

CHEMISTRY AND KINETICS OF THE HYDRO-DESULFURIZATION OF COAL

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INTRODUCTION

Most of the published data on the hydro-desulfurization of coal are unsuitable for detailed kinetic interpretation because equilibrium conditions were partially or wholly achieved. Forty years ago Snow (1) showed almost ten-fold less desulfurization with "fast" heating versus "slow" heating. The present paper describes the theoretical extension and experimental application of the non-isothermal method of Juntgen (2) to the hydro-desulfurization of ten bituminous coals ranging from 1 to 5% sulfur.

This powerful method overcomes the above difficulty by treating temperature as a controlled variable. Essentially continuous measurements of reaction products in a flow system provide experimental functions whose theoretical interpretations identify sets of chemical reactions which are responsible for desulfurization. The kinetics of desulfurization of all ten coals are accounted for satisfactorily by five chemical reaction systems. This method gives activation energies and frequency factors for each chemical reaction.

Independent or idealized experiments were also conducted to test separately these results. In addition, the kinetics of a series of back reactions were also measured including the scavenging of hydrogen sulfide by calcium oxide. In this paper, the theory is summarized, the experimental conditions are described, and the results are summarized, together with a discussion of their significance to processes for control of environmental pollution.

THEORY

The non-isothermal kinetic method circumvents the uncontrolled occurrence of chemical reactions during the time that a sample is being heated to a desired isothermal reaction temperature. This is accomplished by maintaining a constant rate of heat during the experiment. Consider a solid gas reaction in a flow system which produces a new gas as a reaction product. Under the conditions of a constant heating rate of M degrees per minute the usual Arrhenius equations, $k = k_0 \exp(-E/RT)$, can be expressed in terms of the temperature rate of evolution of the new product gas, dV/dT , and the total volume of product gas when the reaction has gone to completion, V_0 .

$$\frac{dV}{dT} = \frac{V_0 k_0}{M} \exp \left\{ - \left[\frac{E}{RT} + \frac{k_0 R T^2}{M E} \right] \right\} \quad (1)$$

where R is the usual gas constant T is the absolute temperature.

The graphical expression of this function of Equation (1) is shown in Figure 1. Three important experimental parameters are obtained from this function, the integral of evolved gas V_0 which is shown as the cross-hatch area under the graph, the temperature of the maximum T_0 , and the temperature rate of evolution of the product chemical at the temperature maximum, $(dV/dT)_{T_0}$. In order to solve this equation for the activation energy, E , and the frequency factor, k_0 , it is convenient to introduce two dimensionless parameters,

$$a = E/RT_0 \text{ and } b = T_0/V_0 (dV/dT)_{T_0} \quad (2)$$

when these dimensionless parameters are substituted in the transcendental Equation (1), we obtain the following relationship

$$a = b \exp(1 - 2/a) \quad (3)$$

which by taking logarithms may be written as

$$\ln a + 2/a = 1 + \ln b \quad (4)$$

We may immediately compute b and, therefore, $1 + \ln b$ from the experimental measurement of the curve in Figure 1. Equation (4) may then be solved graphically by plotting this equation. We can read directly the value of a corresponding to the experimentally determined value of $1 + \ln b$.

Knowing a the activation energy and frequency factors are given by:

$$E - RT_0 a \text{ and } k_0 = (M a/T_0) e^a \quad (5)$$

This derivation is given in greater detail together with extensions to reversible and for back reactions in reference (3).

EXPERIMENTAL

Ten samples of bituminous coal ranging from 1 to 5 percent sulfur were provided by the Illinois Geological Survey and the U.S. Bureau of Mines. These include coals from Illinois, Ohio, Maryland, Pennsylvania and Kentucky. A.S.T.M. analyses were done on these coals for forms of sulfur, mineral analyses, proximate analyses, and sulfur in ash and fixed carbon.

Heating was done with flow hydrogen in a furnace controlled by a linear temperature programmer. Continuous analyses were done with a special mass spectrometer designed and built for this purpose. The experimental set up is shown schematically in Figure 2.

