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CATALYSIS OF THE OXYGEN-CARBON REACTION

BY WATER VAPOR

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ROGER J. ^{JOSEPH} SCHOEPEL

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CATALYSIS OF THE OXYGEN-CARBON REACTION

BY WATER VAPOR

DEDICATION

To those from whose lips encouragement came.

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ABSTRACT

Oxidation of a thin film of relatively pure amorphous carbon has been studied between 400° and 500° C. over a twelve-fold oxygen partial pressure change and a 50,000-fold change in water partial pressure. Water vapor partial pressures varied between 0.00032 and 17.5 mm Hg, the latter corresponding to 100% saturation at room temperature. The carbon was produced in-situ by pyrolytically decomposing methane onto a packed bed of 20-50 mesh Vycor glass particles. A unique recirculation-differential reactor, in which both longitudinal and radial diffusion were negligible, was successfully applied to the oxidation reaction.

Rates of reaction were directly obtained by measuring the steady state rate of product formation, $d(\text{CO}_2)/dt$. Identical results were obtained using measured rates of oxygen conversion and carbon utilization. Measured rates varied from 0.0008 to 0.38 grams of carbon consumed per day, the lower limit corresponding to a 0.0002% change per minute in the weight of carbon present. The only product was carbon

dioxide. Rate data obtained could be correlated according to the kinetic expression

$$-d(C)/dt = k p_{O_2}^{0.3} p_{H_2O}^a$$

where

$$k = 3.64 \times 10^6 \exp(-39,900/RT).$$

The variable exponent on water pressure was found to be a function of both oxygen pressure and reaction temperature. This kinetic expression correlated the experimental data to an average error of 3.2% with a maximum error of 19.8%. Experimental error in the measured rates was about 6%.

The primary finding of this investigation that water partial pressure, a heretofore recognized but uninvestigated parameter in the oxygen-carbon reaction, offers at least a partial explanation for the numerous varying and diverse experimental conclusions so apparent in the literature. Observed transitions in the apparent order on oxygen from nearly zero to first order were resolved in this investigation by determining a water-compensated apparent order with respect to oxygen. The result was a constant 0.3 order on oxygen which held for all experiments. Theoretically this is explained by considering the relative adsorptivity of oxygen and water. The water pressure variable is further demonstrated to be capable of altering a relatively pure carbons reactivity by as much as 700%.

A mechanism is proposed to account for the observed

rate dependence on water pressure. One may assume the existence of two competitive reactions for oxygen which are respectively controlled by the degree of hydrogen imperfections in the solid phase and the amount of extraneous water introduced with the oxygen. Chemically controlled oxidation rates of carbons of high hydrogen content are posed as being essentially independent of water pressure whereas low hydrogen content carbons are suggested as being extremely rate sensitive to minor changes in this variable. A further postulate, of heterogeneous catalysis by simultaneous adsorption with interaction of water and oxygen on neighboring sites, is utilized to explain the pseudo-order variations in oxygen pressure and rate increases due to water vapor. The mechanism proposed is in agreement with the findings of this investigation as well as observations of many other carbon oxidation studies presented in the literature.

CATALYSIS OF THE OXYGEN-CARBON REACTION BY WATER VAPOR

CHAPTER I

INTRODUCTION

Oxidation of carbon and carbonaceous materials is perhaps one of the most useful chemical reactions known to mankind. In addition to either directly or indirectly providing a substantial portion of the world's domestic and industrial energy requirements, carbon oxidation by air contact provides a convenient way of regenerating cracking catalysts in petroleum refining and in the production of oil from geologic strata by underground combustion. The automotive industry has universally sought a catalyst for this reaction ever since its acceptance of the internal combustion engine. On the other hand, other industries have expended considerable effort in attempting to retard the rate of the carbon oxidation reaction. Such is the case for those using graphite as a moderator in nuclear reactors and carbon as an electrode material. Proponents of pyrolytic carbon as a thermal protective coating for rocket and missile nozzles are similarly concerned.

In spite of its technical importance and a great

number of scientific investigations, the manner in which oxygen combines with carbon to produce carbon dioxide and carbon monoxide, or for that matter whether one or the other, or both, is the primary product, has not been well established. The closest agreement among workers on any one issue is in the concept of the formation of a surface carbon-oxygen complex as an intermediate stage in the reaction. Unfortunately, this concept is not presently amenable to prediction of rates of reaction from first principles.

Emphasis in a voluminous sampling of the literature on carbon oxidation has been on carbons derived from impure petroleum coke, coal tar pitch, or similar sources. These are subsequently exposed to various degrees of carbonization and graphitization before exposure to oxygen. Because of the effect on the reaction of impurities and inhomogeneities in the solid phase, it has usually sufficed to use "relatively pure" reactant oxygen and associate all differences in experimental findings with either the solid phase or the reaction system. Recent workers have proposed a more thorough evaluation of the solid phase in hopes of better defining reaction variables. However, preliminary experiments have shown that traces of gaseous impurities may be partly responsible for these differences. This was particularly noted of water vapor. Accordingly, the present investigation was designed to study the effect of water vapor on the oxidation of pure carbon.

CHAPTER II

LITERATURE REVIEW

The reaction of oxygen with carbon has been studied by a multiplicity of experimental approaches in an attempt to define the basic mechanism by which the reaction proceeds. Although the reaction is gradually becoming better understood within the 800° to 2000° C. temperature region, where mass and heat transfer control the reaction, a considerable amount of confusion still exists about the nature of the true chemical mechanism controlling at lower temperatures. Only a few of the many diverse experimental results, which offer clues to this question, are correlatable. The variables which affect the lower temperature process have evidently been either insufficiently defined or controlled, or both.

One of the outstanding features of this review was the significance to which a large number of investigators have attributed to impurities in the solid state. This appeared to be particularly true of hydrogen whether initially present as bound hydrogen or later adsorbed as molecular or nascent hydrogen during activation and/or reaction processes. Its presence has even been considered by several as being

essential to completion of the oxygen-carbon reaction. It is therefore difficult to understand why hydrogen has been neglected in mechanistic postulates except for a vague relationship to so-called "Type I" active sites.

An interesting feature of this review was the degree to which many have supported the existence of a carbon-oxygen surface complex as a separate entity in the reaction. Originated more than a half-century ago, this concept of a reaction intermediate has evolved from one involving multimolecular species to a dual reaction-site hypothesis involving two different types of carbon-oxygen complexes. Numerous attempts have been made to characterize the surface complex by measurements such as weight gain, surface area, preferential adsorption, X-ray diffraction, emission spectroscopy, and destructive distillation. No direct verification, however, has been possible. Primary support for the dual reaction site theory are the singular (CO_2) and dual reaction products (CO and CO_2). These appear to depend on whether a relatively pure or impure sample of carbon is being oxidized. The present work supports the dual site theory while further proposing that one of the sites is common to the carbon and the other is artificially induced during the reaction process.

Assessment of Previous Work

In reviewing previous work, any assessment is made difficult by an apparent multiplicity of variables required

to define the reaction phenomenon. These may be divided into two categories: the quality of the reactants and the mechanical arrangement of the reacting system. Emphasis in the former case has been with the carbon while oxygen purity, for the most part, has been neglected. Differences in carbon reactivities have been found to depend upon almost any variable that alters its physical nature or degree of impurity.

Arrangements of experimental devices have included static and flowing systems where carbon is present as grains, filaments, films or coatings, a single massive piece, suspensions by inert filaments, particles dropped through a hot zone, and packed and fluidized beds. Each system must be assessed as to its ability to give minimum or at least known catalytic effects. Operating variables encompass a wide spread in temperature (from ambient to 2300°C .), pressure (from $1 \mu \text{Hg}$ to 50 atmospheres), gas velocity (from static to 100 m/sec), and reaction time (up to several months). Varying degrees of conversion, from a few ppm change to several weight per cent, are found. Many of the experiments at higher temperatures have utilized inhibitors to suppress undesirable secondary reactions.

Also of interest are the findings for the other gas-carbon reactions. This is particularly true of the reactions of carbon dioxide and steam with carbon which have generally been thought of as possessing mechanisms similar to the oxygen-carbon reaction.

Chemical or Diffusional Mechanism

A considerable amount of experimental effort has been expended to distinguish between chemical controlling mechanisms and those of diffusion. The problem exists because temperature coefficients for the gas-carbon reactions do not show any singular Arrhenius type relationship over broad temperature changes. Instead three general regions of temperature dependence have generally been recognized: 1) low temperature, where the principal controlling mechanism is attributed to chemical reaction from which so-called true activation energies are obtained; 2) intermediate temperature, where the principal mechanism of pore diffusion is attributed with limiting the rate of reaction to yield activation energies which are half their true values; 3) high temperature, where diffusion across a boundary layer controls, resulting in very low apparent activation energies.

Order

By far the majority of lower temperature investigations, conducted under diverse experimental conditions, have found a first, or close to first, order dependence of the oxygen-carbon reaction on oxygen concentration. The implication is that a surplus of active carbon sites exist for the particular experimental situation. This would be the case for a highly reactive carbon. However, in the case of a poorly activated carbon such as graphite, diamond, or other pure form

of carbon, where the concentration of active sites is limited, one could expect a zero, intermediate, or first order dependence on oxygen concentration depending on the relative abundance of oxygen molecules to unoccupied active sites.

Two noteworthy investigations, where zero order dependence on oxygen were found, have been presented by Gulbransen and Andrew¹ and Blyholder and Eyring.² Both investigations used a pure form of graphite and low reaction pressures. Experimental details of these works are deferred to a later section. These reports have attracted considerable interest³ since they contradict the reasoning that high oxygen pressure favors zero order results. Presented herein is additional experimental evidence supporting these zero order findings, with an alternate explanation based on variations in water vapor content.

Reaction Intermediate

The concept of an intermediate reaction in the oxygen-carbon reaction has been popular among workers since first introduced as a multimolecular surface oxide, C_xO_y , by Rhead and Wheeler⁴ in 1913. Their hypothesis was based on observations that a carbon, outgassed after exposure to oxygen, subsequently gave off carbon oxides when the temperature was raised. Investigators have since been interested in these surface oxides to establish 1) the nature of the complex itself, 2) the nature of the primary reaction leading to their

formation, 3) the nature of the complex disintegration reaction and products evolved, 4) the effect of products on the reaction rate, and 5) the controlling mechanism in the reaction sequence.

A. Complex Formation

With regard to the nature of and the primary reaction leading to the carbon-oxygen complex, Langmuir,⁵ in 1915, suggested that when oxygen acts on carbon, part of the oxygen reacts directly to CO_2 and another part forms an adsorption layer with the surface which retards subsequent reaction. He disagreed with the Rhead and Wheeler proposal that the complex consisted of multimolecular chemical species. Instead he postulated an adsorption layer consisting of oxygen atoms chemically combined with edge carbon atoms that formed an extremely stable surface oxide.

Shah,⁶ in 1929, extended Langmuir's model by postulating that, at lower temperatures, more oxygen is retained in second and succeeding layers. With increasing temperatures, Shah proposed that the outer layers were progressively stripped off until only one layer remains. In this way, he was able to explain the diminishing proportion of CO_2 to CO observed with increasing temperatures. Lambert⁷ further developed the model by proposing two distinct processes in the oxidation of carbon: 1) formation of CO_2 by direct impact of oxygen molecules on a clean (pure) carbon, and 2) primary formation of both CO and CO_2 by the decomposition of surface

complexes.

Strickland-Constable⁸ observed, that at 400°C ., CO would not react separately with either carbon or nitrous oxide (N_2O). In the presence of carbon, however, the CO was rapidly oxidized to CO_2 by the N_2O . He proposed the existence of two types of solid oxide complexes labeling them "labile" and "stabile" to explain the phenomenon. These differed in that an intermediate complex has less stability and greater reactivity than does the stabile surface oxide. This latter complex could subsequently react with N_2O , oxygen, or CO to give CO_2 .

A more recent view concerning the nature of the complex is reflected by the Type I and Type II active sites and their ensuing chemical complexes, as described by Blyholder, Binford, and Eyring.⁹ Type I sites are considered as those caused by impurities in the carbon. Type II sites refer to those sites on the pure carbon surface undisturbed by hydrogen or other impurities. Both Type I and Type II sites are capable of reacting with oxygen to form Type I and Type II surface oxides, respectively. Type I surface oxides upon decomposition are capable of producing Type II sites.

While the hypothesis of dual reaction sites for the oxygen-carbon reaction is in general agreement with most postulates since Langmuir, it is interesting to note that one or the other of these sites must also be active to both CO_2 and water. This supposition is essential if, as is usually done,

the mechanistic sequences proposed for the carbon dioxide-carbon and steam-carbon reactions are to be explained by utilization of only a single type of active site.

B. Complex Disintegration

Many clues as to the nature of the carbon-oxygen complex disintegration have been reported. Purely thermal or graphitization experiments with charcoal, petroleum coke, and similar impure sources of carbon have yielded information such as 1) the type and quantity of gases evolved with increasing temperature, 2) simultaneous crystal growth with increasing degree of graphitization, and 3) corresponding changes in adsorption properties. Other gasification-type experiments have evaluated the changes in carbon reactivity as functions of the degree of graphitization and impurities present. Although these experiments vary somewhat in their findings, CO_2 , H_2O , and in some cases CH_4 , appear to be the primary gases evolved up to 600°C . Between 600° and 900°C ., CO is primarily evolved. Hydrogen is given off at higher temperatures, reaching a maximum evolution rate around 1200°C . A prerequisite for simultaneous crystal growth with gas evolution is the release of combined hydrogen which begins at about 900°C .^{10,11} Crystal growth then increases rapidly to 2000°C . and decreases thereafter to 3000°C . Metal impurities have been shown to be completely removed by heating to 3000°C .¹²

Surface Area

Recently it has been popular to characterize carbon activity by surface area measurements taken at some temperature considerably below the reaction temperature. Investigations using this technique have been moderately successful in showing specific surface areas to be a correlative parameter in characterizing carbon both before and during reaction.¹³ However, the usefulness of such measurements, insofar as mechanistic determinations are concerned, is of questionable value. Neither the reaction temperature nor the reactant gas is used in the actual surface area measurement.

Steady State Rates

Investigations using continuous analytical methods have frequently found that carbon oxidation rates become constant after a certain degree of carbon burnoff.^{3,14} This observation is generally accredited to the attainment of a constant carbon activity. Walker, Foresti, and Wright¹³ attempted to clarify this phenomenon for the carbon dioxide-carbon reaction. They found that both surface area and reactivity increased with reaction time until the weight loss approximated ten per cent. Rates then became constant as did surface areas. As an explanation of these findings, Walker and Wright¹⁵ hypothesize that the surface area increase accompanying initial burnoff is due to entrapment of internal surfaces within the bulk sample. They conclude that initial

adsorption of the nitrogen and argon used involves their partial penetration into molecular size capillaries which are quickly closed off by other adsorbed molecules. These gases are then assumed to further penetrate the porous network and, at low temperatures, either lack sufficient energy to diffuse back to the surface or require a much longer time to do so. Their proposal, however, fails to explain the reversible adsorption of carbon dioxide reported.

The above explanation for this constancy in rate of carbon burnoff has been credited to an equilibrium existing within the solid phase between formation of the surface oxygen complex and its removal with a carbon atom. Such an equilibrium could alternately be explained by the attainment of steady state rates of contamination by gaseous impurities, a coincidence which has been observed in this investigation with water vapor.

Reaction Products

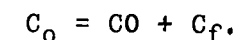
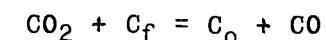
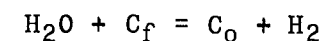
The basic postulate as to the primary product of the oxygen-carbon reaction, CO or CO₂, remains an issue. Numerous workers have concurred that both are primary products as shown by the recent works of Walker, Rusinko, and Austin,³ Rossberg,¹⁶ and Day, Walker, and Wright.¹⁷ Evidence that the question still remains undecided lies in the findings of Blyholder and Eyring^{2,18} who support CO as the primary product, contrasted with Streznewski and Turkevich,¹⁹ and Letart and Magrone,²⁰

who support CO₂ as the primary reaction product. Arthur,²¹ in reviewing the literature, has surmised that most workers have found CO₂ as the primary product for reaction temperatures below 800° C.

Influence of Hydrogen

The subtle role played by hydrogen in governing the rate of gas-carbon reactions is a frequently mentioned but insufficiently stressed variable. For example, when used in the gas phase as an activating agent, hydrogen has been found initially to be very vigorously chemisorbed in small quantities²² with the further capability of reacting with the carbon to remove surface oxides in the form of water.^{23,24} Many workers have credited this initial uptake of hydrogen by carbon to be due in part to adsorption,^{3,5,25-27} which increases with increasing temperature,^{22,28-30} and in part to the reaction which forms methane.

Postulated mechanisms for the steam-carbon and carbon dioxide-carbon reactions^{31,32} hypothesize that a dynamic oxygen exchange exists between the solid and gas phases according to the mechanisms:



The terms C_f and C_o represent a carbon free site capable of reaction and a chemisorbed oxygen-carbon complex respectively.

If these mechanistic steps are representative, then activation of carbon by hydrogen or CO, either in pretreatment or during the course of reaction, should retard the rate of carbon transfer to the gas phase by creating a lower concentration of surface complexes. Such an influence on both the steam-carbon^{26,31-33} and carbon dioxide-carbon^{31,34} reaction has been observed. However, the influence of hydrogen and carbon monoxide on the oxygen-carbon reaction is not as conclusive. Conflicting opinions on this subject have been presented by Armington,³⁵ who found hydrogen pretreatment had no effect, and Bangham,²⁷ who found such pretreatment assisted the gasification reaction. Lowry and Morgan²³ reported a retardation of the oxygen-carbon reaction only after prolonged hydrogen treatment. Addition of CO has been found in one instance to double the rate of the oxygen carbon reaction.³⁶

In the solid phase, hydrogen as an impurity has been found to be very important in determining carbon reactivity. Bangham,²⁷ Rhead and Wheeler,⁴ and Lowry and Morgan²³ have shown that the amount of oxygen chemisorbed by graphite is directly proportional to the hydrogen in the graphite and is independent of the amount of graphite present. Studebaker³⁷ found the same result in working with carbon black. Riley³⁸ also observed this while analyzing for the effect of different degrees of graphitization. Numerous other workers have observed similar results.^{9,11,39,40} The significance of this variable is reflected by the attitude of Jones and Townend⁴¹

who have proposed that the presence of hydrogen atoms is essential for complex formation and thus for the reaction to proceed. More quantitatively, Lowry⁴² found carbon activity to be dependent upon its hydrogen content up to 0.5 per cent and independent of this variable from 0.5 per cent to 2.1 per cent hydrogen. He also observed that carbon reactivity depended upon the maximum temperature used in graphitization and was independent of the atmosphere in which it was prepared.

The amount of residual hydrogen remaining even after extensive graphitization is obviously an important parameter in determining a carbon's reactivity. This variable could account for at least a part of the wide range in reactivity reported in the literature as well as the general inability to correlate data among the various investigators. Nevertheless, except for some vague relationship to Type I active sites, hydrogen has been neglected in previous mechanistic hypotheses.

Influence of Water

The presence of adsorbed water appears to be just as influential in determining carbon reactivity as is the bound hydrogen. However, the nature of the water adsorption process itself has not been well defined. Whereas Walker, Rusinko, and Austin,³ and King and Lawson⁴³ find that water is chemisorbed by carbon, Strickland-Constable⁴⁴ reported the reversible adsorption process applied for charcoal at temperatures up

to 700° C. and for pressures of less than 1 mm Hg. Lawson⁴⁵ qualifies these findings by reporting that an ash-free carbon does not show chemisorption of water. Muller and Cobb⁴⁶ found that chemisorption may be negligible or important depending upon carbon pretreatment.

