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KINETIC STUDY OF THE BOUDUARD REACTION

by

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Bachelor of Technology, Chemical Engineering

University of Madras, 1972

A Thesis

Submitted to the Graduate Faculty

of the

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in partial fulfillment of the requirements

for the degree of

Master of Science

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May
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This thesis submitted by C. Venugopala Rao in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

Wayne R Kube
(Chairman)

Donald E Severson

Clair D. Rowe

A William Johnson
Dean of the Graduate School

Permission

Title KINETIC STUDY OF THE BOUDUARD REACTION

Department Chemical Engineering

Degree Master of Science

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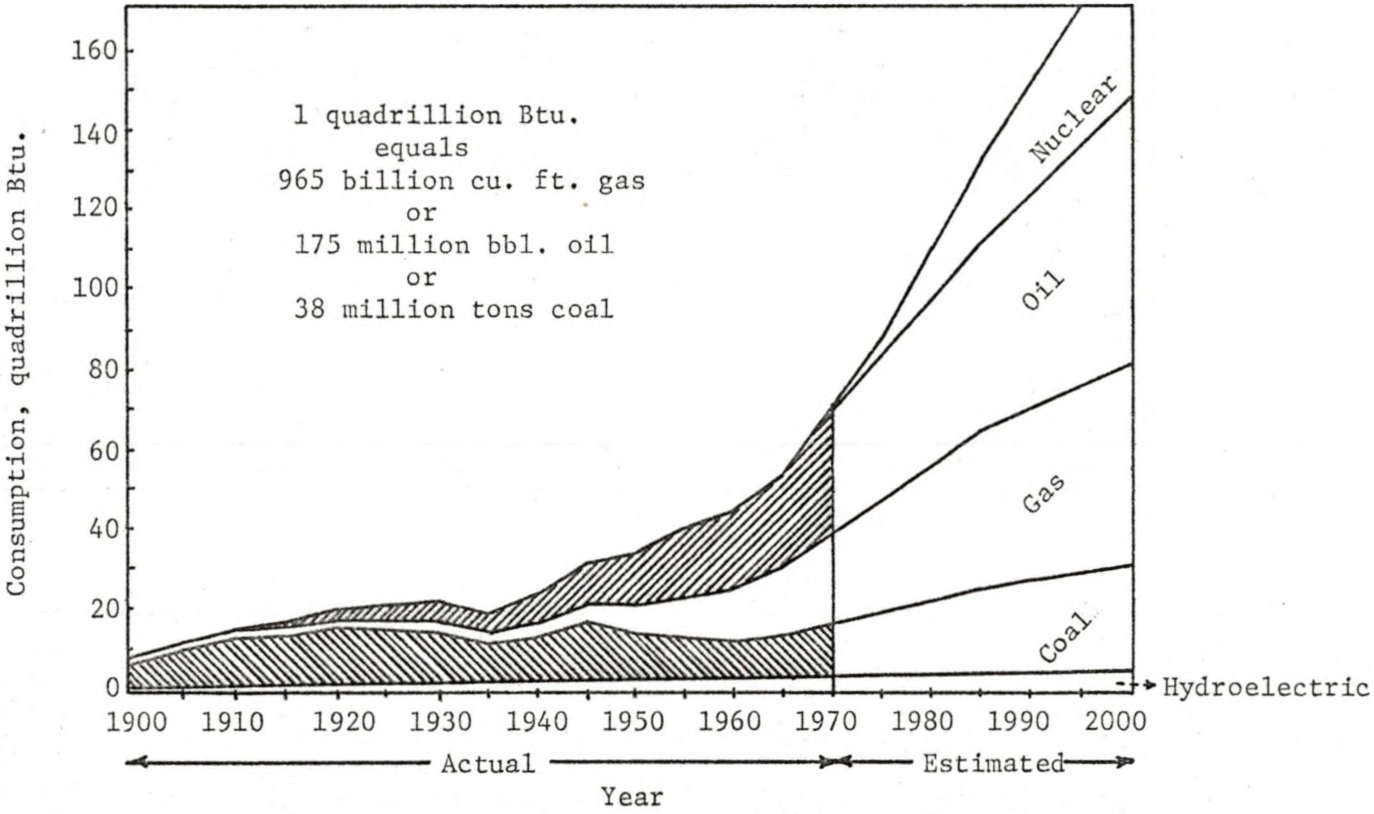
ABSTRACT

Kinetics of the Bouduard reaction (reaction of coal carbon with carbon dioxide) has been investigated in the temperature range 1100°F to 1300°F at atmospheric pressures employing chars from a bituminous coal from West Virginia, a sub-bituminous coal from Montana and two lignites from North Dakota. A simple kinetic model based on the stoichiometric equation $CO_2 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ CO$ was assumed. Rate data were obtained in an electrically heated fixed bed plug-flow reactor. The bed was packed with the coal char and the carbon dioxide delivered from a cylinder. The forward and reverse reaction rate constants were evaluated based on a model allowing for volume changes. The stoichiometric equation did not fit the actual mechanism of the reaction, as indicated by a decrease in the value of k_2 with temperature. Analysis of the factorial design employed indicated that the rate of the Bouduard reaction is significantly dependent on coal type, temperature and space time. The degree of conversion of carbon dioxide to carbon monoxide, for a given space time and temperature, increased with decreasing coal rank.

INTRODUCTION

Americans are the world's greatest energy consumers. Our appetite for heating and cooling, for light, and for transportation (see Figure 1) is outstripping our domestic energy resources. Future production of energy in the United States can be expected to meet increasingly difficult problems. Environmental and safety restrictions as well as quantity, form and location of energy will be important considerations in the total requirements which may increase threefold in the next thirty years (1). The extensive resources of lignite in North Dakota will probably play an important role in the total energy picture of the country.

Lignite can be used to fire boilers for electrical generating stations, in gasification processes to produce synthetic natural gas (SNG), and under proper conditions, liquid fuels. The Bouduard reaction which is the reaction between carbon and carbon dioxide plays an important role in the production of synthetic gas for conversion to SNG. A definite knowledge of the reaction rates would be useful in process control and performance evaluation. For instance, the difficulties in establishing meaningful standards of coke reactivity can be attributed to the limited knowledge of the reaction mechanism. There are applications in which the gasification of carbon is not desired, for example, when it is used as electrode carbon or as moderator in nuclear reactors.



1 quadrillion Btu.
equals
965 billion cu. ft. gas
or
175 million bbl. oil
or
38 million tons coal

Fig. 1.--U. S. ENERGY consumption in the 20th century for the five major sources of fuel.

Again, knowledge of the reaction would assist in controlling the behavior of carbon.

Kinetics of the reactions of carbon dioxide with carbon has been studied by numerous investigators from various countries. While there is some agreement among workers as to the possible sequences of the reaction, disagreements are numerous and confusing. Many models have been proposed for the mechanism of the reaction, but none of them represent all coals under all conditions. In this study, a model has been proposed for the rate equation and the equation is solved by numerical methods to obtain the reaction rate constants.

An electrically heated tubular reactor was used in the present experimental work to obtain rate data. Data was collected to make possible a discussion on the reactivity of carbon dioxide with carbon from different coals under various conditions.

SURVEY OF PREVIOUS WORK

The reaction of carbon dioxide with carbon has been studied by a number of investigators with regard to its mechanism and kinetics although not too much work has been done during the past decade.

Any assessment of previous studies is complicated by the many and varied types of equipment that have been employed and by the multiplicity of operating variables used. The experimental arrangements include gas-flow and static systems in which carbon may be in a fixed or fluidized bed of granular particles, particles falling through a hot zone, a single massive piece, thin filaments or evaporated films. Operating variables encompass a wide range in temperatures (from 200° to 2300° C), pressures (from 10^{-4} mm. Hg to 50 atmospheres) and gas velocities (from zero to 100 m./sec.). Whereas some experiments involved the reaction of an appreciable portion of carbon samples (several weight-per cent), others were confined to reactions of only parts per million.

Langmuir (2) in the year 1915, observed that when carbon dioxide was passed over carbon filament at 1220°K, no change was observed but at 1700°K, the formation of carbon monoxide was limited, but gradually increased with temperature.

Gadsby, Hinshelwood and Sykes (3) experimented with coconut shell charcoal at 700°C and coal charcoal at 800°C. They found that the reaction is of fractional order with respect to carbon dioxide and is strongly retarded by carbon monoxide. The rate of reaction could be represented by an expression of the form

$$\text{rate} = \frac{K_1 p_1}{1 + K_2 p_2 + K_3 p_1} \qquad (1)$$

where p_1 and p_2 are respectively the partial pressures of carbon dioxide and carbon monoxide, and the constants K_1, K_2 and K_3 are functions of one or more of the rate constants, based on an adsorption model.

Reif (4) studied the reaction of carbon dioxide with a high temperature coke at 900°C and under approximately atmospheric pressure and derived a rate expression similar to the one proposed by Gadsby, et al. (3). These investigations show the reaction to be represented by the equations

$$CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (O) + CO \qquad (2)$$

$$C + (O) \xrightarrow{k_3} CO \qquad (3)$$

where (O) represents a molecule chemically bonded to the carbon surface. This mechanism ascribes to the chemical combustion of carbon monoxide with oxygen deposited on the carbon surface by carbon dioxide.

Ergun (5) explains this reaction with dynamic two-phase oxygen exchange reactions represented by the equations

$$CO_2 + C_f \underset{K_2}{\overset{k_1}{\rightleftharpoons}} CO + C_o \qquad (4)$$

$$\text{and} \quad C_o \xrightarrow{k_3} CO + C_f \qquad (5)$$

where C_f represents a free site capable of reaction and C_o an occupied site, i.e. a site possessing an oxygen atom. Equation No. 4 expresses the oxygen-exchange phenomenon. The carbon transfer from solid phase to gas phase originates from occupied sites as represented by Equation No. 5 and is the slowest step of the reactions and is considered as unidirectional. The reaction rate is proportional to the concentration of occupied sites.

The investigations of P. C. Wu (6) suggested on theoretical grounds the possibility of a mechanism represented by

$$CO_2 \longrightarrow (O) + CO \tag{6}$$

$$C + (O) \rightleftarrows CO \tag{7}$$

$$C + (O) \longrightarrow (CO) \tag{8}$$

but no experimental evidence was presented for Equation No. 8.

Clement, Adams and Haskins (7) examined the effect of temperature and gas flow rate on the production of carbon monoxide by the Bouduard reaction. Their experiments were performed by passing a stream of carbon monoxide through a bed of fuel contained in a porcelain tube heated by an electric furnace.

Kauphusman (8) based his study on the study of Clement, <u>et al.</u> (7) and used the following rate expression

$$\frac{d[CO]}{dt} = k_1[CO_2] - k_2[CO]^2 \tag{9}$$

In this study the rank of coal was found to have a definite effect on the conversion of carbon dioxide to carbon monoxide. However, for the reaction there is a net increase of one mole of gas for each mole of gas reacted, and this change in volume was not considered in the above two studies. Equation No. 9 is suitable for a constant volume batch reactor, but, not for a fixed bed plug-flow reactor at constant pressure.

The present study was based on the work of Kauphusman, but, took into account the change in volume that occurs during the reaction. The experiments were performed with lignite, sub-bituminous and bituminous coals.

Information was not available in the literature on the reactivity of lignites and sub-bituminous coals from the United States.

EXPERIMENTAL PROCEDURE

Equipment

Equipment used for investigating the Bouduard reaction included a reactor, a furnace to provide the heat for and maintain the reaction temperature and a system for delivering and metering the flow of carbon dioxide into the reactor. The percentages of carbon monoxide and carbon dioxide in the exit gases were determined by sampling and analyzing with an Orsat apparatus. The schematic flow diagram of the experimental setup is shown in Figure 2.

A tubular reactor in which a fixed bed of char rested on a porous support has been used successfully in similar work and the same concept was employed in this investigation. The final design of the reactor is shown in Figure 3.

The reactor was designed for use with a Burrell model B-1-23 tube furnace capable of maintaining temperatures as high as 2300°F. The heating zone of this furnace is 23 inches long and permits the use of a reactor up to 2 inches in outside diameter. The reactor was designed so that the bed of char would be centered in the heating zone of the furnace.

The temperature of the furnace was controlled and recorded by a Honeywell Electr O Pulse relay controller used in conjunction with a strip chart recorder. The temperature sensor was a shielded chromel-alumel thermocouple.