HYDROGEN SULFIDE EVOLUTION FROM COAL

In a hydrogen atmosphere the sulfur in the coal reacts with hydrogen to produce hydrogen sulfide. A typical H_2S evolution curve for a non-isothermal experiment on coal heated in hydrogen is given in Figure 3. These results were obtained using a hydrogen flow rate of 1 litre per minute over a 250 mg sample of Illinois coal No. 4, as identified in our report, reference (3). The heating rate

was 4°C per minute. Clearly the H₂S evolution does not occur by a single process. Since sulfur exists in coal in many different forms, e.g. pyrite, sulfide, sulfate and several different types of organic sulfur, this result is expected. Each individual reaction of the form, coal + H₂ → H₂S, should yield an H₂S evolution curve similar to that shown in Figure 1. The parameters characterizing that curve T₀, V₀, and (dV/dT)_{T₀} should reflect the kinetics for the individual process. The overall H₂S evolution curve will be composed of the sum of the set of overlapping curves characterizing each of the individual reactions. In the absence of any knowledge on the individual processes an experimental result such as given in Figure 3 can be resolved into individual processes in infinitely many ways. However, if the kinetics of the individual processes are known a priori, a unique resolution of the experimental results can be achieved.

Since iron pyrite is known to be a major source of sulfur in coal, we conducted non-isothermal experiments on samples of iron pyrite obtained from the U.S. Bureau of Mines. In these experiments the back reaction of H₂S with iron was suppressed by using a very high hydrogen flow rate and a very small sample of iron pyrite. The heating rate employed was 4°C per minute. The experimental data on the non-isothermal evolution of H₂S from pyrite are shown in Figure 4. These results clearly indicate two reactions producing hydrogen sulfide; firstly the reduction to FeS and secondly to Fe.

These experimental results on pyrite may be analyzed in a straight forward manner to yield the kinetic parameters for the two reactions. The procedure used is as follows: First we sketch in two peaks of the type shown in Figure 1 which give a reasonable fit to the experimental points. The values of the parameters characterizing the curves are read off of these curves. These parameters are the temperature corresponding to each of the peaks, T₀(°K), the area of the peak, V₀, and the amplitude of the peak at T₀. From these values a dimensionless parameter b as given by Equation (2) is computed and used to graphically obtain a. The values of the activation energies E and pre-exponential factor k₀ are then computed using Equation (5). The results are then double checked by recomputing the H₂S evolution peak corresponding to these parameter values using Equation (1). The calculated peaks are then replotted with the experimental data and the accuracy of the fit is checked. By these procedures we find for the pyrite reaction E = 47 kilocalories per mole and k₀ = 2.8 × 10¹² (atm H₂)⁻¹ min⁻¹ and for the sulfide reduction E = 55 kilocalories per mole k₀ = 2.1 × 10¹³ (atm H₂)⁻¹ min⁻¹. The calculated H₂S evolution curves for these two reactions are compared with the experimental data in Figure 5. The calculated H₂S evolution for the sum of the two processes is shown in the dash line in the figure. The fit between calculation and experimental could obviously be improved by slightly adjusting the amplitudes of the two peaks. However, the amplitudes reflect the stoichiometries of the reaction while the locations and shapes of the peaks reflect the kinetics. These results suggest that the pyrite sample was not pure FeS₂ but rather initially contained a small amount of sulfide.

DESULFURIZATION KINETICS FOR ORGANIC SULFUR

The pyrite sulfur clearly accounts for most of the inorganic sulfur found in coal, but there is also generally substantial amounts of organic sulfur and it is well known that this sulfur may exist in many different kinds of bonding arrange-

ments within the coal. In an attempt to investigate behavior of the organic sulfur on a somewhat simpler, but, related system, we prepared artificially some organic sulfur-containing material. A sample of essentially mineral free charcoal was reacted with hydrogen sulfide in a stream of helium to produce a sulfurated carbon which contained approximately 2.5% sulfur. Non-isothermal measurements on the desulfurization of this material in both hydrogen and helium were carried out. The results of one such experiment are given in Figure 6. In this experiment the sample size and flow rate of hydrogen used were the same as that employed on the major series of non-isothermal experiments on coals. It is clear from the results of studies to date on the sulfurated carbon that a single simple reaction does not account for the behavior of this material. Pending the completion of the kinetic investigation on the complex sequence of reactions involved in the desulfurization of these relatively stable organic sulfur species the empirical result corresponding to the smooth curve shown in Figure 8 has been used in the analysis on the results on coal. We have designated this form of organic sulfur as Organic III.

