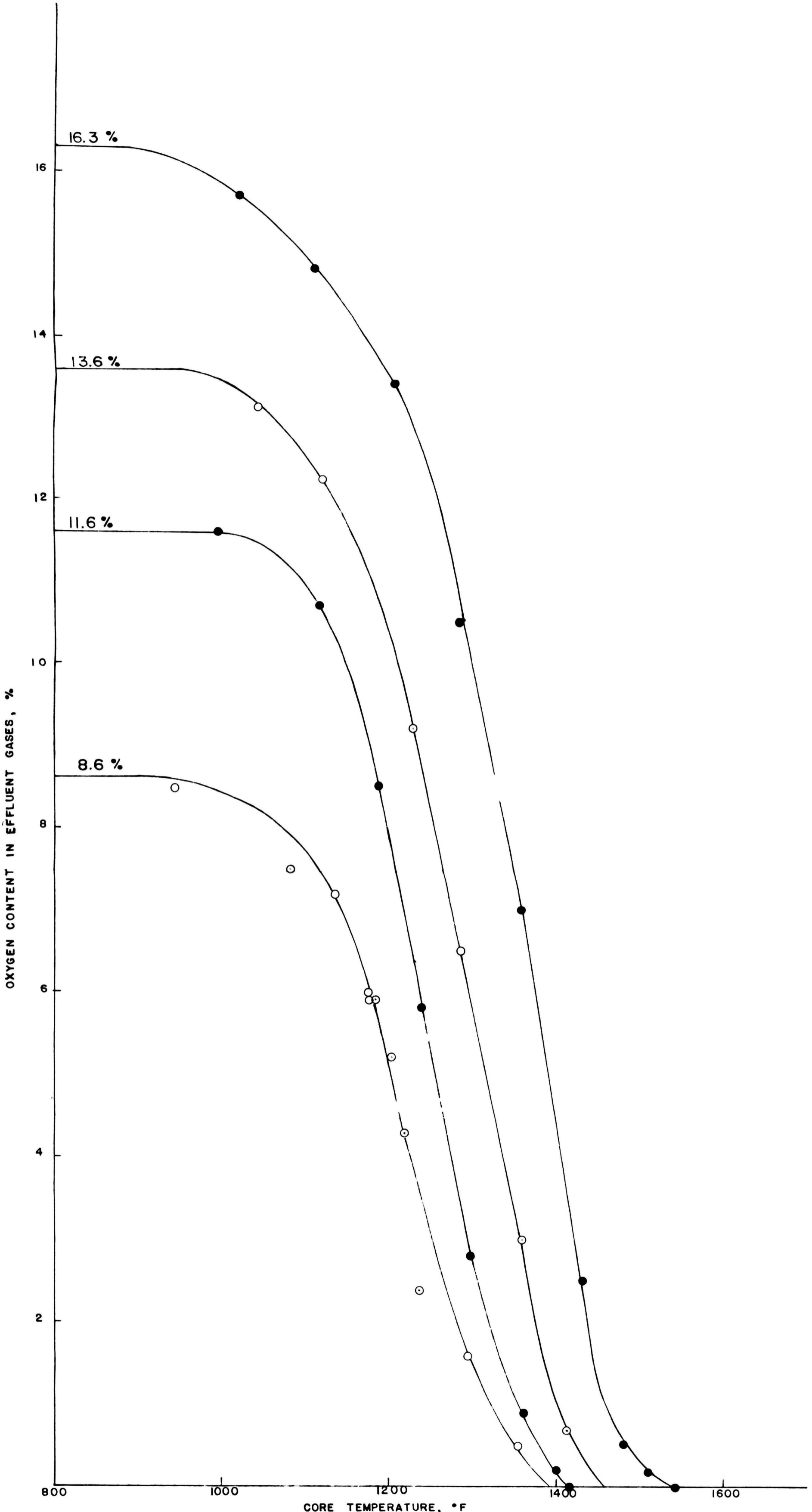


FIGURE 6. VARIATION IN OXYGEN CONTENT OF EFFLUENT GASES