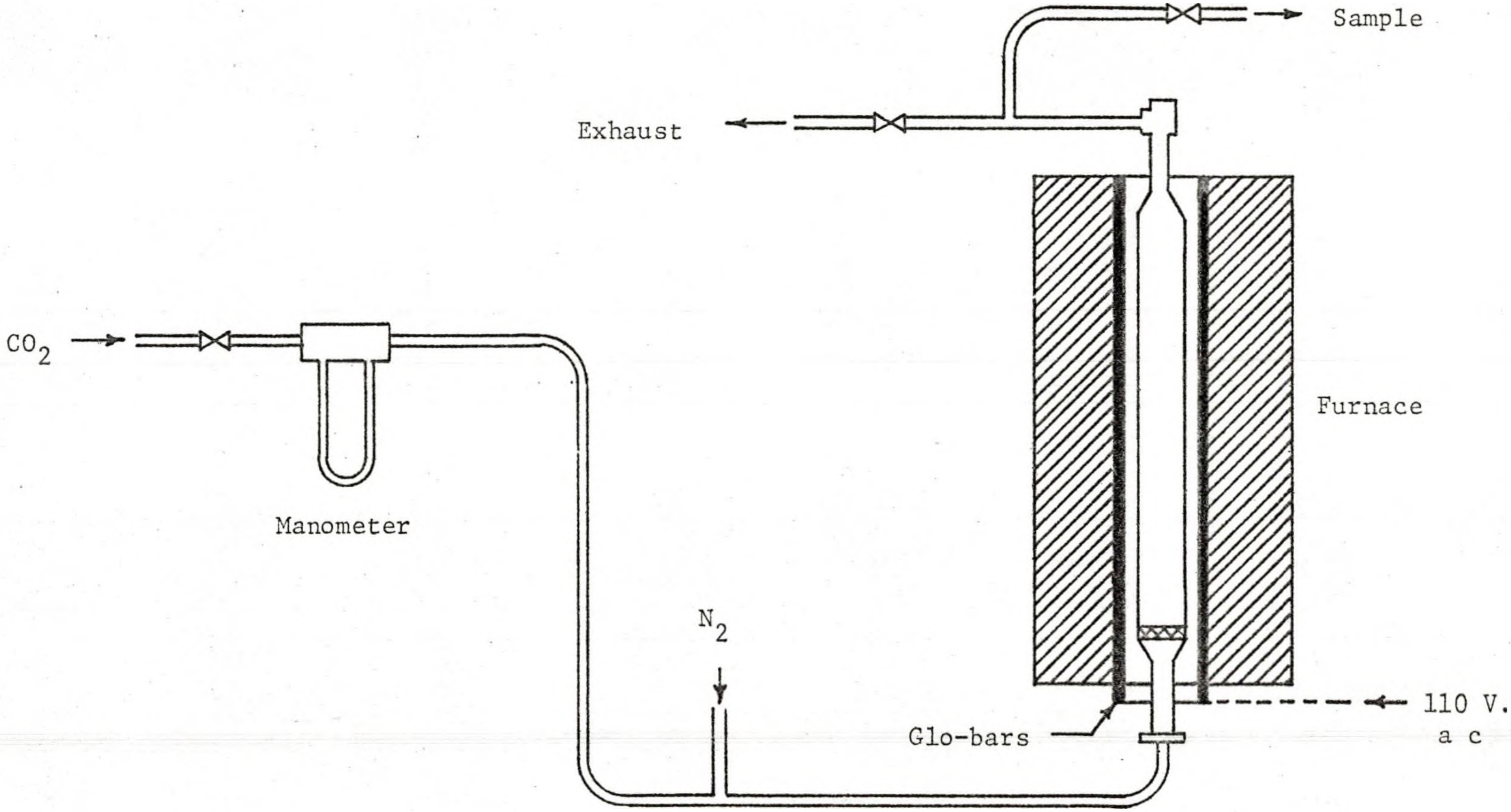


Fig. 2.--Schematic diagram of equipment.

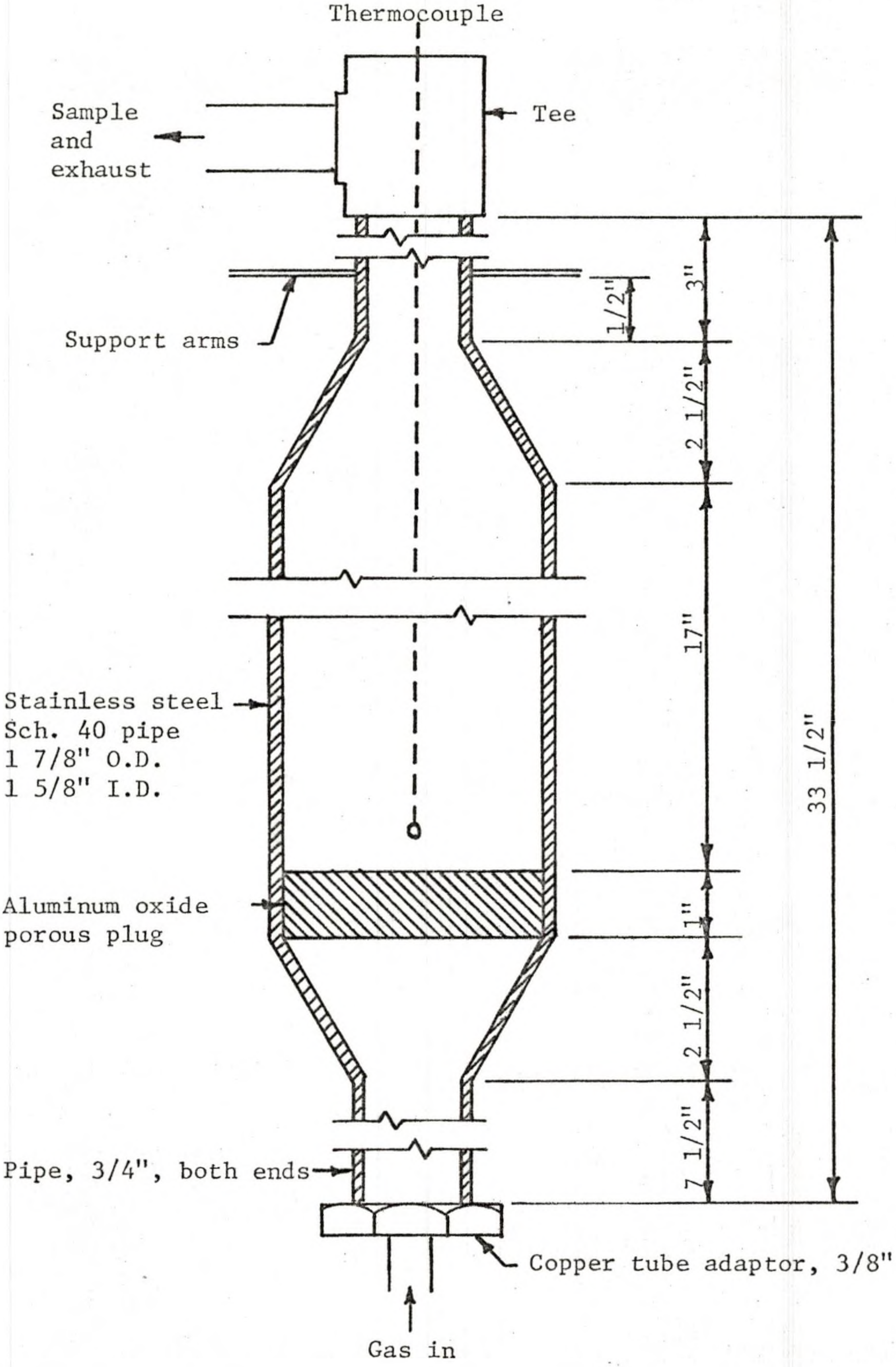


Fig. 3.--Cross section of reaction tube.

The reactor was fabricated of 2-inch nominal outside diameter schedule 40 type 304 stainless steel pipe. Stainless steel was chosen because of resistance to scaling under repeated heating and cooling and to brittling by the carburizing conditions to which it would be exposed.

A porous plug of alumina was fitted to the bottom of the reaction tube. The purpose of this plug was to support the bed of char and to uniformly distribute the carbon dioxide entering the reactor.

The flow of carbon dioxide from the cylinder was easily regulated with a valve in addition to the regulator on the cylinder. A differential manometer indicating the pressure drop across a suitable orifice and calibrated with a standard wet test meter results in a convenient device for flow measurement.

A standard Orsat apparatus with a burette calibrated from 0 to 100 milliliters was used to analyze the gas samples for carbon monoxide and carbon dioxide. The carbon dioxide was absorbed in a contact pipette filled with a KOH solution and the carbon monoxide was absorbed in a bubbler pipette with an acidic cupric chloride solution.

A gas chromatograph was available for use in analyzing the gas samples. Spot checks were made with the gas chromatograph to check the Orsat readings. Gas samples for the chromatograph were taken by using the slight positive pressure in the reactor to force the gas from the discharge line into a sampling bottle where it displaced a collecting fluid to prevent the seepage of air into the sample. The apparatus used for collecting the samples is shown in Figure 4. The collecting fluid was a solution of water, sulfuric acid and sodium sulfate. The low

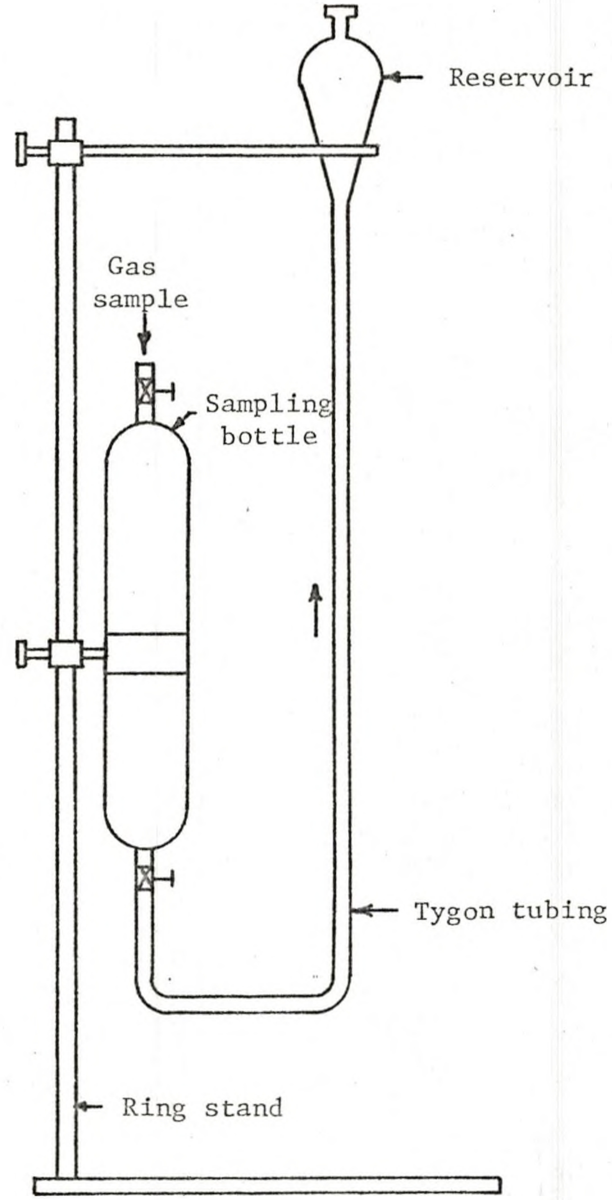


Fig. 4.--Sampling apparatus.

solubility of carbon dioxide in the acid solution reduced errors in the gas analysis due to absorption of carbon dioxide.

Materials Tested

The bituminous coal (A) was obtained from the Arkwright mine at Osage, West Virginia, and the sub-bituminous coal (C) from Colstrip, Montana. The North Dakota lignites (B and D) were respectively from Knife River Coal Mining Company's North Beulah mine at Beulah, Mercer County, and from the Gascoyne mine, Bowman County. As indicated, these coals will be designated A, B, C and D for simplifying future references (see Table 1).

As received (see Table 2), the coals contained volatile matter which would be released on heating in the reactor. The released gases would consist primarily of hydrogen and methane with some carbon dioxide, carbon monoxide and tar vapors included, and would influence the results of the reactivity measurements because of the dilution effects on the gasifying medium.

The volatile matter was reduced by carbonization. A 50-pound sample of each coal was placed in an iron retort, and the retorts were placed in a slot oven at 1000°F at the Grand Forks Energy Research Laboratory. The samples were maintained at this temperature for approximately 7 hours. Coals B, C and D formed unconsolidated chars while coal A formed a hard porous coke. The analysis of the chars are given in Table 3.

The carbon dioxide was a 50-pound cylinder of commercial grade carbon dioxide. The minimum purity for the commercial grade specifies 99.5% carbon dioxide.

TABLE 1.-- COALS TESTED

COAL	TYPE	MINE	TOWN	STATE
A	BITUMINOUS	ARKWRIGHT	OSAGE	WEST VIRGINIA
B	LIGNITE	N. BEULAH	BEULAH	NORTH DAKOTA
C	SUB-BITUMINOUS	COLSTRIP	COLSTRIP	MONTANA
D	LIGNITE	GASCOYNE	GASCOYNE	NORTH DAKOTA

TABLE 2.-- ANALYSIS OF COALS AS RECEIVED

	A	B	C	D
PROXIMATE ANALYSIS				
PERCENT MOISTURE	1.12	28.40	19.01	34.89
PERCENT VOLATILE MATTER	37.81	29.65	32.07	27.91
PERCENT FIXED CARBON	54.22	34.11	41.00	27.57
PERCENT ASH	6.85	7.84	7.92	9.63
ELEMENTAL ANALYSIS				
PERCENT HYDROGEN	5.31	6.09	5.93	6.63
PERCENT CARBON	77.35	46.08	54.88	39.88
PERCENT NITROGEN	1.56	0.67	0.78	0.58
PERCENT OXYGEN	6.82	38.59	29.80	42.26
PERCENT SULPHUR	2.11	0.73	0.69	1.02
PERCENT ASH	6.85	7.84	7.92	9.63
BRITISH THERMAL UNITS / POUND	13860	7640	9410	6700

TABLE 3.-- ANALYSIS OF CHARS AS RECEIVED

	A	B	C	D
PROXIMATE ANALYSIS				
PERCENT MOISTURE	3.30	0.80	0.41	0.77
PERCENT VOLATILE MATTER	5.40	8.68	9.83	13.16
PERCENT FIXED CARBON	81.90	74.18	75.27	63.12
PERCENT ASH	9.40	16.34	14.49	22.95
ELEMENTAL ANALYSIS				
PERCENT HYDROGEN	1.87	1.46	2.01	2.15
PERCENT CARBON	84.06	79.43	79.65	70.01
PERCENT NITROGEN	0.33	0.41	0.43	0.55
PERCENT OXYGEN	2.48	1.02	2.47	2.36
PERCENT SULPHUR	1.86	1.34	0.95	1.98
PERCENT ASH	9.40	16.34	14.49	22.95
BRITISH THERMAL UNITS / POUND	12730	12281	12678	11322

Sample Measuring and Charging

It was necessary to insure that the same volume of char was placed in the reactor for each experiment because the space time is dependent on the void volume of the reactor. A piece of 2-inch schedule 40-pipe was cut to a length of 30 centimeters, the same as the bed depth desired, and one end was closed with a flat plate. By filling the pipe and levelling the top, the correct volume of char could be measured. The weights of the samples were recorded for each experiment and are given in Table 4.