To proceed further in our analysis of the experimental result given in Figure 3 it is necessary to consider the results on all ten coals studied. The results of non-isothermal kinetic experiments for ten coals studied under similar experimental conditions are summarized in Figures 7 and 8. Certain points in common and certain differences should be noted in these results. All of the H_2S evolution curves show a peak in the range between $380^\circ C$ and $430^\circ C$. All of the coals high in pyrite show secondary peaks very close to those found experimentally for the sample of pyrite as illustrated in Figure 5. However, in general for these coals these peaks appear to occur at slightly lower temperatures typically from $10 - 20^\circ C$. If we assume that results on the pyrite are valid for coal we would expect that the presence of the carbon should have little effect on the activation energies for these reactions. But, because of both the production of hydrogen from within the coal and the possibility of the absorption of hydrogen on the carbon surface, we might expect that the pre-exponential factor which is expressed in terms of the concentration of hydrogen in the bulk gas stream might be increased in the case of the coal by these effects increasing surface concentration of hydrogen for a given bulk gas concentration of hydrogen. A downward shift in the temperature corresponding to the peak in the H_2S evolution from pyrite of $20^\circ C$ corresponds to an increase in the pre-exponential factor of about 40%. Data obtained by us and by Powell in his earlier work on the forms of sulfur in char, as a function of carbonizing temperature, support the hypothesis that the secondary peaks in these non-isothermal results do correspond to the reaction of the pyritic and sulfide sulfurs. Similarly this work suggests that the low temperature peaks in the non-isothermal results correspond to the reaction of relatively unstable organic sulfur compounds in coal. A single reaction cannot account for the variation in the location and shape of the low temperature peak for all of these ten coals. However, we have found that two processes, one with T_0 corresponding to $380^\circ C$ and a second with T_0 corresponding to $430^\circ C$ satisfactorily account for the low temperature peak in all ten coals. The kinetic parameters for these two processes which we have designed as Organic I and Organic II are as follows: ORGANIC I, $E = 34.5$ kcal/mole, $K_0 = 3.1 \times 10^{10}$ (atm H_2) $^{-1}$ min $^{-1}$; ORGANIC II : $E = 41.5$ kcal/mole, $K_0 = 2.8 \times 10^{11}$ (atm H_2) $^{-1}$ min $^{-1}$. It is, of course, possible that more than two processes contribute to this low temperature peak, however, only the two are required to account for the experimental

results.

We will now discuss the resolution of the experimental result given in Figure 3 into individual processes. The five processes we have identified in the preceding discussion are three forms of organic sulfur, pyrite, and sulfide. This result in the individual processes were performed graphically by drawing in the peaks corresponding to the individual processes and adjusting the amplitude of the peak without changing the peak location until a best fit to the experimental data is obtained. The fit is determined by comparing the sum of all of the H_2S evolution peaks with the experimental data. The result of this analysis is shown in Figure 9. In the figure the dotted line represents the sum of the individual processes with the amplitudes shown in the figure and the agreement with the experimental points is quite satisfactory with one exception. In the region about $530^\circ C$ there appears to be a significant amount of sulfur evolution which is not accounted for by these five processes. This discrepancy occurs in most of the coals studied but is particularly prominent in coal No. 7, the Maryland coal. This discrepancy may indicate that an additional desulfurization process occurs which we have not taken into account, however, our recent experiments, in an attempt to further understand the Organic III set of reactions, have indicated that the results obtained on the artificial sample of sulfurated carbon may not be directly applicable to coal. It now appears that a proper representation of the Organic III sulfur removal may remove this discrepancy.

One additional point that should be mentioned concerning this analysis of Illinois No. 4 coal is that the total amount of sulfur evolved from the pyrite and sulfide processes appears rather lower than would be expected from the amount of iron pyrite in the coal from the ASTM analysis. However, this coal contains an unusually high calcium content. Our separate experiments on the reaction of H_2S with calcium oxide and calcium carbonate have shown that the reaction of H_2S with these materials in the temperature range above 500° is extremely fast so that nearly one half of the sulfur, which might otherwise be evolved in the pyrite and sulfur peaks, is converted to calcium sulfide and retained in the char. Similar procedures to those described above have been employed in analyzing all ten of the coals studied.

KINETICS OF DESULFURIZATION

We may summarize the chemical reactions and the rate data of coal desulfurization in hydrogen atmospheres by listing our measured kinetics parameters for the five major reactions and two back reactions, as shown in Table I.

