

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
PITTSBURGH MEETING, MARCH 23-26, 1966

A KINETIC STUDY OF THE PYROLYSIS OF A
HIGH-VOLATILE BITUMINOUS COAL

By

Wendell H. Wisler, George Richard Hill, and Norbert J. Kertamus
Fuels Engineering Department
University of Utah
Salt Lake City, Utah

INTRODUCTION

In recent years experimental data from several laboratories have been presented and analyzed in the literature in an effort to arrive at greater understanding of the processes associated with the pyrolysis of coal. Each of these presentations has contributed measurably to an increased understanding, both through the inclusion of experimental data and as a result of interpretations of the data. It is intended that the presentation of experimental data obtained in this laboratory, accompanied by analyses and comparisons with previously reported data, may shed further light upon these very complex processes.

There appear in the literature two basic experimental approaches to this problem:

(1) heating a coal sample to a predetermined temperature where the decomposition processes are studied at constant temperature, and (2) increasing the temperature of the coal sample at a predetermined constant rate. Among those who have pursued their studies at constant temperature, some have heated the coal sample under conditions where the normal coking processes may occur, including the fusion of the sample particles, while others have heated the samples to operating temperatures with the coal particles effectively separated such that attainment of the desired temperature was rapid and fusion of particles was essentially avoided. The results of these various approaches are necessarily varied, but related. The present study is concerned with constant temperature observations of finely divided coal samples under conditions such that fusion of the coal mass may occur in a manner characteristic of coking operations, and at temperatures such that the coal samples pass through the plastic state during the course of the observations.

EXPERIMENTAL PROCEDURE

The equipment used in this study consisted of a vertical tube-type furnace with facility for maintaining constant temperature within $\pm 3^\circ\text{C}$. A stream of nitrogen gas at constant flow rate was admitted at the top of the furnace and flowed downward over the sample. The samples of a Utah high-volatile Bituminous coal, of 47.46 per cent volatile matter on a dry basis, were sized to -40 +60 mesh (particle diameter 417 to 246 microns) and dried at 100°C in a vacuum. Samples of approximately one gram were used in the determinations.

The sample was carefully weighed, then placed in an aluminum foil sample pan and suspended by a nichrome wire from a quartz spring of five gram capacity. A cathetometer measured the deflection of the quartz spring. During the course of pyrolysis, the loss in weight of the sample was recorded, at five minute intervals initially, and at longer intervals after the first 60 minutes. All weight-loss observations, including the initial deflection, were made with a constant flow rate of the nitrogen stream.

RESULTS AND DISCUSSION

Typical fractional weight loss-time curves from this study are shown in Figure 1. It is noted that the later portions of these curves are straight lines, which indicate zero order reaction during these portions, inasmuch as $dx/dt = \text{constant}$. It is noted further that the pyrolysis reaction, as indicated by weight loss of the sample, assumes zero order characteristics at times which decrease in a regular manner from 375 minutes at 409°C to 250 minutes at 497°C , and