The thermocouple was placed in the reactor with the hot junction resting on the porous plug. The sample of char was then poured around the thermocouple without tamping. The thermocouple was then raised one inch from the plug and the fittings holding the thermocouple were tightened to seal the reactor.

Preheating

The electric furnace, temperature recorder and temperature controller were switched on and nitrogen was passed through the reactor. The furnace was maintained at the reaction temperature for approximately eight hours prior to the start of the test. The nitrogen flow was used to flush released volatiles, still remaining from the initial carbonization, from the reactor.

After the heating period was complete, the nitrogen flow was stopped. The carbon dioxide flow was started at the rate necessary to give desired space time. The introduction of carbon dioxide lowered the temperature because of the thermal requirements of the reaction.

TABLE 4.-- WEIGHT OF SAMPLES CHARGED

	GRAMS
COAL A	315
COAL B	367
COAL C	415
COAL D	343

Several minutes were required for the controller to adjust the reactor temperature to the desired level. During the stabilization period, essentially all of the pure nitrogen was flushed from the reactor.

Sampling Procedure

When the reactor temperature stabilized, the valve on the exhaust line was closed and the valve on the sampling line opened. The sampling line was connected to the calibrated burette in the Orsat apparatus. Samples were taken at intervals and analyzed for carbon monoxide and carbon dioxide until the analyses were reasonably constant.

After the reaction had reached a steady state and the analyses had been recorded, the flow rate was changed to provide the next space time. Several minutes were usually required for the reaction to return to a steady state before recording the analysis for the new state.

The sampling procedure was repeated for each contact time and the analyses were recorded. Samples taken at random were analyzed in the gas chromatograph to spot check the Orsat analysis. Since the Orsat analysis and the chromatograph analysis were close and within experimental error, this procedure was later discontinued as the confidence in the Orsat analysis had been established. Carbon monoxide and carbon dioxide represented more than 90 per cent and usually more than 95 per cent of the gases leaving the reactor.

The same procedure was followed in the experiments with the other coals.

EXPERIMENTAL DESIGN

A factorial design (9) is used for the study of the effects of coal, temperature, and space time. This design has distinct advantages over a series of single experiments, each designed to test a single factor.

A factorial experiment can be regarded as a number of simple experiments superimposed on each other. Every observation supplies information on each of the factors studied. One factorial experiment serves the purpose of a number of simple experiments of the same size. A series of simple experiments will throw no light whatever on the interaction of the different factors, which will be shown in a factorial experiment.

In the present study, the independent variables of temperature, space time and type of coal are considered to influence the formation of carbon monoxide. The four coals are taken to be fixed effects while the three temperatures and four space times are considered to be random effects representing a range of possible space times and temperatures. Three variable levels were combined into a mixed model 3 x 4 x 4 factorial design for analysis of variance to determine the possible significance of differences due to these variables. This design requires 48 experiments to be performed (see Table 5).

TABLE 5.-- EXPERIMENTAL DESIGN

TEMPERATURE DEGREES F	SPACE TIME SECS	COAL			
		A	B	C	D
1100	5	1	13	25	37
1100	10	2	14	26	38
1100	15	3	15	27	39
1100	20	4	16	28	40
1200	5	5	17	29	41
1200	10	6	18	30	42
1200	15	7	19	31	43
1200	20	8	20	32	44
1300	5	9	21	33	45
1300	10	10	22	34	46
1300	15	11	23	35	47
1300	20	12	24	36	48

NOTE - NUMBERS IN THE TABLE REPRESENT EXPERIMENT NUMBERS

The significance level selected was 0.05 which means that there was a 0.05 probability of falsely rejecting the null hypothesis.

Of major interest is the null hypothesis that the effects of the coals on the conversion of carbon dioxide to carbon monoxide were all equal to zero. Letting factor B represent the coal effects, this null hypothesis can be written as

$$H_{OB}:\ B_1 = B_2 = B_3 = B_4 = 0 \tag{10}$$

Letting factor A represent the temperature effects and factor C the space time effects, the other null hypotheses are written as

$$H_{OA}:\ A_1 = A_2 = A_3 = 0 \tag{11}$$

$$H_{OC}:\ C_1 = C_2 = C_3 = C_4 = 0 \tag{12}$$

The model equation for the design including the three factors and their interactions is written as

$$\begin{aligned} X_{ijku} &= U + A_i + B_j + C_k + (AB)_{ij} \\ &\quad + (AC)_{ik} + (BC)_{jk} + E_{ijku} \end{aligned} \tag{13}$$

THEORETICAL DEVELOPMENT

The reduction of carbon dioxide to carbon monoxide and the reverse reaction may be expressed as

$$CO_2 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2CO \tag{14}$$

where K_1 and k_2 are the reaction rate constants.

The rate of reaction, expressed as the rate of formation of carbon monoxide is written as

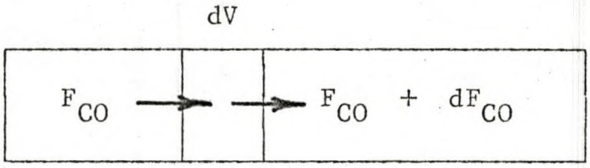
$$r_{CO} = k_1\ [CO_2] - k_2[CO]^2 \tag{15}$$

where $[CO_2]$ and $[CO]$ are the concentrations of carbon dioxide and carbon monoxide expressed as moles/liter respectively.

For a constant volume batch reactor, the rate of reaction is equal to $\frac{1}{V}\ \frac{dN_{CO}}{dt}$, where N_{CO} is the moles of carbon monoxide at time t and V is the volume of the reactor. But, for a plug flow reactor at constant pressure, volumetric flow rate varies because of a net increase of one mole of gas for each mole of gas reacted and so the rate of formation becomes

$$\frac{d[CO]}{dt} = \frac{d\left(\frac{N_{CO}}{V}\right)}{dt} = \frac{1}{V}\ \frac{dN_{CO}}{dt} - \frac{N_{CO}}{V^2}\ \frac{dV}{dt} \tag{16}$$

Consider a reactor of volume V and the reaction taking place in a differential volume dV of the reactor, as follows:



If F_{CO} is the moles per minute of carbon monoxide entering the differential volume dV of the reactor, then $F_{CO} + dF_{CO}$ is the moles per minute of carbon monoxide leaving the differential volume dV. If r_{CO} is the rate of formation of carbon monoxide expressed as moles/liter/minute, then

$$F_{CO} - (F_{CO} + dF_{CO}) + r_{CO}\, dV = 0 \tag{17}$$

and hence

$$dF_{CO} = r_{CO}\, dV \tag{18}$$

If the initial concentration of carbon dioxide is expressed as $[CO_2]_o$ and if y, the mole fraction of carbon monoxide is defined as

$$\frac{[CO]}{[CO] + [CO_2]}$$

and if space time T is defined as $\frac{V}{v_o}$ where v_o is the initial volumetric flow rate of carbon dioxide per minute, then the space time can be expressed as

$$T = \int_o^y \frac{4\, dy}{(2-y)^2 \quad \left\{k_1(1-y) - k_2'(y^2)\right\}} \tag{19}$$

where $k_2' = k_2\, [CO_2]_o$.

Integration gives

$$T = \left[\frac{-1}{2(k_1 + 4k_2')}\right] \times \left[\log \frac{4(-k_1 + k_1 y + k_2' y^2)}{-k_1(2-y)^2}\right]$$

$$- \left[\frac{y}{2(k_1 + 4k_2')\,(2-y)}\right] + \left[\frac{k_1 + 2k_2'}{2(k_1 + 4k_2')\sqrt{k_1(k_1 + 4k_2')}}\right]$$

$$\times \left[\log \frac{\left\{-k_1 - 2k_2'y - \sqrt{k_1(k_1 + 4k_2')}\right\}\left\{-k_1 + \sqrt{k_1(k_1 + 4k_2')}\right\}}{\left\{-k_1 - 2k_2'y + \sqrt{k_1(k_1 + 4k_2')}\right\}\left\{-k_1 - \sqrt{k_1(k_1 + 4k_2')}\right\}}\right] \qquad (20)$$

The equilibrium constant K_p is defined as

$$K_p = \frac{[P_{CO}]^2}{[P_{CO_2}]} = \frac{[P_t[CO]]^2}{P_t[CO_2]} = P_t\frac{[CO]^2}{[CO_2]} = \frac{[CO]^2}{[CO_2]} \qquad (21)$$

where P_{CO} is the partial pressure of carbon monoxide and P_{CO_2} is the partial pressure of carbon dioxide and P_t is the total pressure which is one atmosphere in the present work.

From Equation No. 15 at equilibrium

$$k_1\,[CO_2] = k_2\,[CO]^2 \qquad (22)$$

and so

$$\frac{[CO]^2}{[CO_2]} = \frac{k_1}{k_2} = K_p \qquad (23)$$

Solution of Equation No. 20

Equation No. 20 is space time T expressed as a function of k_1 and k_2'. At a given temperature the experiment yields the variation of y with T. The experiment also yields $K = \frac{k_1}{K}$ calculated from the actual percentages of carbon monoxide and carbon dioxide. Hence, for any assumed k_1, k_2 and consequently k_2' can be attained.

Knowing k_1 (assumed) and $k_2' = \frac{k_1}{K} [CO_2]_o$, a T' can be calculated for every y. If an error term is defined as $\Delta_i = T_i - T_i'$, then the parameter to be minimized is

$$\text{Sigma} = \Sigma \, {\Delta_i}^2 = f(k_1) \tag{24}$$

A search process has to be employed to find the value of k_1 that best suits the experimental data.

Two different search techniques are used in this study, the Monte-Carlo search technique and the Fibonacci search technique. These techniques are explained in Beveridge and Schechter (10). The computer programs used to solve Equation No. 20, employing these search techniques, are shown in Appendices A and B. These programs were written in Fortran IV-G and were solved on the IBM-370 computer at the University of North Dakota computer center.

RESULTS

Gas Analysis

The analysis of the product gases were adjusted to a basis of 100 per cent carbon monoxide and carbon dioxide by the following method:

$$\text{Percent CO} = \frac{\text{Volume CO/100 ml}}{\text{Volume (CO + CO}_2\text{)/100 ml}} \times 100 \qquad (25)$$

$$\text{Percent CO}_2 = \frac{\text{Volume CO}_2\text{/100 ml}}{\text{Volume (CO + CO}_2\text{)/100 ml}} \times 100 \qquad (26)$$

Product gas data after this correction are given in Tables 6 and 7, at various space times based on the flow rate of carbon dioxide in the reactor. The data are graphed in Figures 5, 6 and 7.

The highest ratio of CO to CO_2 for each coal at each temperature was then used to calculate a pseudo-equilibrium constant, K_p, for each char at each temperature. The K_p values calculated from test data do not represent true equilibrium values because the concentrations of CO were observed to be slowly increasing. The values of K_p are shown in Table 8.

