PROBLEMS IN PULVERIZED COAL AND CHAR COMBUSTION

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Abstract

Interest in char combustion derives from the need to utilize the char produced during some gasification processes. Successful use of char in combustion may depend on use with supplementary fuel. The critical factor determining this appears to be the char "reactivity" which may be variations in intrinsic reactivity depending on differences in thermal history, or it may be dependent on differences in internal surface. In preparation for an experimental program to determine the relative significance of these alternatives (or others), what are considered relevant contributions is the existing experimental literature have been re-evaluated. Although overall surface reaction rates have been evaluated for many coal chars there appears to have been a fundamental omission in the kinetic analysis, and an attempt to remedy this has been made. The picture now developed is that of char particles that may burn either in Zone I or Zone II depending on the particle permeability. Zone III combustion is not encountered with particles below about 100 microns. In Zone I and II combustion, however, the intrinsic reaction is evidently a zero order, high activation energy process (E about 45 kcal) at temperatures in the region of 1000°K, changing to a first order, low activation energy process (E about 7 kcal) at temperatures approaching 2000°K, with both processes significant in the transition range between the two limits. This new evaluation modifies the conventional views of reaction order and activation energies.

Introduction

The dwindling supplies of natural gas and the predicted shortage of oil have initiated considerable research concerned with the conversion of coal to easily utilizable synthetic gas and oil. These conversion processes inevitably yield a high proportion of relatively unreactive char as a by-product. In order to render the overall process economically viable, the char must be recoverable as an energy source. This necessity to return to coal has reopened the whole field of study on

p.f. combustion to reanalysis in order to gain deeper understanding of several phases of the general process still not totally understood.

This paper will provide a critical evaluation of the state of the knowledge on the subject of p.f. combustion, reviewing all the possible mechanistic processes involved and distinguishing between those that are generally accepted by the majority of workers in the field and those that are still questionable, either because of inadequate experimental evidence or because of arguable theoretical interpretation.

A theory cannot be acceptable until it is formulated in such a manner that certain definitive experiments are able to substantiate it or disprove it. Mere data gathering is not sufficient; the data must be used to the fullest extent to positively identify the proposed mechanisms. Can certain elusive questions concerning the mechanisms of p.f. combustion be answered by reanalysis of existing data? An attempt to answer this has been made by a reanalysis of rate data for the combustion of a size graded char (1). Nevertheless, the total process is still not fully comprehended. Differences in opinion on many of the issues involved are converging to agreement, but outstanding questions still need answers backed up with the necessary experimental data and theory. Even with the much less complicated reaction of the purest carbon with oxygen, which has been investigated for many years, there are still many unknowns. The coal system is much more complex, involving in many cases simultaneous mechanisms and great advances in comprehending the process have already been made. Hopefully, by isolating the unknown from the known, and by carefully designing experiments to test disputable points, an even finer comprehension of the processes involved in the combustion of p.f. will be obtained.

From a macroscopic viewpoint, the combustion of p.f. particles can be broken down into two main processes: (i) pyrolysis of volatiles and their subsequent combustion, and (ii) heterogeneous combustion of the solid residue. These two processes will be dealt with separately in spite of the frequent overlap of the volatile and heterogeneous regimes.

The following topics and the degree to which they are currently understood will be discussed:

(1) Effect of temperature, time history, rate of heating and environment on the evolution of volatile matter.

(2) The temporal sequence of devolatilization and heterogeneous combustion.

(3) Reaction order in oxidant and activation energies in heterogeneous combustion.

(4) The relative importance of chemisorption and desorption control.

(5) Particle size dependence of combustion characteristics.

(6) Change in total available surface area during combustion: pore size distribution and modification.

(7) Relative importance of mass transfer and chemical control.

(8) Discrepancies between the interpretation of available kinetic data on the combustion of char particles.

(9) Effect of internal diffusion through the porous structure of particles.

(10) Real and apparent orders and activation energies in the combustion process.

Pyrolysis

Introduction

When coal is pyrolyzed the central mechanism can only be the detachment or chemical formation of components of a volatile nature that are then able to escape from the solid involatile matrix under varying circumstances. It should theoretically be possible to isolate four regimes for pyrolysis of coal particles. If the volatile components are able to escape from the matrix as rapidly as they are formed, the overall rate of the pyrolysis will be controlled by the chemical reaction for the volatile formation. When diffusional escape of volatiles takes a finite time which is long compared with the reaction time, the diffusion process will determine the pyrolysis rate. For larger particle sizes or higher heating rates, so that a temperature gradient is generated within the particle, the condition for a pyrolysis wave can be obtained. Here pyrolysis will occur in a zone with unreacted material on the one side and devolatilized char on the other. The pyrolysis rate is then determined by the rate of heat input into the interior of the particle and not by the reaction rate or the diffusional escape. At even higher heating rates, heat reaches the pyrolysis sites faster than it can be utilized and the temperature rises rapidly and the pyrolysis becomes reactivity controlled once more. In the limit the particle could theoretically reach such a temperature that particle burn out could be complete before any significant pyrolysis had time to occur. Such a situation is believed to occur in the explosion flame system.

In the past it has been generally assumed that in pulverized coal flames particle pyrolysis proceeds heterogeneous carbon burn out and that ignition occurs in the volatiles, however there is some evidence (2) to modify this simple concept and their conclusion is that there is parallel pyrolysis and heterogeneous combustion in the flame and that the ignition itself was heterogeneous in origin.

It has been customary to classify coal by means of the proximate analysis test wherein the coal is devolatilized in a crucible under specified conditions of sample size, temperature, and duration of decomposition. Coal has long been considered to be made up of fixed amounts of volatile matter and involatile "fixed carbon" (3), (4), and the proximate test categorizes the coals in terms of percentages of fixed carbon, volatile matter and ash on a dry basis. This test procedure is an example of a medium rate of carbonization. In the pulverized coal flame heating rates may be as high as 10^4 or 10^5 °C/sec., so information obtained about pyrolysis from the proximate analysis test may or may not be relevant to the situation in the p.c. flame. Attempts to approach these high heating rates in the study of pyrolysis and hence more nearly to approximate the conditions in the p.c. flame have been made by several workers.

Loison and Chauvin (5) devolatilized 50-80 micron coal particles on a wire gauze electrically heated to 1000°C (heating rate ≈ 1500 °C/sec.) and found that the yeild of volatiles produced was often greater than the yield of volatiles obtained by the proximate test. They also noted changes in the composition of the volatile products, obtaining a higher ratio of tars to gas at the higher heating rates.

Badzioch and Hawksley (6) designed an apparatus not only to approximate the heating rates in a p.c. system but also to approximate the environment of pyrolysis in those systems. They used an essentially isothermal flow reactor and devolatilized the coal particles (size graded) in nitrogen which acted as dilluent and inert atmosphere. They thereby eliminated the complications of combustion of volatiles and heterogeneous reaction and concentrated only on the pyrolysis process itself. Their results will be discussed in more detail later but the essential results were in agreement with Loison and Chauvin, that the weight loss produced was in all cases greater than the difference in the proximate volatile yield of parent coal and partially pyrolized char.