WITH TEMPERATURE

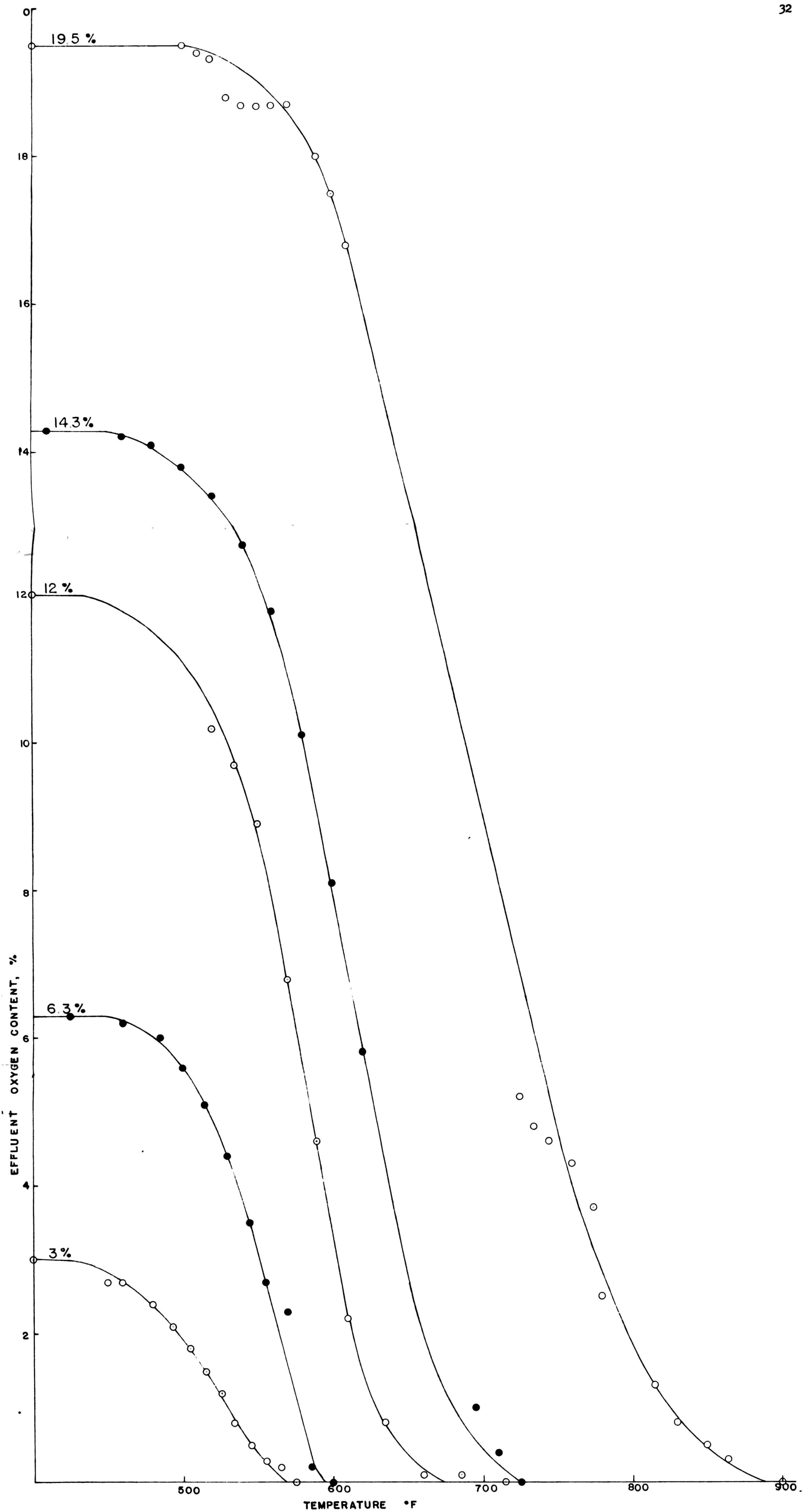
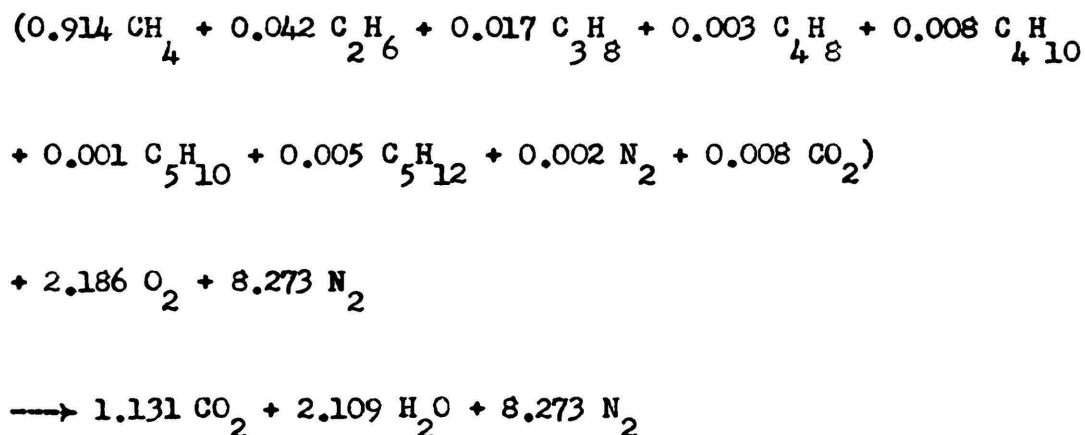