Non-isothermal studies were also made of the removal of H_2S by calcined dolomites and limestones and the regeneration kinetics of the resulting calcium sulfide. The kinetic parameters for these rate data are shown in Table II.

The significance of these results to considerations of sulfur control can be seen by expressing them as rate constants versus temperature over the range of engineering interest. The rate constants for these reactions are shown from $400^\circ C$ to $1000^\circ C$ in Figure 10. There emerges a desulfurization band which encompasses the desulfurization reactions which account for the hydrodesulfurization of the ten bituminous coals studied.

TABLE I

CHEMICAL REACTIONS AND RATE DATA OF COAL DESULFURIZATION
IN HYDROGEN ATMOSPHERES

<u>No.</u>	<u>Reaction</u>	<u>E^{kcal}/mole.</u>	<u>k₀</u>
1	(Org-S) _I + H ₂ → H ₂ S	34.5	3.1 × 10 ¹⁰ (atm H ₂) ⁻¹ min ⁻¹
2	(Org-S) _{II} + H ₂ → H ₂ S	41.5	2.8 × 10 ¹¹ " "
3	FeS ₂ + H ₂ → H ₂ S + FeS	47	2.8 × 10 ¹² " "
4	FeS + H ₂ → Fe + H ₂ S	55	2.1 × 10 ¹³ " "
5	(C-S) + H ₂ → H ₂ S	52	~2 × 10 ¹³ " "
6	Fe + H ₂ S → H ₂ + FeS	18	6.5 × 10 ⁶ (atm H ₂ S) ⁻¹ min ⁻¹
7	Coke + H ₂ S → (C-S) + H ₂	32	2.3 × 10 ⁸ " "

TABLE II

8	CaO + H ₂ S → CaS + H ₂ O	38	4.7 × 10 ¹³ (atm H ₂ S) ⁻¹ min ⁻¹
9	CaS + H ₂ O → CaO + H ₂ S	55	1.0 × 10 ¹⁴ (atm H ₂ O) ⁻¹ min ⁻¹
10	CaCO ₃ → CaO + CO ₂	58	3.0 × 10 ¹² min ⁻¹
11	CaO + CO ₂ → CaCO ₃	17	5.0 × 10 ⁴ (atm CO ₂) ⁻¹ min ⁻¹

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3. (a) Scientific Research Instruments Corporation Report No. SRIC 68-13 (1969), (b) Scientific Research Instruments Corporation Report No. SRIC 69-10 (1969).

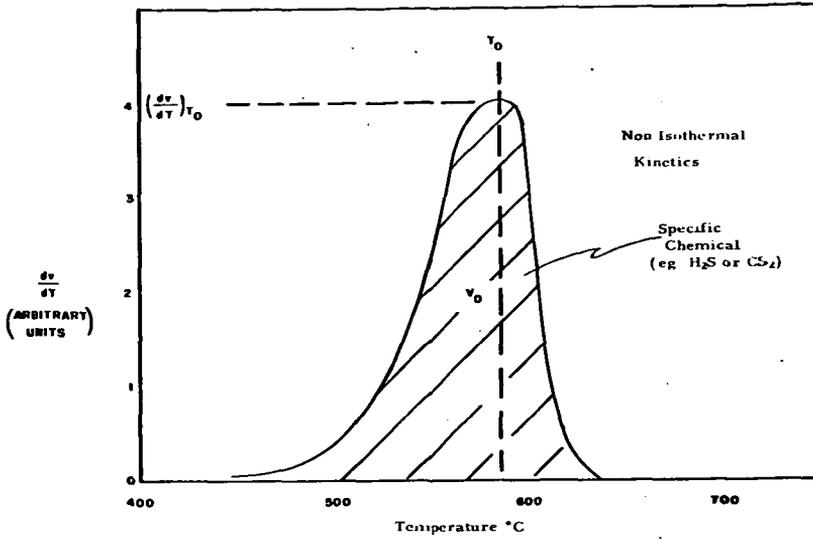


Figure 1. Typical outgassing kinetics curve vs. temperature. T_0 is temperature at peak. $(dV/dT)_{T_0}$ is peak height, V_0 is area.