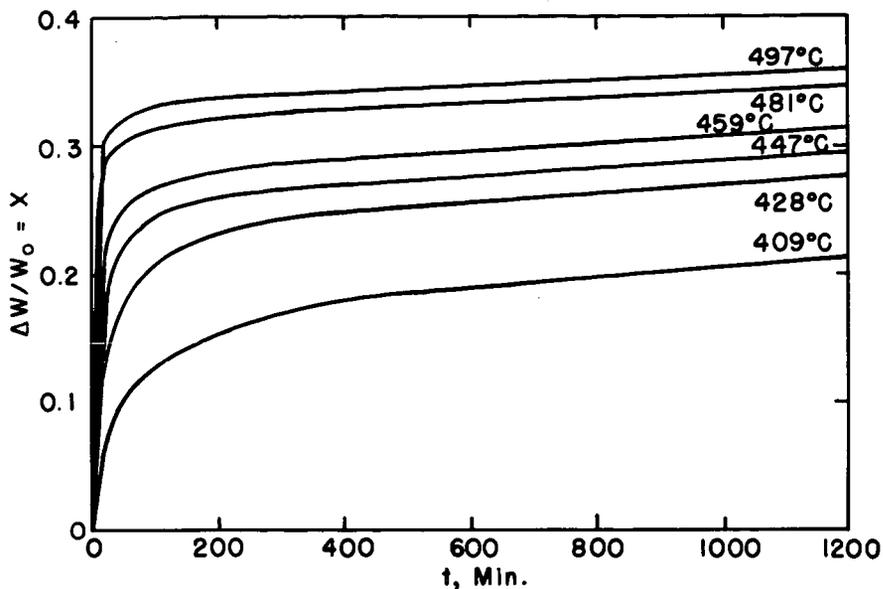


Figure 1. Fractional Weight Loss-Time Curves.

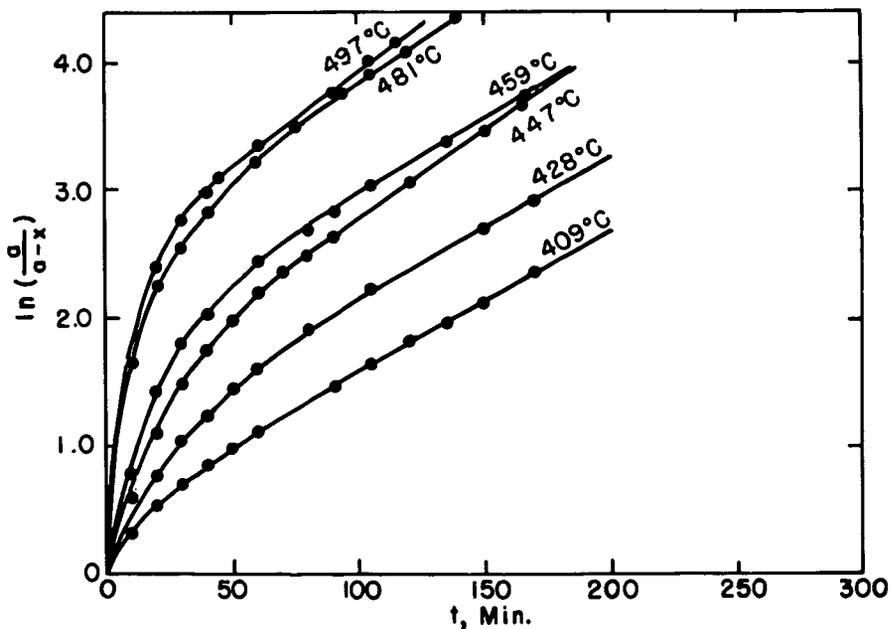


Figure 2. First Order Plot of Data.

continues to be zero order throughout the balance of the determination, which in several cases extends to 1500 minutes. A period of zero weight loss was not attained in any of the determinations.

The analysis of the data for evolution of volatile material for time periods preceding the zero order portions of the curves in Figure 1 involves expressions (e. g. equation 1) wherein the maximum proportion of the coal sample which may ultimately be transformed into volatile products at the temperature concerned must be known or assumed. These quantities were not experimentally observable. Although the nature of the zero order reaction is not known, it is reasonable to assume that it occurs throughout the time of pyrolysis. The reaction velocity constants for this portion of the various curves are determined from the slopes of the straight line portions of the curves in Figure 1, and are observed to be essentially the same for each temperature, with values of the order of 10^{-5} grams per minute. Hence the rate of product evolution, and the quantity of product evolved due to this type of reaction prior to the time when the reaction assumes zero order, are small.

By subtracting the zero order reactions from the weight loss data, values of "a" for the subsequent equations are obtained which characterize the reactions, excluding the slow zero order reaction, occurring to produce most of the volatile material. This was done by extending the straight line portion of the plot of weight loss vs. time to zero time, and subtracting the appropriate quantities, as thus determined graphically, from the observed weight loss values. The intersection of this extended straight line with the ordinate at zero time gives the weight fraction of the sample which would evolve as volatile products if the zero order reaction did not occur, and is thus the value "a" appearing in the differential equations which follow.