Kimber and Gray (7) using essentially the same apparatus as Badzioch and Hawksley also found the weight losses during pyrolysis to be considerably greater than the proximate analysis results. They pyrolized to much higher temperatures (≈1900 °C) and were able to obtain their weight losses by direct measurement, whereas Badzioch and Hawksley used ash as a tracer.

Howard and Essenhigh (2), using a plane flame furnace have studied the devolatilization process in conjunction with the heterogeneous combustion of carbon and the combustion of the volatiles. On the basis of their results, they have formulated an overall picture of the combined process and its temporal sequence, this will be discussed later.

It is thus apparent that the amount of volatiles produced from a coal is not a constant quantity but depends to a greater or lesser extent on the following factors:

1) rate of heating
2) final decomposition temperature obtained
3) duration of the decomposition at that temperature
4) the environment under which the coal is devolatilized

Points of General Agreement

It is now generally agreed that pyrolysis is an activated process and the amount of volatiles produced and their composition will depend on the conditions. Different results are expected between the relatively slow decomposition of particles in a closely packed

bed and rapid decomposition of particles in a dilute suspension, like a dust cloud. In the first case pyrolysis products have time to interact with each other and with other partially pyrolyzed coal particles in their passage through the bed, while in the second case the volatiles are rapidly diluted in a gaseous environment which effectively prevents mutual and particle interactions.

Badzioch and Hawksley (6), postulate that the yield of volatiles depends upon the rate of heating, the final temperature and the duration of heating at that temperature, and on the dilution effect. They devolatilized the coal at short heating times at essentially isothermal conditions so they could not therefore substantiate the first of their postulates. However, they found that the weight loss between the original coal and the char produced was always greater than the change in the proximate volatile matter of coal and char. This change in volatile matter ΔV was measured as a percentage of the original dry ash free coal.

$$\Delta V = VM_o - R$$

where VM_o was the proximate volatile matter of original dry ash free coal and R was the proximate volatile matter of the char produced expressed as a percentage of the weight of the original dry ash free coal.

The weight loss was ΔW where

$$\Delta W = 100 - Y$$

and Y was the yield of char expressed as a percentage of original dry ash free coal. The experimental conditions did not allow them to directly weigh the char produced so they assumed that no ash would be lost during the decomposition process and thus could be used as a tracer. They showed the correlation between ΔW and ΔV to be linear but the regression line did not pass through the origin. This apparent anomaly is discussed later. The constant of proportionality was termed Q so that

$$\Delta W = Q \, \Delta V$$

Kimber and Gray (7), also found Q factors for the coals studied to be greater than one. They found that the devolatilization at higher heating rates appeared to be a two stage process; that the amount of weight loss increases with increasing heating rate although they admitted that at short heating times the effects of rate of heating and final temperature could not be isolated; that the amount of weight loss increased with increased temperature. The important conclusion of Q factors being greater than one is that during pyrolysis either some of the so called fixed carbon is lost as volatile matter and thus the quantity of fixed carbon

determined by proximate analysis decreases, or that the proximate test fails to show all of the possible volatile matter and that some portion of it is somehow captured or otherwise altered by the coal during the carbonization.

Points of Disagreement

Although it is accepted that ΔW is not equal to ΔV, the reasons for this inequality are not fully agreed upon.

The phenomena can be caused by one or a combination of the following:

1) rate of attainment of final pyrolysis temperature
2) value of final temperature and duration of the process
3) devolatilization environment

Badzioch and Hawksley (6), claim that the mechanism and the amount of decomposition depends on the rate of heating. However, in the analysis of their data they subtract out the correction for the heating stage of the particles arguing that since the rate of decomposition is sensitive to temperature the amount of decomposition that occurs during the heating stage is negligible, so actually they observe weight losses for isothermal conditions. Howard and Essenhigh (2), claim that the amount of volatiles produced depends on the final temperature, the duration of the process and the particle size, i.e., when a particle is large enough to sustain a temperature gradient within it. They do not specify the possible effects of the environment of pyrolysis, yet they do warn that considerable discretion must accompany the use of experimental results obtained under conditions differing markedly from those of the application. Preliminary results obtained in this laboratory on the effects of markedly different rates of heating on the amount of volatile matter produced are discussed later.

Badzioch and Hawksley (6), infer from their experimental data that the variation of volatile matter with time for isothermal conditions may be exponential and they expressed the fractional volatile change in the form:

$$\Delta V/VM_o = (1 - C)[1 - \exp(-k\tau)]$$

For decomposition temperature >900°C the proximate volatile matter of the char had almost reached a constant value in the 100 millisecond pyrolysis time considered (8). Kimber and Gray found that for decomposition temperatures above 1000°C the weight loss was even higher and at 1900°C the residual proximate volatile matter in the char approached zero.

The environment of pyrolysis effect has been discussed earlier and it is agreed that the physical conditions under which the decomposition occurs does indeed affect the volatile yield. However, the relative importance of this effect over and above the other factors has never been satisfactorily demonstrated. Recent results obtained in this laboratory shed more light on the quantitative significance of the effect and are discussed below.

Attempted Clarification of Disputed Issues

Badzioch and Hawksley (6), found that the regression line on their plot of ΔW against ΔV did not pass through the origin and dismissed this as an artifact they thought was caused by a loss of ash; however, another explanation could explain the effect. The slope of this plot $\Delta W/\Delta V$ was termed Q and represented a correction factor proposed to account for the fact that actual weight loss incurred during pyrolysis under certain conditions for a coal could be different from that measured by the change in volatiles in the proximate analysis procedure. Dryden (9), has discussed the possibility that volatiles could be entrapped or cracked within the interstices and pores of the coal particles and this could be responsible for a lower yield of volatiles than would have been obtained with finer particles or with a thinner bed or maybe with ambient sweep gas to remove the volatile components rapidly from the vicinity of the pyrolyzing particles. The extreme example of this latter case is, of course, the pyrolysis environment produced in the Badzioch and Hawksley experiments.

The reason for the Q factor being greater than unity would seem therefore to be either the elimination of these entrapments, cracking and back or side reactions or the actual loss of the so called fixed carbon because of conditions not realized in the proximate test. Of course, both effects may be present to varying degrees of significance.

Let us assume there to be a capture factor for the parent coal α such that

$$VM_o = VM_{act}(1 - \alpha)$$

where VM_o is the proximate volatile matter of the original coal and VM_{act} is the "real" volatile matter of the original coal and α is the fraction of the volatile matter that is captured or otherwise lost during the proximate analysis procedure.