Statistical Analysis

The relative reaction rate for the coal was measured for a given space time and temperature conditions by the extent of decomposition of

TABLE 6.-- PERCENTAGE CARBON MONOXIDE IN THE PRODUCT GASES

TEMPERATURE	SPACE TIME	COAL			
DEGREES F	SECS	A	B	C	D
1100	5	3.0	60.9	44.2	49.9
1100	10	4.8	64.0	52.8	57.0
1100	15	6.1	67.6	56.4	61.4
1100	20	8.3	71.0	61.3	65.8
1200	5	15.6	88.7	63.8	80.2
1200	10	21.0	91.2	74.1	86.5
1200	15	26.5	93.1	76.4	89.4
1200	20	40.9	93.5	82.6	92.8
1300	5	35.3	93.4	79.9	91.7
1300	10	51.7	95.1	93.0	95.2
1300	15	58.2	95.8	95.4	96.9
1300	20	65.4	97.0	97.1	97.3

TABLE 7.-- PERCENTAGE CARBON DIOXIDE IN THE PRODUCT GASES

TEMPERATURE	SPACE TIME	COAL			
DEGREES F	SECS	A	B	C	D
1100	5	97.0	39.1	55.8	50.1
1100	10	95.2	36.0	47.2	43.0
1100	15	93.9	32.4	43.6	38.6
1100	20	91.7	29.0	38.7	34.2
1200	5	84.4	11.3	36.2	19.8
1200	10	79.0	8.8	25.9	13.5
1200	15	73.5	6.9	23.6	10.6
1200	20	59.1	6.5	17.4	7.2
1300	5	64.7	6.6	20.1	8.3
1300	10	48.3	4.9	7.0	4.8
1300	15	41.8	4.2	4.6	3.1
1300	20	34.6	3.0	2.9	2.7

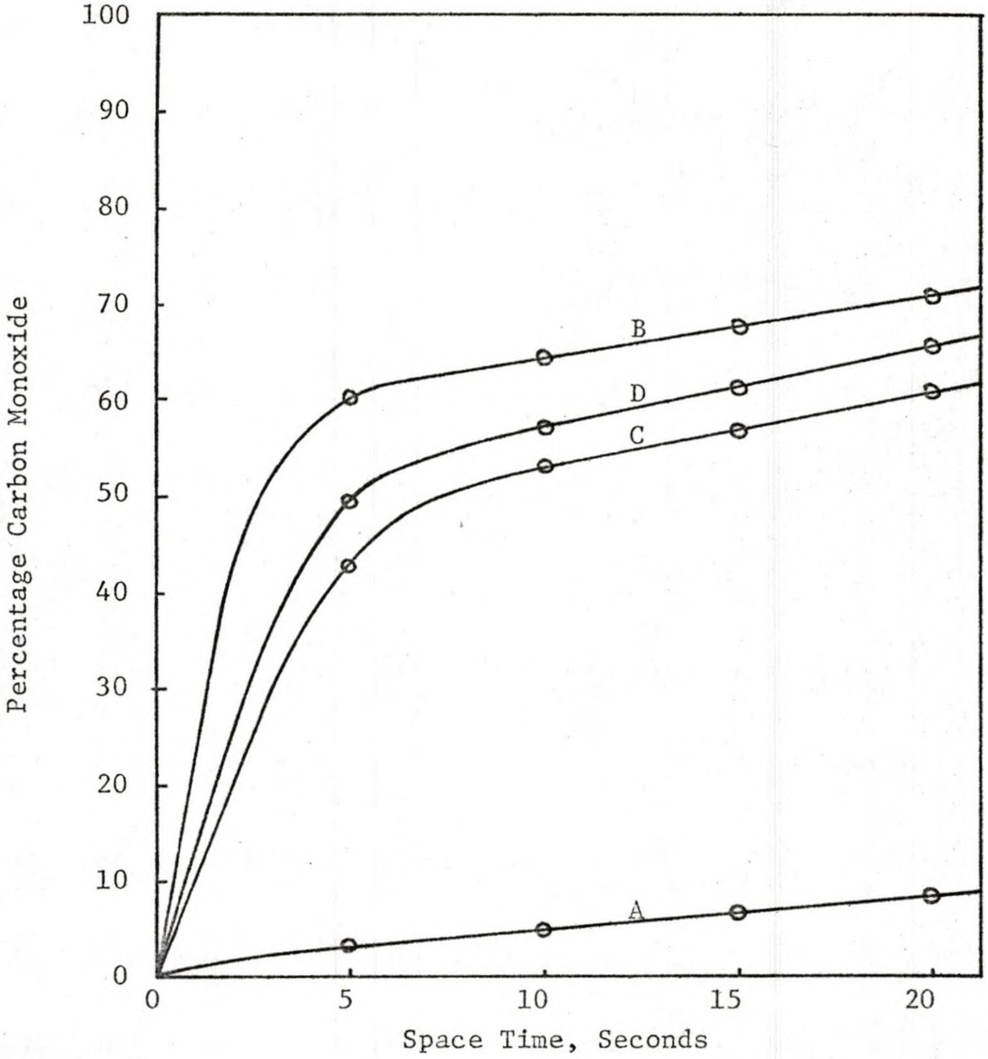


Fig. 5.--Variation of percentage carbon monoxide with space time at 1100°F.

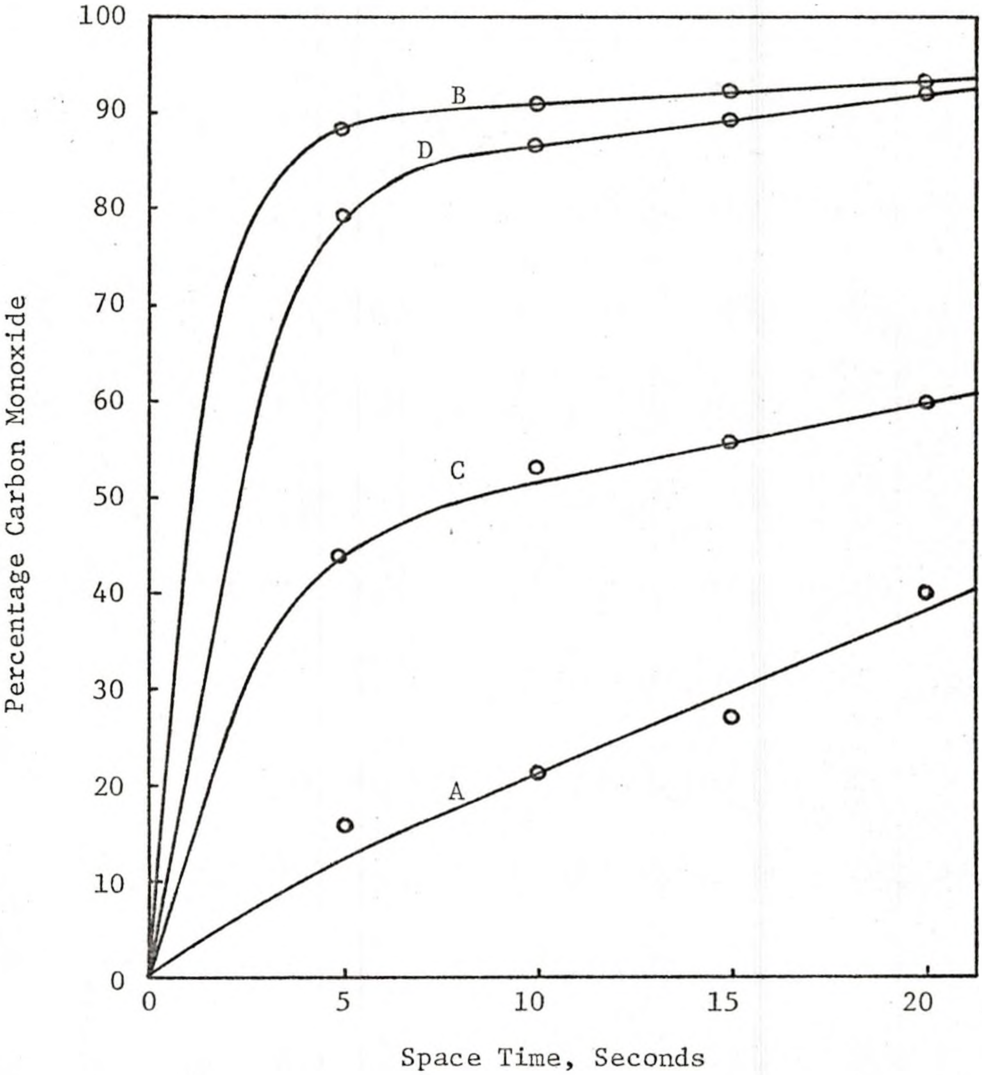


Fig. 6.--Variation of percentage carbon monoxide with space time at 1200°F.

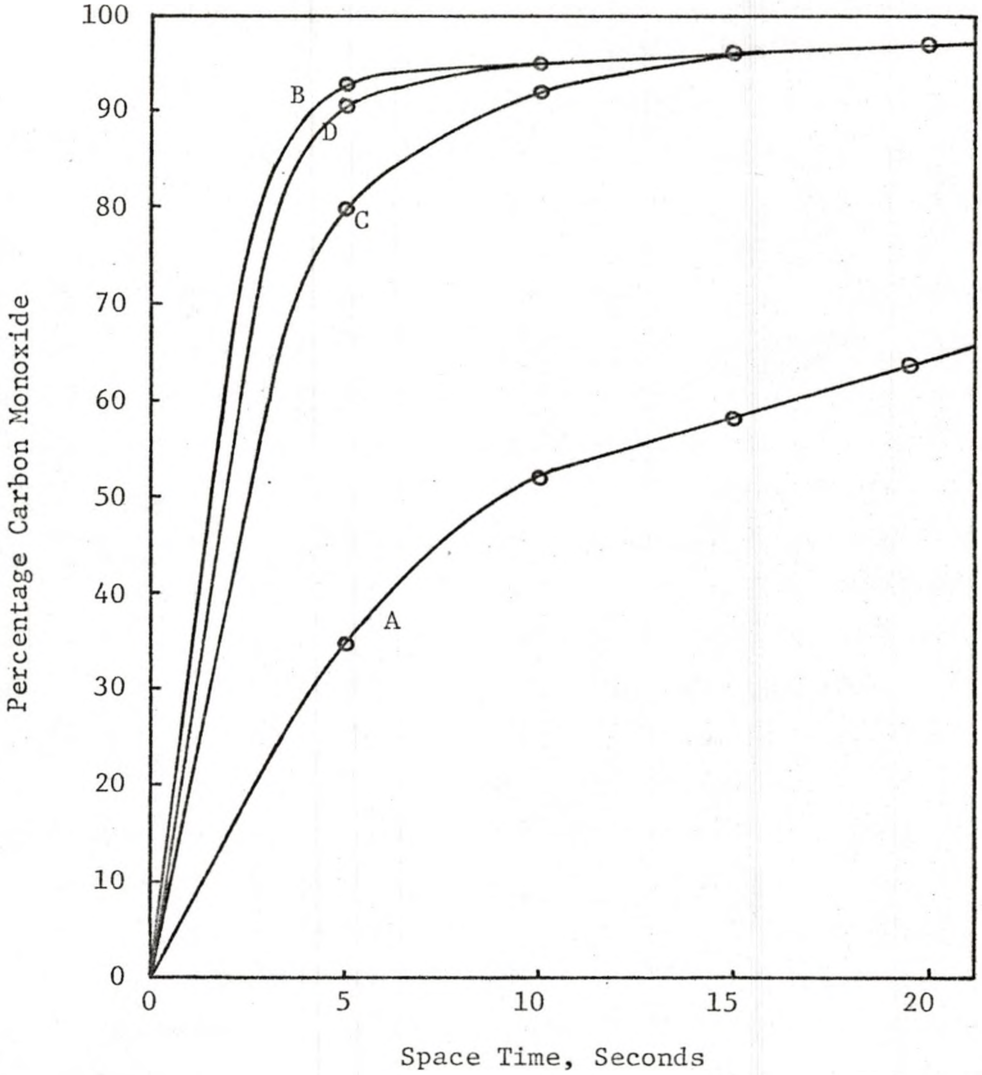


Fig. 7.--Variation of percentage carbon monoxide with space time at 1300°F.

TABLE 8.--RATE CONSTANTS AND EQUILIBRIUM CONSTANTS

Coal	Temperature Degrees F	Sigma	K1	K2	Kp
A	1100	4.7	0.001159	0.155600	0.00745
A	1200	18.4	0.007687	0.027260	0.28200
A	1300	4.2	0.022237	0.019010	1.17000
B	1100	56.1	0.033580	0.020280	1.65600
B	1200	64.9	0.113857	0.008845	12.87200
B	1300	61.9	0.154568	0.005094	30.34400
C	1100	31.2	0.021510	0.023050	0.93300
C	1200	22.0	0.048231	0.012910	3.73500
C	1300	81.2	0.133660	0.004387	30.46500
D	1100	33.6	0.025712	0.020700	1.24200
D	1200	22.9	0.089413	0.007899	11.31900
D	1300	41.1	0.157850	0.004621	34.15800

carbon dioxide. Thus, the degree of decomposition of carbon dioxide is a measure of coal reactivity for the Bouduard reaction. The statistical analysis was made using the percentage of carbon monoxide in the product gases (see Table 6) as the parameter for significance testing.

Influence of Coal Rank

The analysis of variance tests performed on the 3 x 4 x 4 factorial design confirm that there were significant differences in the reactivities of coals as tested. The null hypothesis, which states that the effects of ranks are all equal to zero, could not be accepted at the 0.05 significant level.

The order of reactivity of the coals thus measured from greatest to least was B, D, C and A. The lignites were most reactive followed by sub-bituminous coal and then the bituminous coal. The same order of reactivity was observed for all temperatures and space times investigated, and is confirmed by the order of magnitude of the values of k_1 for the forward reaction (see Table 8).

Influence of Temperature

The analysis of variance (Table 9) shows that the reactivity of coals varied significantly with temperature. The null hypothesis states that the effects of temperature are all equal to zero. The calculated F is greater than the critical F at the 0.05 level, so that the null hypothesis cannot be accepted. These results establish that the Bouduard reaction is significantly temperature dependent for the temperature range and chars tested.