FIGURE 7 RESULTS OF HIGH PRESSURE HYDROCARBON OXIDATION IN POROUS MEDIUM

mixtures studied in the high pressure investigation are: 3.0% O₂; 6.3% O₂; 12.0% O₂; 14.3% O₂; 19.5% O₂. Mixture concentration differs from that in the low pressure study because of difficulty in duplicating samples. The effect of pressure on the experimental results for both methods is shown by the comparison in figure 5 which was obtained from observed low pressure data and interpolation of high pressure results.

The stoichiometric proportion of air in natural gas, in accordance with supplied approximate analysis, is 19.1% oxygen. This result is calculated from the complete combustion equation



where one mole of natural gas reacts with 2.186 moles oxygen. All experimental concentrations studied are considered nonexplosive (17) with exception of the 19.5% O₂ mixture which is in the explosive range.

Observed data relative to the study of effluent analysis as a function of flow rate are listed in table III. The experimental flow rate values are concentrated in the low flow range resulting from a qualifying investigation and are not complete for broad inter-

TABLE III

Experimental Data Showing Effect of Flow Rate on Combustion of
 8.6% O₂/32.6% N₂/58.8% Natural Gas Mixture

Reactor Temp. °F	Flow Rate, cc/min	Residence Time, sec	Exhaust Analysis	
			% Oxygen	% Carbon Dioxide
1193	2.7	112.3	1.8	2.5
1184	3.9	85.4	2.8	1.8
1184	4.2	79.3	2.7	2.0
1190	5.0	66.7	2.8	1.8
1186	6.9	48.3	3.4	1.4
1186	9.1	36.6	4.0	1.2
1184	9.5	35.1	4.5	1.1
1175	10.5	31.7	4.6	1.0
1180	11.8	28.2	5.2	1.0
1185	14.8	22.5	5.7	0.5
1183	16.7*	20.0	5.9	0.9
1174	16.8*	19.8	6.0	0.7
1173	17.4*	19.1	5.9	1.1

* Points plotted in Figure 6.

pretation. Their use here is primarily to outline a kinetic approach which may provide useful information in evaluating oil recovery processes by combustion. The sample gas containing 8.6% oxygen, before reaction, was used in this study.

DISCUSSION OF RESULTS

Oxidation Temperature

Oxidation trends presented in figures 6 and 7 describe the effect of temperature in controlling oxygen conversion through restricted combustion type reactions for two different systems. By following the exhaust oxygen composition with increasing temperatures, each mixture is seen to pass through a point where oxidation is first detectable. Increasingly higher temperatures result in a near linear decline in oxygen composition until complete oxygen utilization is realized. A further increase in temperature tends toward more complete combustion by gradually converting carbon monoxide to carbon dioxide. An interesting side observation at temperatures above 1800 °F (8.6% O₂ sample gas) was that cracking occurred and carbon was deposited. Subsequent carbon oxidation by air injection occurred above about 1050 °F.

In discussing numerical results obtained it should be emphasized that, because of the basic difference in the two experimental apparatus and probable catalytic effect of various mineral surfaces exposed in the sandstone core, there is no guarantee the observed data plotted in figures 6 and 7 and compared directly in figure 5 may be contrasted quantitatively. Inclusion of the high pressure results is to show the analogous type of data obtained where the reaction residence time was about 20 seconds in each experimental setup.