Work which describes the adsorbed carbon-water complex is also of particular interest to this study. King and Lawson⁴³ found that the surface oxide formed with water chemisorption below 400° C. characteristically produced an acidic surface, whereas, above this temperature, another type of surface complex was obviously present. Jones and Townend⁴¹ concluded that the surface oxide, which formed when dry carbon was exposed to moist air, existed as a peroxygen complex. The amount of complex formed in their experiments was roughly proportional to the amount of water adsorbed. This proportionality was reported to hold for different carbons. In an earlier work,⁴⁷ they had proposed that a combination carbon-oxygen-water complex was formed, with the presence of adsorbed water being a requisite for complex formation.

The converse situation has been proposed by Sihvonen⁴⁸ who, in studying the steam-carbon reaction, contends that the reaction is initiated by adsorbed oxygen supplied by the dissociation of water. An identical conclusion has been reached by Binford and Eyring.⁴⁹ In studying the steam-carbon reaction at 1300° C., they observed the rate of carbon utilization was almost linearly dependent upon the amount of oxygen

formed by water dissociation. From this they suggested that adsorbed oxygen acted as a catalyst and that the slowest step in the steam-carbon reaction was the adsorption of oxygen.

As a reaction product in the steam-carbon reaction, carbon monoxide is known to undergo a rapid water-gas shift which is catalyzed by the presence of a carbon surface.⁵⁰ The same type of secondary reaction may take place between CO generated in the oxygen-carbon reaction and oxygen. However, in this connection, Arthur and Bowring⁵¹ have found that adsorption of water on the carbon tends to reduce its catalytic effectiveness resulting in a slower rate of carbon monoxide oxidation.

In postulating mechanisms for the adsorption of water on carbon, Strickland-Constable,⁴⁴ and Gladsby, Hinshelwood, and Sykes³² propose molecular adsorption-desorption processes in accordance with their findings of reversible adsorption. Similarly, a direct interaction between molecular water and a free carbon site has been proposed by Hottel and co-workers⁵² when reaction is involved. Alternately, water is postulated as dissociating into $2H^+$ and O^{--} , which then separately becomes adsorbed on different types of reaction sites, by Long and Sykes,⁵³ and Binford and Eyring.⁴⁹ A similar mechanism with dissociation into H^+ and OH^- radicals has been proposed by Johnstone, Chen, and Scott.³³

The influence of water in the vapor phase on the gas-carbon reactions has not been well established. Whereas Rius

and Fuentes,⁵⁴ and Day⁵⁵ have found that water catalyzes the oxygen-carbon reaction at respectively low and high temperatures, Hoynant and co-workers³⁴ and Lambert⁷ observed that traces of water vapor inhibited this reaction. Presence of water has also been found to catalyze the carbon monoxide oxidation reaction.³ This catalytic effect, coupled with a partial water-gas shift reaction, could account for the increased yield of CO₂ when moist rather than dry air was passed over carbon as observed by Sihvonen and Vuorela,⁵⁶ and Sihvonen.⁵⁷ Sihvonen, however, found that the presence of water vapor had little effect on the oxygen-carbon reaction above 1900° C.

No strong conclusions may be drawn from the literature with regard to the effect of water vapor on the oxygen-carbon reaction. However, as a word of caution in assessing the literature on this point, one must consider the manner in which carbon oxidation rates were obtained as well as the effect of non-carbon surfaces on the measurements. For example, if a carbon steel surface is present, as in the preliminary phase of this investigation, the temporary injection of water vapor was observed to decrease the rate of oxygen conversion while increasing the rate of carbon dioxide production. Thus, if one were determining oxidation rates based on gas analysis, the tag on oxygen would show inhibition by the water vapor whereas carbon dioxide would show a catalytic effect.

Secondary Reactions

The possibility of secondary reactions occurring either simultaneously with, or as a consequence of, the primary oxygen-carbon combination makes any clear interpretation of this reaction difficult. The problem becomes intensified as the temperature level of the investigation is increased. The following side and consecutive reactions must be taken into consideration in a study of the oxidation of carbon:^{1,3}

- 1) $C + O_2 = CO_2$
- 2) $C + \frac{1}{2}O_2 = CO$
- 3) $CO + \frac{1}{2}O_2 = CO_2$
- 4) $C + CO_2 = 2CO$
- 5) $C + H_2O = CO + H_2$
- 6) $CO + H_2O = CO_2 + H_2$
- 7) $C + 2H_2 = CH_4$.

Considering the separate reactions in order, the first three have equilibrium points which are far to the right.⁵⁸ Accordingly, at lower temperatures, the reverse tendencies of these reactions may be neglected. Reaction (3), involving a possible reactant-product combination, has been found to produce less than one per cent CO₂ in the 650° to 700° C. range.⁵⁹ In another investigation appreciable concentrations of CO₂ were formed at 900° C.² High gas velocities and low pressures have been used by a number of investigators as a means of suppressing this reaction.

For reaction (4), where equilibrium theory predicts

equimolar concentrations of CO and CO₂ at 700° C., Shah⁶ was unable to detect any reduction of the CO₂ with charcoal at 500° C. Gulbransen and Andrew¹ concluded from their work that the rate of the carbon dioxide-carbon reaction was negligible below 600° C. and was strongly inhibited at temperature below 700° C. Rhead and Wheeler's findings⁶⁰ further substantiate this conclusion wherein they found reaction (4) to barely be appreciable below 850° C.

The rate at which the reverse of reaction (4) approaches the equilibrium point appears to be much faster than the forward reaction. For example, Hofman⁶¹ found that carbon was capable of forming from CO decomposition in the presence of an iron catalyst at temperatures as low as 400° C. Shah,⁶ however, was unable to detect any such decomposition at 470° C. Deitz and Prosem⁶² concluded this normal decomposition reaction was negligible below 500° C. Rates of the reverse of (4) were measured by Rief⁶³ who found that 2, 17, 44, and 66 per cent of the equilibrium CO₂ concentrations had formed after 90 minutes exposure at temperatures of 700°, 800°, 900°, and 1000° C. respectively.

The tendency of CO₂ to further react with its carbon source has been discussed insofar as its thermodynamic behavior and reactivity are concerned. This product appears to be unreactive in the presence of both carbon and oxygen at lower temperatures as demonstrated by Paxton.³⁶ He found no apparent effect, on the rate of the oxygen-carbon reaction at

500° C., when CO₂ was added to the oxygen feed of his experimental system. However, the effect of an alternate product, CO, was not at all like dilution with CO₂ or N₂. At 450° C. and 1.1 atmosphere total pressure, he found a two-fold increase in the oxygen-carbon reaction with CO dilution as compared to CO₂ or N₂ dilution, the extent of reaction being greatest in the range of oxygen pressures between 0.21 and 0.5 atmospheres. His explanation for this catalysis by CO is its ability to drive the reaction $C_O + CO = CO_2 + C_f$ forward thereby reducing the extent of adsorbed oxygen on the surface.

When water vapor is present, even in minute quantities, the additional reactions (5), (6), and (7) must also be taken into consideration. An evaluation of the rate with which reaction (5) proceeds may be gained by a comparison with reaction (4). Farup⁶⁴ found these two reactions to be comparable in rate at 850° C., while at 800° C., Walker, Rusinko, and Austin³ found reaction (5) to be about three times the rate of reaction (4). At this same temperature, these latter authors report the rate of reaction (4) to be about 3000 times that of reaction (7). Finally the water-gas shift reaction (6) is of importance when water is present below 800° C. or when hydrogen is present above this temperature.¹

From the preceding it may be surmised that, for carbon oxidation below 500° C., reaction (6) and the reverse of

reaction (4) are the only ones of importance from either thermodynamic or kinetic considerations. Unfortunately, both of these reactions have carbon dioxide as their end product.

Low Temperature Oxidation

Of particular interest in a study of carbon oxidation is a digest of experimental findings in the low temperature region roughly defined by the limits of 300° and 800° C. Within this region, it is generally conceded that the measured rates result from true chemical mechanisms distinct from the diffusional mechanisms controlling at higher temperatures. Near the upper limit the temperature coefficient becomes of sufficient magnitude that rates of heat generation exceed those of heat transfer resulting in a rapid increase in temperature. Thereafter the magnitude of reaction variables such as temperature, and reactant and product partial pressures, are not nearly so well defined as they are within the low temperature region.

In one of the earlier works on carbon oxidation, Rhead and Wheeler,⁶⁰ reacted air and pure oxygen with wood charcoal in a constant volume-circulation apparatus at 500° C. and found the rate of oxygen utilization to be directly proportional to its partial pressure. They concluded that local heating of the carbon resulting from CO₂ reduction could not account for all the CO produced and proposed the simultaneous primary production of both oxides. In further experiments,⁴

they found that 1) after a certain time, a mass balance on gas phase oxygen could be made, 2) up to this time, the rate of oxygen uptake was less than that produced as oxides, 3) oxygen fixation was greater on charcoal than on graphite, and 4) a larger proportion of oxygen was adsorbed at lower temperatures.

Langmuir⁵ verified that these findings of Rhead and Wheeler were also characteristic at higher temperatures for the case of metalized filaments made of highly graphitized carbon which were heated with low pressure oxygen in a bulb immersed in liquid air. Langmuir proposed that part of the oxygen reacted directly to form CO₂, the balance forming a surface adsorption layer or complex of great stability which decomposed to CO.

Shah⁶⁵ clarified the nature of the forces involved in forming this surface complex. He found that oxygen was not appreciably adsorbed by sugar charcoal below 0° C., while above this temperature, it was chemisorbed. He extended Langmuir's adsorption model by proposing multi-, rather than single adsorption layers which decomposed with increasing temperature.

Lambert⁷ studied the oxygen-carbon reaction between 250° and 500° C. using two pure and two impure granular carbons in a silica flow reactor, at varying oxygen concentrations. Variations in flow rate were used to vary the reaction time. Feed rates were sufficiently slow so that no local

heating could be detected. Effluent gas analyses were made after about two hours reaction time when an apparent steady state was attained. Almost pure CO₂ resulted from the burning of relatively pure carbon samples while mixtures of both CO and CO₂ were obtained with impure carbons. Carbon oxide concentrations in the exit stream were directly proportional to the initial oxygen concentration and yielded a constant percentage oxygen conversion throughout the range of oxygen concentrations of 20 to 100 per cent. This relationship held for both the pure and impure carbons. In addition, Lambert reported only a small retardation when a CO₂ rather than N₂ diluent was used. Moisture also retarded the formation of CO₂ without altering the activation energy or proportion of CO formed.

Lambert was able to predict reaction rates for the pure carbon by the relation

$$-d(C)/dt = \frac{k(O_2)}{1 + b [(O_2) + (CO_2)]}$$

which was derived on the assumption the CO₂ formed in the reaction provided a surface complex capable of limiting the rate of reaction.

Fluidized beds have been used advantageously to minimize localized over-heating in the oxygen-carbon reaction. In one such investigation, Reichle⁶⁶ cracked a gas-oil on silica-alumina particles to give a carbon deposit which was subsequently regenerated by fluidization with air. He found

the rate of carbon consumption, in grams of carbon removed/100 gms catalyst/sec based on effluent gas analysis, could be expressed as

$$-d(C)/dt = G \left[\frac{P}{760} \right] \left[\frac{492}{T} \right] \left[\frac{454 \times 12}{359 \times 1000} \right] [(CO_2) + \frac{1}{2}(CO)]$$

where G represents the outlet flow rate in ft³/sec. Near differential reactor conditions were claimed in one run. The observed reaction was first order with respect to oxygen.

Lewis, Gilliland, and Paxton⁶⁷ reacted fluidized beds of hardwood charcoal, metallurgical coke, and natural graphite with oxygen over a temperature range of 300° to 950° F. They found the CO/(CO+CO₂) ratio to be essentially constant below 520° F. (about 0.24) and independent of flow rate and the type of carbon. A first order dependence on oxygen was also found, in agreement with many other workers. Six-fold increases in (C), the weight of carbon in the bed, and twenty-fold increases in average oxygen pressure within the bed, (O₂)_{ave}, were correlated by

$$-d(C)/dt = k(C)(O_2)_{ave}$$

The rate constant k varied erratically with carbon burnoff which never exceeded 33 per cent.

A fluidized bed was also used by Haldeman and Botty⁴⁰ to study the kinetics of catalyst regeneration over the temperature range of 500° to 580° C. Carbon used in the study was made from a gas-oil decomposed on silica-alumina particles. The deposit was found to have an atomic C/H ratio varying

between 2.0 and 2.6, depending on the exact pretreatment conditions, and to have high local carbon concentrations in regions of heavy metal concentration. The kinetic study was made under differential conditions using an oxygen partial pressure of 0 to 0.6 atm., initial carbon concentrations of from 0.5 to 6 per cent, initially dry reactant gas, and analyzing the effluent for CO, CO₂, and H₂O. Regeneration kinetics were expressed as a form of

$$\frac{-d(C)}{dt} = k(O_2)^{(0.75 \text{ to } 1.0)}.$$

The reaction approached first order after about 60 per cent burnoff.

Arthur²¹ presented an excellent study of the oxygen-carbon reaction for two carbons of widely different reactivities (artificial graphite and coal char) over a temperature range of 460° to 900° C., using a packed bed-flow reactor. His experiments were designed to inhibit gas phase oxidation of CO. He felt this reaction could be a significant factor in explaining previous findings that, below 800° C., oxygen and carbon combine directly to form CO₂. Phosphoryl chloride (POCl₃) was used for this purpose, being injected in small quantities along with the O₂ and N₂ feed. The POCl₃ was found to suppress the oxidation of carbon as well as CO. Rates of graphite consumption were independent of the mass of carbon present, directly proportional to the oxygen partial pressure, and either independent of, or increased with, the air velocity.

The graphite oxidation rate was independent of velocity changes below 420° C. Above these temperatures the rate was proportional to the flow rate raised to the 0.5 to 0.8 power. Although an appreciable oxygen decrease was measured across the bed, effluent oxygen content was never less than 2 per cent. Substantial amounts of CO were produced on oxidation of the coal char. The ratio of produced oxides (CO/CO₂) was found to be independent of the mass of carbon or the size of particles, air velocity (below 900° C.), and initial oxygen partial pressures (between 38 and 190 mm Hg). It increased with velocity above 900° C. and increased exponentially with temperature between 480° and 900° C. according to the relation

$$\frac{CO}{CO_2} = 10^{3.4} \exp(-12,000/RT).$$

Arthur based his kinetic calculations on effluent O₂, CO, and CO₂ analyses and flow variables according to the equation

$$\frac{-d(C)}{dt} = k' \left[\frac{(CO) + (CO_2)}{(O_2) + (CO_2) + \frac{1}{2}(CO)} \right]$$

where $k' = 12pF/(100 \times 22,400)$. The terms F and p represent the flow rate and oxygen pressure, respectively.

Perhaps the most important work to which the present investigation is related is that of Gulbransen and Andrew.¹ These co-workers investigated the initial reaction of spectroscopic graphite with oxygen in the interval 425° to 575° C. at pressures of 0.15 to 9.8 cm Hg oxygen pressure by suspending 0.25 gram strips of graphite from a sensitive microbalance

operating in a high vacuum system. Experimental burnoffs were limited to less than one-half per cent of the initial carbon charge because of limitations in the system. Prepuri- fication and removal of surface oxides were effected in part by heating under high vacua or in purified H₂ atmospheres. In addition to observing that an un-degassed sample had a higher initial reactivity than either the degassed or hydrogen treated samples, they found that addition of one per cent hydrogen to graphite, undergoing oxidation at 500° C., had no effect on its rate of utilization.

Of greater significance are the constant rate of re- action data obtained by Gulbransen and Andrew at two tempera- ture levels, 450° and 500° C., over a 65-fold change in oxygen pressure. By progressively varying the oxygen pressure between 0.15 and 9.8 cm.Hg, at a constant temperature and for the same graphite sample, they found the rate to increase from nearly zero order in oxygen at the lower pressure to nearly a first order dependence on oxygen at the higher pres- sure. Intermediate pressures gave fractional orders on oxygen. Gulbransen,⁶⁸ in reviewing these results, proposes either mobile adsorption, or immobile adsorption with dissociation, as an explanation to the rate limiting process within the intermediate pressure range. An activation energy of 36.7 kcal/mole, based on initial rate data, was also reported. A higher value of about 40 kcal/mole has been recalculated for the portion of their data representing steady state rates.³

The data of Gulbransen and Andrew for any single ex- periment could be expressed by¹⁴

$$W = K t$$

where W is the weight loss in time t and K is a constant re- presenting the rate of reaction at the experimental tempera- ture and oxygen pressure. Of further significance is the fact that they were able to correlate their rate data as a function of oxygen pressure over the transition period in which the order was changing from zero to unity. The follow- ing equations were found to closely represent this data:

$$\text{For } 500^{\circ} \text{ C.}; K = 1.35 \times 10^{-9} + 0.505 \times 10^{-9} P$$

$$\text{For } 450^{\circ} \text{ C.}; K = 0.23 \times 10^{-9} + 0.083 \times 10^{-9} P$$

where P is given in centimeters of mercury of oxygen and K in units of grams per square centimeter per second (quoted values are listed as gms/cm²-min). An interesting observa- tion associated with these equations is that K tends toward a residual value as P approaches zero. As the reaction is generally considered to be first order in oxygen, one would expect a breaking away of the rate, K, from the above equa- tions at low pressure. These authors did not study nor offer any explanation for this apparent anomaly. Other factors, such as contaminants in the gaseous phase, may have influenced the above results. More will be said on this subject in the discussion of the present results.

The work of Blyholder and Eyring² stands out as the only other experimental verification of a zero order

dependence of the carbon oxidation reaction on oxygen pressure. Their experimental approach consisted of reacting extremely thin graphite coatings on a ceramic base with oxygen at 800° C. From a limited amount of reported data, they found a zero order dependence on oxygen at 100 μ Hg pressure and an activation energy of 80 kcal/mole. The oxygen feed was dried over magnesium perchlorate. Diffusion of oxygen into the pores was concluded to be the rate limiting step. When the specimen coatings were greater than 0.1 mm thick, a half order reaction and an activation energy of 42 kcal/mole were reported.

Reproducibility

Experimental difficulty in duplicating rate data has been reported by a number of investigators of the oxygen-carbon reaction. Langmuir⁵ attributed his difficulty in obtaining reproducible rates to the previous history of the carbons used. Difficulty in reproducing rate constants was also experienced by Lewis, Gilliland, and Paxton.⁶⁷ Their experimental values showed an erratic variation for carbons which were not consumed in excess of 33 per cent burnoff. Armington,³⁵ reacting graphitized carbon blacks and re-graphitized graphite samples with 0.1 atmosphere oxygen between 550° and 600° C. in a vacuum microbalance system, was able to obtain reproducible results only after a minimum burnoff of 2 per cent had been attained.

One of Blyholder and Eyring's² major problems was in experimentally reproducing their results. Their experimental technique consisted of rapidly passing anhydrous dried oxygen over ceramic supported graphite coatings maintained at 800° C. Pressures of less than 100 μ Hg were maintained. Steady state rates of carbon consumption were obtained from the amount of CO₂ removed by a liquid nitrogen trap. They credit their difficulty in reproducing data to variations in total surface area as the sample is consumed and to the adsorption of vapors other than oxygen. This "aging" explanation was used because samples which had been held overnight at either 25° C. or 800° C., under vacuum, lost about 50 per cent of their previously measured reactivity. This reactivity could be restored by a small degree of reoxidation. Since the retarding effect could be artificially induced in a few minutes by passing water vapor over the sample, Blyholder and Eyring regarded their rate variations for identical experiments as understandable trends rather than as random irreproducibilities. More will be said on this apparent poisoning of the carbon surface by water in the discussion of results.

Difficulty in reproducing rate data has also been experienced by Hoynaut and co-workers³⁴ in studying the oxidation of carbon with anhydrous dried air. They claimed traces of hydrogen and water vapor in the feed gas caused a retarding effect to the reaction. Lack of reproducibility in a study of the water-gas reaction by Gadsby, Hinshelwood, and

Sykes³² was accredited to changes in the catalytically active impurities present in the carbon.