TABLE 9

STATISTICAL ANALYSIS--ANALYSIS OF VARIANCE FOR 3 x 4 x 4 FACTORIAL

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Calculated F	Critical F	Estimated Mean Square
Temperature (A)	11662.4	2	5831.2	50.7	F0.05(2,6) = 4.74	$s^2 + 4s_{ab}^2 + 16s_a^2$
Coal (B)	24335.9	3	8112.0	70.5	F0.05(3,6) = 4.76	$s^2 + s_{abc}^2 + 4s_{ab}^2 + 3s_{bc}^2 + 4s_b^2$
Space Time (C)	1228.9	3	409.6	9.9	F0.05(3,44) = 2.83	$s^2 + 4s_{ac}^2 + 12s_c^2$
A x B	690.8	6	115.1	2.8	F0.05(6,44) = 2.33	$s^2 + s_{abc}^2 + 4s_{ab}^2$
B x C	204.3	9	22.7	1.7	F0.05(9,18) = 2.46	$s^2 + s_{abc}^2 + 3s_{bc}^2$
A x C	31.0	6	5.2	0.4	F0.05(6,18) = 2.66	$s^2 + 4s_{ac}^2$
Subtotal	38151.3	29				
Error (AxBxC)	246.3	18	13.7			$s^2 + s_{abc}^2$
TOTAL	38399.6	47				

Influence of Space Time

The percentage of carbon monoxide in the product varied with space time or time of contact of solid and gases. As would be expected, more carbon dioxide was reacted with an increase in space time. The longer the gas is in contact with the coal, the more gas reacts with the coal. This is evidenced by the calculated F being greater than the critical F, substantiating the dependence of reactivity on space time. But, from rate data, it can also be seen that as the temperature increases, the effect of contact time is reduced.

APPLICATION OF THEORY AND DISCUSSION

The mechanism that has been considered in the present study is a simple model based on the stoichiometric equation

$$CO_2 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ CO \tag{14}$$

The rate data obtained from the experiments made possible the evaluation of k_1 and k_2 based on the pseudo-equilibrium constants calculated from the actual percentages of carbon monoxide and carbon dioxide. The values of k_1, k_2 and K_p calculated are shown in Table 8. The results of the computer solution of Equation No. 20 for different coals at different temperature are given in Appendix C. The solution employs a search method using least squares strategy. The error term to be minimized is Sigma (see Equation No. 24). It is observed from the computer output, that the predicted values of k_1 and k_2 fit the experimental data closely.

From the data obtained in the experiments (see Table 8), an Arrhenius-type plot of the reaction rate could be drawn (see Figures 8, 9 and 10). In these plots, the experimental values of k_1, k_2 and K_p are plotted as a function of the temperatures.

Examination of the graph reveals that the slope of the line for k_2 is positive. This means that in the equation $k_2 = A\ e^{\frac{-E}{RT}}$, the term $\frac{-E}{R}$ is positive, thus implying a negative activation energy. A negative

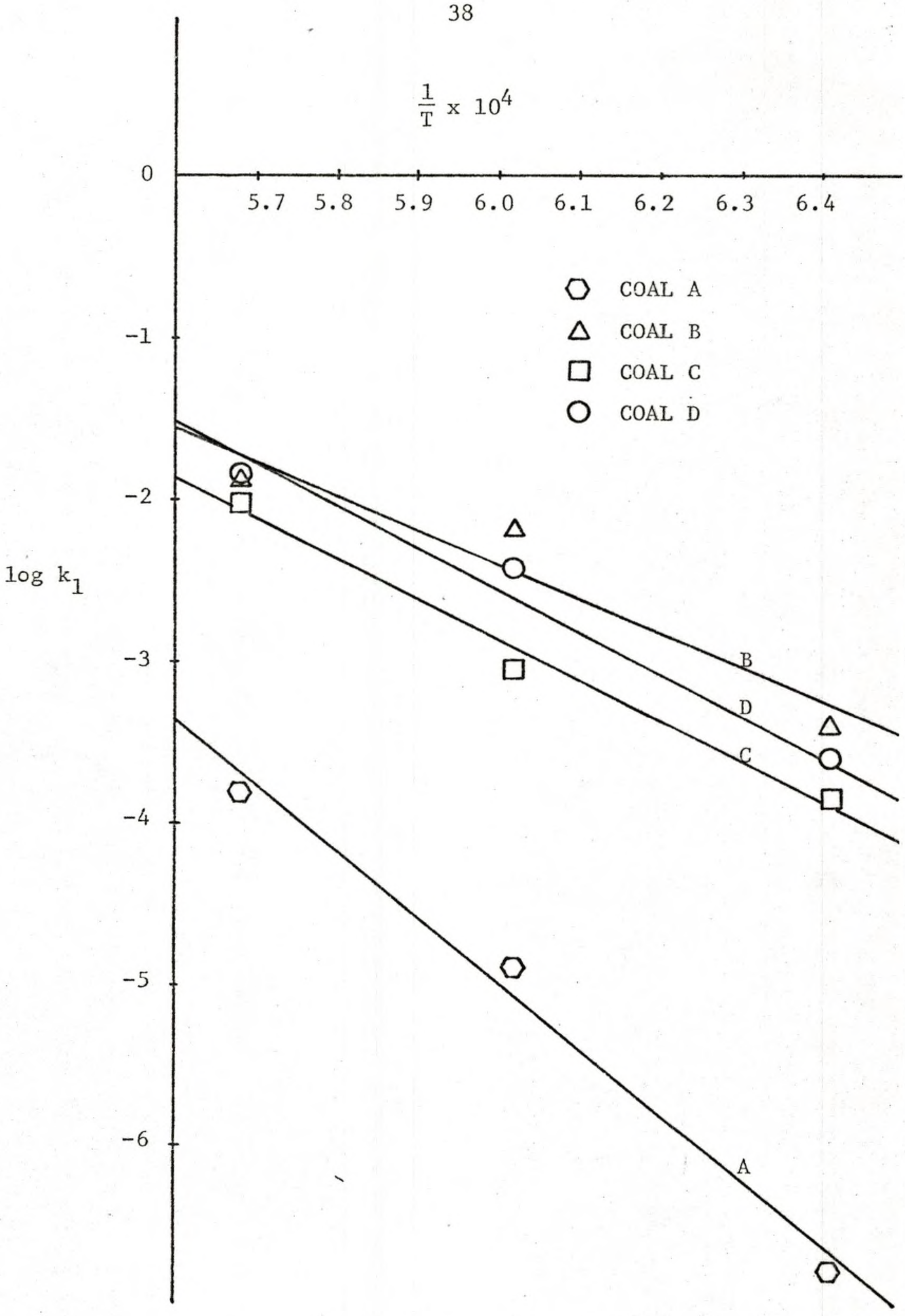


Fig. 8.--Variation of k_1 with temperature.

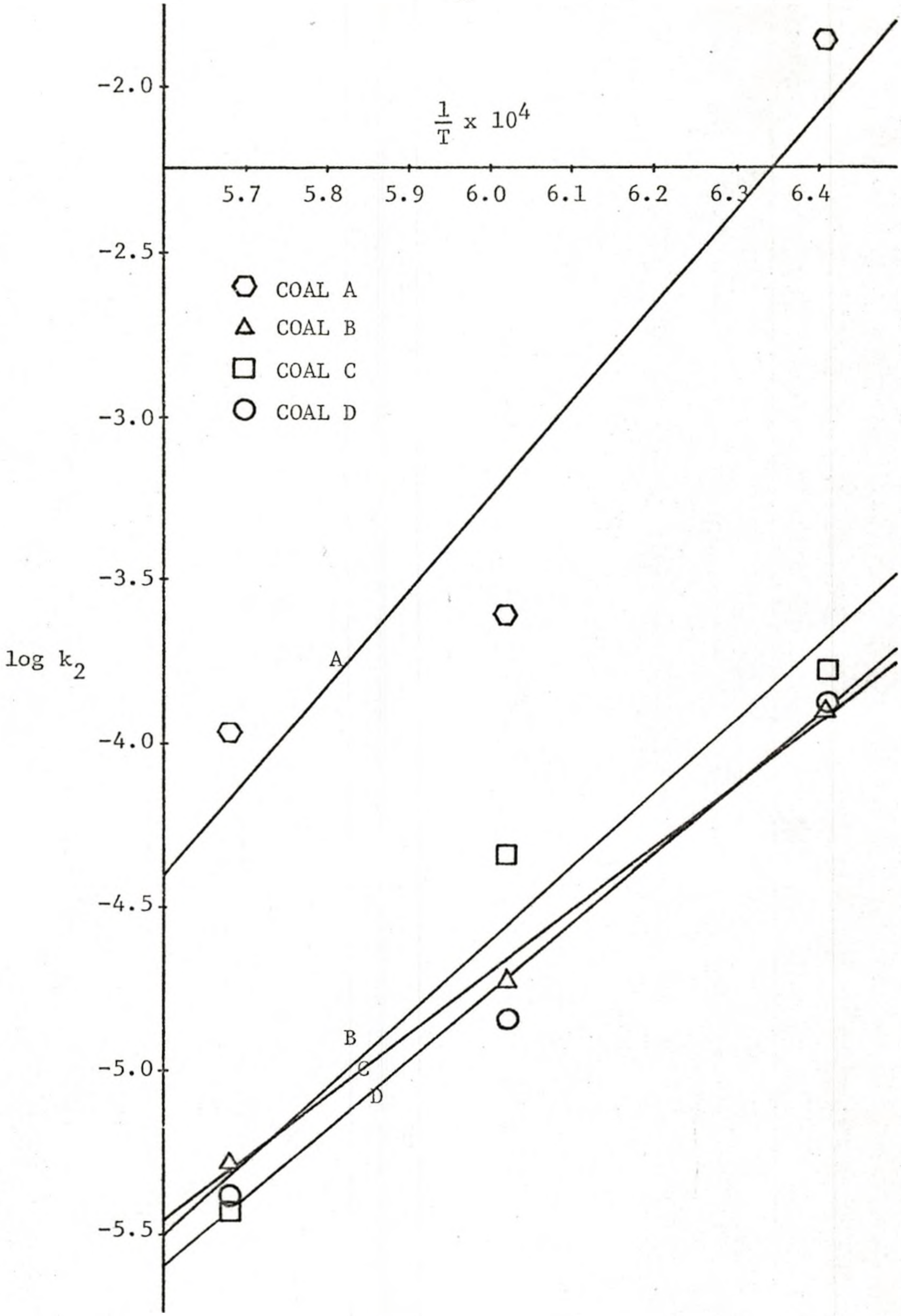


Fig. 9.--Variation of k_2 with temperature.

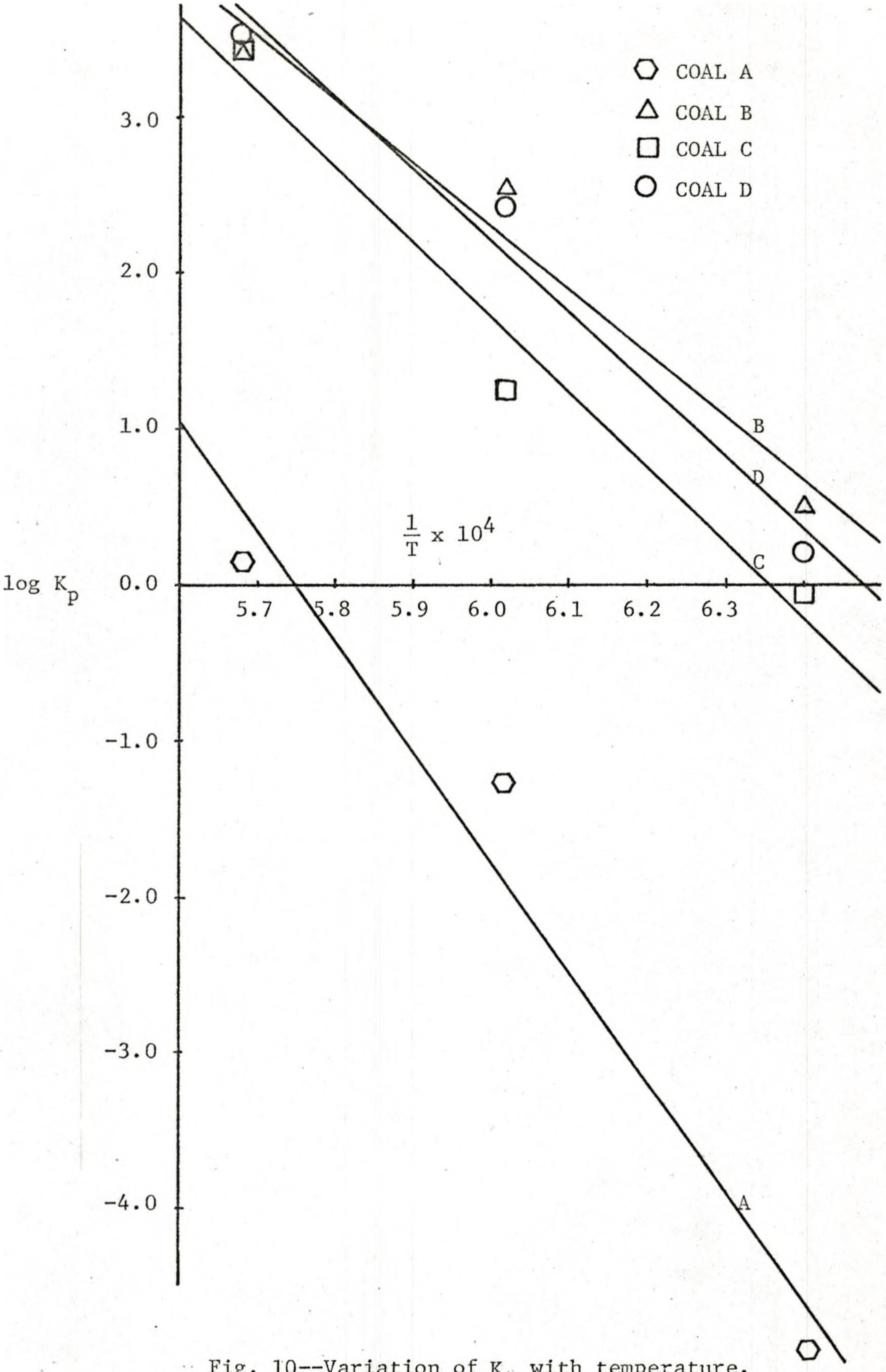


Fig. 10--Variation of K_p with temperature.

activation energy is not interpretable in current reaction theory.