Except for errors in experimental observations, the initial oxidation point for the rich natural gas concentrations shown in figure 6 (atmospheric pressure) is approximately 950 °F. Data presented in figure 7, where experimental pressure is 400 psig, show this point as near 470 °F. The influence of pressure in reducing initial oxidation temperature is considerable but agrees with expected results. According to Le Chatelier's principle, an increase in pressure favors the reactants as the volume increases during combustion and, therefore, should increase rather than decrease the initial oxidation temperature. A complete explanation of this effect is too exhaustive for treatment here. The argument involves the existence of an activated complex which accounts for the increase in reaction rate at higher pressures by considering a relatively long time lag between activation and decomposition.

(21) In discussing parameters involved in explosive combustion, Lewis and von Elbe (25) state that because of these pressure-temperature relations an increase in pressure decreases ignition temperature while increasing the reaction rate. For reactions dependent on some power of the pressure, they present the general relationship

$$\log P = A/T + B$$

where: A = overall activation energy/gas constant

B = constant depending on the system

for which a plot of this form has been found to agree with many experimental observations.

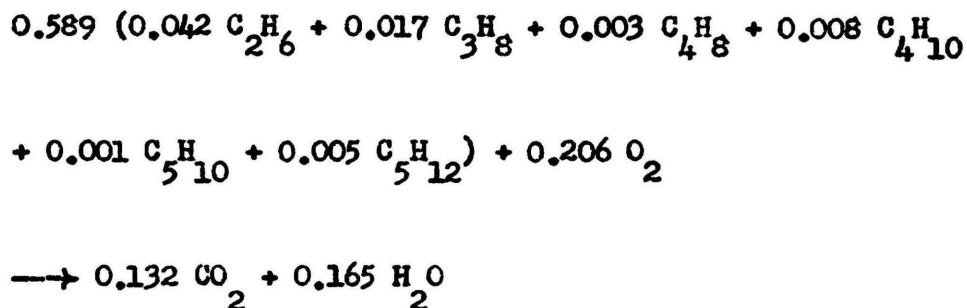
Returning to the results at hand, the balance of data contained on each graph of figures 6 and 7, as well as trends in the declining

free oxygen composition, pertain to the specific experimental conditions and are not readily applicable to other systems. This effect is perceived, for example, by doubling the experimental reactor length (other factors constant) again measuring effluent products. The increased volume provided the reacting molecules increases the time contained within the reactor zone thereby permitting the reaction to go further toward completion. This change will, in effect, give a smaller temperature increment before complete oxygen utilization is realized and result in a greater (in the negative direction) slope of the linear portion of each plot. In an extremely long reactor, the combustion process would be complete prior to the gases reaching the reactor outlet. The influence of other controlling variables will be explained more fully in the section undertaking a kinetic approach to the overall combustion reaction.

Use of the multi-component fuel in the investigation prohibits a thorough analysis of the combustion data with reference to any one compound or group of components. This restriction follows from interpretation of the degree of oxygen utilization presented in figure 6 and the ideal combustion reaction.

In previous discussion, it was shown the less volatile constituents of natural gas could be expected to ignite at lower temperatures than methane. The analogy is made that these components, in individual non-explosive mixtures with air, follow a like order of ignition temperature when ignited in a porous medium. Based on this interpretation the curve representing 8.6% initial oxygen indicates very little, if any, methane oxidation as suggested by the following complete combustion equation for the heavier components.

For 8.6% oxygen (58.9% natural gas, 41.1% air):



The above stoichiometric reaction requires 0.206 moles of oxygen to burn the combustibles (other than methane) contained in 0.589 moles of natural gas. The available oxygen is only 0.086 moles or 41.8% of the quantity necessary. For mixtures containing a higher oxygen concentration and corresponding lower natural gas content, the relative amounts of oxygen necessary for complete combustion of ethane and heavier components for the remaining low pressure sample gas mixtures are:

<u>Oxygen concentration in sample gas, %</u>	<u>Relative amount oxygen available to completely burn ethanes plus, %</u>
8.6	41.8
11.6	67.9
13.6	111.4
16.3	209.0

Preliminary Kinetic Application

Results obtained through variation in flow rate for one sample gas mixture permit a limited kinetic analysis, of effluent concentration of the reactant oxygen, utilizing the pseudo-order concept. The study consists of applying experimental data to apparent first- and second-order rate equations in an effort to obtain approximate pseudo-order relationships for the complex combustion system. For the thor-

ough evaluation of combustion behavior applying chemical kinetics, one must vary the reactants ratio while analyzing the reaction characteristics at the same pressure and temperature. (26) Also the use of a more liberal integrated equation would be helpful in determining whether the order of combustion reaction specific to oxygen was integral, fractional, or did not follow any set pattern.