Then the weight loss is

$$\Delta W = \frac{VM_o}{1 - \alpha} - \frac{R}{1 - \beta}$$

where R is (as defined by Badzioch and Hawksley) the proximate volatile matter of the char and β is the capture factor for the char, which because of partial devolatilization and physical changes in nature is assumed to be different from that of the parent coal.

$$\Delta V = VM_o - R \quad \text{by definition}$$

$$\text{thus} \quad \Delta W = \frac{\Delta V + R}{1 - \alpha} - \frac{R}{1 - \beta}$$

$$\text{and} \quad \Delta W = \frac{\Delta V}{1 - \alpha} + R \left[\frac{1}{1 - \alpha} - \frac{1}{1 - \beta}\right]$$

But R is not a constant so we substitute $(VM_o - \Delta V)$ for R in the above; thus

$$\Delta W = \frac{\Delta V}{1 - \beta} + VM_o \left[\frac{\alpha - \beta}{(1 - \alpha)(1 - \beta)}\right]$$

$$\text{thus} \quad \Delta W = Q\Delta V - Q(\beta - \alpha)VM_o/(1 - \alpha)$$

$$\text{where} \quad Q = \frac{d(\Delta W)}{d(\Delta V)} = \frac{1}{1 - \beta}$$

This represents the equation of a straight line with slope $1/(1 - \beta)$ and intercept $Q(\beta - \alpha)\ VM_o/(1 - \alpha)$.

When $\Delta W = 0$, $\Delta V = VM_o\ (\beta - \alpha)/(1 - \alpha)$

and if $\beta > \alpha$, then $\Delta V > 0$

When $\Delta V = 0$, $\Delta W = QVM_o(\alpha - \beta)/(1 - \alpha)$

and if $\beta > \alpha$, then $\Delta W < 0$

Although this adequately explains the intercept obtained on the ΔW against ΔV plot, it was necessary to determine the expected magnitude of a capture factor effect in the proximate analysis test, so a series of experiments were performed in this laboratory, whereby the percentage weight loss obtained in the test was plotted as a function of the depth of coal (proportional to weight) in the crucible. The experiments were carried out to the exact specifications of the ASTM test procedure apart from the variation in the quantities of coal used. The results obtained are shown graphically in Figure I. It can be seen that there is a significant effect that can be attributed to a capture factor, yet the effect is not of sufficient

magnitude by itself to explain a Q factor as high as 1.5 or 1.8. The effect shown is of the order of 10 percent. For a Q factor of 1.5 the effect would have to be on the order of 30 percent. Thus although volatile capture does apparently occur in the proximate test, the effect is not large enough to cause the difference between ΔW and ΔV produced in the Badzioch and Hawksley, and Kimber and Gray experiments. The only other explanation is that some of the "fixed carbon" is actually lost during the devolatilization produced under the conditions of their experiments. This almost certainly means that a similar process is occurring in p.c. systems.

In Figure I the squares represent pyrolysis at 1200°C and there is no difference in percentage weight loss than at 950°C. The lower points show devolatilization under conditions of very slow rates of heating, approximately 20-30°C/minute. There is a significant lowering of percentage weight loss under these conditions which suggests that the rate of heating does have an effect upon the quantity of volatiles produced.

As an extension to the two component hypothesis of coal, it appears as if there is a transitional component between the fixed carbon and the volatile component parts which may become volatile or involatile depending on the conditions of decomposition. If the pyrolysis is rapid the thermal energy flux is high enough to promote a substantial portion of the transitional component to the vapor phase. With slow decomposition, preferential polymerization occurs with the evolution of a smaller proportion of volatile matter, the remainder adding to the fixed carbon. This three component hypothesis of coal seems to be well supported from the experimental evidence quoted in this paper.

Remaining Questions

A knowledge of the processes occurring during pyrolysis of coal is required for understanding the combustion of coal particles in p.c. flames, and the way in which the pyrolysis results are used in calculations of p.c. systems will depend on just when and in what order pyrolysis and heterogeneous combustion occur. Essenhigh and Howard (2), suggest that the heterogeneous combustion and pyrolysis occur simultaneously in the plane flame system, but the complexities of studying both combustion and decomposition together make such conclusions extremely difficult to establish.

Although it is accepted that pyrolysis is an activated process, values for activation energies are varied. Juntgen's studies (10), showed that the activation energies for the processes could be divided into two ranges; either 15 or 30 kcal/mole which he identified as activated diffusion and chemical decomposition respectively. He used an average or global activation energy concept in his

analysis of the pyrolysis of coal (11). Badzioch and Hawksley obtained an activation energy of approximately 18 kcal/mole for all the coals that they studied, while the activation energy quoted by Van Krevelen (12), for coal carbonization is about 56 kcal/mole.

The modes of devolatilization and their dependence on particle size are now beginning to be understood, and it should now be possible to assign limits to the various pyrolysis regimes already mentioned. Two models for pyrolysis are proposed by Essenhigh and Howard (2), the first assumes devolatilization occurs uniformly throughout the particle, so the rate of reaction at any time is proportional to the mass (or volume) of unreacted material remaining in the particle, i.e., pyrolysis is a volumetric reaction. Since the total mass of material is independent of the size of particles containing it, the model indicates that pyrolysis should be independent of particle size. The second model assumes pyrolysis to occur in a thin zone surrounding a core of undecomposed material, here the mass of volatile matter present in the zone is proportional to the surface area of the particle, thus the pyrolysis should show a particle size dependence. For the p.c. system they eliminated the latter model on grounds that: 1) the observed time required for pyrolysis was much greater than that predicted from the model for both physical and chemical control, 2) that evidence from Ishihama (13) indicated that there is no size dependence below 60 microns diameter, and 3) an estimation of the temperature distribution inside the particle in a flame indicated that the pyrolysis could not be a surface reaction due to a temperature gradient inside the particle for diameters less than about 50 microns. Thus for particles smaller than approximately 50 microns, the rate of pyrolysis should become independent of particle size and be first order in unreacted volatile material.

Heterogeneous Combustion

Generally Accepted Mechanisms*

In the reaction of a gaseous component with a solid surface it is generally agreed that the process can be divided into three basic steps:

i) Transfer of the gaseous reactant to the solid surface

ii) Chemical reaction of gas with the surface

iii) Diffusion of the products of the reaction away from the surface

Considering now the carbon oxygen system we can say that the rate of weight loss of carbon per unit external surface area R_t is given by the so called "resistance equation":

$$1/R_t = 1/R_{mt} + 1/R_{chem}$$

Here R_{mt} represents the rate at which oxygen molecules are transported across the boundary diffusion layer to the surface where they immediately react to form products and R_{chem} represents the case when there is no resistance to transport of oxygen molecules to the surface but that the reaction takes a finite time. Thus R_{mt} and R_{chem} are the limiting values for mass transfer and chemical reaction.

If the rate is controlled exclusively by the mass transfer process, this implies that the concentration of the oxidant at the surface is effectively zero so the particles if spherical can be treated as impervious spheres, no matter what their internal structure is, which shrink from the outside surface inwards as the reaction proceeds at constant density, thus:

$$\frac{-dm}{dt} = -4\pi r^2 \sigma_A \frac{dr}{dt} = 4\pi r^2 R_t$$

$$\text{and} \quad \tau = -\frac{\sigma_A}{R_t} \int_{r_o}^{o} dr \qquad (1)$$

where σ_A is the density and τ is the burning time when $r = 0$.