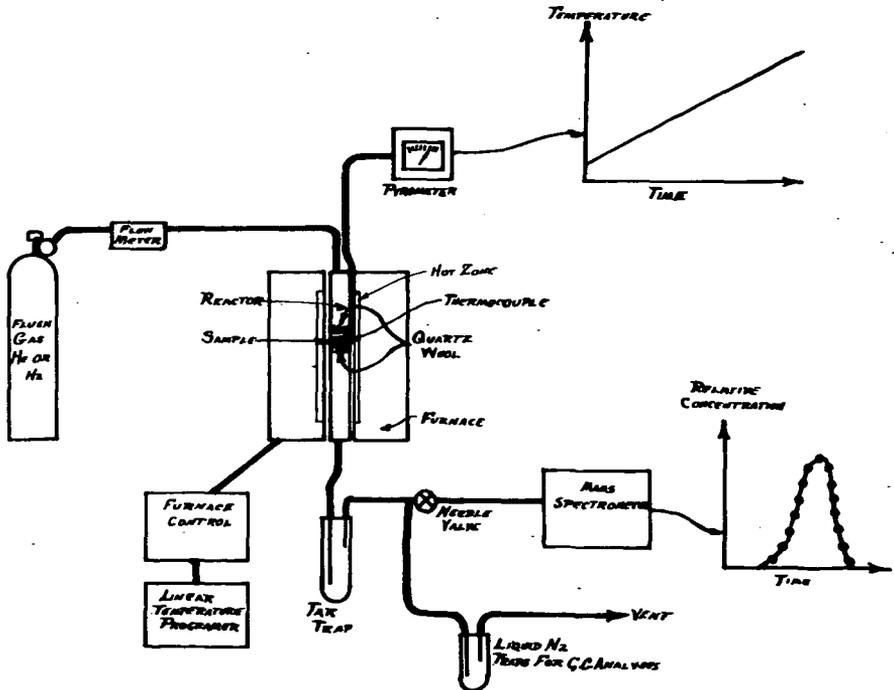


Figure 2. Schematic diagram of experimental apparatus.

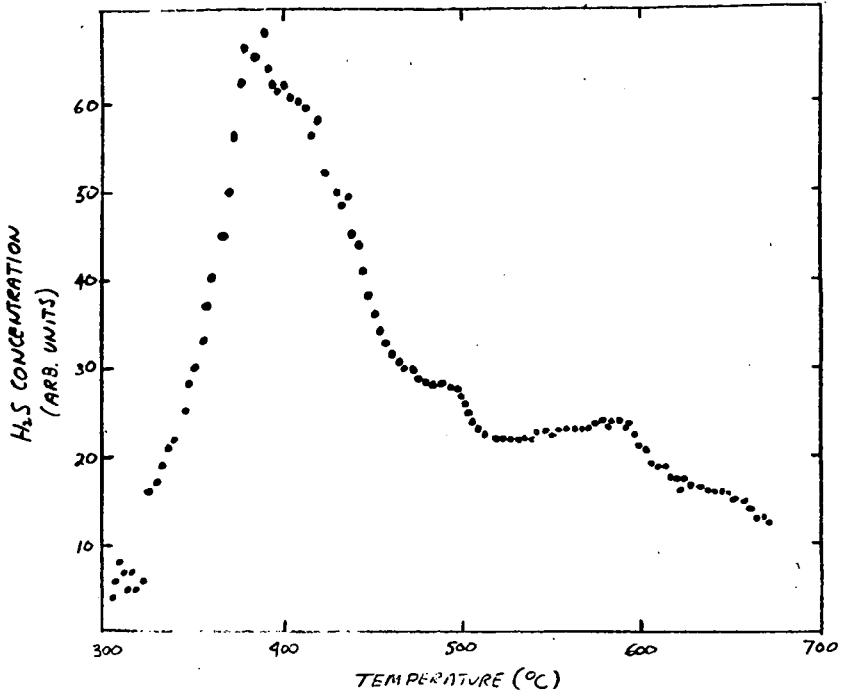


Figure 3. H₂S evolution in a non-isothermal experiment at one atmosphere of hydrogen on Illinois 5% sulfur coal, SRI No. 4.