The positive slope of the line also means that the rate of the reverse reaction decreases with temperature. But, the rate of a simple reaction step should increase with temperature, in contrast to the results observed here.

These two observations clearly indicate that the simple mechanism considered, based on the stoichiometric equation, does not represent the actual mechanism of the reaction. The assumption that the forward reaction is of first order and the reverse reaction is of the second order is not correct. The correction for volume change during reaction employed in derivation of the equation did not correct the simple equation mechanism.

An attempt was made to fit the rate data into the mechanism proposed by Reif (4).

$$CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (O) + CO \qquad (2)$$

$$C + (O) \xrightarrow{k_3} CO \qquad (3)$$

The rate of reaction for this mechanism is expressed by an equation of the form

$$\text{rate} = \frac{K_1 p_{CO_2}}{1 + K_2 p_{CO} + K_3 p_{CO_2}} \qquad (27)$$

where K_1, K_2 and K_3 are functions of the rate constants k_1, k_2 and k_3. The available data were not sufficient to do a meaningful analysis.

The reaction of carbon dioxide with carbon is heterogeneous, and cannot be explained by a simple mechanism based on the stoichiometric equation. A more complex mechanism using the concept of reaction rates is necessary.

The heterogeneous reaction occurs by way of a series of diffusional and chemical steps, described as follows:

> 1. Mass Transfer and diffusion of reactants from the gas through a relatively stagnant film to the solid surface and to available capillary areas of pore structure.
> 2. Adsorption, physical and/or chemical, of reactants on the solid.
> 3. Surface chemical reaction, which may be preceded by reactant dissociation.
> 4. Release of surface reaction products, and
> 5. Diffusion and mass transfer of products to the bulk of the gas stream (11).

Thus in a broad sense, the heterogeneous reaction mechanism comprises a diffusional part, the rapidity of which depends on concentration differences and molecular velocities of gases near the surface and in the porous structure; and a chemical kinetic part, which essentially consists of chemisorption of the reactants and desorption of the products and of the chemical reaction on the surface.

Materials with small particle size have a large ratio of external surface to available pore surface. Hence the effect of internal diffusion on overall rate is small. Thus the effect of diffusion is only being offered by the resistance to transfer to and from the surface. But, with large, porous particles, the reaction rate is significantly influenced by internal diffusion. Hence measured reaction rate will always include some effects of the resistance due to internal diffusion.

The relative importance of diffusion increases with reactivity of the carbon surface, particle diameter, pore size and distribution.

The pore geometry and degree of penetration of the reacting gases into the solid becomes important when there is appreciable diffusional resistance. In a strict sense, the true chemical kinetic effects can only be determined if all diffusional resistances are made negligible.

Under steady state conditions, the total external diffusion rate equals the total reaction rate, and the internal diffusion rate is essentially equivalent to the reaction rate in the pore structure. The rate of reaction at the external surface would be equal to the difference between external and internal diffusion rates.

If the diffusional resistance is nearly the total resistance, the reaction is "diffusion controlled." Conversely, the reaction is "kinetically controlled" at negligible diffusional resistance.

A common assumption in gasification reactions is the existence of active carbon-free sites distributed in small concentration throughout the carbon structure. These sites are capable of chemisorbing the reacting gas molecules forming a complex occupied site.

The rate and the order of the reaction depend on the formation and removal rates of these surface complexes and on the number and extent of coverage of the active carbon-free sites. The gasification rate could be defined as being proportional to the number of occupied sites (see Equation No. 5).

Based on the above discussion, if one may assume the external surface to be negligible compared to the pore surface, the Bouduard reaction can be represented by the following steps:

$$\mathrm{CO}_{2\ \text{Bulk}} \xrightleftharpoons[k_2]{\substack{k_1 \\ \text{External Diffusion}}} \mathrm{CO}_{2\ \text{Surface}} \tag{28}$$

$$\mathrm{CO}_{2\ \text{Surface}} \xrightleftharpoons[k_4]{\substack{k_3 \\ \text{Internal Diffusion}}} \mathrm{CO}_{2\ \text{Pores}} \tag{29}$$

$$\mathrm{CO}_{2\ \text{Pores}} \xrightleftharpoons[k_6]{\substack{k_5 \\ \text{Adsorption}}} \mathrm{CO}_{2\ \text{Adsorbed}} \tag{30}$$

$$\mathrm{CO}_{2\ \text{Adsorbed}} + \mathrm{C} \xrightleftharpoons[k_8]{\substack{k_7 \\ \text{Reaction}}} 2\ \mathrm{CO}_{\text{Adsorbed}} \tag{31}$$

$$\mathrm{CO}_{\text{Adsorbed}} \xrightleftharpoons[k_{10}]{\substack{k_9 \\ \text{Desorption}}} \mathrm{CO}_{\text{Pores}} \tag{32}$$

$$\mathrm{CO}_{\text{Pores}} \xrightleftharpoons[k_{12}]{\substack{k_{11} \\ \text{Internal Diffusion}}} \mathrm{CO}_{\text{Surface}} \tag{33}$$

$$\mathrm{CO}_{\text{Surface}} \xrightleftharpoons[k_{14}]{\substack{k_{13} \\ \text{Bulk Diffusion}}} \mathrm{CO}_{\text{Bulk}} \tag{34}$$

Any one or more of the above steps could be rate controlling, and the other steps then neglected for rate considerations in comparison with the rate controlling step.

CONCLUSIONS

1. The stoichiometric equation $CO_2 + C \rightleftharpoons 2\ CO$ does not reveal the mechanism of the reaction.

2. The rank of coal has a significant effect on the reactivity of carbon dioxide with coal.

3. With the increase in rank of coal, the reactivity, with carbon dioxide, decreases.

4. These high reactivities may make low rank coals suitable for the production of synthetic natural gas.

5. Temperature has a significant effect on the Bouduard reaction, as does space time.

SUGGESTIONS FOR FUTURE WORK

Based on the overall reaction, the rate of the reaction can be expressed by an expression of the form

$$\text{rate} = k_1[CO]^n - k_2[CO_2]^m \tag{35}$$

where k_1 and k_2 are the reaction rate constants of the forward and reverse reactions respectively, and m and n are the forward and reverse orders of the reaction respectively. With sufficient rate data some form of a regression technique may be used to solve this equation to give k_1, k_2, m and n. These rate constants thus calculated are not the rate constants of the rate controlling step, but are related to the true rate constants. A knowledge of the reaction rate constants k_1 and k_2 and the orders of the reaction, m and n would aid in the prediction of a mechanism for the Bouduard reaction from all the possible steps.

One of the possible conclusions that could be drawn from the collected data and calculated results is that the reaction may be controlled by diffusional effects. Effects of particle size of the coal on the reaction rate can be studied. If the order of magnitude of mass transfer rate due to diffusion is found much higher than that of the actual reaction rate then it could be concluded that diffusion is not the controlling step. If this is not true, then diffusion is also important. This study will be able to explain the deviation of the true order of the reaction from the apparent order as given by the stoichiometric equation.

Once this is determined, attempts could be made to collect rate data after eliminating diffusional effects. Attempts could be made to fit the collected data into an adsorption model as follows:

$$CO_2 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CO_2)_{ads}$$

$$(CO_2)_{ads} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2(CO)_{ads}$$

$$(CO)_{ads} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} CO$$

Of these any one step could be assumed to be rate controlling and the data could be tested to fit this model. If the data fit, the assumption could be valid. If not, another step could be assumed to be rate controlling and the procedure repeated.

APPENDIX A

PROGRAM TO SOLVE THE RATE EQUATION

THE MONTE-CARLO SEARCH TECHNIQUE

APPENDIX - A

PROGRAM TO SOLVE THE RATE EQUATION - THE MONTE-CARLO SEARCH TECHNIQUE

```
      DIMENSION TAU(4),Y(4),COAL(2)                                     MONT-001
      DATA IX/65547/                                                    MONT-002
   90 FORMAT (2F7.5)                                                    MONT-003
  999 READ (5,90) A1,A2                                                 MONT-004
      IF (A1 .EQ. 0 .AND. A2 .EQ. 0) GO TO 1000                         MONT-005
      READ (5,60) (TAU(N),Y(N),N=1,4),COAL(1),COAL(2),TEMP,EQBMKP       MONT-006
   60 FORMAT (4(F2.0,3X,F5.3,5X),2A4,F4.0,2X,F6.3)                      MONT-007
      WRITE (6,70) COAL(1),COAL(2),TEMP                                 MONT-008
   70 FORMAT ('1'////21X,'RATE CONSTANTS FOR',2A4,' AT TEMPERATURE OF ',FMONT-009
     $6.1,' DEGREES FAHRENHEIT'//)                                      MONT-010
      WRITE (6,80) (N,TAU(N),Y(N),N=1,4)                                MONT-011
   80 FORMAT (21X,'FOR GIVEN VALUES OF'/21X,6X,'TAU',6X,'Y',/,4(21X,I2,3MONT-012
     $X,F4.1,4X,F5.3/)/)                                                MONT-013
      WRITE (6,260)                                                     MONT-014
  260 FORMAT (20X,'      LIMITS OF K1'/20X,'  LOWER',5X,'UPPER',10X,'K1',1MONT-015
     $5X,'K2',14X,'SIGMA'/)                                             MONT-016
      PBYRT=1.0/(0.08025)/(((TEMP-32.0)*5.0/9.0)+273.2)                 MONT-017
      DELTA=(A2-A1)/10.0                                                MONT-018
      A2=A1                                                             MONT-019
      A3=A1                                                             MONT-020
      SUMALL=10.0E+10                                                   MONT-021
      NUM1=10                                                           MONT-022
      NUM2=500                                                          MONT-023
      NUM3=1                                                            MONT-024
  120 DO 100 I9= 1,NUM1                                                 MONT-025
      A1=A2                                                             MONT-026
      A2=A1+DELTA                                                       MONT-027
      SUM=10.0E+10                                                      MONT-028
      DO 210 J = 1,NUM2                                                 MONT-029
```

```
      CALL RANDU (IX,IY,YFL)                                            MONT-030
      AK1=A1+DELTA*YFL                                                  MONT-031
      AK2=AK1*PBYRT/EQBMKP                                              MONT-032
      SUMSQU=0.0                                                        MONT-033
      P=AK1+4.0*AK2                                                     MONT-034
      P1=AK1*P                                                          MONT-035
      Q=SQRT(P1)                                                        MONT-036
      C1=-1.0/(2.0*P)                                                   MONT-037
      C2=(AK1+2.0*AK2)/(2.0*P*Q)                                        MONT-038
      DO 500 I=1,4                                                      MONT-039
      U=Y(I)                                                            MONT-040
      W1=(4.*(-AK1+AK1*U+AK2*U*U)/(-AK1*(2.-U)*(2.-U)))                 MONT-041
      W=C1*ALOG(W1)-U/(2.*P*(2.-U))                                     MONT-042
      C3=((AK1+2.*AK2*U+Q)*(-AK1+Q))/((-AK1-2.0*AK2*U+Q)*(AK1+Q))       MONT-043
      TAUP=W+C2*ALOG(C3)                                                MONT-044
      V=TAU(I)-TAUP                                                     MONT-045
      SUMSQU=SUMSQU+V*V                                                 MONT-046
  500 CONTINUE                                                          MONT-047
      IF (SUMSQU .LT. SUM) GO TO 140                                    MONT-048
      GO TO 110                                                         MONT-049
  140 SUM=SUMSQU                                                        MONT-050
      ANS1=AK1                                                          MONT-051
  110 IX=IY                                                             MONT-052
  210 CONTINUE                                                          MONT-053
      ANS2=ANS1/EQBMKP                                                  MONT-054
      IF (NUM3 .EQ. 0) GO TO 150                                        MONT-055
      WRITE (6,250) A1,A2,ANS1,ANS2,SUM                                 MONT-056
  250 FORMAT  (22X,2(F5.3,5X),3(E12.6,5X))                              MONT-057
      IF (SUM .LT. SUMALL) GO TO 130                                    MONT-058
      GO TO 100                                                         MONT-059
  130 A3=A1                                                             MONT-060
      SUMALL=SUM                                                        MONT-061
  100 CONTINUE                                                          MONT-062
      A2=A3                                                             MONT-063
      NUM1=1                                                            MONT-064
```

```
      NUM2=2000                                                         MONT-065
      NUM3=0                                                            MONT-066
      GO TO 120                                                         MONT-067
  150 AK1=ANS1                                                          MONT-068
      AK2=AK1/EQBMKP                                                    MONT-069
      WRITE (6,160) AK1,AK2,EQBMKP,SUM                                  MONT-070
  160 FORMAT (/20X,35('**')//20X,' FINAL ANSWER'/20X,' ------------'/33XMONT-071
     $,'RATE CONSTANTS',5X,'K1 = ',E12.6/52X,'K2 = ',E12.6/48X,'EQBMKP =MONT-072
     $ ',E12.6//49X,'SIGMA = ',E12.6//20X,35('**'))                     MONT-073
      GO TO 999                                                         MONT-074
 1000 WRITE (6,1001)                                                    MONT-075
 1001 FORMAT ('1')                                                      MONT-076
      STOP                                                              MONT-077
      END                                                               MONT-078
```