The likelihood exists that many such similar problems of obtaining reproducibility have been observed but never reported. Nevertheless, the above mentioned investigations are sufficient to pose the existence of at least one uncontrolled reaction parameter responsible for this behavior. Also involved is the previous inability to predict rates from first principles. This difficulty has generally been attributed to changes within the carbon structure. Perhaps other influences have been underestimated.

Investigations Using Pyrolytic Methane Carbon

Pyrolytic carbon formed by methane decomposition has received limited application as a fuel by investigators of carbon gasification reactions. Meyer⁶⁹ decomposed methane onto filaments for his source of carbon to study its reaction with oxygen at low pressures and high oxygen flow rates between temperatures of 500° to 2000° C. He found a different type reaction occurred from 500° to 1200° C. in comparison to that occurring from 1300° to 2000° C. Below 1200° C. the reaction was first order in oxygen dependence. In an extension of this work, using the same streaming method and methane as a carbon source, Martin and Meyer⁷⁰ studied the effect of product gases in their investigation of the carbon dioxide-carbon reaction at temperatures to 2325° C. Chen, Christensen,

and Eyring⁷¹ used a similarly made pyrolytic carbon film deposited on a ceramic base to study the oxygen-carbon reaction between 350° and 500° C.

On the Nature of Pyrolytic Methane Carbon

The methane decomposition reaction has been quite extensively investigated.⁷² However, the nature of the amorphous solid phase formed is not so readily characterized. It has only been recently that such properties as surface areas, pore distributions, crystallographic parameters, and average crystallite sizes and orientations of carbon have been determinable for such carbons.

Wheeler⁷³ has pointed out that it is erroneous to conclude that methane when "cracked" gives only brilliant carbon, as at least three different types of carbon are identifiable. These vary with the nature of the cracking surface and the temperature and speed of the gas. Gibson, Riley and Taylor⁷⁴ prepared filamentous carbon by cracking CH₄ diluted with H₂, N₂ and CO on an Fe surface at 1000° C. X-ray analysis showed the carbon to have an amorphous structure.

Iley and Riley⁷⁵ observed results similar to those of Wheeler. They identified the three forms of carbon deposited between vitreosil tubes as vitreous and columnar, soft-black pulverulent, and filamentous. These were arranged zonally from the hotter to the cooler ends. They all resembled

macrocrystalline graphite in their reactivity to oxygen. Carbons produced in this manner were found to be pure with the exception of a fraction of a percentage of hydrogen.

Summary of Literature Review

An attempt has been made to present a comprehensive review of those portions of the literature which appeared to be pertinent to this work. Very few positive conclusions may be drawn because of the differing experimental findings and interpretations. Therefore quantitative results, for the most part, have been overlooked as these have not yet proven to be of significance to a fundamental understanding of the oxygen-carbon reaction. The following generalizations and hypotheses about the oxygen-carbon reaction are accordingly restricted.

1. Localized overheating is one phenomenon which characterizes the transition from chemical to diffusion controlling mechanisms. Inferences drawn about the true chemical mechanism when such an experimental condition exists are questionable. Very few near-differential reactor experiments on the oxidation of carbon have been performed in which temperature gradients were negligible.

2. Experimental conditions are usually such that an apparent first, or close to first, order reaction with respect to oxygen is observed. Two noteworthy exceptions have found the rate to be nearly independent of oxygen pressure. In one case, a transition in order from zero to unity was accompanied by an increase in oxygen

pressure. Zero order results were observed at low oxygen pressures. Chemical reaction kinetics predicts, for this reaction, a first order dependence on the reactant in limited supply. Therefore there must exist at least one accompanying pressure dependent variable whose influence on the reaction has previously been neglected. Such a situation could explain the inability to define the basic mechanism by which the oxygen-carbon reaction proceeds. Previous emphasis in defining additional reaction variables has been directed toward a more thorough evaluation of the solid state carbon while gaseous contaminants, for the most part, have been neglected.

3. The concept of a stable carbon-oxygen surface complex, while well supported, has eluded direct experimental verification. This is clearly evidenced by the precise work of Gulbransen⁶⁸ who, using a microbalance sensitive to carbon weight changes of 0.0001%, reportedly found ". . . no evidence of an initial pickup of oxygen to form a surface oxide as predicted by Rhead and Wheeler."

4. At lower reaction temperatures, pure carbon combines with oxygen to yield carbon dioxide while impure carbons yield both the monoxide and the dioxide. The mechanisms by which these reactions occur are not well understood. Most carbon oxidation studies have been

made using relatively impure carbon.

5. Surface area measurements have not yet attained the degree of sophistication to be of direct significance in determining the rate or chemical controlling mechanism of the oxygen-carbon reaction.

6. Depending upon experimental conditions, carbon oxidation rates may become constant after a certain degree of carbon burnoff indicating the attainment of steady state conditions within the reactor. The steady state carbon oxidation rate is independent of the mass of the carbon in the reactor when this quantity is large in proportion to the amount of oxygen passed through the reactor and/or differential reactor conditions exist. That is, the steady state rate may persist through a fairly large change in carbon concentration.

7. Neglecting the influence of other contaminants, the oxidation rate of impure carbon is proportional to the amount of bound hydrogen present in the sample. Oxidation rates accordingly decrease in the order charcoal, coke, graphite and diamond. This influence of hydrogen has previously been neglected in mechanistic proposals for the oxygen-carbon, carbon dioxide-carbon and steam-carbon reactions.

8. Water vapor has been shown to influence the rate of carbon oxidation although no thorough investigation

has been reported to show its quantitative importance. Observations of both catalysis and inhibition of the oxygen-carbon reaction by water appear to be equally well founded.

9. The decomposition of carbon monoxide to carbon and carbon dioxide and the water-gas shift are the only secondary reactions of importance in a study of pure carbon oxidation below 500° C.

10. Most carbon oxidation rate investigations have attempted to correlate their results according to the mass law form. Controversial points have arisen over the apparent order on oxygen, activation energy, rates of reaction, and the influence of contaminants. Activation energies are reported to vary from 17 to 100 kcal/mole with the lower energies compatible with mass transfer control of the reaction. Reports of chemical controlled rate dependence upon temperature frequently fall within the 40 to 80 kcal/mole range.

11. Difficulty in obtaining reproducibility indicates a lack of experimental control over all of the factors influencing the oxygen-carbon reaction.

12. Carbons used in most experiments have been obtained from impure petroleum coke, coal tar pitch, or similar sources. Although they have subsequently been exposed to differing degrees of purification by heating and graphitization, there still exists an abundance of

hydrogen in the solid phase. In contrast, pyrolytic carbons, particularly those made by methane decomposition in an inert atmosphere, contain only a few tenths per cent hydrogen. These latter type carbons have received limited use in studying the oxygen-carbon reaction.

13. The diluent used in most investigations reviewed was nitrogen. The possibility of secondary reactions involving this component does exist. Strickland-Constable⁸ has shown that, at 400° C., carbon monoxide is readily oxidized by nitrous oxide in the presence of charcoal. He also found the nitrous oxide-carbon reaction to be appreciable at 400° C. yielding almost pure carbon dioxide. This point will not be discussed further since helium was used as a diluent in the present investigation.

CHAPTER III

EXPERIMENTAL APPARATUS AND MATERIALS

In the course of this work, a recirculation differential reactor was constructed to study the kinetics of the oxidation of amorphous carbon. The carbon was present in the reactor in the form of a thin film, deposited by cracking methane on a bed of non-porous "Vycor" brand glass particles. Neither an experimental system of this design nor this type of carbon-coated packed bed had been previously reported in the literature on carbon oxidation.

Criteria

The experimental recirculation differential reactor system was selected in an attempt to overcome many of the problems encountered in obtaining precise kinetic data in flow systems. This type system has been shown to be capable of permitting high gas velocities through the reactor while avoiding an excessive use of reactants.⁷⁸ Interpretation of recirculating reactor data is similar to that used in evaluating once-through reactor data if process variables are measured upstream and downstream from the recirculating portion of the reactor system. Such an application was selected for this investigation, the details of which are included as Appendix VI.

The big advantage of recirculating a portion of the

reactor effluent, over a once-through type reactor, lies with the degree of conversion necessary to overcome analytical limitations. In a once-through reactor, if conversions are sufficiently small to justify using an average bed temperature and average reactant composition in the flow stream, then analytical errors make precise kinetic determinations questionable. On the other hand, if sufficiently large conversions are permitted so that a more reasonable error analysis results, then a precise knowledge of the reaction temperature and reactant composition along the bed becomes questionable. This problem becomes particularly important in studying reactions which have large temperature coefficients. By recirculating a portion of the reactor outlet stream, one is able to more closely approximate differential reactor conditions, maintain a lower temperature gradient through the bed, increase the conversion required of analytical methods by monitoring the flow upstream and downstream from the recirculating system, and more closely ascertain the reactant composition within the reactor. Other desirable features of the system include lower diffusional effects, both radial and longitudinal, which result from the lower conversions per pass of reactant through the reactor.

One apparent disadvantage of the recirculating process, that of recirculation of products along with reactants, is offset by the emphasis this technique places on the influence of products on the reaction. Interpretation of rate data

from once-through reactors too frequently assumes this latter effect to be negligible. A further discussion of the recirculating reactor system is outside the scope of this work and may be found in the literature.⁷⁷⁻⁸⁶

The carbon selected for this study was one which could be deposited as a coating and yet be of a purity which could be accurately determined. The relatively pure amorphous form used was conveniently generated by pyrolytically decomposing methane. Non-porous, low activity, Vycor glass was selected as a support for the deposit in order to minimize diffusional and catalytic effects during oxidation.

Sensitive analytical techniques for determining the carbon content of the bed, feed composition, and effluent gas analyses for oxygen and carbon dioxide, as well as for traces of hydrogen, methane, and carbon monoxide, including an analytical determination of water content, were incorporated with the recirculation system. A very stable feed control is essential to insure constancy of flow at steady state conditions.

Description of the Process

Referring to Figure 1, and the photograph of Figure 2, the high pressure oxygen-helium feed, premixed and of established composition, was expanded through a pressure regulator to about 40 psi and then passed through a differential flow controller into the stream being recirculated. The composite stream, consisting of a fixed ratio of recycle to feed gases,

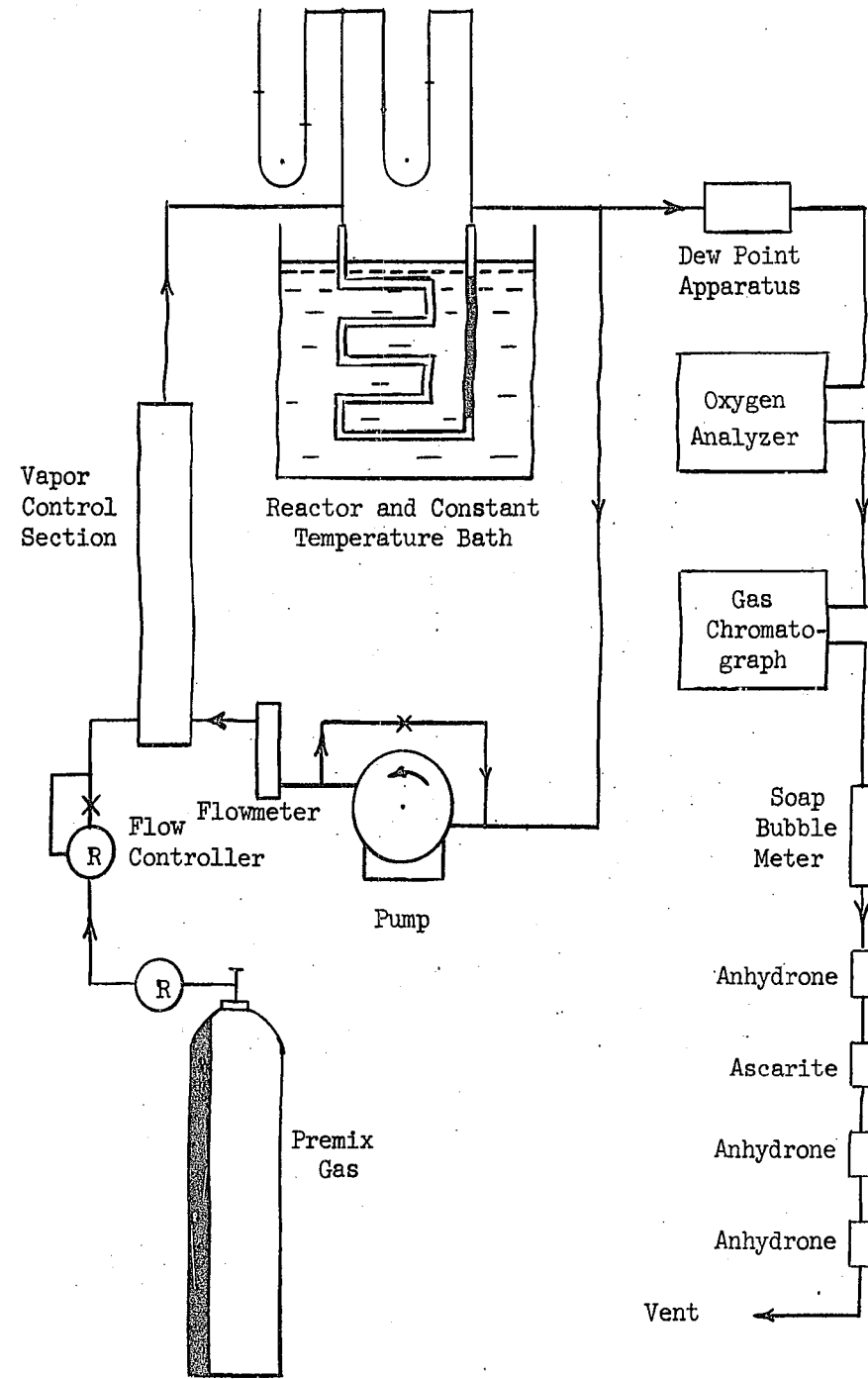


Figure 1. Schematic of Experimental Apparatus

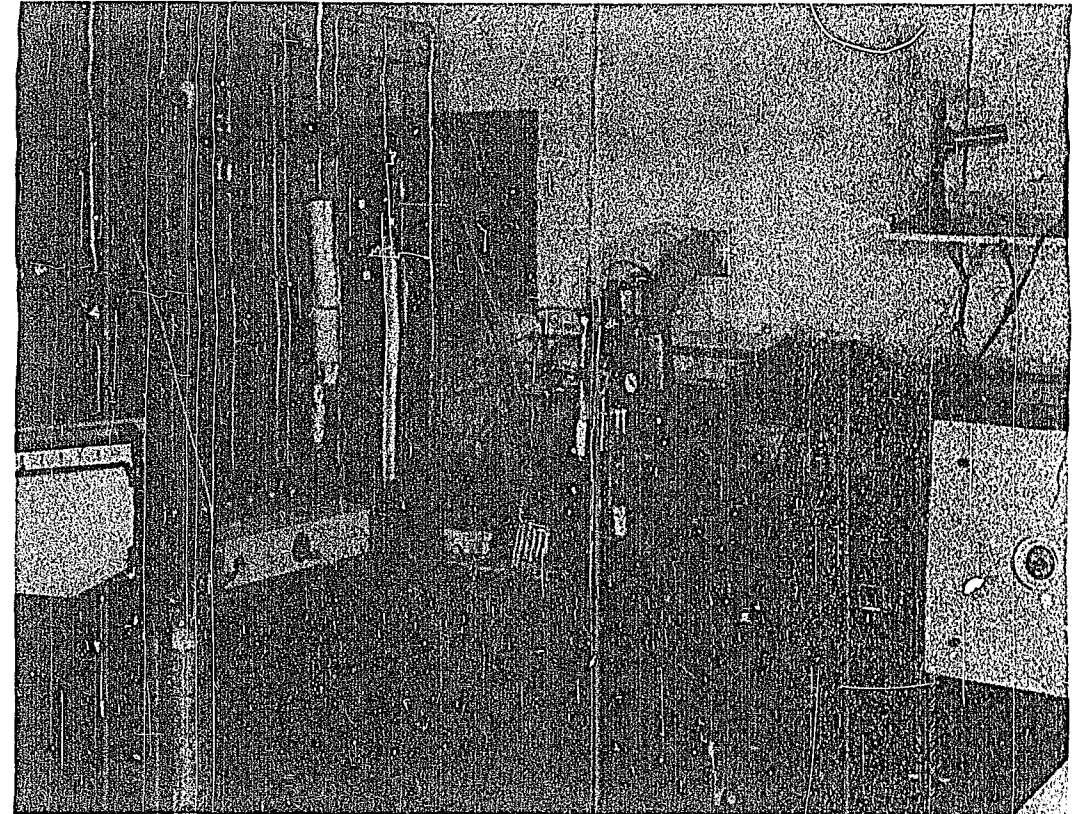


Figure 2: Photograph of Experimental Apparatus

was then directed through one of three routes at the vapor control section. This facility, wherein a broad range of water vapor contents could be incorporated with the gas, is shown as Figure 3. The ensuing mixture then flowed through a preheating section and into the packed bed reactor (Figure 4), both of which were immersed in a constant temperature bath. Construction of the constant temperature bath is illustrated in Figure 5. The stream leaving the reactor was cooled and subsequently divided into effluent and recycle portions, the latter passing in series through a flow meter and recycle pump to be mixed with fresh feed gas.

The effluent portion first passed through a dew point tester capable of determining saturation temperatures from below -200° F. to ambient temperatures. It was then routed through an oxygen analyzer coupled with a gas chromatograph for effluent gas analysis. The flowing gas was next directed through a flow meter of the soap bubble type and then through an ascarite-anhydron adsorption train where carbon dioxide was removed. The adsorption train was weighed frequently to give both the incremental and cumulative weights of CO_2 produced. The gas was then vented.

Description of the Equipment

1. Differential Flow Controller. The feed flow control device was a Moore Model 63BD-L controller capable of controlling downstream flow rates to within ± 0.5 per cent.