To analyze the data prior to the time of over-all zero order reaction, the differential equation is written:

$$\frac{dx}{dt} = k_1 (a-x) \quad (1)$$

where "x" is the observed weight loss at time "t", as a fraction of the initial sample weight, and "a" is the maximum weight loss obtainable (excluding the zero order reaction as explained above). The constant "k₁" is the reaction velocity constant. Integrating equation (1), and evaluating the constant of integration with x = 0 when t = 0, yields

$$\ln \frac{a}{a-x} = k_1 t \quad (2)$$

In Figure 2, $\ln \frac{a}{a-x}$ is plotted versus time. It is noted that the data produce straight lines, and hence are first order, at times above about 90 minutes. The slope of the straight line is equal to "k₁" of equation (2) for that temperature, and over the range of data where the straight line is observed.

For a second order reaction, the following differential equation applies:

$$\frac{dx}{dt} = k_2 (a-x)^2 \quad (3)$$

Integrating and evaluating the constant of integration with x = 0 when t = 0,

$$\frac{x}{a(a-x)} = k_2 t \quad (4)$$

Plotting $\frac{x}{a(a-x)}$ vs. t yields a straight line for the first 60 minutes for some temperatures but a slight curvature at the lower and higher temperatures.

A rate equation of general form is written:

$$\frac{dx}{dt} = k_n (a-x)^n \quad (5)$$

where n ≠ 1 and denotes the order of the reaction. Integrating, and evaluating the constant of integration with x = 0 when t = 0,

$$\frac{a^{1-n} - (a-x)^{1-n}}{1-n} = k_n t \quad (6)$$

This equation is applied to the data for the first 60 minutes, when the larger portion of the product evolution occurs, by selecting values for n at each temperature until a straight line is produced for that temperature over the 60 minute period on a plot of

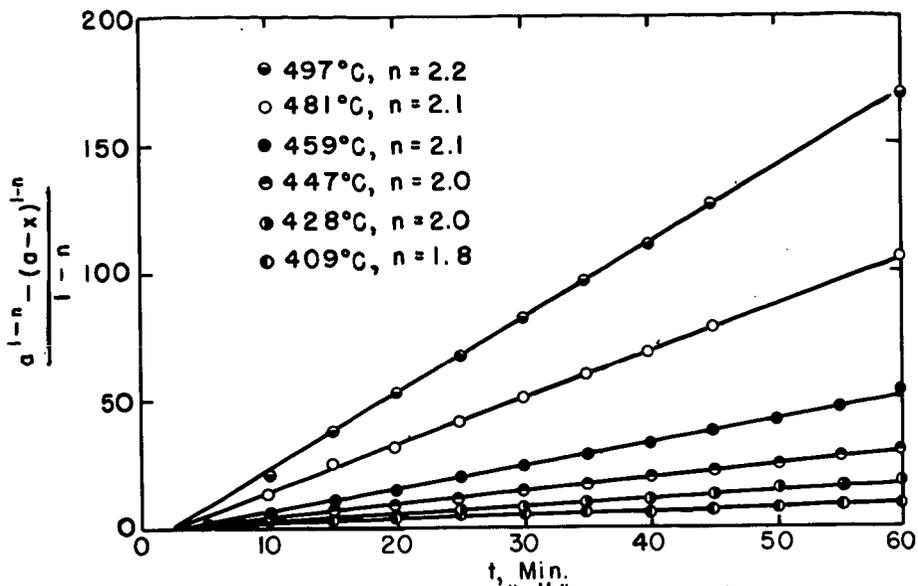


Figure 3. Plot of "n'th" Order Equation.