If there is turbulent mixing throughout the system of oxidant gas and carbon or coal particles and thus relative motion between gas and particles, the boundary layer thickness can be reduced and mass transfer across it is enhanced. It can be shown that for a relative velocity of u, the rate of mass transfer is given by:

*The authors of this paper are indebted to the excellent review article of Mulcahy and Smith (14) for the formulation of this section.

$$R_{mt}(u>0) = R_{mt}(u = 0)\ [1 + a\ (N_{Re})^b (N_{Sc})^c] \qquad (2)$$

where N_{Re} is the gas-particle Reynolds number, N_{Sc} is the Schmidt number and a, b, and c are constants. By taking values for the constants a, b, and c and evaluating the ratio $R_{mt}(u>0)/R_{mt}(u = 0)$ for various particle sizes at different values of the acceleration, the conclusion arrived at (14) is that in the p.f. size range very little increase in mass transfer results even with an acceleration of 1000 g. It is then reasonable to assume that p.f. particles are effectively stationary relative to their gaseous environment.

It is then permissible to use Nusselt's (15) treatment for the calculation of R_{mt} assuming Fick's Law of Diffusion. The result of this treatment is:

$$R_{mt} = 48\ (D_o(f_m/d)\rho_o)(T/_{To})^{0.75}/32 \qquad (3)$$

where f_m is the mass fraction of oxidant in the bulk phase, d is the particle diameter, ρ_o is the gas density and T is the reaction temperature, the subscript o refers to standard conditions. This shows that the rate is proportional to 1/d and has a small temperature coefficient. The derivation of the above assumes that one oxygen molecule liberates two carbon atoms as CO. If account is taken of Stefan flow (16),(17) the above expression is modififed to:

$$R_{mt} = -48\ [(D_o/d)\rho_o(T/T_o)^{0.75}\ \ln(1-\gamma f_m)/\gamma]/32 \qquad (4)$$

Since this equation shows that the rate of mass transfer is inversely proportional to the particle diameter, as d becomes small enough R_{mt} will become large so that below a certain particle size $R_{mt} >> R_{chem}$. When this condition is met the chemical reaction rate will become the rate controlling process. We can then elaborate upon point (ii) above and differentiate between the process of chemisorption and desorption, either one of which can be the rate controlling step.

Expressions for the maximum rates of chemisorption and desorption in gas/solid systems have been derived (18), (19) and are:

for chemisorption (adsorption)

$$R_{chem} = [2M_O P_{O_2}/(2\pi RTM_{O_2})^{1/2}]\ \exp\ (-E_{ads/RT})\ \ gm/cm^2\ sec. \qquad (5)$$

where E_{ads} is the activation energy for chemisorption. This rate is seen to be first order in oxygen concentration.

for desorption (from absolute rate theory (7))

$$R_{chem\ des} = C_s\ k\ \frac{k_B T}{h}\ \frac{f^+}{f_s}\ \exp\ (-E_{des/RT})\ \ gm/cm^2\ sec. \qquad (6)$$

$$\text{or } R_{chem\ des} = [(12RTC_s)/(N^2h)]\ \exp\ (-E_{des/RT})\ \ gm/cm^2\ sec. \qquad (7)$$

where C_s = number of carbon atoms/cm^2 of graphite lattice

k = transmission coefficient

k_B = Boltzmann constant

f^+, f_s are partition functions

E_{des} is the activation energy for desorption

In this case, the rate is seen to be independent of oxygen concentration, i.e., zero order in oxygen.

The transition between a system whose rate is controlled by chemical reaction to one whose rate is controlled by mass transfer is often depicted on an idealized Arrhenius diagram as shown in Fig. II. For a fixed particle size as the temperature is increased the rate of the chemical reaction will increase much faster than the rate of mass transfer until above a critical temperature T_c the mass transfer limits the overall rate of the reaction. The temperature at which this transition occurs depends on particle size since R_{mt} is proportional to 1/d while R_{chem} is independent of the particle diameter. Mulcahy and Smith (14) attempted to estimate the value of T_c that would hold for a 40 micron particle if the chemical rate was calculated from equations 5 and 7 and the mass transfer rate was given by equation 4. However, the assumptions they had to make in order to evaluate these rates from the equations, especially for the desorption rate are probably unrealistic so that any conclusions obtained from this ideal analysis should be used cautiously. Nevertheless their conclusion is that if E_{ads}>5 kcal/mole, combustion at atmospheric pressure of virtually all particles in the p.f. range will be chemically controlled.

After Nusselt's work it was generally assumed that the rate of mass transfer to a particle could be automatically equated to the rate of combustion, but Hottel and Stewart (21) found evidence of chemical rate control in a reanalysis they performed on some existing data. Essenhigh (22) and Essenhigh and Beer (23) found strong evidence of chemical rate control from their experimental data and subsequent workers (24), (25) have supported these conclusions. Mulcahy and Smith (14) have plotted rate data derived from investigations on the combustion of anthracites, bituminous coals, soots, charcoals

and bulk graphites on an Arrhenius diagram. They have plotted on the same diagram the theoretical line for mass transfer to a 40 micron particle and although the plotted rates are considerably scattered, they are all less than the rate of this mass transfer to a 40 micron particle. Also the strong dependence of the rate on the fuel type is very indicative of chemical control. All this evidence tends to strongly imply that chemical control is operative in the combustion of p.f. sized particles at atmospheric pressure.

In the above discussion we have been implicitly considering the particles to be impervious and that they burn at constant density as progressively shrinking spheres. Although this is implied it in no way changes the qualitative conclusions that have been arrived at. However, in order to study practical systems of combusting particles, we must realize that this simple model is often incorrect. The variation in chemical reactivity of a particle can depend on the intrinsic chemical nature of the material or on the physical structure of the material. The most likely factor determining the reactivity is the total surface area available to the oxidant, this in turn depends on the roughness of the surface and the porosity of the particle, i.e., on the internal structure and extent of micro, transitional and macropores. When the particle is porous and oxidant can penetrate into the interior, the pore structure is modified during the reaction as the walls of the pores are themselves consumed during the combustion process. It might be expected that the rate of oxidation would increase from low to 50 percent burn off as the accessibility of surface increases, and then decrease as pores coalesce and reduce the total internal surface area. Microscopic and photographic examination of coals and chars during various conditions of heating and combustion have been undertaken (26)-(32) and in some cases combustion has been observed to occur in the pores. The only conclusion from this is that the effect of porosity with the possibility of internal burning must be considered in any discussion of combustion processes of p.f. particles.

The schematic Arrhenius plot of Fig. III shows the case for an impervious sphere as well as the case for a porous particle. This latter case shows three regimes which are now briefly discussed.

In zone I the oxidant concentration is the same throughout the particle and equal to that of the bulk phase. The reaction rate per unit total surface area is

$$R_{chem,\ tot} = A\ C^n \exp\ (-E/RT) \qquad (8)$$

where n and E are the true order and activation energy for the reaction.