APPENDIX B

PROGRAM TO SOLVE THE RATE EQUATION

THE FIBONACCI SEARCH TECHNIQUE

APPENDIX - B

PROGRAM TO SOLVE THE RATE EQUATION - THE FIBONACCI SEARCH TECHNIQUE

```
      COMMON TAU(4),Y(4),PBYRT,EQBMKP,AK1,AK2,SUMSQU                    FIBO-001
      DIMENSION F(30),AK1I(10),AK2I(10),SUMI(10),COAL(2)                FIBO-002
  999 READ (5,10) OSINTL,OSINTU,ALPHA                                   FIBO-003
   10 FORMAT (3F7.5)                                                    FIBO-004
      IF (OSINTL .EQ. 0.0 .AND. OSINTU .EQ. 0.0 .AND. ALPHA .EQ. 0.0) GOFIBO-005
     $ TO 1000                                                          FIBO-006
      FLAST=1.0/ALPHA                                                   FIBO-007
      N=1                                                               FIBO-008
      ANUM1=0.0                                                         FIBO-009
      ANUM2=1.0                                                         FIBO-010
   20 F(N)=ANUM1+ANUM2                                                  FIBO-011
      ANUM2=ANUM1                                                       FIBO-012
      ANUM1=F(N)                                                        FIBO-013
      NLAST=N                                                           FIBO-014
      N=N+1                                                             FIBO-015
      IF(ANUM1 .LT. FLAST) GO TO 20                                     FIBO-016
      WRITE (6,30) ALPHA                                                FIBO-017
   30 FORMAT ('1',/////,21X,'FIBONACCI SERIES TO BE USED'/,21X,'GIVEN ALFIBO-018
     $PHA = ',F8.5,//,31X,' N',5X,'F(N)',/)                             FIBO-019
      DO 40 I=1,NLAST                                                   FIBO-020
      N=I-1                                                             FIBO-021
   40 WRITE (6,50) N,F(I)                                               FIBO-022
   50 FORMAT (' ',30X,I2,3X,F8.1)                                       FIBO-023
      READ (5,60) (TAU(N),Y(N),N=1,4),COAL(1),COAL(2),TEMP,EQBMKP       FIBO-024
   60 FORMAT (4(F2.0,3X,F5.3,5X),2A4,F4.0,2X,F6.3)                      FIBO-025
      WRITE (6,70) COAL(1),COAL(2),TEMP                                 FIBO-026
   70 FORMAT ('1'////21X,'RATE CONSTANTS FOR',2A4,'AT TEMPERATURE OF ',FFIBO-027
     $6.1,' DEGREES FAHRENHEIT'//)                                      FIBO-028
      WRITE (6,80) (N,TAU(N),Y(N),N=1,4)                                FIBO-029
```

```
   80 FORMAT (21X,'FOR GIVEN VALUES OF'/21X,6X,'TAU',6X,'Y',/,4(21X,I2,3FIBO-030
     $X,F4.1,4X,F5.3/)/)                                                FIBO-031
      WRITE (6,260)                                                     FIBO-032
  260 FORMAT (20X,'    LIMITS OF K1'/20X,'  LOWER',5X,'UPPER',10X,'K1',1FIBO-033
     $5X,'K2',14X,'SIGMA'/)                                             FIBO-034
      PBYRT=1.0/(0.08025)/(((TEMP-32.0)*5.0/9.0)+273.2)                 FIBO-035
      ZINT=(OSINTU-OSINTL)/10.0                                         FIBO-036
      N3=NLAST-3                                                        FIBO-037
      CL=ZINT                                                           FIBO-038
      B1=OSINTL                                                         FIBO-039
      DO 90 I=1,10                                                      FIBO-040
      AI=I                                                              FIBO-041
      A1=B1                                                             FIBO-042
      B1=A1+ZINT                                                        FIBO-043
      SL=(F(NLAST-2)/F(NLAST))*ZINT                                     FIBO-044
      X1=A1+SL                                                          FIBO-045
      X2=B1-SL                                                          FIBO-046
      AK1=X1                                                            FIBO-047
      CALL THEQAN                                                       FIBO-048
      SUM=SUMSQU                                                        FIBO-049
      AK1=X2                                                            FIBO-050
      CALL THEQAN                                                       FIBO-051
      IF (SUMSQU .LT. SUM) GO TO 110                                    FIBO-052
      B1=X2                                                             FIBO-053
      NCOUNT=0                                                          FIBO-054
      GO TO 120                                                         FIBO-055
  110 SUM=SUMSQU                                                        FIBO-056
      A1=X1                                                             FIBO-057
      NCOUNT=1                                                          FIBO-058
  120 DO 170 K=2,N3                                                     FIBO-059
      CL=B1-A1                                                          FIBO-060
      SL=(F(NLAST-(K+1))/F(NLAST-(K-1)))*CL                             FIBO-061
      X1=A1+SL                                                          FIBO-062
      X2=B1-SL                                                          FIBO-063
      AK1=X1                                                            FIBO-064
```

```
      IF(NCOUNT .EQ. 1) AK1=X2                                          FIBO-065
      CALL THEQAN                                                       FIBO-066
      IF (NCOUNT .EQ. 1) GO TO 130                                      FIBO-067
      IF (SUMSQU .LT. SUM) GO TO 140                                    FIBO-068
      A1=X1                                                             FIBO-069
      NCOUNT=1                                                          FIBO-070
      GO TO 170                                                         FIBO-071
  140 SUM=SUMSQU                                                        FIBO-072
      B1=X2                                                             FIBO-073
      NCOUNT=0                                                          FIBO-074
      GO TO 170                                                         FIBO-075
  130 IF (SUMSQU .LT. SUM) GO TO 160                                    FIBO-076
      B1=X2                                                             FIBO-077
      NCOUNT=0                                                          FIBO-078
      GO TO 170                                                         FIBO-079
  160 SUM=SUMSQU                                                        FIBO-080
      A1=X1                                                             FIBO-081
      NCOUNT=1                                                          FIBO-082
  170 CONTINUE                                                          FIBO-083
      AK1=(A1-B1)/2.0+10.0E-7                                           FIBO-084
      CALL THEQAN                                                       FIBO-085
      IF (SUMSQU .LT. SUM) GO TO 180                                    FIBO-086
      IF (NCOUNT .EQ. 1) AK1=X2                                         FIBO-087
      AK1=X1                                                            FIBO-088
  180 AK1I(I)=AK1                                                       FIBO-089
      AK2I(I)=AK1/EQBMKP                                                FIBO-090
      SUMI(I)=SUM                                                       FIBO-091
      A1=OSINTL+(AI-1.0)*ZINT                                           FIBO-092
      B1=A1+ZINT                                                        FIBO-093
      WRITE (6,250) A1,B1,AK1I(I),AK2I(I),SUMI(I)                       FIBO-094
  250 FORMAT  (22X,2(F5.3,5X),3(E12.6,5X))                              FIBO-095
      B1=OSINTL+AI*ZINT                                                 FIBO-096
   90 CONTINUE                                                          FIBO-097
      L=1                                                               FIBO-098
      DO 200 I = 2,10                                                   FIBO-099
```

```
      IF (SUMI(I) .LT. SUMI(L)) L=I                                     FIBO-100
  200 CONTINUE                                                          FIBO-101
      WRITE (6,210) AK1I(L),AK2I(L),EQBMKP,SUMI(L)                      FIBO-102
  210 FORMAT (/20X,35('**')//20X,' FINAL ANSWER'/20X,' ------------'/33XFIBO-103
     $,'RATE CONSTANTS',5X,'K1 = ',E12.6/52X,'K2 = ',E12.6/48X,'EQBMKP =FIBO-104
     $ ',E12.6//49X,'SIGMA = ',E12.6//20X,35('**'))                     FIBO-105
      GO TO 999                                                         FIBO-106
 1000 WRITE (6,1001)                                                    FIBO-107
 1001 FORMAT ('1')                                                      FIBO-108
      STOP                                                              FIBO-109
      END                                                               FIBO-110


      SUBROUTINE THEQAN                                                 FIBO-111
      COMMON TAU(4),Y(4),PBYRT,EQBMKP,AK1,AK2,SUMSQU                    FIBO-112
      AK2=AK1/EQBMKP                                                    FIBO-113
      AK2P=AK2*PBYRT                                                    FIBO-114
      SUMSQU=0.0                                                        FIBO-115
      P=AK1+4.0*AK2P                                                    FIBO-116
      P1=AK1*P                                                          FIBO-117
      Q=SQRT(P1)                                                        FIBO-118
      C1=-1.0/(2.0*P)                                                   FIBO-119
      C2=(AK1+2.0*AK2P)/(2.0*P*Q)                                       FIBO-120
      DO 500 I=1,4                                                      FIBO-121
      U=Y(I)                                                            FIBO-122
      W1=(4.*(-AK1+AK1*U+AK2P*U*U)/(-AK1*(2.-U)*(2.-U)))                FIBO-123
      W=C1*ALOG(W1)-U/(2.*P*(2.-U))                                     FIBO-124
      C3=((AK1+2.*AK2P*U+Q)*(-AK1+Q))/((-AK1-2.0*AK2P*U+Q)*(AK1+Q))     FIBO-125
      TAUP=W+C2*ALOG(C3)                                                FIBO-126
      V=TAU(I)-TAUP                                                     FIBO-127
      SUMSQU=SUMSQU+V*V                                                 FIBO-128
  500 CONTINUE                                                          FIBO-129
      RETURN                                                            FIBO-130
      END                                                               FIBO-131
```