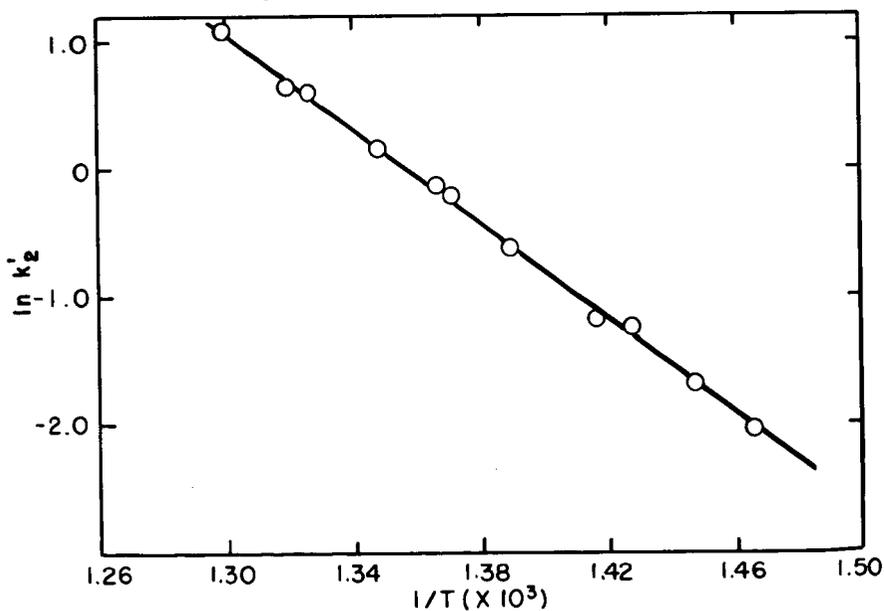


Figure 4. Plot of Arrhenius Eq., First 60 Minutes.

$$\frac{a^{1-n} - (a-x)^{1-n}}{1-n} \text{ vs. } t.$$

The order of the reaction thus determined for the first 60 minutes (with the zero order reaction subtracted, as explained above) ranges from 1.8 at 409°C to 2.2 at 497°C, with a gradual and progressive increase in order noted with increase in temperature. These results are shown in Figure 3. The slopes of the lines in Figure 3 equal " k_n " from equation (6) for each temperature as indicated.

A region of transition from approximately second order to first order is noted, spanning a time of about 30 minutes. A similar region of transition between first order and zero order portions of the data is also observed.

The specific rate of most chemical reactions can be related to the temperature at which the reaction occurs by the Arrhenius equation:

$$k' = Ae^{-E/RT} \quad (7)$$

where E is the energy of activation and A is a quantity which is independent of or varies little with temperature. Over narrow temperature ranges, E and A may be considered to be constant.

Equation (7) may be written in the form

$$\ln k' = \ln A - E/RT \quad (8)$$

A plot of the natural logarithm of the rate constant k' vs. the reciprocal of the absolute temperature should yield a straight line with slope equal to $-E/R$. Figure 4 presents such a plot for the observed reactions of the first 60 minutes. From the slope of the line in Figure 4, an energy of activation of 36.6 kcal. per mole is obtained for the reactions of the first 60 minutes. A similar plot for the first order region yields an activation energy of 5.36 kcal. per mole for that region.

In the use of equation (7), the activation energy, E, varies slightly with temperature, and A involves an entropy term. Strictly speaking, the factor which determines the rate of a reaction is the free energy of activation, ΔF^\ddagger . We may therefore properly write: (4)

$$k' = Ae^{-\Delta F^\ddagger/RT} \quad (9)$$

$$k' = Ae^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (10)$$

where ΔF^\ddagger , ΔH^\ddagger and ΔS^\ddagger are the free energy, heat and entropy of activation, respectively.

The factor "A" in equation (10) is termed the frequency factor, and accounts for the rate of decomposition of the activated complex to form products, which rate of decomposition can be shown to be $\frac{kT}{h}$, where k is the Boltzmann constant, and h is the Planck Constant. Also, it is possible that not every activated complex leads to formation of products. Allowance is made for this possibility by introducing a term, \mathcal{H} , called the transmission coefficient. ($\mathcal{H} \leq 1$, and represents the fraction of activated complexes which does become products.)