In zone II the concentration of oxidant within the porous structure is not constant but varies from effectively zero at the center of the particle to the bulk phase value at the periphery. Thus the rate of reaction is in part determined by the internal diffusion of oxidant through the porous structure (33). The rate of reaction is then given by (14):

$$R_{chem} = 2N\pi r_p[(r_p D_p A C^{n+1} \exp(-E/RT))(n+1)^{-1}]^{1/2} \qquad (9)$$

The apparent order is then (n+1)/2 where n is the true order and the apparent activation energy becomes E/2 where E is the activation energy in zone I, since both expressions appear under the square root sign in the rate equation.

In zone III the increase in temperature has increased the reaction rate so that it has become too fast to control the overall rate and oxidant molecules react as soon as they arrive at the particle surface. The overall rate is then controlled by mass transfer. It is important to realize that there is no sharp cut off from one zone to another, but rather a continuous transition between the zones.

Another regime exists characterized by a solid whose reactivity is great enough to prevent oxidant penetration further than the mean free path λ, but not fast enough to cause mass transfer control. This regime is termed the "outer kinetic region" (17) and has zone I kinetic characteristics. However in this case there is an increased area for reaction because of the external roughness of the surface of the particle.

The regime in which the reaction is occurring can be determined by calculating the depth to which the oxidant can penetrate into the particle. If the depth of penetration is L, then from our definitions above we see that for rough sphere particles $L<\lambda$; for zone I $L>>r$ (the particle radius); and for zone II $\lambda<L\leq r$. Mulcahy and Smith (14) adopting the idealized pore model of Wheeler (34) used observed combustion rates to estimate values of L as a function of the particle porosity (θ) and the mean pore radius ($\bar{r}_p$) using the relation for zone II conditions:

$$L\ (C = 0) = D_p \Theta C_s / [(n + 1)^{1/2} R_{chem}] \qquad (10)$$

where C_s is the concentration at the surface.

They found that $L>\lambda$ for reasonable values of the porosity when $\bar{r}_p>0.1$ microns for a reactive coal and $\bar{r}_p>.01$ for a less reactive coal. Values of $\bar{r}_p$ below .05 microns for reactive coal and 0.005 microns for less reactive coal gave rise to rough sphere conditions, i.e., $L<\lambda$. For $\bar{r}_p \geq 1$ micron all particles

in the p.f. range were found to be completely penetrated at the lower chosen value for R_{chem}. At the same pore size and highest R_{chem}, particles <20 microns were found to be completely penetrated (zone I kinetic region) and 100 micron particles were 40 percent penetrated. Thus the conclusions of this analysis were that if all the porosity was contained in micropores rough sphere kinetics would always apply, but if the particle were macroporous, then zone II conditions would be applicable.

Thus chars produced from anthracites and brown coals which are highly microporous would be expected to combust under rough sphere conditions. The conclusions just stated were arrived at by applying the simple cylindrical pore model developed orginally by Wheeler (34) to place reactions within porous catalysts on a theoretical basis. Evidence from microscopy hardly supports this simple model, many pyrolized particles have complete voided structures varying from "pop corn" type through lacy to hollow cenospheres (35). However the important points to emerge from this analysis are firstly that the value of the rate of chemical reaction at the start of the combustion process may not remain constant throughout the whole burn-out period even in isothermal conditions because of the evolution of the internal structure of the particle, and secondly that the temperature and oxidant concentration are not the only variables to consider when interpreting the kinetics of such reactions.

Disputed Issues

For a simple reaction the rate per unit surface area can be expressed as

$$R_{chem\ tot} = A\ C^n \exp(-E/RT) \qquad (11)$$

where n and E are the true order and activation energy of the reaction independent of temperature, and A has only a slight temperature dependence in comparison to the exponential term. The true parameters n and E in combustion systems have been extremely difficult to determine for several reasons. Among these reasons are:

(i) the difficulty in avoiding zone II and III conditions

(ii) the difficulty in controlling the particle temperature because of the high heat of reaction

(iii) the change in the available surface area during the course of the combustion process

Therefore there is still considerable uncertainty pertaining to values of E and n for impure carbons. This uncertainty even applies to the case of pure carbons where although many investigations to determine the values of these parameters have been undertaken,

there is still considerable inconsistancy and uncertainty in the experimental results. Walker (36) et al have reviewed the carbon oxygen system and point out that as Θ' (the surface coverage) tends to unity, that the reaction order would be expected to be zero with respect to covering agent and when Θ' tends to zero, a first order dependence is predicted. These authors correctly imply that an important factor affecting Θ' is the pressure of oxidant but also the temperature of the particle surface is probably an equally important factor. This factor may explain why Gulbransen and Andrews (37) obtain a zero order dependence at relatively low pressures in a low temperature range of 400-500°C, and similarly Blyholder and Eyring (20) obtain a zero order dependence at 800°C at low pressures. Orders intermediate between zero and one have been found by several workers (38)-(42) using highly purified graphites.

Variations in activation energies between about 80 kcal/mole down to zero have been obtained under various conditions for the oxygen pure carbon system and for the impure carbon system, similar, but not so large, variations in activation energy have been found, with the value often being strongly temperature dependent.

Disagreement also exists in the p.f. system as to the value and temperature dependence of activation energies. Smith in two papers on the kinetics of combustion of size graded particles (43), (44) finds activation energies on the order of 17 kcal/mole and an order of unity in surface oxygen concentration. He represents R_{ac}, the rate per unit external surface area, by an Arrhenius expression of the form:

$$R_{ac} = A \exp(-E_a/RT_p) \quad gm/cm^2 \text{ sec atm } O_2 \qquad (12)$$

where T_p is the particle temperature calculated from a simple heat balance on the particle assuming CO to be the primary product (45).

Field (1), (46) in experiments on the rates of combustion of size graded fractions of char attempted to fit his data to an expression of the Arrhenius form, but found that the activation energy could not be taken as constant, but would need to vary as a function of temperature, decreasing from about 35 kcal/mole at 1300°K to about 10 kcal/mole at 1800°K. Smith in an attempt to account for the non-linearity of Field's Arrhenius plot suggested that Field's data is compatible with a transition between rate control in zone I to zone II, brought about possibly by the differences in pore structure of the chars used. However, if this were the explanation, the activation energy in Field's data should never fall below a value of E/2, where E is the value obtained in zone I, hence Field's activation energy should never be less than 17 kcal/mole, whereas in fact the activation energy falls to 10 kcal/mole and apparently is still falling with increasing temperature. The scatter in Smith's data makes it difficult to say whether E_a is constant or does in fact level off slightly in the higher temperature region as does Field's data.

Another possible explanation as to this change in activation energy with temperature is given in the next section (Attempted Clarification of Disputed Issues by a Reanalysis of Existing Data), where some of Field's original data is reanalyzed.