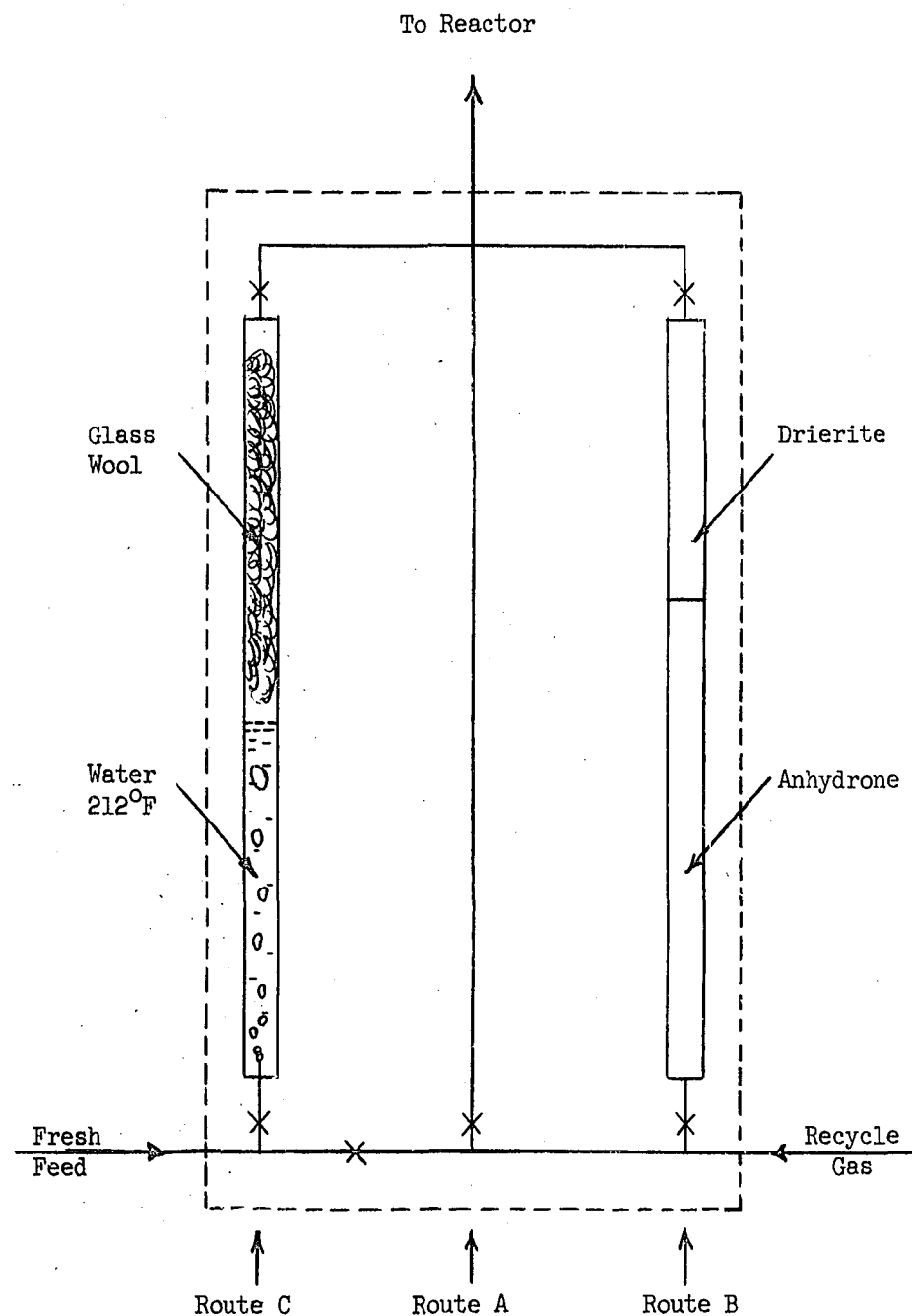


Figure 3. Detail of Vapor Control Section

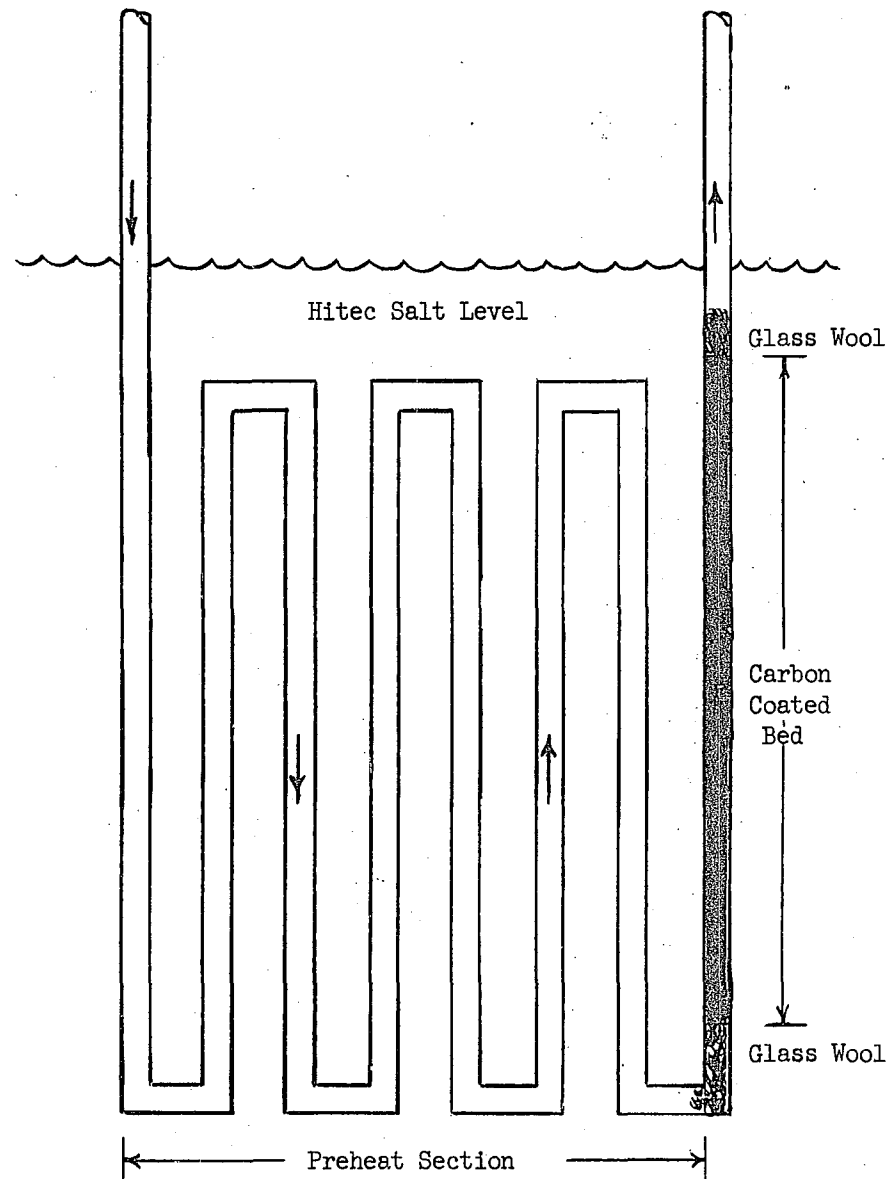
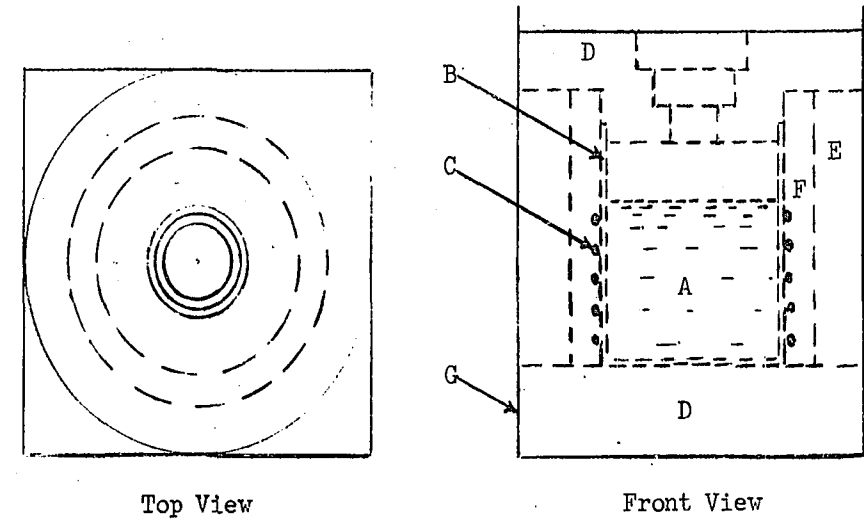


Figure 4. Vycor Glass Reactor



Symbols:

- A Hitec Heat Transfer Salt
- B Stainless Vessel
- C Nichrome Wire
- D Thermobestos Block Insulation
- E Nominal 17"x 3" Thermobestos Pipe Insulation
- F Nominal 12"x 2" Thermobestos Pipe Insulation
- G Wood Framing

Figure 5. Constant Temperature Bath

2. Vapor Control Section. Three general levels of water vapor content were obtained by flowing the gas through one of three routes in this section. Route A (Figure 3) is merely a by-pass so that the steady state water content becomes essentially that of the premixed feed gas. For very low water content, the gas is passed through route B consisting of a combination drierite-anhydrous adsorption column. The steady state water content obtained through this section, as determined by an analysis of the effluent gas, was a gas of about -90° F. dew point corresponding to a saturation vapor pressure over ice of 0.0027 mm Hg.^{87,88} Water Vapor contents approaching saturation at ambient temperatures were obtained by directing the gas through the heated-bubble saturator of route C. The water refluxing action obtained in the operation of this saturator gave water vapor content which varied slightly with contact time and saturator pressure, as above.

3. Preheating Section and Reactor Shell. This Vycor glass element is shown in Figure 4. Eight feet of 9 mm OD x 7 mm ID tubing were continuously spiraled for immersion into the constant temperature bath. The first 6 feet amounted to a preheating section with the carbon bed being contained within the next seven inches. Pyrex wool plugs were used to contain the bed. Upstream and downstream pressures were obtained at locations immediately adjacent to the Vycor element.

4. Constant Temperature Bath. The constant temperature

bath was constructed as shown in Figure 5. Hitec salt, a eutectic mixture of sodium nitrate and sodium nitrite, was used for a heat transfer medium. This material was contained within a 12" ID x 13" steel vessel. A stirrer was used to equalize bath temperatures. Two 980 watt Nichrome wire heaters, separated from the vessel by asbestos sheeting, were connected to 118 volt variable transformers which in turn were connected to a 1500 watt constant voltage regulator. One heater supplied the major portion of power required while the other was used for control purposes. Heat insulation was provided by six inches of Thermobestos insulation. The constant temperature bath was designed for a maximum operating temperature of 1200° F.

Temperature control was manual with $500 \pm 1^{\circ}$ C. easily sustained over several hour periods without requiring frequent adjustments. The constant voltage regulator, in conjunction with a circulating fan directed on the variable transformer coils, and a constant ($\pm 1^{\circ}$ C.) temperature room, aided substantially in temperature control.

5. Recycle Flow Meter. The meter used to measure the recycle gas flow was a Brooks "Shorate 150," size No. 2, of the tapered tube type. A stainless steel ball float gave satisfactory "on scale" readings.

6. Recirculating Pump. The recycle pump was of the vibrating diaphragm type similar to a previously reported design.⁷⁶ Essential elements used in the construction were

four 1963 Buick fuel pumps whose fabric reinforced diaphragms were connected as per the referenced design. Pump operation was satisfactory and no excessive pulsations were noticed. A by-pass arrangement around the pump, as shown in Figure 1, enabled flow control of the stream actually recycled.

7. Dew Point Apparatus. Figure 6 shows a modified version of the standard Bureau of Mines type dew point tester which was used for analysis of water contents in the effluent gas stream. Construction and operating details for the standard instrument are contained in ASTM Standards D-1142. The lower temperature range of the conventional instrument was extended by the adaptation of an elongated heat transfer mandrel connected to the copper rod basic to the instrument. The mandrel, replacing the gas expansion element of conventional design, could be immersed in different coolant liquids enabling varying degrees of temperature sensitivity. Ice-water, dry ice-acetone, and liquid nitrogen coolants were used with which mirrored surface temperature depressions of from ambient to below -254° F. were obtained. The temperature of the mirrored surface was measured by means of an iron-constantan thermocouple located within the thermometer well in physical contact with the mirrored surface plate of the standard instrument.

Operation of the modified dew point apparatus was similar to that of the commercial instrument down to temperatures of about 0° F. The dew point of the gas became more

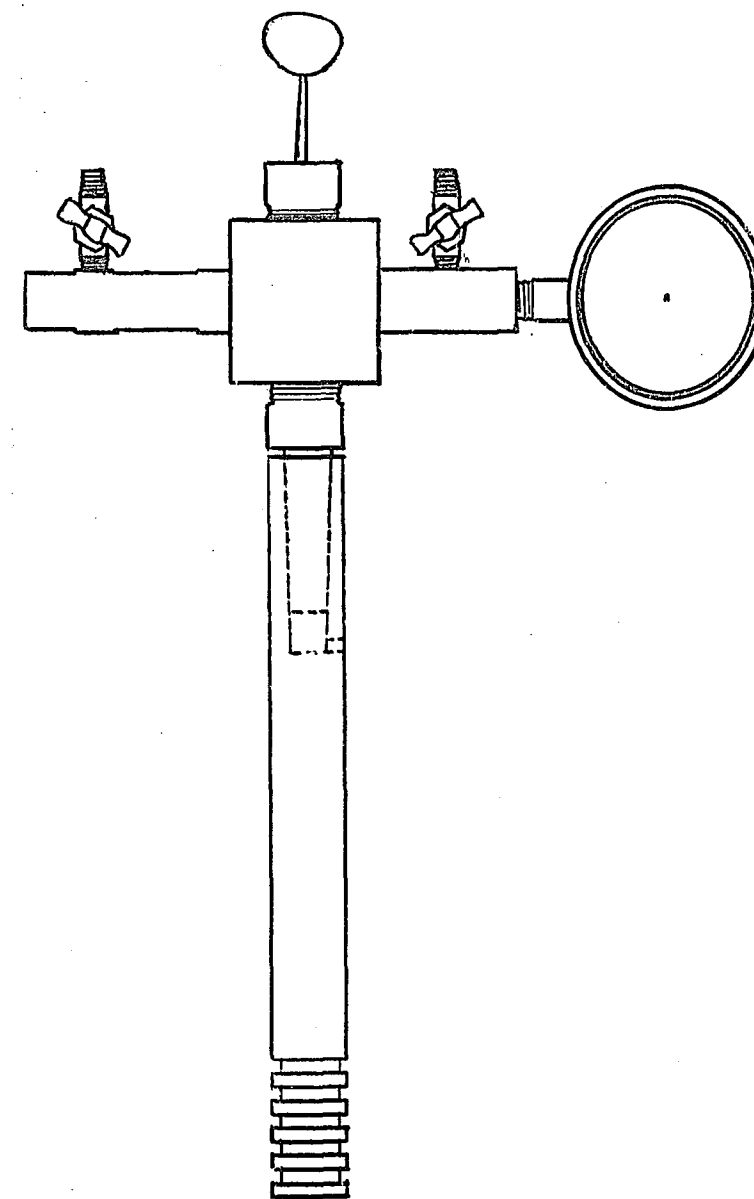


Figure 6. Modified Dew Point Apparatus

difficult to recognize at lower temperatures because ice crystals, rather than liquid droplets, then formed. For such cases, the temperature where ice crystals first began to form was taken as the dew point. This observation was facilitated by use of a magnifying lens and good illumination of the mirrored surface.

8. Oxygen Analyzer. A Beckman Model E-2 oxygen analyzer was used for analysis of oxygen in the feed and effluent flow streams. Five ranges of oxygen sensitivity were available with the instrument: 0-2%; 2-3%; 3-4%; 4-5%; 5-10%. Instrument accuracy was $\pm 1\%$ of the measuring range span. Accuracy claimed could only be substantiated by calibration after each oxygen analysis.

9. Gas Chromatograph. Gas analyses for O_2 , CO_2 , and a check for traces of H_2 , CH_4 , and CO in the effluent stream were made available through the use of a Beckman GC-2 gas chromatograph and a 0-1 mv recorder. Helium was used for the carrier gas. The stock instrument was modified for dual column operation by a toggle and check valve arrangement. Analyses for CO_2 were obtained through use of a nine inch column of 14-20 mesh Silica Gel packing while O_2 analyses, and a check for traces of H_2 , CH_4 , and CO , were made with a nine inch column of 20-50 mesh Molecular Sieve 5A packing. Good peak resolution was obtained with these column lengths for constant operating variables of 30 psi carrier gas feed pressure, a 300 ma conductivity cell current, and $70^\circ C$. column

temperature. The chromatograph was electrically operated from the constant voltage regulator previously mentioned. A fairly constant base line tracing was obtained at maximum sensitivity.

10. Adsorption Train. The cumulative weight of carbon dioxide produced in the oxidation of a carbon sample was obtained by frequently weighing an ascarite-anhydrone adsorption train. As shown in Figure 1, the effluent gas passed through an anhydrone column to remove excess water vapor, through the ascarite where CO_2 was adsorbed, and then through another anhydrone column to remove the water liberated by the ascarite in the adsorption of CO_2 . A final anhydrone column was used to prevent atmospheric contamination of the weighing section. Accurate weighings were made with a Mettler type 15H balance of 160 gram capacity and ± 0.05 mg accuracy.

Carbon Fuel and Coking Furnace

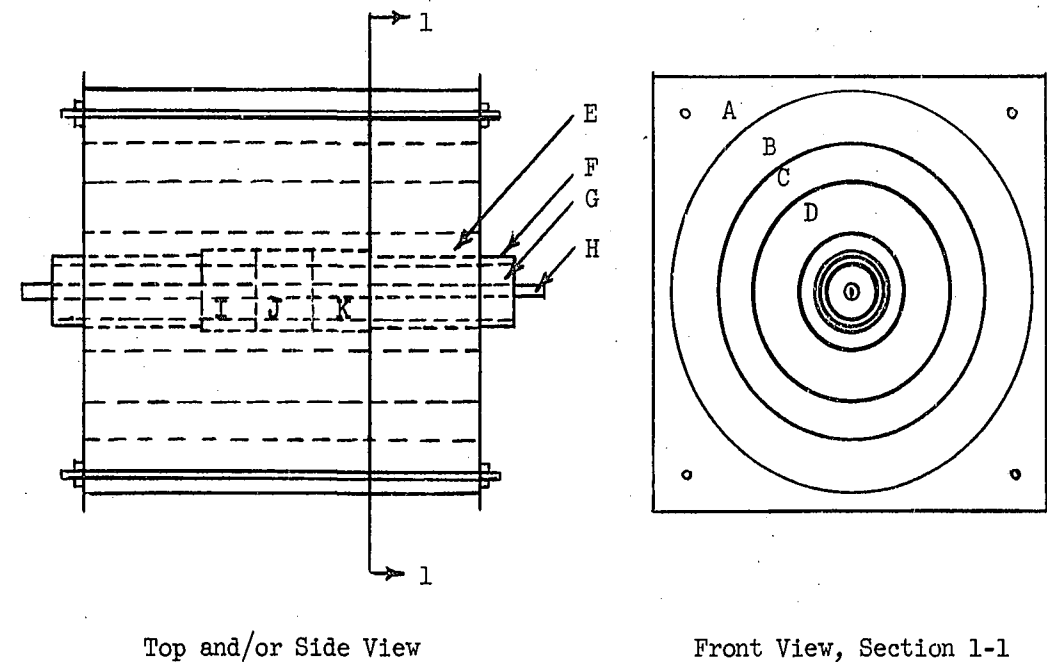
A solid amorphous deposit was produced by passing methane through a heated porous bed of 20-50 mesh non-porous Vycor glass particles (cullet, ground and screened). The bed was contained within a 25 mm OD x 22 mm ID x 36" Vycor glass tube. Pure Grade methane containing at least 99 per cent CH_4 as per the supplier, Phillips Petroleum Company, was used.

The decomposition reaction took place quite readily at $1940^\circ F$. resulting in a film-type coating which consolidated the particles. Methane was fed to the decomposition reactor at 1.3 SCFH over about a five hour period in each

coking operation. The effluent was burned. Sufficient decomposition experiments were made until an ample supply of 20-50 mesh gray carbon coated particles remained after crushing and rescreening. Since the residence time of the coking operations varied somewhat, the composite sample of coated particles was thoroughly stirred in order to insure a uniform sample source for the oxidation experiments. This bulk sample was stored in a desiccator until used. Three random samples, each containing two to five grams of coated particles, were completely oxidized with air in a metallurgical furnace operated at 600°C . The carbon content was found to be $3.81 \pm .01$ per cent by weight in all cases.

The tube-type coking furnace, constructed for the decomposition experiments, incorporated six Hevi-Duty type 24 KSP semi-cylindrical heating units (4" OD x 3" ID x 3", 2200°F . rating, 700 watts each set). Each pair of resistance elements was separately operated from a variable transformer for control of the linear temperature gradient within the reactor. Heat insulation was provided by a two inch thick layer of insulating refractory concrete, six inches of Superex pipe insulation, and six inches of Thermobestos pipe insulation. A schematic drawing of the furnace is shown in Figure 7.

The decomposition reactor was contained within the furnace by two half cylinders of molded castible refractory. A sliding wire chromel-alumel thermocouple, contained within an Alundum thermowell, provided linear temperature measurements



Symbols:

- | | |
|---------|--|
| A | Transite Sheet |
| B | Nominal 17"x 3" Thermobestos Pipe Insulation, 1200°F |
| C | Nominal 12"x 2" Thermobestos Pipe Insulation, 1200°F |
| D | Nominal 6" x 3" Superex Pipe Insulation, 1900°F |
| E | Casted Refractory, 2400°F |
| F | Alundum Tube |
| G | Casted Refractory, 2400°F |
| H | Vycor Glass Tube |
| I, J, K | 118 Volt Heater Units |

Figure 7. Schematic of Coking Furnace

within one of the half cylinder molds. Operation of the furnace was satisfactory although a considerable warm-up period was required and thermocouple life was short. Measured temperature fluctuations of $\pm 20^{\circ}$ F. were probably caused by line voltage variation and inadequate warm-up time. In one test near 1940° F., the linear temperature gradient in the thermowell was less than two degrees per inch along the middle five inch section of the furnace.