For a heterogeneous system such as coal pyrolysis, the number and nature of reaction sites changes with time. Accordingly an expression for the rate of reaction in such a system includes a term of the form:

$$\frac{\text{molar concentration of sites}}{\text{gram}}$$

Equation (10) thereby becomes, for a coal pyrolysis system⁵

$$k' = \frac{\text{molar conc. of sites}}{\text{gram}} \mathcal{H} \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (11)$$

which may be written in the form:

$$\ln \left(\frac{h}{\mathcal{H}k} \frac{k'}{T} \right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \frac{\Delta S^\ddagger}{R} + \ln [C^\ddagger] \quad (12)$$

where $[C^\ddagger]$ denotes the molar concentration of active sites per gram of coal. The transmission coefficient, \mathcal{H} , is usually taken as unity. A plot of

$\ln \left(\frac{h}{\mathcal{H}k} \frac{k'}{T} \right)$ vs. $\frac{1}{T}$ will yield a straight line of slope $-\frac{\Delta H^\ddagger}{R}$ and intercept $\left(\frac{\Delta S^\ddagger}{R} + \ln [C^\ddagger] \right)$.

Such a plot is contained in Figure 5 for the data of the first order region, which yields a value for ΔH^\ddagger of 4.1 kcal. per mole for this region. A similar plot of the data for the first 60 minutes yields a value for ΔH^\ddagger of 35.6 kcal. per mole for that region. The intercepts at $1/T = 0$ yield values for the quantity $(\Delta S^\ddagger + R \ln [C^\ddagger])$ of -12 and -63 for the first 60 minutes and the first order region, respectively.

An expression has been derived by Eyring, et. al. (4) whereby the entropy of activation for a heterogeneous reaction may be calculated from experimentally determined reaction rates and energies of activation:

$$k' = e^{-(\Delta n^\ddagger - 1) \frac{kT}{h}} e^{-E/RT} e^{\Delta S^\ddagger/R} \quad (13)$$

where Δn^\ddagger is the increase in the number of molecules accompanying the formation of the activated complex. The standard state assumed in the use of this equation includes unit concentration of reaction sites. If, as indicated earlier, the reaction during the first 60 minutes is approximately second order, followed by a period of first order reaction, Δn^\ddagger becomes -1 and zero for the two regions, respectively. Equation (13) then yields values of ΔS^\ddagger of -12 e.u. for the first 60 minutes of the pyrolysis reaction, and -63 e.u. for the first order region.

An entropy value of -63 e.u. is unrealistic for the pyrolytic decomposition of coal. Further, it is unlikely that a change in entropy of activation of more than a few (say three or four) entropy units would be observed during the pyrolytic reactions, as an entropy change would reflect a corresponding change in the complexity of the activated complex. Equation (12) demonstrates that the entropy values as determined experimentally, and as calculated from equation (13), include the possible variations in molar concentration of active sites, and reason leads to the conclusion that the concentration of sites is perhaps very different from 1 mole per sq. cm. of surface, as discussed later. Further, the large change in ΔS^\ddagger as determined from equation (12) is perhaps best explained in terms of a change in concentration of active sites.

If it were to be assumed that the entropy does not change during the course of the reaction (which would imply that the nature of the activated complex remains essentially constant), and that the change in apparent entropy is to be accounted for completely by a change in concentration of active sites, combining the expressions

$$\Delta S^\ddagger + R \ln [C_1^\ddagger] = -12 \text{ and } \Delta S^\ddagger + R \ln [C_2^\ddagger] = -63,$$

we get:

$$\frac{[C_1^\ddagger]}{[C_2^\ddagger]} = 10^{11} \quad \text{or} \quad [C_2^\ddagger] = 10^{-11} [C_1^\ddagger] \quad (14)$$

indicating a decrease in concentration of active sites as the reaction proceeds, of the order of 10^{-11} .

It has been observed (2) that the constant "A" in the Arrhenius equation assumes values of the order of 10^{13} for unimolecular reactions, and of the order of 10^{10} for bimolecular reactions. Inasmuch as the apparent order of reaction changes from approximately second order in the initial stages to first order after 90 minutes, allowance may be made in the entropy consideration for a change in "A" of 10^3 (bimolecular to unimolecular). In addition, noting that an entropy change of 4.6 units ($2.3 \times R$) corresponds to a change in concentration of active sites by a factor of 10, we may consider that the entropy decreases by this amount during the course of the reaction. An entropy change greater than this is very improbable. The sum of these two factors for maximum effect would account for a change in apparent entropy of -18 units. Accordingly a decrease in concentration of active sites at least of the order of 10^7 is indicated, corresponding to a change in apparent entropy of -33 units.