Attempted Clarification of Disputed Issues by a Reanalysis of Existing Data

Changes in the temperature dependence of a reaction that can be depicted on an Arrehnius diagram are consistent with change from chemical to mass transfer dominance as discussed earlier, or change from zone I to zone II kinetic dominance, also discussed above. However, the temperature variation of the activation energy and apparent (or real) order in oxygen can also be explained by a transition from desorption to chemisorption dominance in the reaction. Chemisorption is known to occur extensively on carbons at room temperature (47), so it is reasonable to expect the activation energy for chemisorption to be low, with the order in oxygen being unity. Activation energies for desorption are expected to be high (20) and an order in oxygen of zero. So we can expect at low temperatures, where the chemical rate is slow, the surface to be covered with oxidant so the reaction rate must be controlled by the desorption process. In this case, the order in oxygen should be zero for zone I conditions and 1/2 for zone II. The activation energy E_{des} is expected to be high, perhaps in the region of 40-80 kcal/mole. As the temperature increases, so does the reaction rate and the surface coverage tends to zero, so that the process now limiting the reaction rate is the chemisorption of oxidant onto the surface of the carbon. This would lead to an apparent and real order of unity and a low value for the activation energy (E_{ads}). To lend support to this hypothesis, the results of Field (1) have been reanalyzed in the discussion contained below.

Field (1) shows his results plotted on a linear plot of K_s (surface reaction rate coefficient gm/cm^2 sec atm) against surface temperature T_s °K. The exponentially rising curve shown also on the same graph represents the best fit to the data of past workers at atmospheric pressure and at temperatures above 1000 °K, as given in the review by Field, Gill, Morgan and Hawksley (49). The curve is given by:

$$K_s = A \exp(-E/RT_s)$$

where $A = 8710$ gm/cm^{2}sec atm

$E = 35{,}700$ cal/mole

$R = 1.986$ cal/mole °K (13)

This exponential curve is based on measurements from other workers below 1650°K, and it is evident from the graph that the new measurements of Field are consistent with the curve up to this temperature. However,

for temperatures above 1650°K, the values of Field's data fall considerably below the extrapolated exponential curve.

Field therefore represents his data by a linear relationship of the form:

$$K_s = -0.49 + 3.85 \times 10^{-4} T_s \qquad (14)$$

$$\text{or} \quad K_s = K_o + A T_s$$

In Field's second paper on combustion rates of p.c. (46), he represents his rate variance with temperature by the following expression for various coals:

$$K_s = K_{s,1600\,°K} + A (T_s - 1600) \qquad (15)$$

The simple model assumed for the interpretation of Field's data is that of the Langmuir Adsorption Isotherm (50). Although this model is necessarily subject to the underlying assumptions of this theory (47), the general conclusions derived from this treatment are applicable.

From Langmuir's treatment, we can say that the rate of reaction is given by:

$$\text{Rate} = \frac{K_1 K_2 p_s}{K_1 p_s + K_2} \qquad (16)$$

where K_1 and K_2 are the rates for chemisorption and desorption respectively, and p_s is the oxygen concentration at the surface. Expressing the rate in terms of Field's nomenclature (1) we have:

$$K_s p_s = \frac{K_1 K_2 p_s}{K_1 p_s + K_2}$$

$$\text{and} \quad 1/K_s p_s = 1/K_2 + 1/K_1 p_s$$

where $K_1 = k_1 \exp(-E_1/RT_s)$ and $K_2 = k_2 \exp(-E_2/RT_s)$. Here, k_1 and k_2 are the pre-exponential factors for chemisorption and desorption respectively, and E_1 and E_2 are the activation energies for chemisorption and desorption respectively. Rearranging the above expression leads to:

$$1/K_s = \frac{\exp(E_1/RT_s)}{k_1} + \frac{p_s \exp(E_2/RT_s)}{k_2} \tag{16a}$$

$$1/K_s = (1/k_1) \exp(E_1/RT_s) \{1 + \frac{k_1 p_s}{k_2} \exp[(E_2 - E_1)/RT_s]\} \tag{17}$$

$$\ln K_s = \ln k_1 - \frac{E_1 + RT_s \ln\{1 + b \exp[(E_2-E_1)/RT_s]\}}{RT_s}$$

This last expression gives an apparent activation energy E_a, where

$$E_a = E_1 + RT_s \ln[1 + b \exp(\Delta E/RT)] \tag{18}$$

Here there are three variable parameters E_1, b and ΔE, where $\Delta E = E_2 - E_1$ and $b = k_1 p_s/k_2$.

Field's expression for his temperature dependent activation energy is:

$$E = RAT_s^2/K_s \quad \text{(eq. 10 ref. (46))} \tag{19}$$

Values of activation energy E were calculated from equation (19) at various temperatures T_s. A least squares fit of the activation energies calculated from equation (19) was performed using the functional form of equation (18). The fitting parameters that were varied to obtain the best least squares fit were E_1, b and ΔE. The results obtained from this analysis were:

$E_1 \simeq 6{,}000$ cal/mole

$E_2 \simeq 37{,}000$ cal/mole

$b \simeq 0.000126$

Using these values of the three fitting parameters, equation (18) matches equation (19) almost exactly.

Starting with equation (16a), we can rearrange it in the following forms:

$$1/K_s = (p_s/k_2)\ \exp(E_2/RT_s)\ \{1 + (k_2/k_1p_s)\ \exp[(E_1-E_2)/RT_s]\}$$

$$1/K_s = (p_s/k_2)\ \exp(E_2/RT_s)\ \{1 + (1/b)\ \exp(-\Delta E/RT_s)\} \qquad (20)$$

$$\text{and } 1/K_s = (p_s/k_2)\ \exp\ (E_2/RT_s)\ [1 + X] \qquad (21)$$

Equations (17) and (20) are equivalent forms of equation (16a). As the temperature T_s tends to zero, X tends to zero, and we see from equation (21) that K_s approaches $(k_2/p_s)\exp(-E_2/RT_s)$, or that K_sp_s approaches $k_2\ \exp(-E_2/RT_s)$. Thus we find that as T_s tends to zero, we tend towards a zero order rate expression whose limit is $k_2\ \exp\ (-E_2/RT_s)$ or K_2.

It is interesting to determine the value of X with increasing temperature, and hence the departure of the rate expression from the pure zero order dependence component K_2. Below 1400°K, X<<1 (in fact less than .01) and the low temperature limit is applicable. In the range of temperatures 1400°K to 2000°K, the value of X grows from 1.47×10^{-2} to 0.763 (see Table I). At approximately 1600°K, ten percent divergence from a pure K_2 dependence would be incurred, with ever increasing divergence occurring at higher temperatures as is shown in Fig. III.

Referring to Field's statement (1) that data from previous workers at lower temperatures (<1650°K) could be fitted with an Arrhenius rate expression with an activation energy of 35,700 cal/mole, it is not surprising to obtain this result in view of the above analysis. Recall that E_2, the low temperature limit activation energy for the desorption process, was calculated to be approximately 37,000 cal/mole, and that significant divergence from this simple Arrhenius expression occurs only above 1650°K. The oxygen dependence was also shown to be zero order for the temperature range in the analysis presented here.

The above explanation and analysis appear to fit the facts as far as order in oxygen and temperature dependence of activation energy are concerned, especially for the data of Field. More precise rate determinations are required, especially in the high temperature region, if more experimental substantiation of this theory is to be obtained.