Assumption of apparent first- and second-order behavior led to the use of equations 8, 10, 13, and 15. Observed data applied to the respective equation resulted in calculated reaction velocity constants shown in table IV. Calculated k values obtained are smaller for relations involving no change in volume during reaction, as computed by equations 8 and 13, than for increasing volumes computed with equations 10 and 15. Second-order rate constants calculated are also larger than first-order by factors ranging between 10 and 30, depending on the basis of comparison. The deviation between both computations of first- and second-order relationships increases with increasing flow rate or decreasing conversion. Errors in assuming constancy of reactant concentration, other than oxygen, will increase with increased residence time or oxygen conversion because the quantity of reactants consumed will be proportionately greater. Also diffusional effects were not included which, at low flow rates and high temperatures, could cause considerable variation in calculated results. Since the experimental pressure of one atmosphere remained essentially constant, the different values calculated result from concentration expressions contained within brackets of each equation.

Residence time calculations used in the formulas are based on apparent dimensions of the reaction system and the flow rate at the peak

TABLE IV
 Calculated Reaction Rate Constants Based on Pseudo-Order Rate
 Equations 8, 10, 13, and 15

Residence Time, sec	$k_1 \times 10^7$, Pseudo-First-Order*		$k_2 \times 10^7$, Pseudo-Second-Order*	
	<u>Equation 8</u>	<u>Equation 10</u>	<u>Equation 13</u>	<u>Equation 15</u>
112.3	6.20	7.55	175	193
85.4	5.85	6.65	126	143
79.3	6.52	7.39	143	161
66.7	7.50	8.51	161	182
48.3	8.57	9.90	165	187
36.6	9.33	11.00	164	189
35.1	8.21	9.94	135	158
31.7	.80	10.70	142	168
28.2	7.90	10.95	121	145
22.5	8.17	10.92	118	146
20.0	8.44	11.60	119	149
19.8	8.08	11.28	114	144
19.1	8.85	12.18	125	157

* Note: Refer to table III for observed data. Example calculations are included in the text. Dimensions of reaction rate constants calculated are as follows:

$$k_1 = \text{gm moles/sec-cc reactor volume-atm}$$

$$k_2 = \text{gm moles/sec-cc reactor volume-atm}^2$$

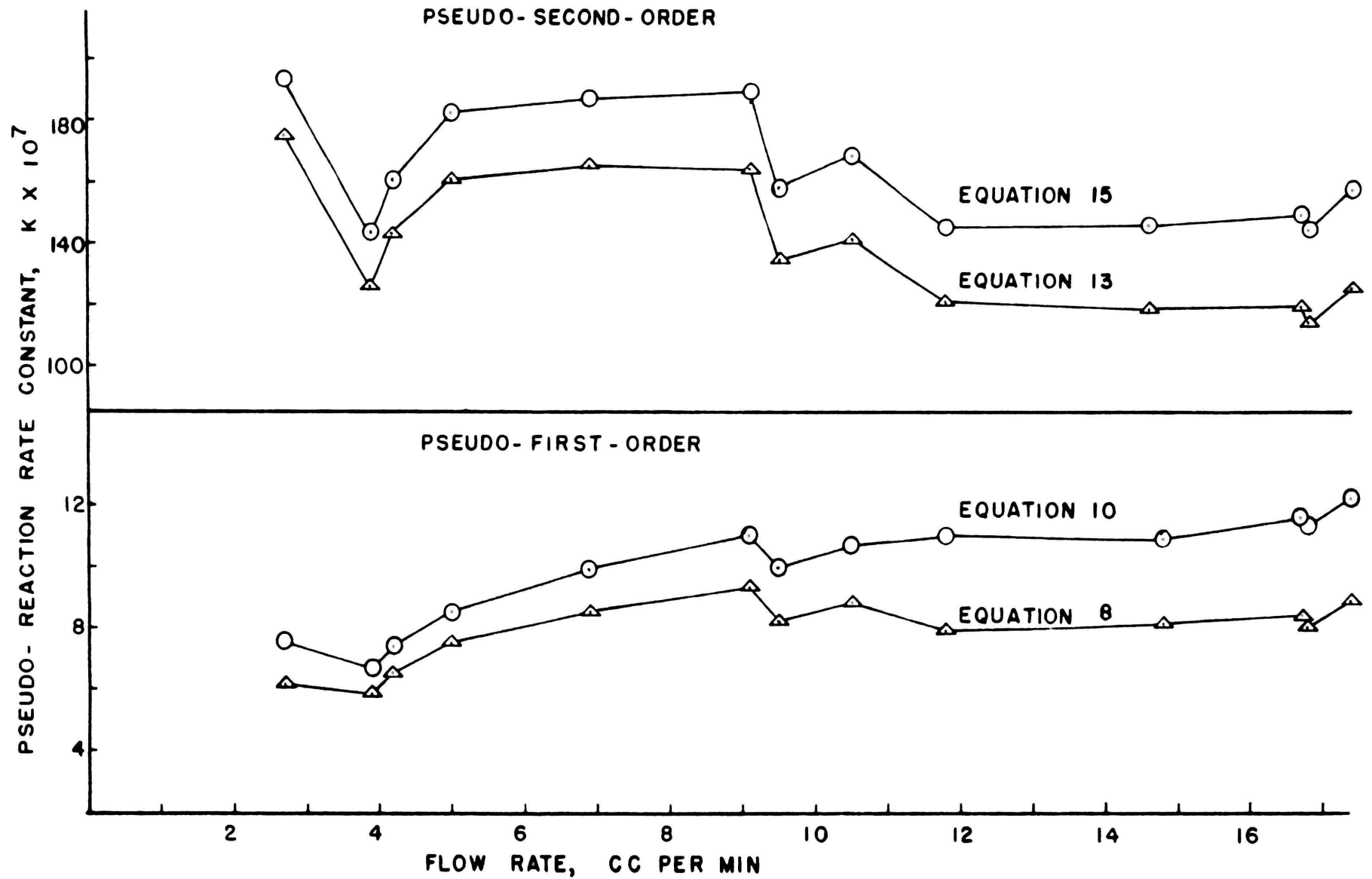


FIGURE 8. GRAPH SHOWING VARIATION OF CALCULATED PSEUDO-REACTION RATE CONSTANT

temperature within the reactor. Use of this procedure excludes added effects resulting from reaction during the preheating or cooling stages as the gases move through the system. The time allotted for fluids contained within the peak temperature zone was calculated in the following manner:

Reactive system: Combustion tube of 25 mm ID packed with ground glass to 34.5% porosity; 4" isothermal peak temperature zone maintained at respective temperature T; gas volume referred to 70 °F.

Residence time in seconds

$$= \frac{0.75 \times (2.5)^2 \times 4 \times 2.54 \times 60 \times 0.345 \times 530}{fT}$$

where: f = steady state flow, cc/min.

T = reactor peak temperature, °R.

Equation 16

Experimental k values calculated are plotted in figure 8 for ease in comparison. Numerical values obtained from the apparent first-order expressions give a slightly negative slope to the general shape of the two curves while the apparent second-order relationships give slightly positive slopes. Theoretical analysis demands a slope equal to zero, i.e., one in which k remains constant.

An apparent fractional-order rate expression, between first- and second-order rate dependence for oxygen, is indicated by the overall experimental results; however, a reasonably constant k value was obtained for the first-order rate calculation through the use of equation 8.

The agreement for low residence time at high flow rates is particularly good above six cc/min flow giving an average value for k of 8.48×10^{-7} moles-sec-cc-atm. The original assumption of constancy in fuel reactant concentration is rendered less valid below this flow rate (greater residence time) due to high oxygen conversion. Rate constants calculated for flow in excess of the six cc/min rate vary by 10% above and 7% below the mean 8.48×10^{-7} value. Among other variables, the deviation at lower flow than the six cc/min rate could be due to an induction period before rapid oxidation or the oxidation of higher molecular weight hydrocarbons.