As a coal sample is heated at a slow and constant rate a period of rapid evolution of volatile material is observed in the vicinity of 400°C , at temperatures when the fluidity of the coal is rather rapidly increasing. Several investigators (3, 11) have concluded that the plastic state is the result of the decomposition reactions occurring in this temperature range. These initial reactions, at least some of them, appear to be extremely rapid, as indicated by the work of Shapatina, et. al. (9), and of Stone and coworkers (10), where the coal samples were heated under conditions such that the small coal particles remained effectively separated during heating and attained the temperature of the reaction zone very rapidly. The data of Shapatina indicate that the particles attained thermal equilibrium with the reaction zone within 0.5 second after introduction into the heated region. Under these conditions, of the maximum volatile product yield obtainable at 450°C , 32% was evolved during the first 0.8 second after introduction into the heated zone. It should be noted that under the conditions of the experiment escape of the volatile matter in these initial seconds was not impeded by fusion of the coal particles. In contrast to the very rapid heating rates attained by Shapatina, times up to five minutes in length were required to attain thermal equilibrium in the present study, as reported also by Berkowitz (1) in his studies.

Shapatina noted in the initial seconds a rapid evolution of CO_2 , H_2O and CO , accompanied by a somewhat slower and more extended evolution of tar, gaseous hydrocarbons and hydrogen,

with further evolution of CO and CO₂. Previous studies (12) have demonstrated that when a high volatile coal is heated at constant rate, CO₂, CO and H₂O, apparently physically adsorbed within the coal pores, are liberated at temperatures below 200°C. At temperatures approaching 400°C. further evolution of these gases occurs, believed to be associated with chemical decomposition of the coal structure. Kessler (7) noted the occurrence of reactions in this temperature range whereby aliphatic chains were split off and evolved from the coal. Stone, et. al. observed the evolution of appreciable quantities of methane and lesser amounts of other hydrocarbons in this temperature range. Several investigators have noted, as in the present experiments, the appearance of oily products in the volatile matter at temperatures when the coal enters the plastic state. These products have been reported (12) to be initially paraffinic in nature, with naphthenes appearing as the temperature is increased.

It seems probable that during the time of these initial rapid reactions, thermal decomposition is occurring within the coal mass, as well as at sites on the surfaces, both external and internal, which existed in the original coal sample. The products of the primary decomposition, called "fluid coal" by Fitzgerald (3) and "metaplast" by van Krevelen, et. al. (11) being thus dispersed throughout the coal mass, impart a degree of plasticity to it. Whereas in the studies of Shapatina and of Stone the coal particles were effectively separated during this initial period such that the volatile products could rather readily escape from the small particles, in an actual coking operation, as under conditions obtaining in the present study, as well as in the investigations of Fitzgerald, van Krevelen, and Berkowitz, the particles fuse together, inhibiting the escape of the volatile products and resulting in a pressure build-up within the pore spaces within the coal mass. Such a pressure build-up has been extensively discussed by Berkowitz. (1)

Fitzgerald observed that, at 407°C, a state of maximum fluidity in the coal mass was achieved after 25 minutes, following which a decay in the plastic state occurred, with an effective period of plasticity of some 80 to 90 minutes at this constant temperature. Van Krevelen observed that, as the temperature of the test was increased, the time required to attain maximum fluidity was decreased, and the rate of decay of the plastic state increased. It should be noted that the degree of fluidity continues to increase for appreciable times, up to 25 minutes, after the coal has attained the predetermined constant temperature, indicating that some of the primary decomposition reactions are still in progress.