More evidence to support this hypothesis comes also from the study of pure carbon systems. Rosner and Allendorf (48) found in

their study of the reaction of oxygen with pure graphite at high temperatures that the activation energy changed from 31 kcal/mole at 1300°K to 0 at 1600°K. At 1200°K the apparent order was 0.56, which implies that the real order is zero, if pore diffusion is present and the reaction is in the desorption controlled regime. At 1440°K the apparent order is unity and this is compatible with chemisorption control. So perhaps detailed mechanistic arguments were not that premature from their data.

Blyholder and Eyring (20) find a zero order reaction with an activation energy of 80 kcal/mole at 800°C for very thin coatings of graphite rubbed on ceramic rods. This was twice as large as the activation energy observed for samples 1 mm. thick where the rate is obviously pore diffusion controlled. The order in this case was found to be 1/2 in oxygen.

Departures of the activation energy at high temperatures towards the limiting value of chemisorption control may not occur to any substantial extent until very high combustion temperatures are reached, as was shown from the above analysis. Also, much of the existing data on burn out of small p.f. particles is expectedly quite scattered because of the difficulties involved in extracting reliable data from such systems, so direct substantiation of the proposed picture set out in this paper may be difficult. However, this has been an attempt to consolidate some results in the carbon oxygen system, especially as it is applicable to p.f. systems, and fit them into a workable, although simplistic model.

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Table I

T °K	$\frac{\Delta E}{RT}$	exp $(-\Delta E/RT)$	$(\frac{1}{b})$ exp $(-\Delta E/RT)$
0	∞	0	0
1000	18.5	9.25×10^{-9}	7.35×10^{-5}
1200	15.4	2.05×10^{-7}	1.63×10^{-3}
1400	13.2	1.85×10^{-6}	1.47×10^{-2}
1600	11.6	9.17×10^{-6}	7.28×10^{-2}
1800	10.3	3.36×10^{-5}	0.267
2000	9.25	9.61×10^{-5}	0.763

Figure I

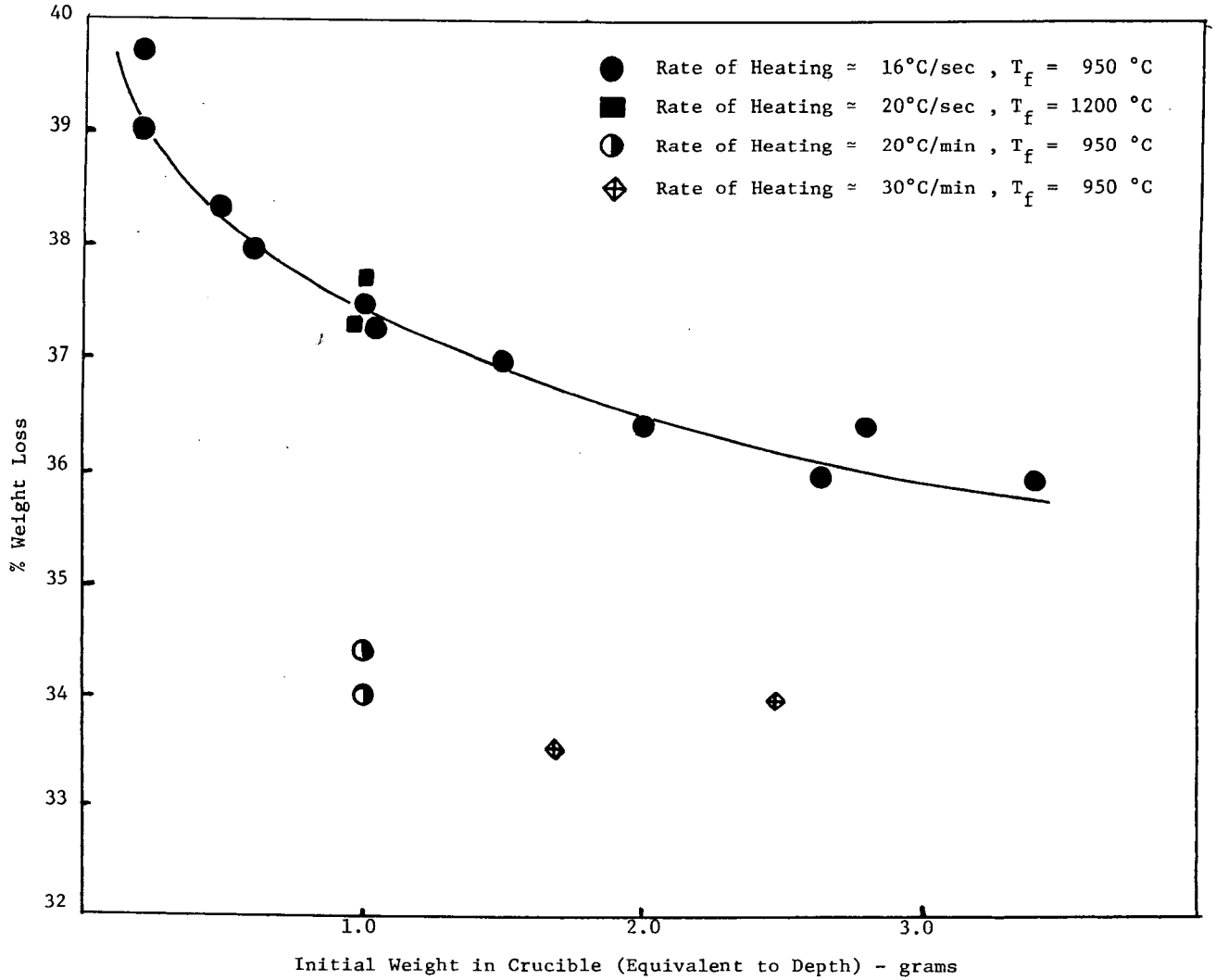
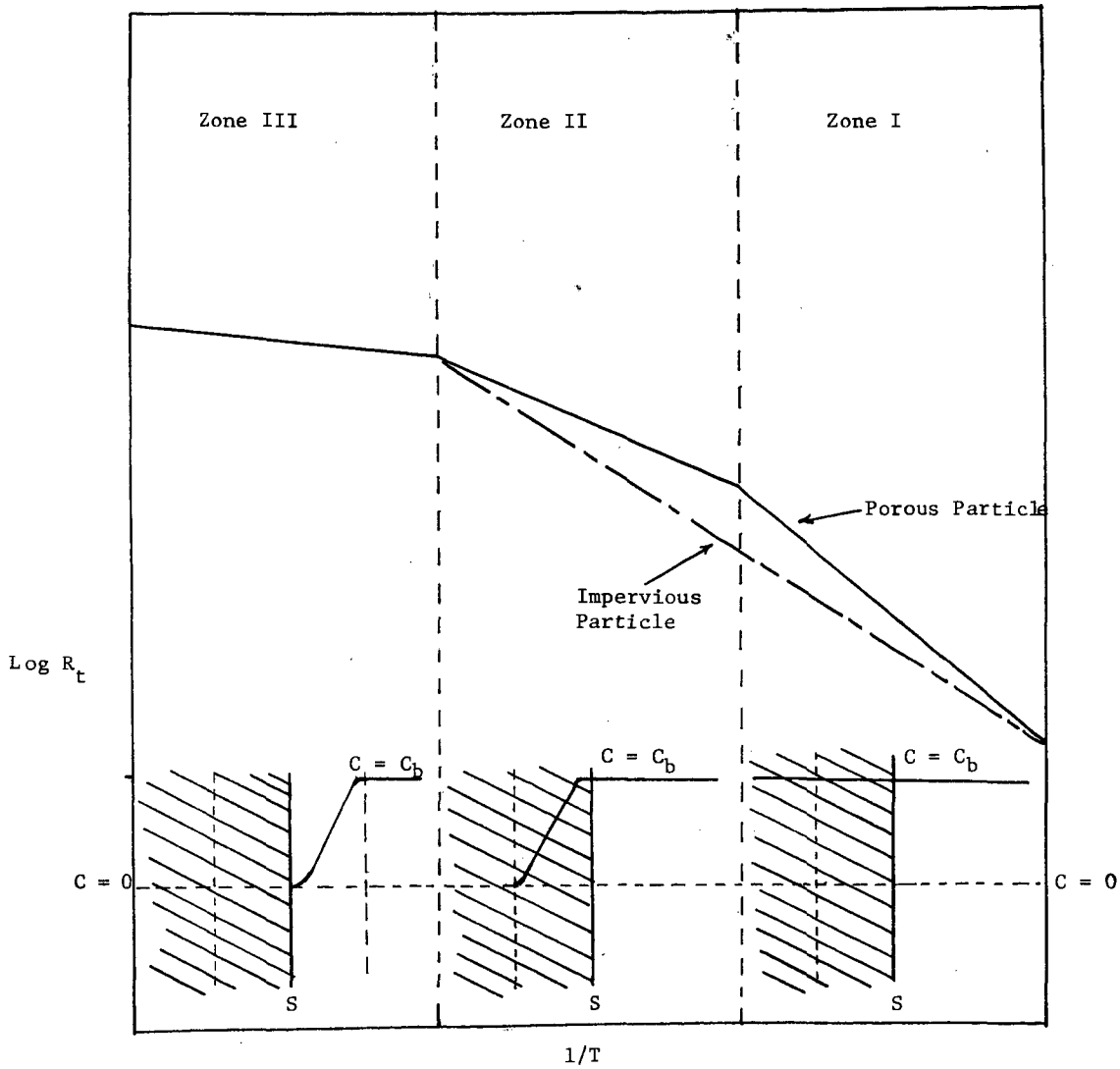