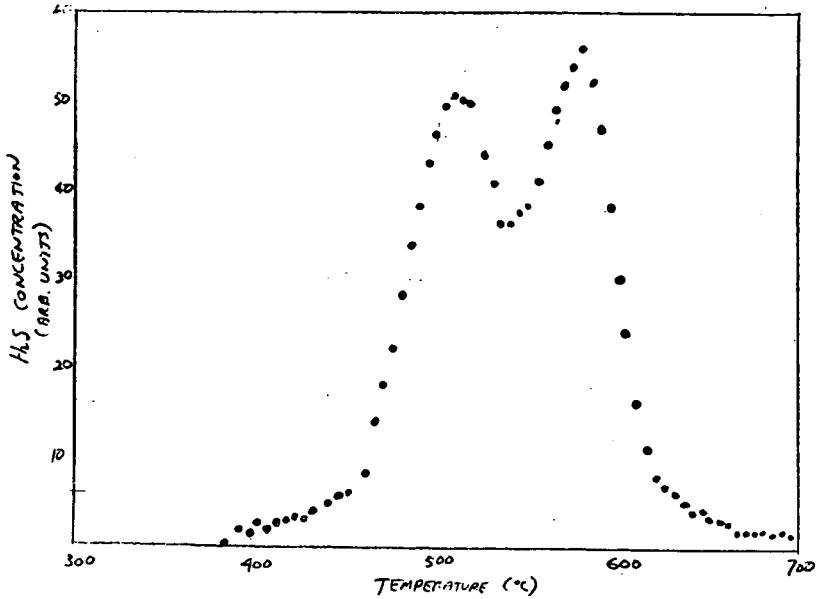


Figure 4. H₂S evolution in a non-isothermal experiment at one atmosphere of hydrogen on pyrite.

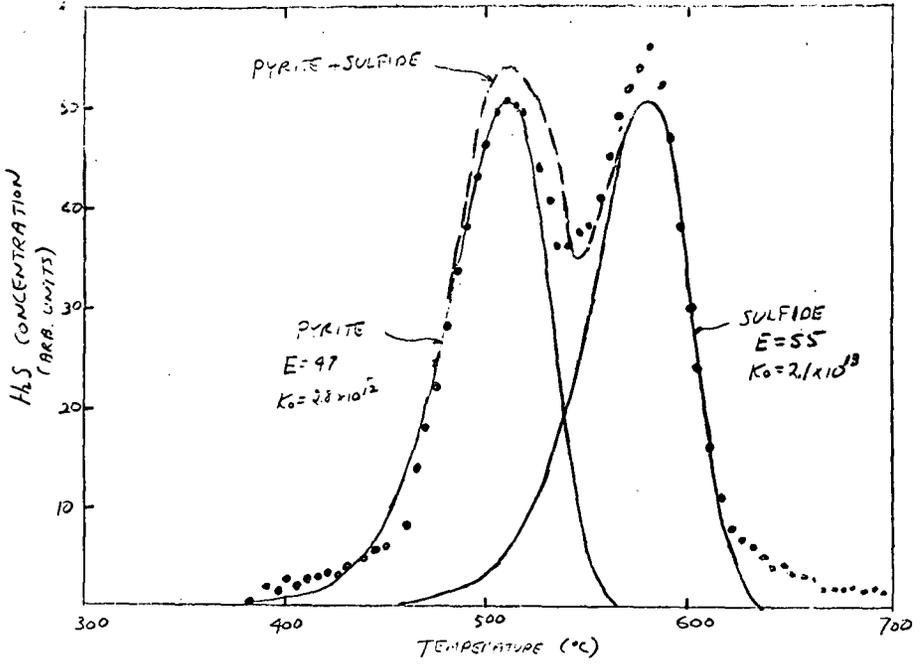


Figure 5 . Kinetic analysis of the non-isothermal measurement on pyrite.

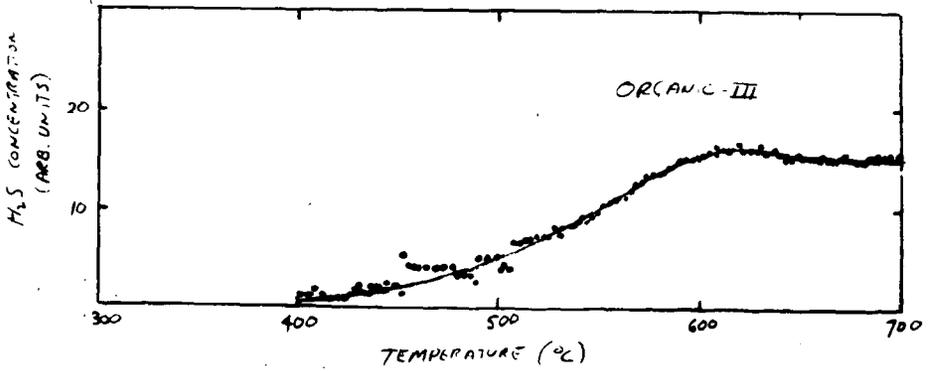


Figure 6. H₂S evolution in non-isothermal experiment at one atmosphere of hydrogen on sulfurated carbon prepared from charcoal.