The initial period of 50-60 minutes, during which the over-all reaction order as observed ranges from 1.8 to 2.2, spans the time when the coal manifests a measurable degree of fluidity, and as depicted in the models of Fitzgerald and of van Krevelen, includes the Primary decomposition reactions which produce the plastic or fluid material as well as the secondary reactions which result in the disappearance of the plastic condition. The coal is in a state of measurable fluidity throughout most of this period such that reactions may be considered to occur throughout the coal mass, and not be restricted to sites associated with surfaces. Each of the reactions, considered separately, may be considered as a first approximation to be unimolecular and first order, inasmuch as most decomposition reactions are of such a nature. However the picture of simultaneous occurrence of reactions of both types indicated here becomes further complicated by diffusion problems produced by the appearance and subsequent decay of a plastic state. This combination would not necessarily produce a rate of change in the rate of escape of volatile materials which would follow a first order rate law. The observed gradual increase in reaction order as temperature increases lends support to the proposition that a physical phenomenon, such as diffusion, plays an important role in the processes of this period.

The observed sequence of events of the present study include the following: (1) an initial rapid evolution of volatile products with an observed rate of decrease in the rate of evolution through the first 50-60 minutes such as to approximately fit the equation $\frac{dx}{dt} = k_2(a-x)^2$; (2) a period of changing rate of decrease in rate of product evolution, of approximately 30 minutes duration, whereby the second order rate decays to a first order rate; (3) a period of some 100 minutes wherein the rate of decrease in the rate of product evolution fits the equation $\frac{dx}{dt} = k_1(a-x)$; (4) a second period of decay in the rate of decrease in the rate of

product evolution, of varying duration depending upon the temperature, reaching a period of observed zero order rate; (5) a long period of slow but steady rate of product evolution according to the equation $\frac{dx}{dt} = k$. The series of events, steps (2) through (5), all included, cannot be

conceived to be due to diffusional control throughout, as was proposed by Berkowitz. It is doubtful that diffusion plays a major role in the observed rates of product evolution after the first 90 minutes, or after the observed rate is first order. Rather it is believed that the first order period represents an actual first order reaction, with energy of activation of the order of 5.36 kcal. per mole as observed. It should be noted that in the studies of Shapatina and of Stone

a first order region was observed to follow the period of rapid evolution of volatile products, with energy of activation of 5.3 kcal. per mole in Shapatina's work and 6.7 kcal. per mole in the work of Stone.

It was noted above that the progress of the pyrolytic reaction is accompanied by a change in the quantity $\Delta S^\ddagger + R \ln [C^\ddagger]$, as determined from plotting equation (12), from -12 units in the initial stages to -63 units in the first order region. It has been observed that in a bond-breaking unimolecular reaction the activated complex is often very much like the original reactant, in which case the value of ΔS^\ddagger is zero. If it is assumed that the reactions occurring in the thermal decomposition of coal are of this nature, the value of -12 units must be associated with the concentration of reacting sites.

In using equation (13) to calculate the entropy of activation for the initial 60 minutes of pyrolysis, which also yields a value of -12 units, the assumption was made that the standard state of unit concentration of reacting sites obtained. It is apparent this assumption is not valid. It was observed earlier that an apparent entropy change of 4.6 units was equivalent to a change in concentration of reacting sites by a factor of 10. Hence the value of $\Delta S^\ddagger + R \ln [C^\ddagger] = -12$ could be explained if the actual number of reacting sites is smaller than the assumed value by $\frac{12}{4.6}$ or by a factor of 410. If a model (6) for the structure of coal is examined, one may readily conclude that only a small fraction of the existing bonds would be of such nature as to rupture at the temperatures here indicated, to lead to the products which have been observed to evolve at these temperatures.

The decrease in value for $\Delta S^\ddagger + R \ln [C^\ddagger]$ from -12 to -63 units was observed to represent a decrease in concentration of reacting sites per gram of coal of the order of 10^7 , if the initial period of 50-60 minutes represents a bimolecular reaction, or a decrease of the order of 10^{11} if both periods were characterized by unimolecular reactions. The sites available for the thermal decomposition reactions believed to occur in the initial moments of pyrolysis, associated largely with the plastic state, would be large in number and not restricted to surfaces in existence in the original coal. However the reactions occurring during the first order period, following the resolidification of the coal, would occur only at selected sites upon existing surfaces, internal or external. The large negative value of -63 units, as indicated above, requires that the concentration of reacting sites be low, and this in turn could explain the slow rate of product evolution in spite of the low activation energy of 5.36 kcal. per mole.