Feed Materials

Cylinders of Bone Dry aviators breathing oxygen (purity 99.5%), Grade A helium (purity 99.99%), and Bone Dry-Research Grade carbon dioxide (purity 99.8%) were used. The purity claimed by the suppliers was not substantiated. Test mixtures of gas were formulated by combining these gases, at high pressure, in the approximate desired proportions. Subsequent mixture analysis was by either the oxygen analyzer or gas chromatograph. At 1600 psig, for a final mixture of 8.20 per cent O_2 in He, a two week mixing period was required before a homogeneous gas mixture resulted. Mixing times were decreased thereafter by use of a heat source at the bottom of the cylinder.

CHAPTER IV

EXPERIMENTAL TECHNIQUES

Calibrations

The recycle gas flow meter was calibrated by passing variable flow rates of helium through the meter and measuring the downstream rate with a soap bubble meter. Appropriate corrections for pressure, temperature, and density (molecular weight) were made when experimental gas volumes were measured.

The iron-constantan thermocouples used in determining reaction temperature were checked for accuracy against a platinum resistance thermometer. The comparison was made within the well-stirred constant temperature bath previously described. Thermocouple measurements at about 400° C. and 500° C., after correction for cold junction temperatures, gave readings within ± 0.5 per cent of the absolute temperatures indicated by the readings from the platinum resistance thermometer.

The accuracy of the iron-constantan thermocouple used in dew point determinations was within ± 3 per cent of the absolute temperature at a -92° F. dew point level and within ± 1 per cent near the freezing point of water. This calibration

was made by comparing cold junction compensated thermocouple temperatures with liquid bulb thermometer readings when both were respectively immersed in stirred dry ice-acetone and ice-water baths.

Two instrument calibrations were required for accurate analysis with the oxygen analyzer. Both were performed in accordance with the manufacturer's recommendations. One, the zero setting, was made after thoroughly purging the instrument with nitrogen. This was an infrequently required operation. The span calibration was made after similarly purging the instrument with a standard oxygen-nitrogen sample. The standard sample was procured from The Matheson Company and contained $9.80 \pm .01$ per cent oxygen, by their analysis. Since slight changes in barometric conditions affected the span calibration, the instrument accuracy was maintained by making a span calibration after each analysis for oxygen in an unknown sample.

The gas chromatograph provided a qualitative check on O_2 , H_2 , CH_4 , and CO , the first named showing changing effluent gas compositions as steady state was approached. Calibration of the instrument for steady state CO_2 compositions was made by comparing the planimetered peak areas obtained from gases of known CO_2 content. Unknown steady state carbon dioxide contents so determined were always within a few per cent of the average found by weighing the adsorption train columns over a time increment.

Run Technique

The reactor was charged with a 7.5 gram sample of carbon coated particles (0.2858 gms carbon) at the beginning of each series of experiments. The feed-recirculation-exhaust system was allowed to come to steady state conditions at the test feed rate with the reactor maintained at room temperature. Steady state was then determined by gas chromatograph and oxygen analyzer readings. Approximately one hour was required to reach this condition. The purged adsorption train was then weighed and the reactor immersed in the constant temperature bath. Approximately 30 minutes was required for the bath to regain the steady desired temperature level. Steady effluent gas compositions were regained only after from 1 to 3 hours at the reaction temperature. The experiment was continued until about 5 mg of CO_2 had been produced under non-varying conditions. The reactor was then cooled, one of the process variables under study was then changed, and the procedure was repeated starting with the attainment of steady state conditions while the reactor was at room temperature. A new series of experiments was started when one-third of the carbon deposit had been consumed.

The temperature of the molten salt bath was taken as the reaction temperature. This was done to facilitate the measurements since no measurable temperature gradient could be detected across the bed with the steel reactor in which rates were a maximum. Iron-constantan thermocouples were then located in the gas stream immediately upstream and downstream from the bed.

effect of the reaction product on the oxygen-carbon reaction. Observed experimental data are included in Appendix I. Comparison of rates for comparable oxygen and water contents shows that little, if any, effect was caused by the presence of large concentrations of carbon dioxide.

Water vapor, carried through the system by helium, was passed over a carbon bed maintained at 500° C. in another experiment. The purpose was to check for the existence of either a simultaneous steam-carbon reaction or for any external effect which would influence the major experimental results. No trace of carbon reaction with steam was found at this temperature.

Also worth noting is the difficulty in obtaining reproducible results in preliminary experiments in which a stainless steel reactor was used. Observed rates under apparently identical conditions varied by as much as 800 per cent. They appeared to depend on the previous history of the steel surface and particularly upon previous adsorption of water vapor. As there was more mill scale following use of high water concentrations in the feed, as well as proportionate carbon dioxide production, the likelihood is that under comparable conditions the oxidizing qualities of the steel may have overshadowed that of the carbon. Fabrication of the reactor from Vycor glass alleviated the problem.

CHAPTER V

EXPERIMENTAL RESULTS

Quantitative experimental results are listed in Appendix I. Presented are measured rates of carbon oxidation with corresponding experimental data of temperature, oxygen content in the feed gas, the flow rate across the recirculating portion of the system, and analyses of exhaust gases for oxygen, carbon dioxide, and water vapor. Rates were measured over the 400° to 500° C. temperature interval using three different concentrations of oxygen in the feed. The effect of three levels of water content on the rate was explored for each oxygen concentration. A sample calculation of rate data is included as Appendix II.

An important result of this investigation is the finding of only one reaction product: carbon dioxide. No trace of carbon monoxide production was found. Rates at steady state remained constant and were independent of the mass of carbon present in the bed through 33 per cent carbon consumption.

Carbon dioxide was used as a diluent, in place of helium, in one experiment. The purpose was to check for the

CHAPTER VI

ANALYSIS OF DATA

Rates of reaction presented in Appendix I, measured at temperatures of 400° , 450° and 500° C., have been plotted as a function of effluent oxygen pressure in Figure 8. Rates measured at each temperature level are contained within the three outlined areas. The lower line of each area represents oxidation rates under relatively "dry" reactive conditions. Likewise, the upper line represents oxidation rates at considerably higher water vapor contents. These lines represent related, rather than constant, water contents and should be so construed. An attempt to compensate for the effect of differing degrees of water content on the rate will be described later.

The purpose in presenting the data as in Figure 8 is to show the conventional interpretation techniques for rate data obtained in the oxidation of carbon. A horizontal line of zero slope would, in this case, represent an apparent or pseudo-zero order reaction with respect to oxygen. A slope of unity would indicate a first order reaction in oxygen. Intermediate slopes would give fractional orders with respect to

SYMBOL	WATER VAPOR PRESSURE mm Hg
A	0.00032
B	0.05
C	17.2
D	14.8

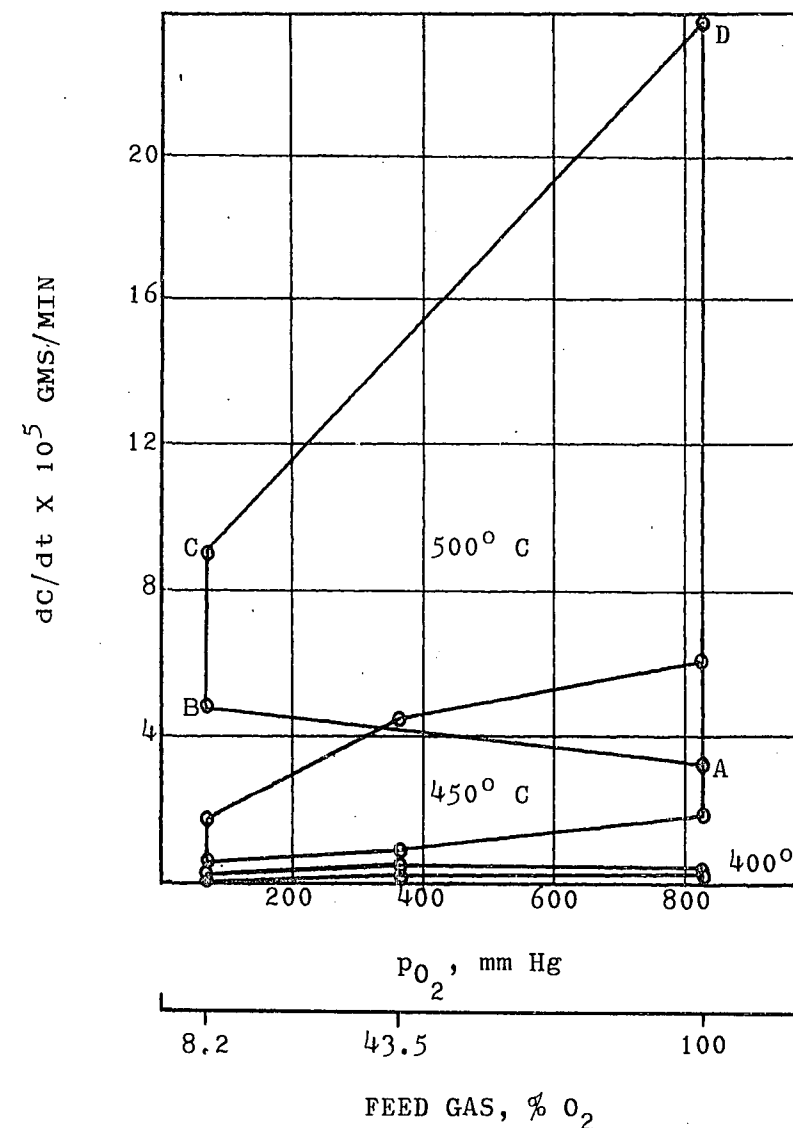


FIGURE 8. RATES OF REACTION VS OXYGEN CONTENT SHOWING EFFECTS OF VARIATION IN WATER CONTENT

oxygen pressure. One of the disadvantages in utilizing this technique of analyzing rate data is that all parameters influencing the rate are accredited to oxygen. Accordingly, the concept of an "apparent order with respect to oxygen" should be emphasized.

Inspection of Figure 8 shows that, within the temperature range of 400° to 500° C.:

1. At the lower temperature, the rate of carbon oxidation is essentially independent of oxygen pressure for both relatively "dry" and "wet" reactive conditions.

2. With relatively low water vapor contents, the rate of carbon oxidation is essentially independent of oxygen pressure over the entire temperature range of 400° to 500° C. However, the influence of minor changes in water pressure under these conditions becomes more pronounced at the higher temperature. The magnitude of this effect is illustrated by the negative slope of the lower 500° C. region. Here the rate using an 8.2% oxygen feed containing water at 0.05 mm Hg pressure was found to be almost three times that for a pure oxygen feed of 0.00032 mm Hg of water pressure. If this variation in water content were not considered, one would have to conclude an apparent negative order on oxygen pressure.

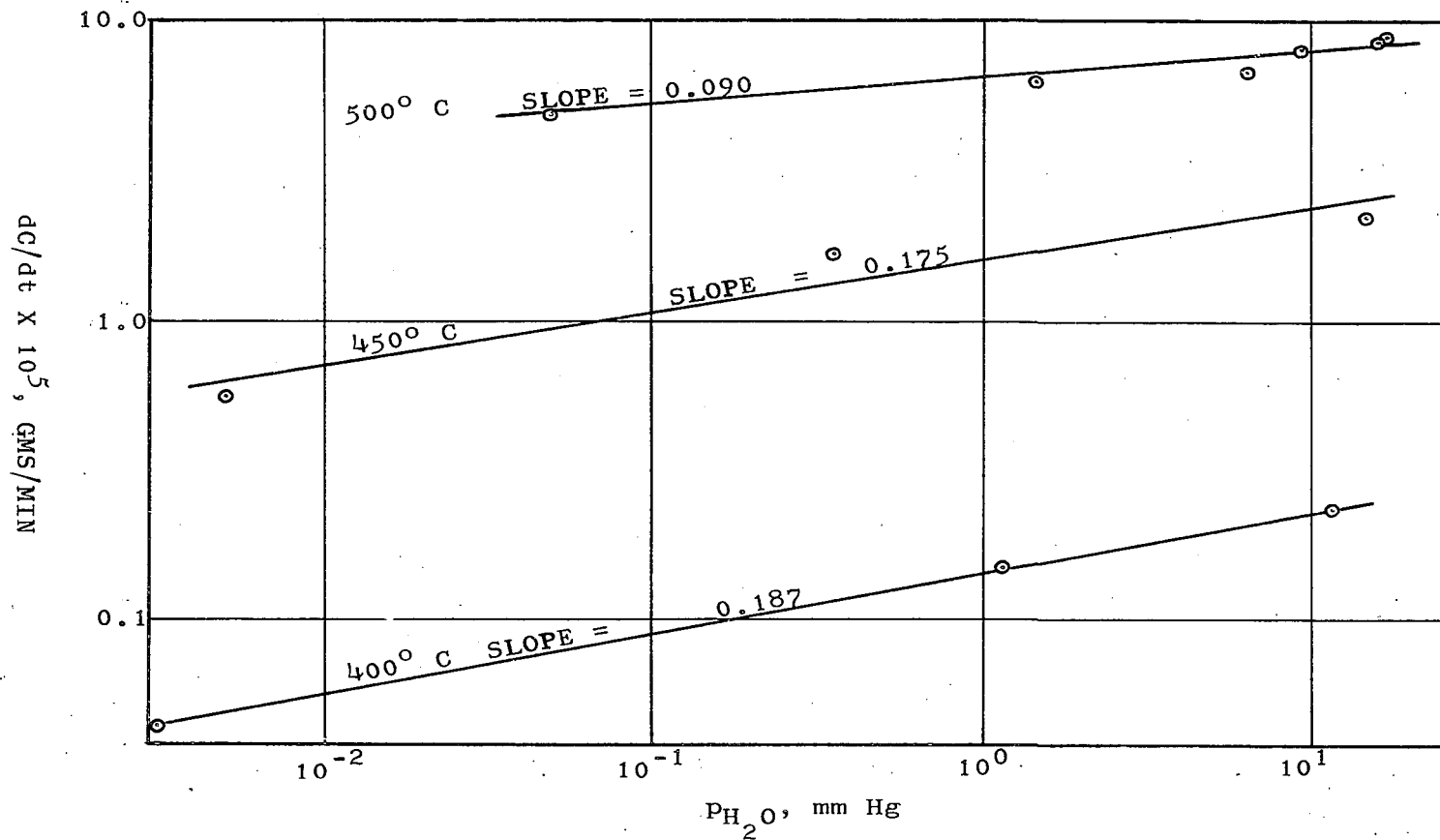
3. At the higher temperature (and at relatively high water vapor contents), the influence of water vapor is sufficient to give rates of carbon oxidation which are

nearly first order with respect to oxygen pressure.

4. That water pressure is indeed a parameter in the oxygen-carbon reaction may be seen from the magnitude of rate changes at the 500° C. temperature level. Rate variations of 200% were caused by a 350-fold change in water pressure with the 8.2% oxygen feed, as represented by the left side of the 500° C. area. On the right hand side of the same area, corresponding to a pure oxygen feed, a 50,000-fold change in water pressure resulted in an increase in rate of 700%.

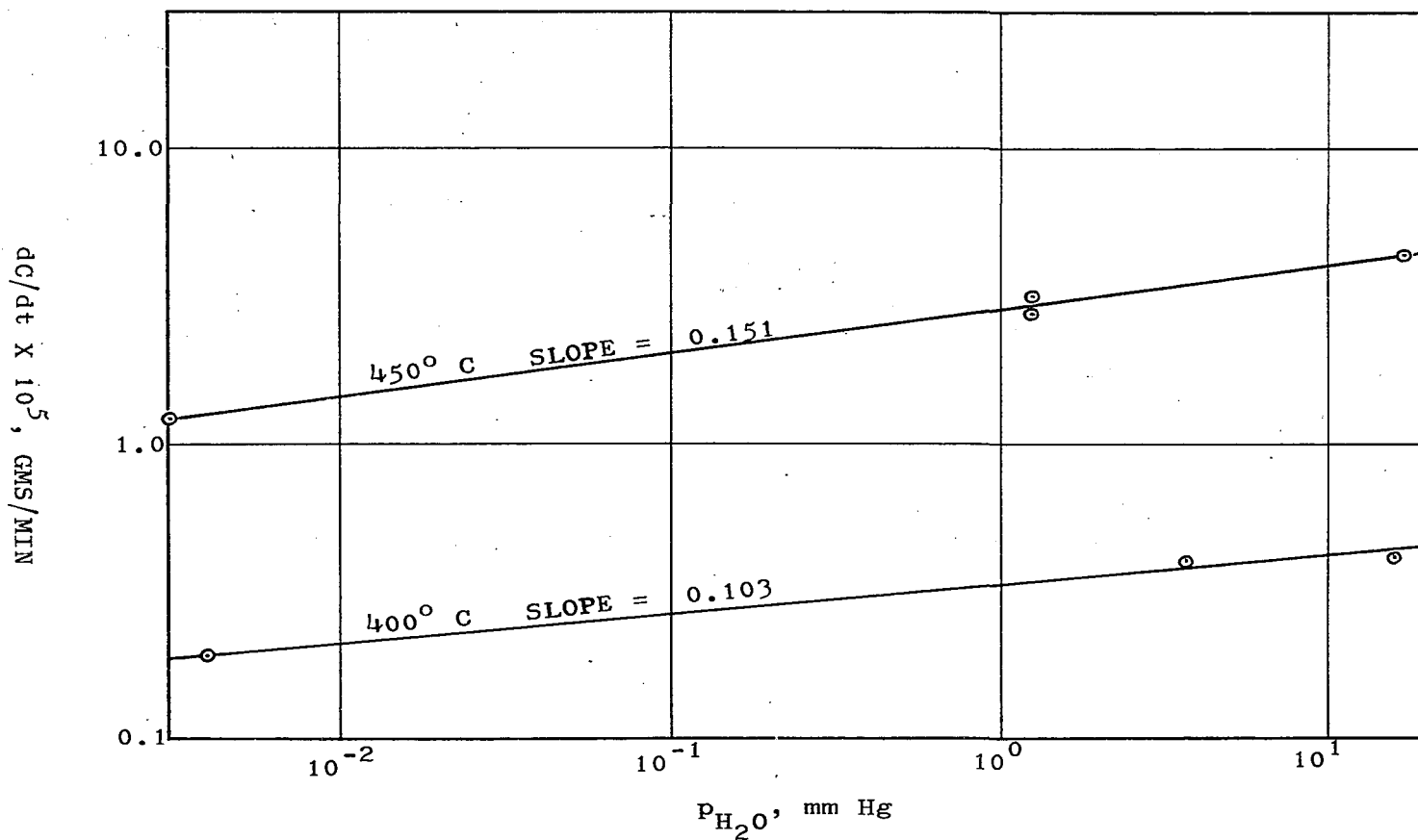
Changes in order suggested above are frequently interpreted as due to changes in the basic mechanism controlling the reaction. Such a hypothesis is advanced herein. Variations in the magnitude of rates for two reactions competing for oxygen, one of which is dependent on water vapor content is the basis for the postulate.