APPENDIX C

RESULTS OF COMPUTER SOLUTION OF THE RATE EQUATION

```
FIBONACCI SERIES TO BE USED
GIVEN ALPHA =  0.00001

              N       F(N)

              0          1.0
              1          1.0
              2          2.0
              3          3.0
              4          5.0
              5          8.0
              6         13.0
              7         21.0
              8         34.0
              9         55.0
             10         89.0
             11        144.0
             12        233.0
             13        377.0
             14        610.0
             15        987.0
             16       1597.0
             17       2584.0
             18       4181.0
             19       6765.0
             20      10946.0
             21      17711.0
             22      28657.0
             23      46368.0
             24      75025.0
             25     121393.0
```

```
RATE CONSTANTS FOR COAL A AT TEMPERATURE OF 1100.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
        TAU        Y
  1      5.0      0.030
  2     10.0      0.048
  3     15.0      0.061
  4     20.0      0.083


    LIMITS OF K1
  LOWER       UPPER            K1                   K2                   SIGMA

  0.0         0.001       0.999983E-03        0.134226E 00        0.234288E 02
  0.001       0.002       0.115859E-02        0.155516E 00        0.466420E 01
  0.002       0.003       0.200001E-02        0.268457E 00        0.136564E 03
  0.003       0.004       0.300002E-02        0.402688E 00        0.285455E 03
  0.004       0.005       0.400000E-02        0.536913E 00        0.380745E 03
  0.005       0.006       0.500002E-02        0.671144E 00        0.444590E 03
  0.006       0.007       0.600005E-02        0.805376E 00        0.489933E 03
  0.007       0.008       0.700001E-02        0.939599E 00        0.523681E 03
  0.008       0.009       0.800002E-02        0.107383E 01        0.549737E 03
  0.009       0.010       0.900002E-02        0.120806E 01        0.570444E 03

*************************************************************************

FINAL ANSWER
------------
               RATE CONSTANTS       K1 = 0.115859E-02
                                    K2 = 0.155516E 00
                                EQBMKP = 0.745000E-02

                                 SIGMA = 0.466420E 01

*************************************************************************
```

```
RATE CONSTANTS FOR COAL A AT TEMPERATURE OF 1200.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
        TAU          Y
 1       5.0       0.156
 2      10.0       0.210
 3      15.0       0.265
 4      20.0       0.409


    LIMITS OF K1
 LOWER       UPPER              K1                    K2                   SIGMA

 0.0         0.001        0.999983E-03         0.354604E-02         0.327429E 05
 0.001       0.002        0.199998E-02         0.709214E-02         0.593581E 04
 0.002       0.003        0.299998E-02         0.106382E-01         0.180485E 04
 0.003       0.004        0.399991E-02         0.141841E-01         0.640197E 03
 0.004       0.005        0.499993E-02         0.177302E-01         0.229773E 03
 0.005       0.006        0.599989E-02         0.212762E-01         0.762520E 02
 0.006       0.007        0.699972E-02         0.248217E-01         0.254296E 02
 0.007       0.008        0.768690E-02         0.272585E-01         0.183624E 02
 0.008       0.009        0.800118E-02         0.283730E-01         0.194847E 02
 0.009       0.010        0.900017E-02         0.319155E-01         0.339202E 02

***********************************************************************************

FINAL ANSWER
------------

                 RATE CONSTANTS          K1  =  0.768690E-02
                                         K2  =  0.272585E-01
                                     EQBMKP  =  0.282000E 00

                                      SIGMA  =  0.183624E 02

***********************************************************************************
```

```
RATE CONSTANTS FOR COAL A AT TEMPERATURE OF 1300.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
          TAU        Y
  1       5.0      0.353
  2      10.0      0.517
  3      15.0      0.582
  4      20.0      0.654


   LIMITS OF K1
 LOWER       UPPER              K1                   K2                    SIGMA

 0.010       0.013        0.129996E-01         0.111107E-01          0.379718E 03
 0.013       0.016        0.159999E-01         0.136751E-01          0.117095E 03
 0.016       0.019        0.189994E-01         0.162388E-01          0.256972E 02
 0.019       0.022        0.219996E-01         0.188031E-01          0.428605E 01
 0.022       0.025        0.222305E-01         0.190004E-01          0.420772E 01
 0.025       0.028        0.250008E-01         0.213682E-01          0.134017E 02
 0.028       0.031        0.280002E-01         0.239318E-01          0.359361E 02
 0.031       0.034        0.310005E-01         0.264961E-01          0.639700E 02
 0.034       0.037        0.340000E-01         0.290599E-01          0.936601E 02
 0.037       0.040        0.370001E-01         0.316241E-01          0.123133E 03

*****************************************************************************

FINAL ANSWER
------------
                RATE CONSTANTS         K1 = 0.222305E-01
                                       K2 = 0.190004E-01
                                   EQBMKP = 0.117000E 01

                                    SIGMA = 0.420772E 01

*****************************************************************************
```

```
RATE CONSTANTS FOR COAL B AT TEMPERATURE OF 1100.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
        TAU        Y
 1      5.0      0.609
 2     10.0      0.640
 3     15.0      0.676
 4     20.0      0.710


   LIMITS OF K1
 LOWER       UPPER              K1                      K2                    SIGMA

 0.020       0.023        0.229997E-01           0.138887E-01           0.202005E 03
 0.023       0.026        0.259986E-01           0.156996E-01           0.114561E 03
 0.026       0.029        0.289996E-01           0.175118E-01           0.731324E 02
 0.029       0.032        0.319994E-01           0.193233E-01           0.576932E 02
 0.032       0.035        0.335853E-01           0.202810E-01           0.560704E 02
 0.035       0.038        0.350004E-01           0.211355E-01           0.572661E 02
 0.038       0.041        0.380022E-01           0.229482E-01           0.656058E 02
 0.041       0.044        0.410003E-01           0.247586E-01           0.789998E 02
 0.044       0.047        0.440003E-01           0.265702E-01           0.952352E 02
 0.047       0.050        0.470001E-01           0.283817E-01           0.112922E 03

**********************************************************************

 FINAL ANSWER
 ------------
               RATE CONSTANTS        K1 = 0.335853E-01
                                     K2 = 0.202810E-01
                                 EQBMKP = 0.165600E 01

                                  SIGMA = 0.560704E 02

**********************************************************************
```

```
RATE CONSTANTS FOR COAL B AT TEMPERATURE OF 1200.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
       TAU        Y
 1      5.0     0.887
 2     10.0     0.912
 3     15.0     0.931
 4     20.0     0.935


   LIMITS OF K1
 LOWER      UPPER           K1                  K2                  SIGMA

 0.100      0.103      0.102900E 00       0.799410E-02       0.722557E 02
 0.103      0.106      0.105898E 00       0.822698E-02       0.684120E 02
 0.106      0.109      0.108938E 00       0.846316E-02       0.660804E 02
 0.109      0.112      0.111729E 00       0.867999E-02       0.651240E 02
 0.112      0.115      0.113857E 00       0.884531E-02       0.648694E 02
 0.115      0.118      0.115408E 00       0.896579E-02       0.651358E 02
 0.118      0.121      0.118435E 00       0.920095E-02       0.660042E 02
 0.121      0.124      0.121167E 00       0.941320E-02       0.675639E 02
 0.124      0.127      0.124021E 00       0.963497E-02       0.697742E 02
 0.127      0.130      0.127269E 00       0.988730E-02       0.727275E 02

*********************************************************************

FINAL ANSWER
------------

          RATE CONSTANTS        K1 = 0.113857E 00
                                K2 = 0.884531E-02
                            EQBMKP = 0.128720E 02

                             SIGMA = 0.648694E 02

*********************************************************************
```

```
RATE CONSTANTS FOR COAL B AT TEMPERATURE OF 1300.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
      TAU        Y
 1     5.0     0.934
 2    10.0     0.951
 3    15.0     0.958
 4    20.0     C.97C


  LIMITS OF K1
 LOWER      UPPER            K1                  K2                  SIGMA

 0.140      0.143      0.142570E 00      0.469845E-02       0.664468E 02
 0.143      0.146      0.145850E 00      0.480654E-02       0.643036E 02
 0.146      0.149      0.148735E 00      0.490163E-02       0.629425E 02
 0.149      0.152      0.151744E 00      0.500080E-02       0.623304E 02
 0.152      0.155      0.154568E 00      0.509384E-02       0.618750E 02
 0.155      0.158      0.156237E 00      0.514887E-02       0.621579E 02
 0.158      0.161      0.159674E 00      0.526211E-02       0.625903E 02
 0.161      0.164      0.161525E 00      0.532313E-02       0.634676E 02
 0.164      0.167      0.164370E 00      0.541689E-02       0.645394E 02
 0.167      0.170      0.167427E 00      0.551762E-02       0.662417E 02

*********************************************************************

FINAL ANSWER
------------
            RATE CCNSTANTS        K1 = 0.154568E 00
                                  K2 = 0.509384E-02
                              EQBMKP = 0.303440E 02

                               SIGMA = 0.618750E 02

*********************************************************************
```

```
RATE CONSTANTS FOR COAL C AT TEMPERATURE OF 1100.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
        TAU        Y
 1       5.0      0.442
 2      10.0      0.528
 3      15.0      0.564
 4      2C.0      C.613


   LIMITS OF K1
 LOWER      UPPER           K1                 K2                 SIGMA

 0.010      0.013      0.129991E-01       0.139326E-01       0.339443E 03
 0.013      0.016      0.159996E-01       0.171485E-01       0.116499E 03
 0.016      0.019      0.189995E-01       0.203639E-01       0.437357E C2
 0.019      0.022      0.215127E-01       0.230575E-01       0.311589E 02
 0.022      0.025      C.220023E-01       0.235823E-01       0.315157E 02
 0.025      0.028      0.250003E-01       0.267956E-01       0.451487E 02
 0.028      0.031      C.280005E-01       0.300113E-01       0.697504E C2
 0.031      0.034      0.310002E-01       0.332264E-01       0.984894E 02
 0.034      0.037      0.340003E-01       0.364419E-01       0.128126E C3
 0.C37      C.040      C.370003E-01       0.396573E-01       0.157109E 03

**********************************************************************

FINAL ANSWER
------------
            RATE CONSTANTS          K1  = 0.215127E-01
                                    K2  = 0.230575E-01
                                EQBMKP  = 0.933000E 00

                                 SIGMA  = 0.311589E 02

**********************************************************************
```

```
RATE CONSTANTS FOR COAL C AT TEMPERATURE OF 1200.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
        TAU        Y
 1       5.0     0.638
 2      10.0     0.741
 3      15.0     0.764
 4      20.0     0.826


   LIMITS OF K1
 LOWER      UPPER             K1                  K2                   SIGMA

 0.030      0.033       0.329979E-01        0.883477E-02         0.178632E 03
 0.033      0.036       0.359988E-01        0.963824E-02         0.107081E 03
 0.036      0.039       0.389995E-01        0.104416E-01         0.634628E 02
 0.039      0.042       0.419994E-01        0.112448E-01         0.384311E 02
 0.042      0.045       0.449989E-01        0.120479E-01         0.259591E 02
 0.045      0.048       0.479756E-01        0.128449E-01         0.220682E 02
 0.048      0.051       0.482305E-01        0.129131E-01         0.220368E 02
 0.051      0.054       0.510057E-01        0.136561E-01         0.240782E 02
 0.054      0.057       0.540017E-01        0.144583E-01         0.301409E 02
 0.057      0.060       0.570013E-01        0.152614E-01         0.389843E 02

**************************************************************

FINAL ANSWER
------------
           RATE CONSTANTS        K1 = 0.482305E-01
                                 K2 = 0.129131E-01
                             EQBMKP = 0.373500E 01

                              SIGMA = 0.220368E 02

**************************************************************
```

```
RATE CONSTANTS FOR COAL C AT TEMPERATURE OF 1300.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
       TAU        Y
 1      5.0     0.799
 2     10.0     0.930
 3     15.0     0.954
 4     20.0     0.971


   LIMITS OF K1
 LOWER       UPPER              K1                   K2                   SIGMA

 0.120       0.123        0.122933E 00        0.403523E-02         0.117885E 02
 0.123       0.126        0.125844E 00        0.413075E-02         0.961372E 01
 0.126       0.129        0.128907E 00        0.423133E-02         0.833703E 01
 0.129       0.132        0.130162E 00        0.427249E-02         0.818264E 01
 0.132       0.135        0.133663E 00        0.438744E-02         0.812023E 01
 0.135       0.138        0.135371E 00        0.444350E-02         0.850949E 01
 0.138       0.141        0.138433E 00        0.454399E-02         0.957724E 01
 0.141       0.144        0.141494E 00        0.464448E-02         0.116028E 02
 0.144       0.147        0.144157E 00        0.473190E-02         0.132049E 02
 0.147       0.150        0.147691E 00        0.484790E-02         0.164809E 02

*******************************************************************************

FINAL ANSWER
------------
            RATE CONSTANTS         K1 = 0.133663E 00
                                   K2 = 0.438744E-02
                               EQBMKP = 0.304650E 02

                                SIGMA = 0.812023E 01

*******************************************************************************
```

```
RATE CONSTANTS FOR COAL D AT TEMPERATURE OF 1100.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
       TAU         Y
 1      5.0      0.499
 2     10.0      0.570
 3     15.0      0.614
 4     20.0      0.658


  LIMITS OF K1
 LOWER      UPPER           K1                 K2                 SIGMA

 0.010      0.013      0.129999E-01       0.104669E-01       0.715184E 03
 0.013      0.016      0.159994E-01       0.128820E-01       0.295867E 03
 0.016      0.019      0.189992E-01       0.152972E-01       0.122169E 03
 0.019      0.022      0.219997E-01       0.177132E-01       0.536246E 02
 0.022      0.025      0.249964E-01       0.201260E-01       0.341077E 02
 0.025      0.028      0.256709E-01       0.206690E-01       0.335712E 02
 0.028      0.031      0.280005E-01       0.225447E-01       0.384889E 02
 0.031      0.034      0.310005E-01       0.249601E-01       0.546671E 02
 0.034      0.037      0.340004E-01       0.273755E-01       0.764669E 02
 0.037      0.040      0.370002E-01       0.297908E-01       0.100623E 03

*****************************************************************************

FINAL ANSWER
------------
            RATE CONSTANTS        K1 = 0.256709E-01
                                  K2 = 0.206690E-01
                              EQBMKP = 0.124200E 01

                               SIGMA = 0.335712E 02

*****************************************************************************
```

```
RATE CONSTANTS FOR COAL D AT TEMPERATURE OF 1200.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
      TAU       Y
 1     5.0    0.802
 2    10.0    0.865
 3    15.0    0.894
 4    20.0    0.928


  LIMITS OF K1
 LOWER      UPPER            K1                  K2                  SIGMA

 0.070      0.073      0.728622E-01       0.643716E-02       0.594117E 02
 0.073      0.076      0.759743E-01       0.671210E-02       0.447798E 02
 0.076      0.079      0.788963E-01       0.697025E-02       0.351890E 02
 0.079      0.082      0.819773E-01       0.724245E-02       0.285383E 02
 0.082      0.085      0.848986E-01       0.750054E-02       0.247502E 02
 0.085      0.088      0.878328E-01       0.775976E-02       0.230786E 02
 0.088      0.091      0.898518E-01       0.793814E-02       0.229398E 02
 0.091      0.094      0.911601E-01       0.805372E-02       0.231907E 02
 0.094      0.097      0.940954E-01       0.831305E-02       0.248812E 02
 0.097      0.100      0.970552E-01       0.857454E-02       0.276251E 02

*************************************************************************

FINAL ANSWER
------------
                RATE CONSTANTS       K1 = 0.898518E-01
                                     K2 = 0.793814E-02
                                 EQBMKP = 0.113190E 02

                                  SIGMA = 0.229398E 02

*************************************************************************
```

```
RATE CONSTANTS FOR COAL D AT TEMPERATURE OF 1300.0 DEGREES FAHRENHEIT


FOR GIVEN VALUES OF
       TAU       Y
 1      5.0    0.917
 2     10.0    0.952
 3     15.0    0.969
 4     20.0    0.973


   LIMITS OF K1
 LOWER       UPPER             K1                   K2                  SIGMA

 0.150       0.153       0.151148E 00        0.442497E-02        0.424379E 02
 0.153       0.156       0.155062E 00        0.453955E-02        0.412932E 02
 0.156       0.159       0.157848E 00        0.462112E-02        0.410646E 02
 0.159       0.162       0.160148E 00        0.468844E-02        0.411909E 02
 0.162       0.165       0.162772E 00        0.476526E-02        0.419036E 02
 0.165       0.168       0.165998E 00        0.485972E-02        0.429463E 02
 0.168       0.171       0.168436E 00        0.493107E-02        0.441745E 02
 0.171       0.174       0.171965E 00        0.503440E-02        0.461810E 02
 0.174       0.177       0.174263E 00        0.510168E-02        0.478419E 02
 0.177       0.180       0.177136E 00        0.518578E-02        0.500031E 02

**************************************************************

FINAL ANSWER
------------
           RATE CONSTANTS         K1 = 0.157848E 00
                                  K2 = 0.462112E-02
                              EQBMKP = 0.341580E 02

                               SIGMA = 0.410646E 02

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