Example Calculations

Measured data: (see table III)

Reactor temperature, °F	1190
Flow rate, cc/min	5
Injected oxygen concentration, %	8.6
Effluent oxygen concentration, %	2.8
Experimental pressure, atm	1

Calculated data:

$$\begin{aligned} \text{Residence time} &= \frac{0.785 \times (2.5)^2 \times 4 \times 2.54 \times 60 \times 0.345 \times 530}{5 \times 1650} \\ &= 66.7 \text{ sec.} \end{aligned}$$

$$\begin{aligned} F/VP &= \frac{1}{\text{Residence time} \times 22,400} \\ &= \frac{1}{66.7 \times 22,400} \\ &= 6.7 \times 10^{-7} \text{ gm moles/sec-cc reactor volume-atm.} \end{aligned}$$

Equation 8:

$$\begin{aligned} k_1 &= 6.7 \times 10^{-7} \ln (0.086/0.028) \\ &= 7.5 \times 10^{-7} \text{ gm moles/sec-cc reactor volume-atm.} \end{aligned}$$

Equation 10:

$$\begin{aligned} k_1 &= 6.7 \times 10^{-7} (0.086 + 0.028)/(1 + 0.028) \\ &\quad + (1 + 0.086) \ln ((0.086 \times 0.028 + 0.086)/ \\ &\quad (0.086 \times 0.028 + 0.028)) \\ &= 8.51 \times 10^{-7} \text{ gm moles/sec-cc reactor volume-atm.} \end{aligned}$$

Qualitative Interpretation

The lack of complete agreement of this experimental analysis with theory restricts the study to a qualitative interpretation based on observed results and relationships indicated by the flow equations. Equation 8, for example, shows that reactant conversion in an isothermal flow system (at essentially constant pressure) is a function only of residence time and initial concentration.

Discussions in the previous sections offer a better understanding of the data presented in figure 6, with particular emphasis on the shape of the 8.6% oxygen curve. The portion of the study concerning variation in flow rate was made within the 20 °F differential bounded by 1173 °F and 1193 °F. By decreasing the flow rate in this region from an average 17 cc/min (plotted curve) to 2.7 cc/min (see table III), the curve becomes almost vertical. This effect causes a shifting of the plotted 1.8% O₂ point from 1286 °F to 1193 °F, a decrease of 93 °F. The slope of the straight line segment of each curve on the graph may then be interpreted as indicative of the flow rate relative to a specific re-

actor volume. A decrease in flow rate produces essentially the same result as increasing reactor volume, increasing the slope of this line accordingly. Alternately, increasing the flow causes a wider variation between initial oxidation temperature and temperature of complete conversion.

Application of similar studies to thermal recovery by subsurface combustion methods requires a knowledge of heat zone width as well as temperature distribution across the thermal wave. If the combustion zone width is narrow, relative to flowing gas velocity, the time in residence will be short and inefficient oxygen utilization may result. On the other hand, where thermal zones are relatively wide with respect to the velocity of flowing gases, nearly complete heat utilization should be effected.

CONCLUSIONS

A brief discussion of a few of the many parameters affecting natural gas combustion within restrictive environments has been presented. The problem of understanding combustion reactions of this nature is complex and involves a large number of variables which are difficult to separate for thorough evaluation. The author has, therefore, performed a preliminary investigation to determine which of certain variables were controlling, to analyze how they are related, and to show some of their relationships by preliminary laboratory experiments. The following points should prove useful for a more exhaustive evaluation of parameters relevant to this type combustion process:

1. Depletion of oxygen, in the exhaust stream, is indicative of reaction progression and has been determined for a specific set of

experimental conditions. Field application of this procedure in evaluating combustion zone characteristics should proportionately weigh dilution, absorption, adsorption, and other effects such as low temperature oxidation.

2. Oxidation reactions of natural gas, in varying concentrations with air, may be of flameless nature when ignited in porous media of a size normally found in petroleum reservoirs.

3. Combustion behavior of near stoichiometric and normally flammable concentrations of natural gas in air is dependent on the same parameters as are normally considered nonexplosive mixtures when burned in a porous medium. Further, the oxidation reaction is incapable of spontaneous propagation through pore restrictions of a size comparable to most petroleum reservoirs. This conclusion is evidenced by the explosive gas shown as the 19.5% oxygen curve of figure 7 where any degree of reaction completion was possible through either temperature or residence time variation.

4. Natural gas reactions taking place within a heated porous medium will reach near equilibrium conditions within a relatively short time in residence. Experimental residence time in the order of 20 seconds permitted reproducible oxygen conversions provided rock temperature remained constant. Therefore, only a relatively narrow combustion zone width is necessary to obtain combustion in field projects, the width decreasing with decreasing gas velocity as the injected gases progress radially away from an injection well bore.