A more quantitative representation of water vapor on the rate of the oxygen-carbon reaction is shown by the logarithmic plots of Figures 9, 10 and 11. Although there is some scatter in the data, each plot shows a fairly consistent catalytic effect by water (as proposed in the discussion) for any one temperature level. Experimental oxygen pressures were constant to about $\pm 6\%$ in each run. Variations in the concentration of this component were caused by different degrees of oxygen conversion, water pressure, barometric changes, and minor fluctuations in flow rate. The slope of the $\ln(\text{Rate})$ vs P_{H_2O} plots of Figures 9, 10 and 11 represents the apparent



66

FIGURE 9. PLOT TO DETERMINE APPARENT ORDER ON WATER PRESSURE, 8.2% O₂ FEED



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FIGURE 10. PLOT TO DETERMINE APPARENT ORDER ON WATER PRESSURE, 43.5% O₂ FEED

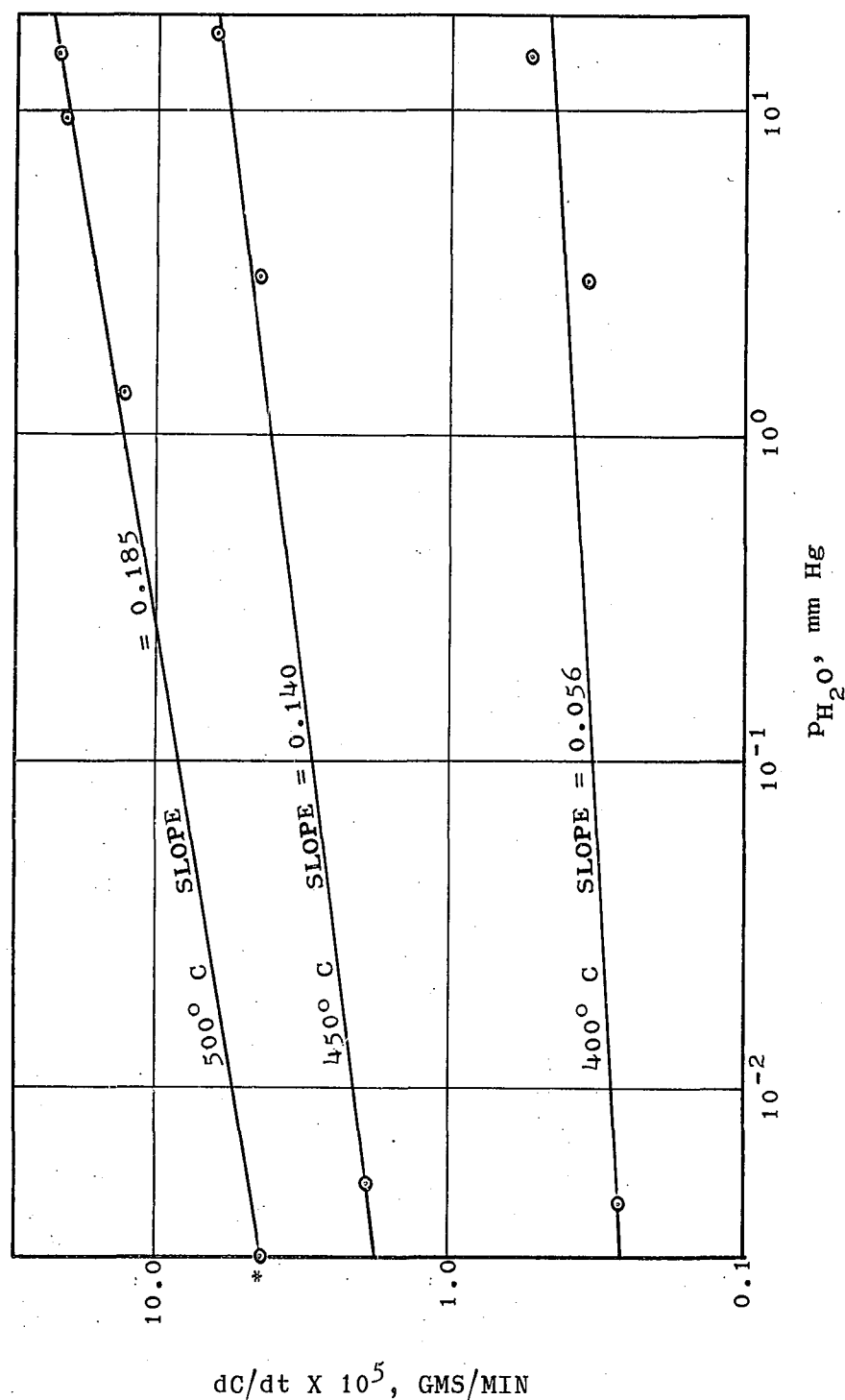


FIGURE 11. PLOT TO DETERMINE APPARENT ORDER ON WATER PRESSURE, 100% O₂ FEED

order of the reaction with respect to water pressure for each oxygen pressure and temperature studied. In comparison with Figure 8, in addition to excluding temperature variations, these plots have excluded the effect of oxygen pressure on the apparent order of the reaction with respect to water pressure. The slope of each curve is seen to decrease from 0.187 to 0.090 as the temperature is increased from 400° to 500° C. for the 8.2% oxygen feed data. The opposite effect is noted for the 43.5 per cent and 100 per cent oxygen feed data of Figures 10 and 11. An explanation for this phenomenon based on relative adsorption rates, is presented in the discussion. Neglecting these variations, an average slope of 0.138 (\pm about 43%), corresponding to about 1/7th fractional order on water, is found for the 100° C. temperature range and oxygen pressures studied in this investigation.

It has been shown by Figure 8 that, at 500° C., apparent orders on oxygen may vary between zero and unity depending on the relative amount of water vapor. Figures 9, 10 and 11 have shown a rate dependence with water pressure which is constant for any specific oxygen pressure and reaction temperature. These apparent orders on water may now be used to separate out the reaction dependence of water from that of oxygen. Accordingly, in Figure 12 is plotted measured rates of reaction corrected for the effect of water pressure versus oxygen pressure. The observed exponent on water pressure for the specific reactive conditions has been used in calculating

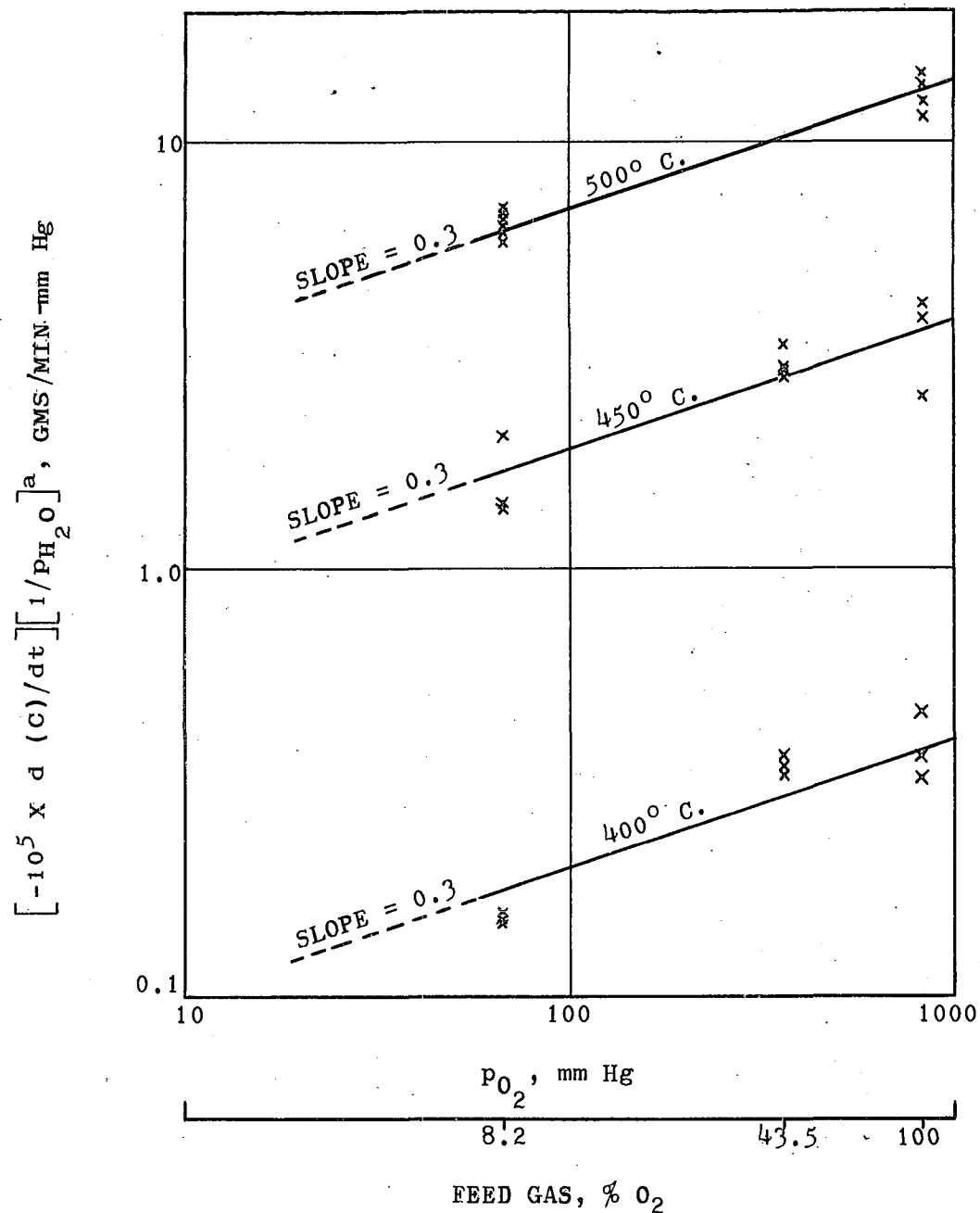


FIGURE 12. COMPENSATED RATES VS OXYGEN CONCENTRATION

ordinate values. This variable exponent was obtained from the slopes of the curves represented in Figures 9, 10 and 11. Experimental errors and perhaps minor influences on the rate by unidentified contaminants in the gaseous and solid phases are believed to account for the spread in data at each temperature level.

The most important conclusion to be drawn from Figure 12 is that the "water compensated" rate dependence on oxygen pressure is neither zero nor first order, shown as bounds in Figure 8, but a constant 0.3 order for all the experimental data involved at the three temperature levels. The resulting kinetic equation takes the form

$$-d(C)/dt = k \cdot P_{O_2}^{0.3} P_{H_2O}^a$$

Arrhenius type plots were made from rate data obtained from the smoothed curves of Figures 9-11 at water partial pressures of 0.005, 0.2, 1.0 and 10.0 mm Hg. An activation energy of 39.9 kcal/mole was calculated from the slope of the curves which was in fair agreement among all four water pressures. A plot of the 1.0 mm Hg water pressure situation is shown by Figure 13 for the three oxygen concentrations studied. An exponent of 0.30 on oxygen at this water content would account for the shifts in the curve with increasing oxygen concentration. The rate constant (k) in the preceding equation may be evaluated from Figure 13 and the exponential rate expression $k = A \exp(-E/RT)$ to give the final empirical

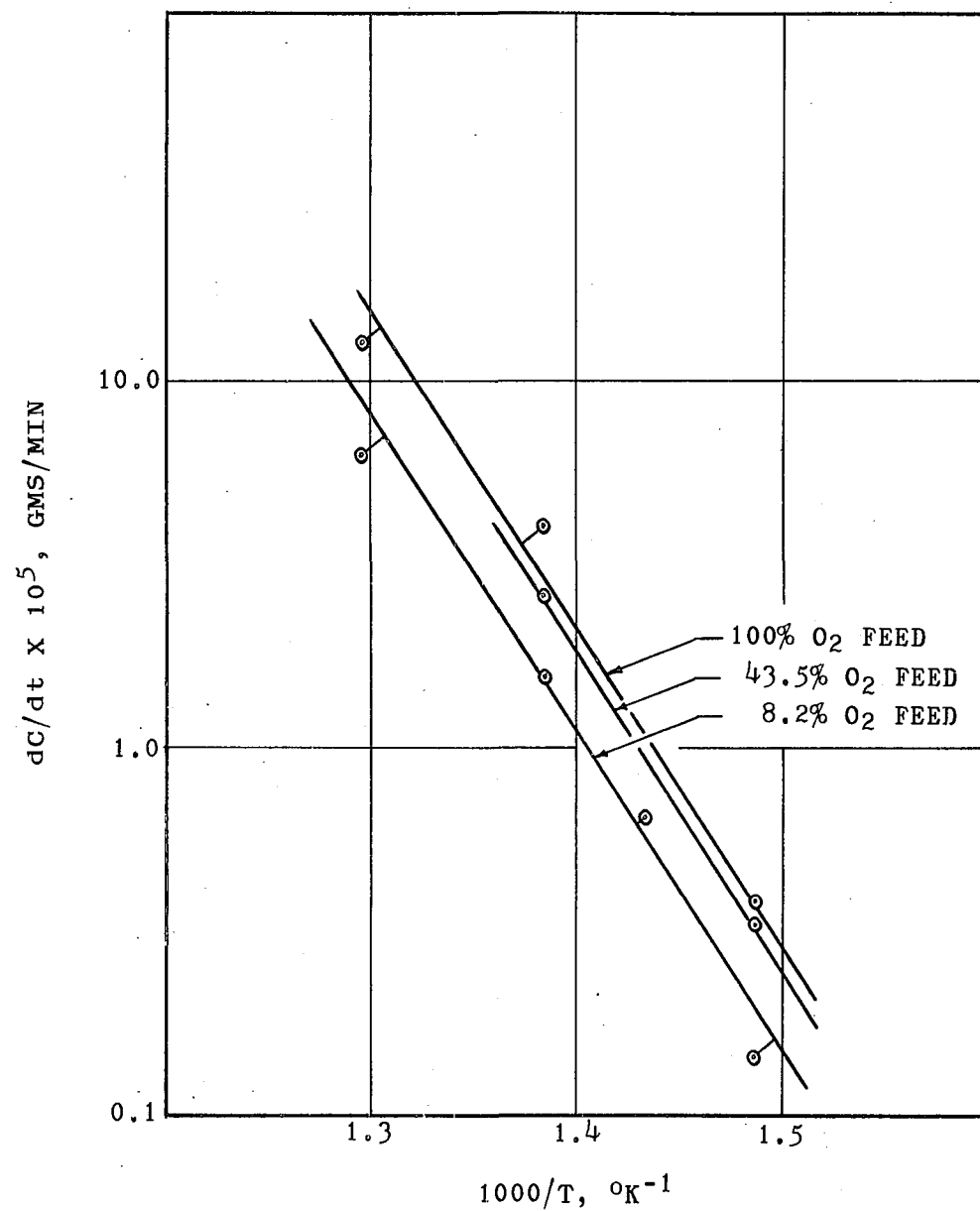


FIGURE 13. ARRHENIUS TYPE PLOT OF LOG RATE VS 1/T

equation:

$$-d(C)/dt = 3.46 \times 10^6 \exp(-39,900/RT) p_{O_2}^{0.3} p_{H_2O}^a$$

In this expression, $-d(C)/dt$ is evaluated in grams of carbon consumed per minute, T in $^{\circ}K.$, and p_{O_2} and p_{H_2O} in mm Hg of oxygen and water pressure, respectively. An alternate form for the rate constant will be presented in the discussion of results.

Assessment of Errors

Rates of reaction were obtained directly from weight measurements as heretofore described. Simple conversions were then made to put the data in a more presentable form. An example calculation has been presented in Appendix II. The maximum error in the measured rate data is estimated to be $\pm 6\%$ as analyzed in Appendix III.

apparent order on oxygen has twice been reported in the literature. However, no previous quantitative connection between either the order on oxygen or the oxidation rate with water pressure has been mentioned.

The rate dependence of the oxygen-carbon reaction on water pressure alone, at a constant oxygen pressure, was found to be

$$\left[-d(C)/dt \right]_{T, p_{O_2}} \propto p_{H_2O}^a$$

where (a), the apparent order on water pressure, varied between 0.056 and 0.187 for the range in experimental variables investigated. The numerical value of this exponent was found to be relatively constant over a 50,000-fold change in water pressure. It varied slightly with both reaction temperature and oxygen pressure.

It is possible to separate out this influence of water on the reaction by utilizing a "water compensated apparent order of reaction with respect to oxygen" concept. This concept is demonstrated by the mass law result

$$\left[-d(C)/dt \right] (1/p_{H_2O})^a \propto p_{O_2}^{0.3}$$

where the numerical value of the water compensated exponent on oxygen has been found in these experiments, to a close approximation, to be independent of both temperature and water pressure. Upon evaluating the proportionality, the final

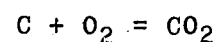
CHAPTER VII

DISCUSSION OF RESULTS

Review of Findings

Results obtained in this investigation are unique in that an experimental system was applied which gave unusually high precision for kinetic data. These results were further improved through strict control of the purity of the materials used. Experimentally measured rates of carbon oxidation were low thus precluding localized overheating by mass transfer restraints.

The observed chemical reaction was



with no carbon monoxide being found. The kinetic data at 500° C. showed a mass law proportionality to oxygen pressure of

$$\left[-d(C)/dt \right]_T \propto p_{O_2}^{0 \text{ to } 1}$$

where the coefficient on oxygen was found to vary with water vapor partial pressure. The relationship was such that carbon oxidation rates were proportional to oxygen pressure at relatively high water vapor pressures and independent of this variable under relatively dry reactive conditions. Zero

empirical equation is found for representing the experimental data obtained in this study:

$$-d(C)/dt = 10^{-5} \exp\left[\frac{E(1/T^* - 1/T)}{R}\right] p_{O_2}^{0.3} p_{H_2O}^a$$

Rates are expressed in grams of carbon consumed per minute. Experimental variables were T , p_{O_2} and p_{H_2O} expressed as $^{\circ}K.$, and mm Hg pressure respectively. An activation energy, E , of 39,900 calories/mole was calculated from an Arrhenius plot. The term T^* , which may be of fundamental significance in characterizing a carbon's residual reactivity, was evaluated to be $749^{\circ} K.$ or $476^{\circ} C.$ Substitution of these constants resulted in the more generally used form

$$-d(C)/dt = k p_{O_2}^{0.3} p_{H_2O}^a$$

where

$$k = 3.46 \times 10^6 \exp(-39,900/RT).$$

Comparison of experimentally measured rates with those predicted by the preceding equation is as presented in Appendix V and graphically by Figure 14. The average error between calculated and measured rates, which represents the average agreement of the correlation with the experimental data, is 3.2%. The absolute error, which indicates the maximum scatter of the experimental data with respect to the correlation, is 19.8%. If the first 26 of the 29 data points of Appendix V are considered, the average error is reduced to 0.3% and the absolute error is 18.8%.