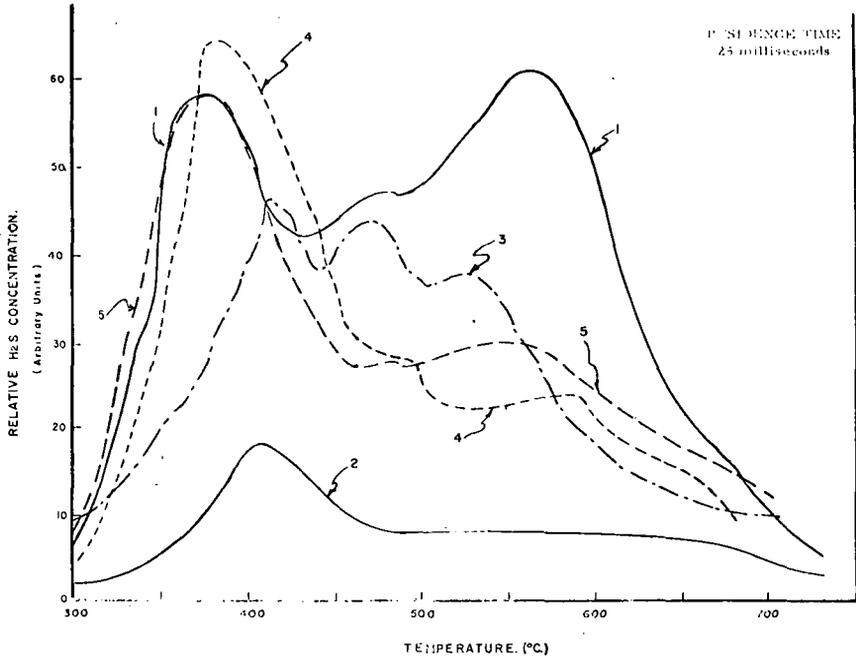


FIGURE 7. NON-ISOTHERMAL H_2S EVOLUTIONS IN H_2 FROM COALS SRI NUMBERS 1 THROUGH 5.

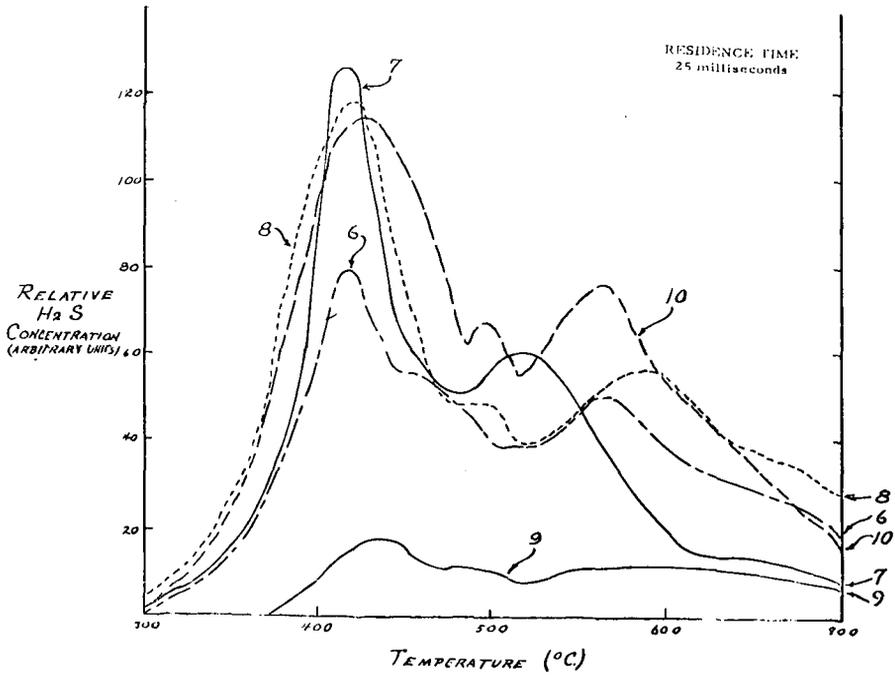


FIGURE 8. NON-ISOTHERMAL H_2S EVOLUTIONS IN H_2 FROM COALS SRI NUMBERS 6 THROUGH 10.