Rate of Heating ≃ 16°C/sec , T_f = 950 °C
Rate of Heating ≃ 20°C/sec , T_f = 1200 °C
Rate of Heating ≃ 20°C/min , T_f = 950 °C
Rate of Heating ≃ 30°C/min , T_f = 950 °C
% Weight Loss
40
39
38
37
36
35
34
33
32
1.0
2.0
3.0
Initial Weight in Crucible (Equivalent to Depth) - grams

Figure II

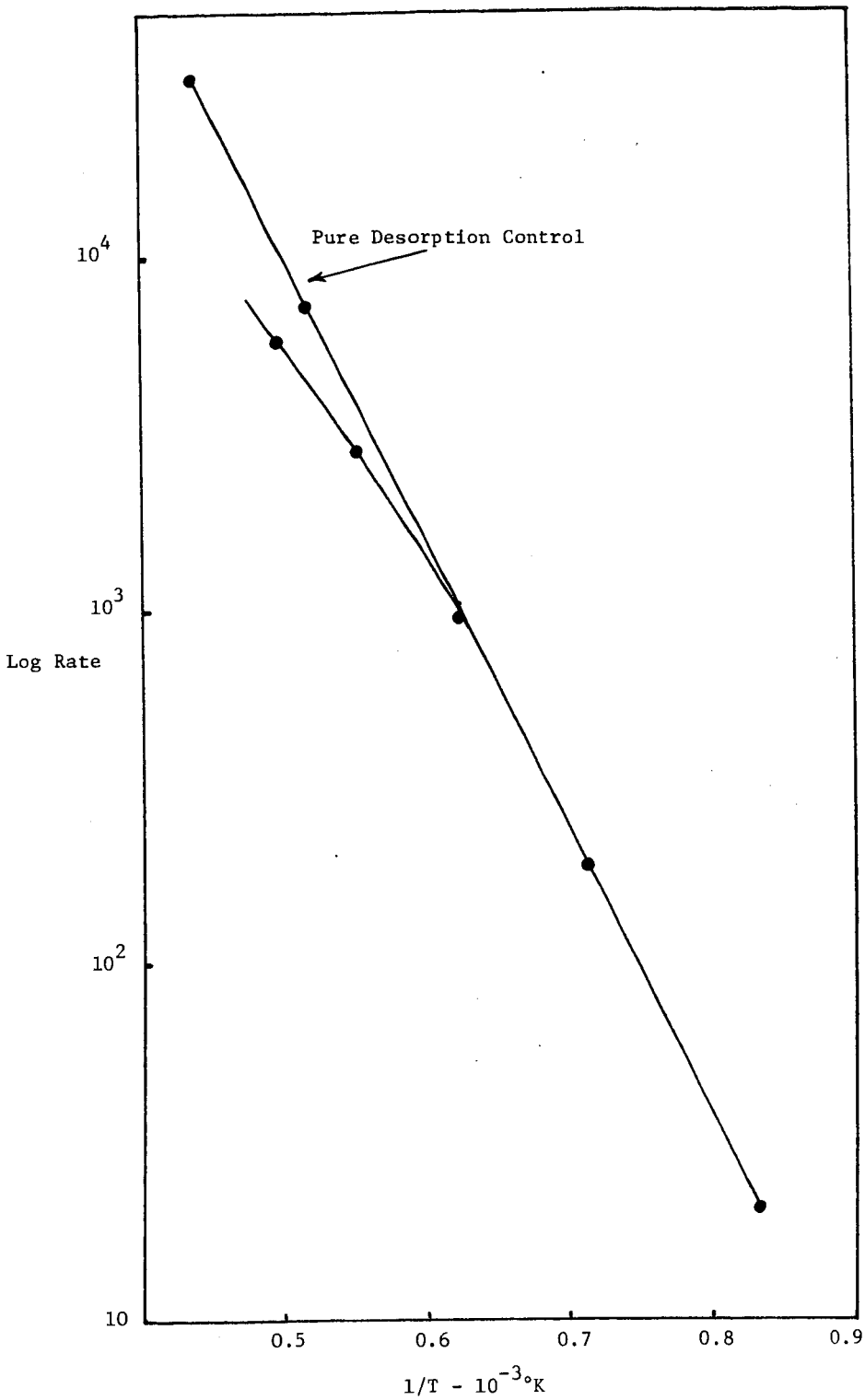
Arrhenius Diagram Showing Rate Controlling Regimes in Gas-Solid Reactions



S = Particle Surface

C_b = Bulk Concentration

Figure III


Pure Desorption Control
10^4
10^3
10^2
10
Log Rate
0.5
0.6
0.7
0.8
0.9
$1/T - 10^{-3}$°K