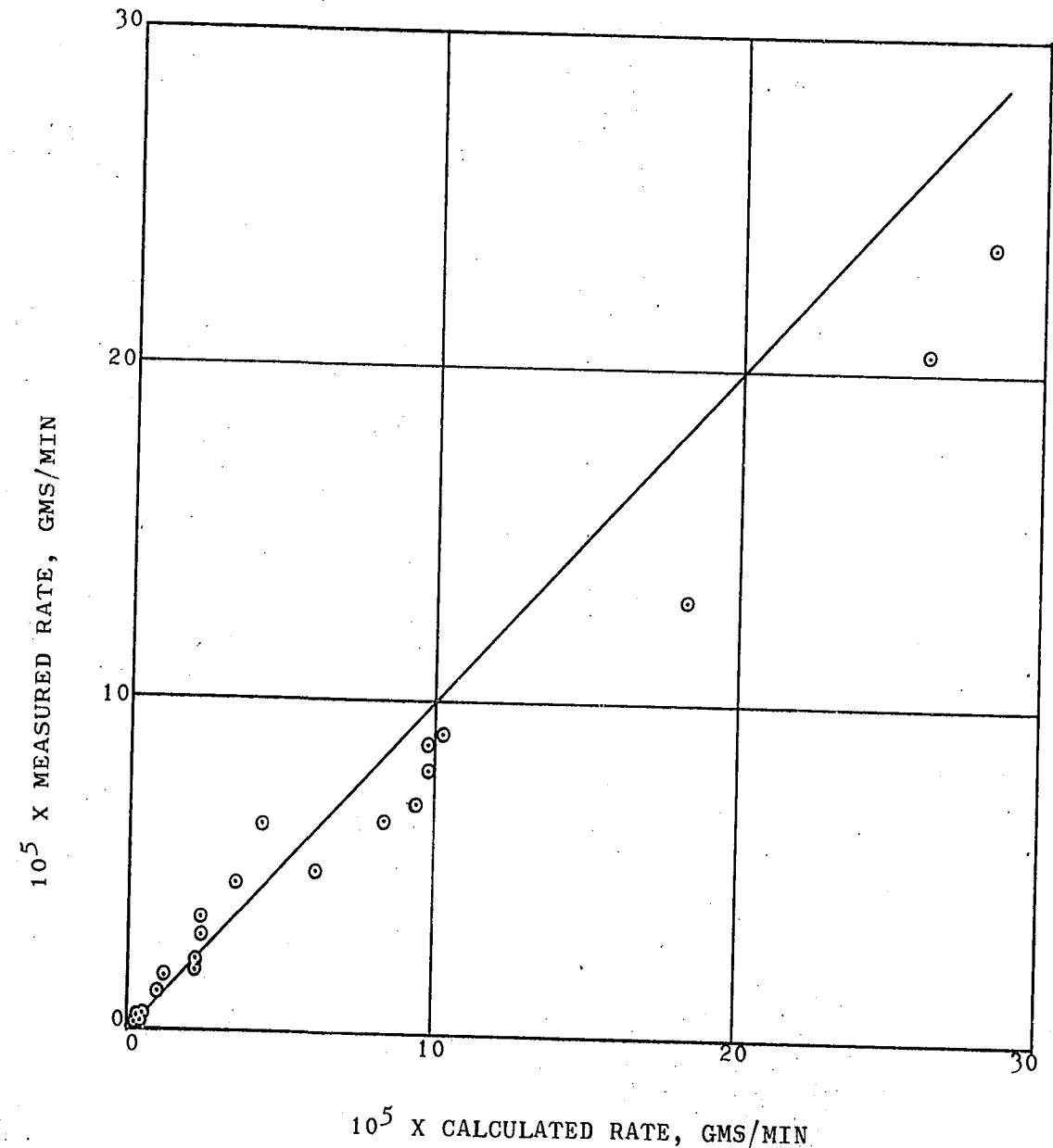


FIGURE 14. MEASURED VS CALCULATED RATES

Interpretation of Results

It is fairly obvious from the preceding that water vapor is capable of enhancing the oxygen-carbon reaction rate. An explanation for this phenomenon, which is also in agreement with existing knowledge and concepts about the oxygen-carbon reaction, is not available in the literature. In an attempt to clarify this role of water in the mechanism of the oxygen-carbon reaction, the following hypotheses and deductions are made. A more detailed proposal is presented in Appendix IV.

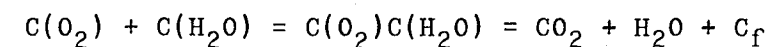
1. Competitive reactions for oxygen occur between
a) bound hydrogen, carbon and oxygen and b) water vapor, carbon and oxygen. Only the latter type reaction is of significance in the case of a relatively pure carbon undergoing oxidation at low to moderate reaction temperatures where mass and heat transfer effects are of no consequence in the reaction mechanism.

2. Active carbon sites of pure carbons compete for the adsorption of gaseous oxygen and water. Conversely stated, oxygen and water (as well as diluents) compete for adsorption on carbon. The degree to which either is adsorbed depends upon the nature of the carbon surface, the respective partial pressures of the species involved and the temperature.

3. Simultaneous and neighboring adsorption of oxygen and water, or simultaneous adsorption with rearrangement,

is a necessary step in the overall sequence of the reaction of oxygen with pure carbon.

A mechanism which is consistent with the above, and developed in more detail in Appendix IV, is



where C_f represents a carbon free site capable of adsorption and $C(O_2)C(H_2O)$ represents an intermediate oxygen-carbon-water complex. Catalysis by water is supported by this mechanism. The mechanistic sequence involved in formation and decomposition of the intermediate three-species complex is not clear. The existence of such a peroxidic complex, however, has previously been proposed.⁴¹

The following theoretical rate expression, which is compatible with the above and the hypotheses and criteria for selection of a mechanism as listed in Appendix IV, has been derived therein. Depending on the values of the adsorption coefficient and partial pressure of each species, the derived expression

$$\text{Rate} = \frac{k K K' p_{O_2} p_{H_2O}}{(1 + K p_{O_2} + K' p_{H_2O})^2}$$

may be seen to be proportional to $p_{O_2} p_{H_2O}$ under certain

conditions, or to be proportional to $p_{\text{H}_2\text{O}}$ and independent of p_{O_2} , or to p_{O_2} and independent of $p_{\text{H}_2\text{O}}$ under other conditions. The first two situations have been demonstrated in this investigation. The reverse situation, that of an apparent catalysis of the steam-carbon reaction by oxygen, is in agreement with the third condition and has been observed by Sihvonen⁴⁸ and Binford and Eyring.⁴⁹ The form of the above expression is identical to the Langmuir-Hinshelwood type mechanism involving interaction between two adsorbed species. However, one major distinction in the mechanism represented may be noted. In the Langmuir-Hinshelwood mechanism, reaction is considered to be between adsorbed species with the solid adsorbent acting as a catalyst. In the present hypothesis, one of the adsorbed species is considered to be the catalyst.

Unfortunately it is not quantitatively possible, on the basis of present experimental evidence, to evaluate K and K' in the preceding relation. This is because adsorption data, which involve reactant gases at temperatures where reaction rates are appreciable, are not available. In interpreting adsorption data, it must be recognized that gases which are non-reactive to carbon become less strongly adsorbed with increasing temperatures whereas the reverse is the case for gaseous reactants of carbon. Thus, the degree to which different gases are attracted to carbon is a variable. For example, below a certain temperature, which could also vary with diluent and the type and degree of carbon impurity,

oxygen is physically sorbed by carbon. The phenomenon is characterized by an apparent reversibility and a low heat of adsorption. With higher temperatures, the desorption process takes place more slowly reflecting the higher heats in chemisorption. Although the literature is not in complete agreement on this point, in general, oxygen adsorption appears to be reversible below about 0°C . and water adsorption is reversible through considerably higher temperatures. It is also noted that the more strongly a reactant gas is adsorbed by carbon at lower temperatures, the greater is its reactivity at higher temperatures. This is true at least for oxygen and water. A comparison of their rates of reaction at 800°C . and 0.1 atmospheres pressure has shown oxygen to be capable of reacting about 10^5 times faster than the corresponding steam-carbon reaction.³

In further support of the mechanism proposed are preferential adsorption studies of gases exposed to clean carbon surfaces. Ethylene, for example, has been found to be more strongly adsorbed on an active carbon than carbon dioxide. The presence of a high carbon dioxide concentration lowered its adsorption only slightly. However, small amounts of ethylene considerably lowered the adsorption of the less adsorbable carbon dioxide gas.⁹⁰ Many such examples of preferential adsorption are contained in the literature on gas chromatography.

Changes in the magnitude of the order dependence on

water with temperature, as noted in Figures 9, 10 and 11, also are suggestive of a dual adsorption type mechanism. This is shown more clearly in Figure 15. As previously mentioned, these data show opposing trends for the 8.2 per cent oxygen feed as compared with the 43.5 per cent and pure oxygen feeds although the changes are consecutive. The exponent on water at 500° C. is seen to increase with increasing oxygen pressure indicating an increased dependence on the concentration of this species. Opposite effects may be noted for the values at 400° C. This reversal of data for the specific carbon used is explainable in terms of competing adsorption reactions by oxygen and water as proposed.

Selective adsorption and the form of the theoretical rate equation proposed may also explain the experimental data of Gulbransen and Andrew¹ in which an increase in order in oxygen with an increase in oxygen pressure was observed. Although the water vapor content was not measured in their work, one might assume a relatively consistent experimental procedure was used so that water pressure varied in direct proportionality with oxygen pressure. At the 1.5 mm Hg oxygen pressure and assumed proportionately low water vapor partial pressures, a relatively lower adsorptive capacity, coupled with a varying coefficient on water vapor partial pressure, could understandably produce the observed results.

The zero order experimental conclusions of Blyholder and Eyring² could be explained by similar considerations.

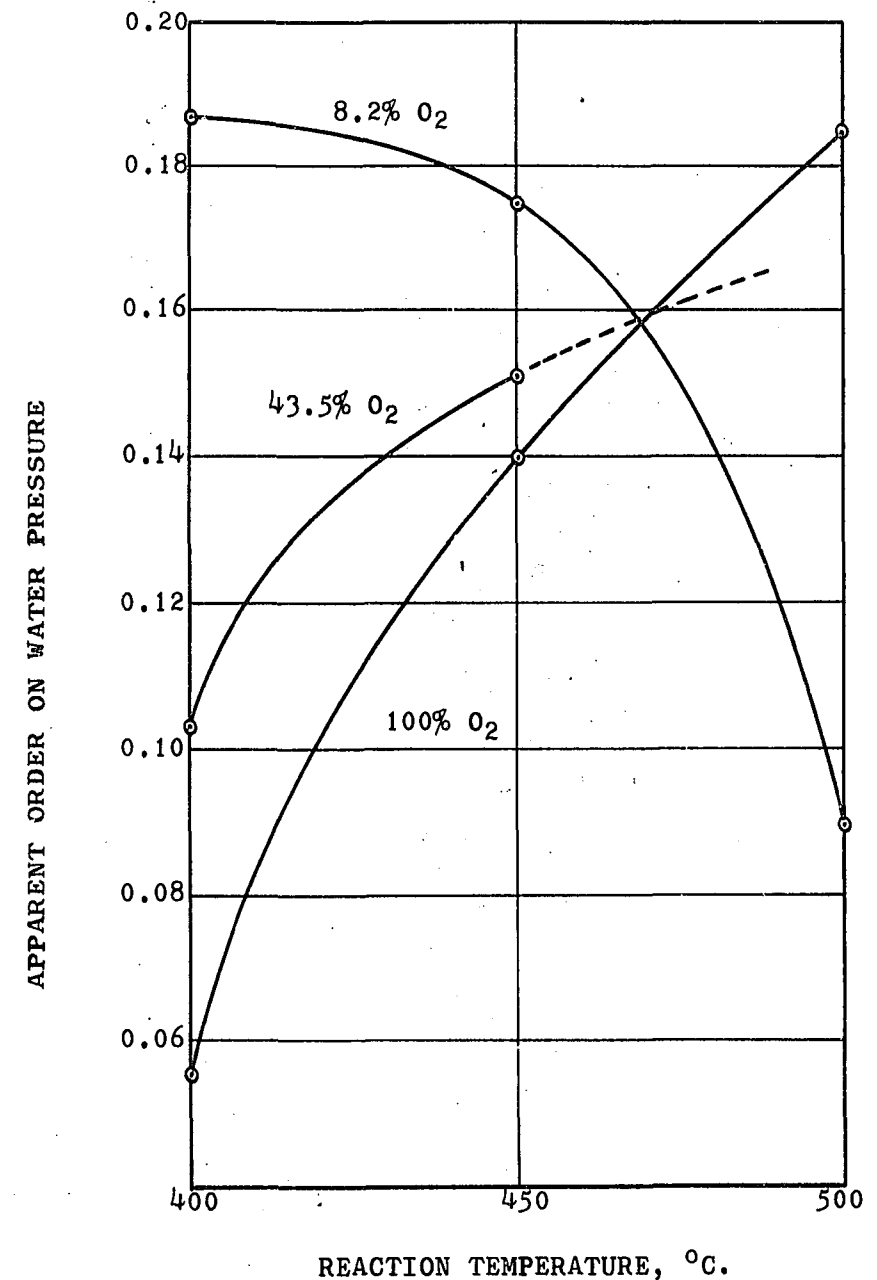


FIGURE 15. TRANSITION IN APPARENT ORDER ON WATER PRESSURE WITH TEMPERATURE AND FEED COMPOSITION

Their observation of rapid poisoning when water vapor was passed over the carbon is also in agreement with the concept of relative adsorption of water and oxygen in influencing the rate of carbon oxidation. At high water vapor pressures, the degree of adsorption of this component should be correspondingly high thereby reducing the number of unoccupied active carbon sites available for subsequent oxygen adsorption and reaction. According to this explanation and for a constant oxygen pressure, one would predict an optimum water vapor pressure from which either an increase or decrease in the amount of this component present would reduce the rate of reaction. A similar variation for the optimum oxygen pressure, at a constant water pressure, would also be expected. Such conclusions are in agreement with the theoretical rate expression proposed in Appendix IV.

The 500° C. temperature data of Gulbransen and Andrew¹ may be re-examined as has been done by Blyholder and Eyring² for their 450° C. experiments. These latter authors conclude that the 450° C. data could be better expressed as a half-order reaction over the entire pressure range. Indeed, with exception of one of the ten data points reported which may not have been experimentally reproducible, the same conclusion may be drawn for the 500° C. temperature data. That is, for both temperature levels,

$$\left[-d(C)/dt \right]_T \propto p_{O_2}^{0.5}$$

where any influence due to variations in water pressure would be incorporated within the proportionality relating the rate with oxygen pressure.

Another significant finding of Gulbransen and Andrew¹ is the anomaly that their 500° C. data, as represented by the equation

$$-d(C)/dt = 1.35 \times 10^{-9} + 0.505 \times 10^{-9} p_{O_2},$$

did not break away to a zero rate as pressure diminished. No attempt was made to explain the phenomenon nor to further investigate the situation. Such an observation does, however, lend support to the breakdown of the reaction sequence as proposed in Appendix IV. Therein is made the postulate of a carbon's "residual reactivity" which is primarily a function of the amount of bound hydrogen native to the sample. According to this hypothesis, all impure forms of carbon could be expected to possess a basic or residual reactivity which is characterized by the reaction temperature and oxygen partial pressure as this latter variable approached zero pressure.

Experimental results presented herein are individually in agreement with those of numerous other investigators in the field of carbon oxidation. Observations in this work which are also in direct support of those previously reported are as follows:

1. An apparent catalysis by water vapor.
2. Nearly zero, fractional, and first order dependence

of the rate on oxygen pressure depending on the amount of water vapor present.

3. Reaction rates which were independent of the amount of carbon present through 30% carbon burnoff.

4. Rapid attainment of steady state oxidation rates in which the rate of oxidation remained constant. (In this work, the attainment of a steady state oxidation rate was coincident with the attainment of a steady state water vapor partial pressure.)

5. Carbon dioxide as the sole product in the oxidation of a pure carbon.

6. Simultaneous adsorption effects in the oxidation of carbon.

7. An activation energy in close agreement with that generally recognized for this reaction.

8. Coherence with some sort of dual mechanistic sequence involving Type I (bound hydrogen dependent) and Type II (proposed as water vapor dependent in this work) sites.

9. The influence of varying stream velocities on the effluent oxygen and product concentrations.

10. A negligible steam-carbon reaction at 500° C.

11. A small to negligible influence of the carbon dioxide product on the rate of carbon oxidation.

12. The experimental data can be correlated by the Arrhenius type equation.

Significance of Investigation

An attempt has been made to present a critical review of basic concepts and apparently significant parameters in the oxygen-carbon reaction. To this has been added the findings of the present investigation. The next logical step appears to be an evaluation of the overall field of carbon oxidation in terms of conclusions suggested by this study.

One major problem, that of quantitatively assessing previous literature on the subject, appears insurmountable. Part of the problem stems from the variety of experimental techniques and reactant materials used in studying the reaction. Another facet of the problem stems from the fact that many investigators do not describe their experiment in quantitative enough terms. It appears that part of the confusion about the nature of the reaction could be resolved by more carefully weighing those data in which neither the water vapor content in the reactant stream nor the influence of non-carbonaceous but adsorbent surfaces in the reaction system can be established. Another apparently significant variable which should be defined for any quantitative comparison of carbon reactivity is a carbon's basic hydrogen content.

Comparison of reaction rates of carbons oxidized in the same or different systems has yielded results of little theoretical significance. In an attempt to clarify the problem, Walker et al,³ have recommended that rates for comparative purposes should be taken only after steady state rates of

reaction have been attained. A further effect that must be recognized in any such comparison is the frequently reported independence of the rate on the mass of carbon present through a considerable degree of carbon burnoff. If this effect is observed then, during the period of constant rate of reaction, the reaction must be limited by something other than the number of carbon sites available. Accordingly, comparative rates of reaction expressed on a per gram of carbon basis are meaningless during this interim and the rate must be made specific to some other limiting criterion. On the other hand, specific reaction rates could be of more comparative significance if the measurement were made at the critical carbon mass concentration immediately subsequent to the period of constant rate of carbon consumption.

Caution should be exercised in assuming the results of this investigation can be applied indiscriminately to the whole field of carbon oxidation. In this regard it is probably wise to point out that, even though a 50,000-fold change in water vapor pressure has been studied, the lower and upper limits of water vapor content correspond to dew points of -112° F. and $+75^{\circ}$ F., respectively. Also the carbon oxidized was amorphous in form with a purity closely akin to that of diamond. Furthermore, the helium diluent could account materially for influences not observable with nitrogen dilution and vice versa.

Be this as it may, the work presented herein clarifies the role of one significant parameter which makes it inherently

easier to use existing data in a more realistic manner. The very fact that carbon occurs in many forms and structures each of which have some effect, makes it unrealistic to expect that the development of an overall, all encompassing, theory is feasible. Rather, practical understanding will have to evolve from quantitative studies of individual parameters as reported herein.

CHAPTER VIII

CONCLUSIONS

Oxidation of a relatively pure amorphous form of pyrolytic carbon is shown to undergo an apparent catalysis by water vapor over the 400° to 500° C. temperature interval. This finding, of water vapor partial pressure as heretofore a recognized but uninvestigated parameter in the oxygen-carbon reaction, offers at least a partial explanation for the numerous varying and diverse experimental conclusions so readily apparent in the literature. The variable has been demonstrated to be of sufficient importance to govern a pure carbon's reactivity and the apparent order with respect to oxygen pressure. Water vapor partial pressures up to 100% saturation at room temperature were studied.

Experimental conclusions of nearly zero, fractional and first order dependence of the rate on oxygen pressure were possible when the influence of varying water pressure was neglected. However, by adjusting the measured rates for the influence of water vapor, a "water compensated order on oxygen pressure" was obtained which remained constant over all experimental conditions. The mass law kinetic relationship

$$-d(C)/dt = k p_{O_2}^{0.3} p_{H_2O}^a$$

where (a) is an experimentally measured value and the rate constant is determined from

$$k = 3.64 \times 10^6 \exp(-39,900/RT)$$

was found to represent the experimental data with an average error of 3.2%. An activation energy of 39,900 calories per mole was calculated.

A mechanism is proposed to account for the influence of water vapor which postulates the existence of two competitive reactions for oxygen which are controlled respectively by the amounts of hydrogen originally bound to the carbon and that introduced as extraneous water. For a relatively pure carbon exposed to oxygen at moderate reaction temperatures, the latter is posed as overshadowing the former to a degree such that the measured rate of reaction is proportional to the number of simultaneously occupied neighboring sites.

The overall mechanism proposed represents an extension over those previously reported by 1) including the water vapor partial pressure variable, 2) accounting for variations in carbon reactivity due to varying degrees of hydrogen impurity, 3) pointing out the influence of trace hydrogen impurities on the reaction mechanism when the rate of reaction is low, 4) offering a detailed mechanism for one type of active site participation, 5) supporting an adsorption/desorption mechanism similar in form to that generally recognized for the

steam-carbon and carbon dioxide-carbon reactions, 6) considering a gaseous species to act as a catalyst when in an adsorbed state and 7) accounting for the qualitative observations of pseudo-zero, fractional and first order dependence of the rate on oxygen pressure. Although it has not been possible to quantitatively test the mechanism proposed, it qualitatively supports the findings of this investigation in addition to being consistent with a number of other observations reported in the literature.

The differential reactor system with recirculation has been shown to be an applicable experimental technique for studying the oxygen-carbon reaction. A type of carbon-coated packed bed, which had not been previously reported on in the literature on carbon oxidation, was utilized.