Finally it may be noted that observations were made with sample of -200 +250 mesh (74 to 60 microns particle diameter) and the results compared with those from the -40 +60 mesh (417 to 246 microns) used throughout this study. No significant difference in the weight loss-time curves was observed. Decreasing the particle size in the degree indicated would increase the external surface area not more than a factor of 10 in the range 10^{-3} to 10^{-2} square meters per gram. Determinations of the total surface area of coal samples of -40 +60 mesh have yielded values of 50 to 200 square meters per gram. (8) Thus reactions occurring on surfaces or within the mass would not be appreciably altered in this regard. The rate of attaining thermal equilibrium may be increased under certain conditions by decreasing the particle size, thus displacing the curve, but such did not occur in the present study.

ACKNOWLEDGMENT

The Research reported herein was supported by the U. S. Office of Coal Research and by the University of Utah under Contract #14-01-0001-271.

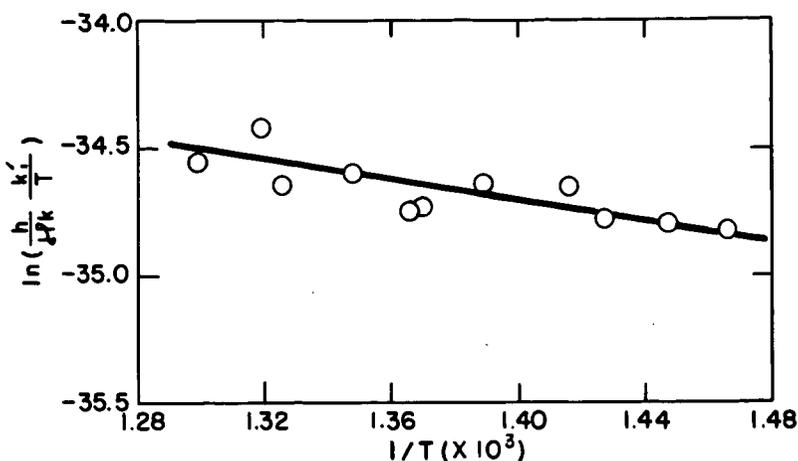


Figure 5. Eyring Plot for Evaluating ΔH^\ddagger and ΔS^\ddagger ,
First Order Region.

LITERATURE CITED

- (1) Berkowitz, N., *Fuel*, **39**, 47 (1960).
- (2) Daniels, F., and Alberty, R. A., "Physical Chemistry", New York, Wiley (1961).
- (3) Fitzgerald, D., *Fuel*, **35**, 178 (1956).
- (4) Glasstone, S., Laidler, K. J., and Eyring, H., "Theory of Rate Processes", New York, McGraw-Hill (1941).
- (5) Hill, G. R., "Experimental Energies and Entropies of Activation--Their Significance in Reaction and Rate Prediction for Bituminous Coal Dissolution", paper submitted for publication in *Fuel*.
- (6) Hill, G. R., and Lyon, L. B., *Ind. and Eng. Chem.*, **54**, 36 (1962).
- (7) Kessler, M. F., and Vecerikova, V., *Brennstoff-Chem.*, **40**, 52 (1959).
- (8) Kini, K. A., *Fuel*, **42**, 103 (1963).
- (9) Shapatina, E. A., Kalyuzhnyi, V. V., and Chukhanov, Z. F., *Doklady Acad. Nauk S.S.S.R.*, **72**, 869 (1950).
- (10) Stone, H. N., Batchelor, J. D., and Johnstone, H. F., *Ind. and Eng. Chem.*, **46**, 274 (1954).
- (11) van Krevelen, D. W., Huntjens, F. J., and Dormans, H. N. M., *Fuel*, **35**, 462 (1956).
- (12) Wilson, P. J., Jr., and Wells, J. H., "Coal, Coke and Coal Chemicals", New York, McGraw-Hill (1950).