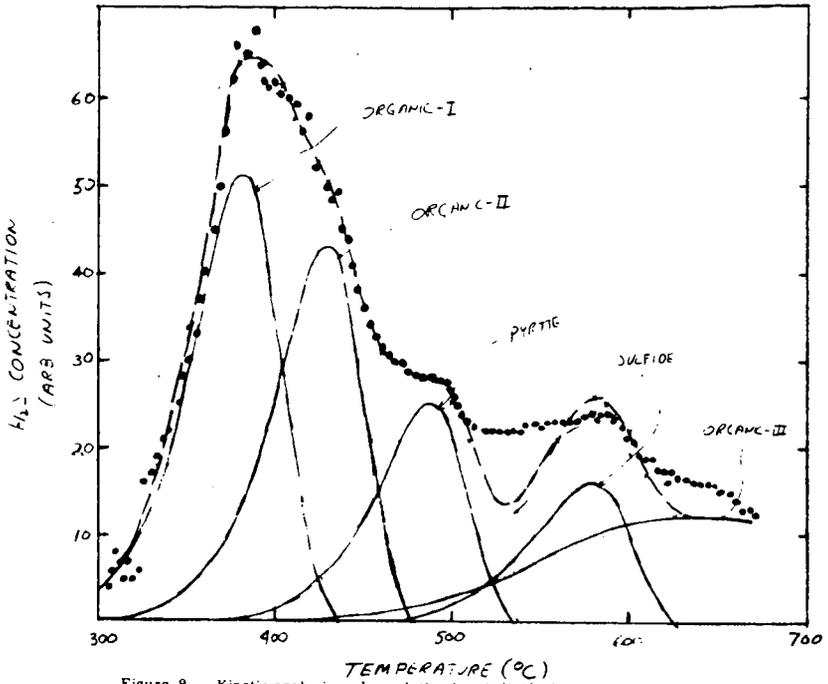


Figure 9. Kinetic analysis and resolution into individual processes of the H_2S evolution in a non-isothermal experiment at one atmosphere of hydrogen on Illinois 5% sulfur coal, SRI No. 4.

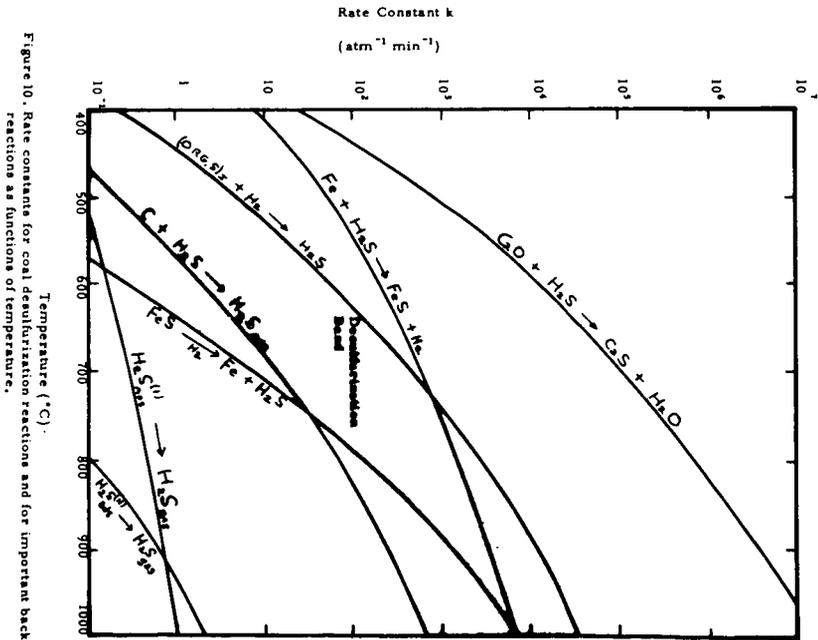


Figure 10. Rate constants for coal desulfurization reactions and for important back reactions as functions of temperature.