CHAPTER IX

RECOMMENDATIONS

The true chemical mechanism and kinetics governing the sequence of events in carbon oxidation have eluded scientific interpretation since the reaction first became intensively studied after the turn of the century. Present precepts about the problem generally involve an undetermined variable within the solid phase. The present work has alternately shown water vapor to play a dominant role in the reaction of a pure carbon for which proper compensation in the mechanism must be made. One such attempt has been made herein in which broad but justifiable generalizations were necessary in order to approach the problem from a fundamental point of view. Much work remains to be done to further qualify the chemical mechanism and kinetics involved. In this regard, the following problems appear to be particularly worth while investigating.

1. Clarification of the phenomenon associated with water vapor catalysis in the oxidation of carbons of varying hydrogen content.
2. A clearer definition of the residual reactivity

concept and its fundamental significance.

3. The roles of selective and relative adsorption of oxygen, water and common diluents on active carbon sites and means for identifying and measuring same.
4. Characterization of the dual carbon site theory.
5. Experimental proof of the existence of a stable surface oxide complex of carbon.
6. The roles of oxygen and water contamination in the carbon dioxide-carbon reaction and of oxygen contamination in the steam-carbon reaction.

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APPENDICES

APPENDIX I--EXPERIMENTAL RESULTS

Feed % O ₂	Reactor Temperature		Efflux SCC/min	P _{H₂O} mm Hg	P _{O₂} mm Hg	P _{CO₂} mm Hg	Rate of Reaction, gms C consumed/min x 10 ⁵	
	Approx. °C	Actual °F						
8.2 (in He)	400	753.5	45.7	.0032	67.9	.019	.0545	
		749.8	43.1	1.14	67.4	.054	.154	
		750.4	50.4	11.7	65.8	.074	.239	
	425	797.3	47.1	1.16	67.2	.220	.672	
		450	842.0	47.9	.0051	68.8	.089	.563
			839.9	48.1	.363	69.4	.551	1.71
	475	842.2	44.2	14.7	65.2	.768	2.21	
		500	884.5	45.3	1.14	66.1	1.90	5.56
			933.0	49.0	.05	58.0	1.36	4.87
		930.4	48.7	1.44	65.5	2.05	6.38	
		930.1	30.2	6.24	64.0	3.53	6.86	
		931.7	49.3	9.34	64.9	2.49	7.95	
	934.0	37.2	16.1	61.8	3.61	8.69		
		932.7	53.6	17.2	62.1	2.60	9.03	
		43.5 (in He)	400	749.3	37.7	.0038	364.5	.081
749.7	44.9			3.68	356.5	.143	.421	
747.7	50.1			16.0	362.4	.135	.435	
450	838.3		41.1	.0030	362.8	.319	1.203	
	842.9		48.7	1.22	364.7	.923	2.87	
	844.0		42.7	1.22	362.1	1.26	3.46	
843.7	49.3	17.2	365.4	1.43	4.48			

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(continued)

APPENDIX I--EXPERIMENTAL RESULTS
(continued)

Feed % O ₂	Reactor Temperature		Efflux SCC/min	P _{H₂O} mm Hg	P _{O₂} mm Hg	P _{CO₂} mm Hg	Rate of Reaction, gms C consumed/min x 10 ⁵
	Approx. °C	Actual °F					
100 (in He)	400	750.8	42.1	.0044	839.9	.101	.272
		748.2	23.8	2.98	826.3	.224	.345
		747.6	39.6	14.7	820.1	.213	.541
	450	841.4	47.1	.0051	823.9	.614	1.88
		843.3	41.5	3.07	836.2	1.70	4.49
		842.4	44.3	17.5	821.8	2.21	6.24
	500	931.7	47.8	.00032	828.9	1.08	3.32
		931.7	44.8	1.35	826.0	4.55	13.11
		931.0	57.9	9.48	815.0	5.50	20.54
		932.1	53.5	14.8	808.3	6.90	23.81
9.2 (in CO ₂)	500	932.0	58.4	1.57	74.4	759.0	9.70

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APPENDIX II

EXAMPLE CALCULATIONS

Run #33 Room Temperature, 77° F.
 Feed, 8.20% O₂ (in Helium) Reactor Pressure, 830 mm Hg
 Reactor Temperature, 933° F. Barometric Pressure, 732 mm Hg
 Effluent Flow Rate, 49 SCCM Recycle Flow Rate, 240 SCCM
 Weight of Ascarite Column at Start of Test, 129.8306 ± .0001 gms
 Weight of Ascarite Column at End of Test, 129.8406 ± .0001 gms
 Length of Test, 56 min.
 Weight of Carbon Dioxide Produced during Test, 0.0100 gms
 Weight of Carbon Consumed in Test, $0.0100 \times 12/44 = 273 \times 10^{-5}$ gms
 Rate of Carbon Utilization = $\frac{273 \times 10^{-5}}{56} = 4.87 \times 10^{-5}$ gms/min
 Probable Analytical Error in Rate Measurement = $\pm \frac{.0002 \times 100}{0.01} = 2\%$
 Effluent Dew Point Temperature, -58° F.
 Water Vapor Pressure of Effluent, 0.05 mm Hg
 Oxygen Analyzer Measurement of Effluent, 7.92% O₂
 Effluent Analysis:

$$p_{\text{H}_2\text{O}} = 0.05 \text{ mm Hg}$$

$$p_{\text{O}_2} = 0.079 \times 732 = 58 \text{ mm Hg}$$

$$p_{\text{CO}_2} = \frac{0.0100 \times 22,400 \times 732}{56 \times 44 \times 49} = 1.36 \text{ mm Hg}$$

$$p_{\text{H}_e} \text{ (by difference)} = 672.59 \text{ mm Hg}$$

APPENDIX III

ASSESSMENT OF ERRORS

Experimental rates of reaction were accurately determined in this investigation through selection of a differential reacting system and precise analytical methods. Analytical accuracy was further improved by recirculating the major portion of the reactor exhaust. Experimental reaction rates may be determined directly from weight measurements with such a reactor system. Since rates were measured under steady state conditions and the oxygen was premixed with the diluent, errors in the measurement are influenced only by the uncertainty in the controlling variables of flow rate and temperature. The latter is the more significant because of the exponential dependence of reaction rate on temperature. The influence of variations in this parameter may be seen by the following considerations.

If the rate constant is only dependent on temperature, then the exponential form of the Arrhenius relation

$$k = A \exp(-E/RT)$$

may be expressed as:

$$dk = (AE/RT) \left[\exp(-E/RT) \right] dT/T.$$

By taking their ratio, a final relative form

$$dk/k = (E/RT) dT/T$$

is obtained from which an estimate of temperature errors in rate data may be obtained. Upon using the 39.9 kcal/mole activation energy found in this study and a $500^\circ \pm 1^\circ$ C.

temperature control of the reactor, the uncertainty in rate data due to temperature errors is seen to be

$$\begin{aligned} dk/k &= \left[39,900 / (1.99 \times 773^2) \right] dT \\ &= 0.034 dT. \end{aligned}$$

Since rates are proportional to rate constants, an error of uncertainty of less than four per cent is calculated for the one degree variation in temperature. Adding this to the two per cent error in rate due to analytical measurements as per Appendix II gives an average error of about six per cent in the measured rates at 500° C.

APPENDIX IV

PROPOSED MECHANISM

Criteria for the selection of a mechanism were as follows:

1. Oxidation rates of carbons containing an appreciable amount of bound hydrogen are a strong function of the quantity of this element present.
2. Oxidation rates for carbons of low hydrogen content are strongly influenced by the concentration of vapor phase water present.
3. Oxidation rates of low hydrogen carbons at moderate reaction temperature are independent of oxygen concentration under relatively dry reactive conditions and proportional to the concentration of this component at higher water vapor contents.
4. The primary reaction product of the pure carbon-oxygen reaction is carbon dioxide.
5. The activation energy for the reaction is large and positive.
6. The mechanism selected must be consistent with other known facts about the chemistry of the reaction.

It has been fairly well established that, excluding the influence of oxygen and temperature, oxidation rates of carbons containing varying amounts of bound hydrogen are a

function of the quantity of this element present. On the other hand, oxidation rates of carbons of low hydrogen content have been shown to be strongly influenced by the concentration of vapor phase water. Any postulated mechanism must support the two situations since both appear to be well founded.

Proposal I--Competitive Reactions

If rates of hydrogen-laden carbon are a function of oxygen pressure, and rates of pure carbons are more dependent on water pressure at lower water concentrations, then the possibility is suggested of competitive reactions for oxygen. For a constant level in oxygen pressure, the rate may then be expressed as

$$\text{Rate} = f(\underline{H}, p_{\text{H}_2\text{O}}) \quad (1)$$

where \underline{H} and $p_{\text{H}_2\text{O}}$ represent the concentration of bound hydrogen in the carbon and the water vapor partial pressure, respectively. If, in any one sample, the amount of bound hydrogen remains in constant proportion to the amount of carbon present, then the rate may be given by

$$\text{Rate} = \text{constant} + f'(p_{\text{H}_2\text{O}}) \quad (2)$$

or

$$\text{Rate} = \text{Rate 1} + \text{Rate 2} \quad (3)$$

where the two processes are assumed to be independent of each other. If an appreciable amount of hydrogen is present in

the carbon, and Rate 1 \gg Rate 2, then

$$\text{Rate} \approx \text{Rate 1.} \quad (4)$$

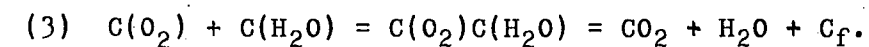
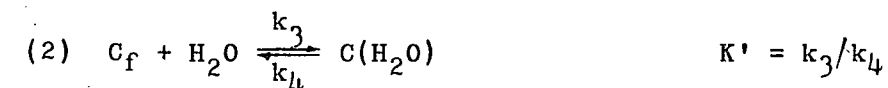
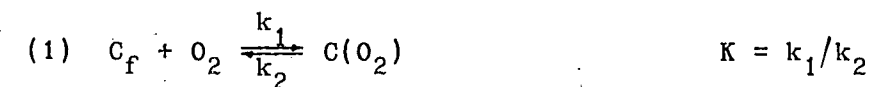
On the other hand, if the carbon is relatively pure, the reaction temperature is moderate, and water vapor is in abundance, then Rate 1 \ll Rate 2, and

$$\text{Rate} \approx \text{Rate 2.} \quad (5)$$

This latter situation is suggested as an explanation of data for the case at low temperatures where reaction rates are moderate. According to this proposal, it is obvious that the importance of trace amounts of hydrogen in a relatively pure carbon becomes pronounced as the reaction rate diminishes at lower water vapor partial pressures.

Proposal II--Water Catalysis

There are several hypothetical mechanisms which give the required form of rate equation (5). As one possibility, the following steps are postulated:



The term C_f represents a carbon free site capable of adsorption and $\text{C}(\text{O}_2)$ and $\text{C}(\text{H}_2\text{O})$ represent carbon-oxygen and carbon-water complexes. These basic steps may be alternately

detailed. However, the general scheme presented is one of catalysis by water, involving simultaneous adsorption of oxygen and water. A subsequent interaction of adsorbed complexes is a necessary step in the reaction mechanism.

Proposal III--Simultaneous and Neighboring Adsorption

There is general agreement that experimental evidence on the carbon dioxide-carbon reaction fits an equation of the form³

$$\text{Rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (6)$$

where p_{CO} and p_{CO_2} are the partial pressures of carbon monoxide and carbon dioxide and the constants k_1 , k_2 and k_3 are functions of one or more rate constants. Experimental data on the steam-carbon reaction likewise generally fit an equation of the form³

$$\text{Rate} = \frac{k_1 p_{\text{H}_2\text{O}}}{1 + k_2 p_{\text{H}_2} + k_3 p_{\text{H}_2\text{O}}} \quad (7)$$

where terms are similarly defined. Both expressions are based on simultaneous adsorption mechanisms.

A similar relationship may be derived for the oxygen-carbon reaction considering only the relative adsorption of both oxygen and water. Assume first a steady state exists in the rates of formation and decomposition of surface

complexes as in the proposed mechanistic reactions (1) and (2). If θ_1 and θ_2 are the fractions of active carbon sites occupied by oxygen and water, respectively, then the fraction of free sites unoccupied at any time is $(1-\theta_1-\theta_2)$. Therefore

$$k_1 p_{\text{O}_2} (1 - \theta_1 - \theta_2) = k_2 \theta_1 \quad (8)$$

$$k_3 p_{\text{H}_2\text{O}} (1 - \theta_1 - \theta_2) = k_4 \theta_2 \quad (9)$$

The fraction of surface covered by oxygen and water is, from equations (8) and (9),

$$\theta_1 = \frac{K p_{\text{O}_2}}{1 + K' p_{\text{H}_2\text{O}} + K p_{\text{O}_2}} \quad (10)$$

and

$$\theta_2 = \frac{K' p_{\text{H}_2\text{O}}}{1 + K' p_{\text{H}_2\text{O}} + K p_{\text{O}_2}} \quad (11)$$

Since the rate of reaction is equal to the rate of decomposition of the adsorbed carbon-oxygen complex, which in turn is proportional to the fraction of the surface covered by oxygen, then

$$\text{Rate} = k_2 \theta_1 \quad (12)$$

Substituting for θ_1 from equation (10) gives the final expression for the case of simultaneous adsorption of oxygen and water in which there is no chemical interaction with the adsorbed water:

$$\text{Rate} = \frac{k_1 p_{O_2}}{1 + K' p_{H_2O} + K p_{O_2}} \quad (13)$$

where $K = k_1/k_2$, $K' = k_3/k_4$, and the rate constants are as shown with reactions (1) and (2). Such an expression is consistent with reaction (1) and (2) and may conceivably resolve to either first or zero order dependence on oxygen depending on the magnitude of the adsorption coefficient and pressure of each species. The equation does not, however, predict an increase in rate with increasing water pressure as has been experimentally observed in the present investigation.

A more acceptable rate expression may be obtained if, in addition to simultaneous adsorption of oxygen and water, is made the further stipulation of neighboring occupancy with chemical interaction.⁸⁹ In agreement with reaction (3) of the mechanism, the kinetics may be deduced as follows: If the rate is proportional to the concentration of simultaneously occupied neighboring sites, then

$$\text{Rate} = k \theta_1 \theta_2 \quad (14)$$

Substitution for θ_1 and θ_2 from equations (10) and (11) yields the final rate expression proposed:

$$\text{Rate} = \frac{k K K' p_{O_2} p_{H_2O}}{(1 + K' p_{H_2O} + K p_{O_2})^2} \quad (15)$$

APPENDIX V

COMPARISON OF EXPERIMENTAL AND CALCULATED RATES*

Rate of Reaction x 10 ⁵ , gms/min		
Measured	Calculated	% Error**
.0545	.0610	+11.9
.153	.182	+18.9
.239	.280	+17.2
.563	.554	- 1.6
1.71	1.17	-31.6
2.21	2.19	- 0.1
4.87	6.10	+25.3
6.38	8.36	+31.0
6.86	9.48	+38.2
7.95	9.88	+24.3
8.69	9.88	+13.7
9.03	10.30	+14.1
.194	.166	-14.4
.421	.336	-20.2
.435	.393	- 9.7
1.203	.956	-20.5
2.87	2.37	-17.4
3.46	2.36	-31.8
4.48	3.54	-21.0
.272	.280	+ 2.9
.345	.401	+16.2
.541	.438	-19.0
1.88	2.19	+16.5
4.49	3.46	-22.9
6.24	4.38	-29.8
3.32	3.92	+18.1
13.11	18.31	+39.7
20.54	26.15	+27.3
23.81	28.32	+18.9

* Sequence of measured rates identical to that of Appendix II for 400°, 450° and 500° C. data.

** Ave. error = $\Sigma \text{Error} / 29 = 3.2\%$

Abs. error = $\Sigma |\text{Error}| / 29 = 19.8\%$

APPENDIX VI

INTERPRETATION OF RECIRCULATING DIFFERENTIAL REACTOR DATA

Use of a differential reactor flow system with recirculation of a portion of the exhaust flow has been shown to be most successful with moderately complex reactions which lend themselves to sensitive analytical determination. Recirculation of as large a volume as is experimentally feasible, while simultaneously maintaining minimum desired temperature and pressure gradients, results in an optimum designed system. A corresponding prerequisite is a degree of reactant conversion which is sufficiently large to overshadow analytical accuracy. Recirculation is particularly advantageous in studying the chemical mechanism of the carbon oxidation reaction because the high heat release, coupled with poor heat transfer characteristics, frequently causes localized overheating in near differential reactors.

Analysis of reaction kinetics for a differential reactor with recirculation may be simplified by restricting kinetic considerations to the inlet and exhaust sections in which no recirculation occurs. This case is analogous to the kinetics of a straight differential reactor. However, emphasis is placed on the effect of products on the reaction by the recirculation technique, a point too frequently neglected in differential reactor studies where only the first element of the reactor bed is exposed to a product-free flow stream. Letting X_i represent the inlet oxygen concentration and F_i

the total inlet flow in moles/sec, then the moles of oxygen per second entering the reactor and recirculating system is $X_i F_i$. Similarly, if X_o and F_o represent the respective exhaust oxygen concentration and flow, then the moles of oxygen leaving the system in unit time will be $X_o F_o$. By material balance, the rate of oxygen utilization within the reacting system is then

$$\text{Rate of oxygen utilization} = -d(O_2)/dt = X_i F_i - X_o F_o$$

where only flow rates and oxygen concentrations are necessary to determine the rate of oxygen disappearance. This may or may not be equal to the rate of carbon oxidation which depends on the products formed. If CO is the only product (theoretical case), then there will be a volume increase during reaction equal to twice the volume of oxygen utilized. In such a case, the following holds true:

$$F_o - F_i = 2(X_i F_i - X_o F_o)$$

$$\text{Rate of carbon oxidation} = -d(C)/dt = -2d(O_2)/dt$$

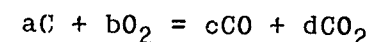
$$-d(C)/dt = 2F_o \left[(X_i + 2X_i X_o) / (1 + 2X_i) - X_o \right].$$

If the oxygen utilized is equally shared by both CO and CO₂, resulting in CO/CO₂ = 2, then a volume increase equal to half the volume of oxygen utilized will be realized giving

$$F_o - F_i = X_i F_i - X_o F_o$$

$$-d(C)/dt = -1.5d(O_2)/dt = 1.5F_o \left[(X_i + X_i X_o) / (1 + X_i) - X_o \right].$$

In general, for the chemical reaction



where

$$-d(C)/dt = -(a/b) d(O_2)/dt = (a/c) d(CO)/dt = (a/d) d(CO_2)/dt,$$

the volume increase upon reaction and kinetics are given by

$$F_o - F_i = r(X_i F_i - X_o F_o)$$

where

$$r = c/b = Z_o/(X_i - X_o)$$

Z_o = exhaust CO concentration

and the general rate expression is

$$-d(C)/dt = F_o \left[(Y_o + 0.5Z_o)/(X_i - X_o) \right] \left[(X_i + rX_iX_o)/(1+rX_i) - X_o \right]$$

where

Y_o = exhaust CO_2 concentration.

The simplest case is the reaction in which only CO_2 is formed as in the case of pure carbon oxidation at low temperatures. Since there is no volume change upon reaction,

$F_i = F_o$ and the rate of carbon oxidation is identical to both the rate of oxygen utilization and the rate of carbon dioxide production. Thus

$$\begin{aligned} -d(C)/dt &= -d(O_2)/dt = d(CO_2)/dt \\ &= F_o(X_i - X_o) \\ &= F_oY_o \end{aligned}$$

and the instantaneous rate may be measured directly. If steady state conditions have been reached and analytical accuracy restricts the lower limit for which differential conversions are accurate by the instantaneous analysis, then an average differential rate may be obtained by measuring,

for example, the cumulative carbon dioxide produced over a finite time interval. The only limit in time by this latter technique is a continuation of the steady state.