5. Presence of increasing quantities of the less volatile constituents in natural gas does not affect the initial oxidation temperature to an appreciable extent, as evidenced by the initial oxidation

temperatures of the nine mixtures represented in figures 6 and 7.

6. An increase in pressure above one atmosphere reduces oxidation temperatures of natural gas confined to a porous medium. Increased effects of rapid activated complex disintegration, chemisorption, and/or the heterogeneity of the chemical reaction, with pressure, are believed to be primarily responsible for this result.

7. Minimum temperatures of rich natural gas oxidation, within the porous environments studied, are near 950 °F at atmospheric pressure and 470 °F at 27.65 atmospheres absolute pressure when the gas is allowed about 20 seconds reaction time. Complete oxygen conversion of rich natural gas and air mixtures is possible above these temperatures if a longer time period in residence is provided. These temperatures may be lowered somewhat if a longer period in residence is permitted.

8. The chemical kinetic procedure herein presented offers an approach to the solution of some of the most important variables involved in complex natural gas combustion reactions. Parameters affecting natural gas combustion within a porous matrix are initial fuel or air concentration, type of fuel utilized, flux, pressure, temperature, and dimensions of the reactive system.

9. Future experimentation attempting to analyze combustion kinetics would benefit through use of a pure component fuel with variable reactants ratios to cover the range of interest. The experimental analysis, if performed in a flow type system, should involve measuring the effects of different flow rates through the reactor at the same pressure and temperature. For quantitative application of results, calibration of temperature sensing devices at the test condition is necessary. Application of experimental results in determining order

with respect to a limiting reactant may be of some real and useful value but is difficult to evaluate in a multi-component system. Use of a more general integrated equation enabling the direct solution of pseudo-reaction order either fractional, or otherwise, is suggested.

APPENDIX

Development of First-Order Steady State Flow Equation

The rate of a chemical reaction is determined by the decrease in reactant concentration, or increase in product concentration, per unit time. The mathematical expression representing this relationship for a "batch" (static) system, where C is the reactant concentration at any time t , is as follows:

$$r = -dC/dt \quad \text{Equation a}$$

According to accepted kinetic theory, the rate of a first-order reaction is directly proportional to the concentration, as expressed by the relation

$$r = -dC/dt = k C \quad \text{Equation b}$$

where k is the constant of proportionality for the experimental temperature. Use of equation b demands the reaction be carried out at constant volume and temperature. For "flow" (dynamic) systems, the reactor volume changes as the fluid is displaced along the reactor and equation b could not be expected to apply in its present form. Also for steady state conditions of flow, temperature, pressure, etc., time is not a variable except in determining the distance a certain quantity of flowing fluid has traveled and thereby the volume through which a certain reaction has occurred. For such a dynamic situation, the time function in the above equations may be replaced by the ratio

of reactor volume to flow rate (volume/time), V/F , the differential of which is:

$$dt = d(V/F) = (F dV - V dF) / F^2 \quad \text{Equation c}$$

Considering only the flow of reacting gases and assuming the rate of reactant consumption to follow first-order kinetics and equal to the rate of product formation, substitution of equation c in equation a reduces to the general rate equation for flow systems:

$$r = -F dC / dV \quad \text{Equation d}$$

Incorporating the concentration proportionality of equation b, the relation

$$r = -F dC / dV = k C \quad \text{Equation e}$$

is obtained which yields, upon integration,

$$k = (F/V) \ln (C_1/C_2) \quad \text{Equation f}$$

the kinetic flow equation for first-order reactions under steady state conditions. Accounting for the effect of pressure in reducing flow volume, the final equation

$$k = (F/PV) \ln (C_1/C_2) \quad \text{Equation g}$$

is obtained where C_1 and C_2 signify entering and exit concentrations after passage of PV/F units of time.

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VITA OF ROGER J. SCHOEPPEL

Born:

June 23, 1929

Chester, Ill'nois

Marital Status:

Married, 2-children

Formal Education:

Bachelor of Science, 1952

Mining Engineering, Petroleum Engineering Option

Missouri School of Mines and Metallurgy

Rolla, Missouri

Armed Service:

U. S. Army, 1946-47

U. S. Army, 1952-53

Employers:

Stanolind Oil and Gas Company, 1951, 1952, 1953-55

Sinclair Research Laboratories, Inc., summers, 1956, 1957

Gulf Research and Development Company, summer, 1958

Missouri School of Mines and Metallurgy, 1955-date