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A MATHEMATICAL MODEL FOR THE PYROLYSIS OF
OIL SHALE USING DISTRIBUTION OF
ACTIVATION ENERGY KINETICS

By

John Arthur Marlatt

A THESIS

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ABSTRACT

A MATHEMATICAL MODEL FOR THE PYROLYSIS OF OIL SHALE USING DISTRIBUTION OF ACTIVATION ENERGY KINETICS

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Mathematical simulations of commercial oil shale retort operations require an understanding of the rate processes which occur in individual oil shale particles. Previously, the kinetics of oil shale devolatilization have been modeled using simple kinetic schemes but have failed to predict the production of volatile products over a wide range of pyrolysis conditions. A prototype model was developed in this study which incorporated the kinetics of devolatilization, a mechanism for intraparticle mass transport of volatile products, and the kinetics for intraparticle product degradation. The complex kinetics associated with oil shale devolatilization were interpreted using the distribution of activation energies theory developed previously for coal pyrolysis. A Gaussian distribution function was used to represent the activation energies for the reactions producing volatile products. The parameters in the model were estimated from isothermal weight loss data

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for western oil shale. A favorable comparison was made between the model prediction and data from a nonisothermal experiment.

Dedicated to
Janet Lee Marlatt

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LIST OF NOMENCLATURE

A	collection of constants given on page 44 $[\frac{(kg \ sec)}{m^3}]$
b	heating rate $[^{\circ}K/sec]$
B	collection of constants given on page 44 $[\frac{kg}{(m^3 \ sec)}]$
C_{iR}	mass concentration of a reactive volatile species i in the gas phase of the particle $[kg/m^3 \text{ of gas phase in the particle}]$
C_{iBR}	mass concentration of a reactive volatile species i bound in the solid phase of the particle $[kg/m^3 \text{ of solid phase in the particle}]$
C_{iBR}^0	initial mass concentration of a reactive volatile species i bound in the solid phase of the particle $[kg/m^3 \text{ of solid phase in the particle}]$
$C_{iR\infty}$	mass concentration of a reactive volatile species i in the sweep gas far from the particle $[kg/m^3 \text{ of gas phase in the particle}]$
C_{iNR}	mass concentration of a nonreactive volatile species i in the gas phase of the particle $[kg/m^3 \text{ of gas phase in the particle}]$
C_{iBNR}	mass concentration of a nonreactive volatile species i in the solid phase of the particle $[kg/m^3 \text{ of solid phase in the particle}]$
C_{iBNR}^0	initial mass concentration of a nonreactive volatile species i bound in the solid phase of the particle $[kg/m^3 \text{ of solid phase in the particle}]$
$C_{iNR\infty}$	mass concentration of a nonreactive volatile species i in the sweep gas far from the particle $[kg/m^3 \text{ of gas phase in the particle}]$

C_R	total mass concentration of all reactive volatile species in the gas phase of the particle [kg/m^3 of gas phase in the particle]
C_{NR}	total mass concentration of all nonreactive volatile species in the gas phase of the particle [kg/m^3 of gas phase in the particle]
$C_{R\infty}$	total mass concentration of all reactive volatile species in the sweep gas far from the particle [kg/m^3 of gas phase in the particle]
$C_{NR\infty}$	total mass concentration of all nonreactive volatile species in the sweep gas far from the particle [kg/m^3 of gas phase in the particle]
C^*	total volatile content of the particle [kg/m^3 of solid phase in the particle]
C_p	heat capacity of the solid phase of the particle [$\text{J}/(\text{kg}^\circ\text{K})$]
D	diameter of the particle [m]
D_e	effective diffusion coefficient [m^2/sec]
E_i	activation energy associated with the devolatilization reaction liberating species i [$\text{cal}/\text{g-mole}$]
E	activation energy [$\text{cal}/\text{g-mole}$]
E_o	mean activation energy associated with the Gaussian distribution function [$\text{cal}/\text{g-mole}$]
$f(E)$	distribution function for the activation energies
g	ratio defined in Eq. (4)
h	convective heat transfer coefficient between the sweep gas and the particle surface [$\text{J}/(\text{m}^2^\circ\text{K sec})$]
ΔH	heat of reaction for each devolatilization reaction liberating species i [J/kg]
k_i	Arrhenius rate constant associated with the reaction liberating species i [sec^{-1}]
k_{oi}	Arrhenius frequency factor associated with the rate constant k_i [sec^{-1}]
k_o	Arrhenius frequency factor for any reaction i [sec^{-1}]

k''	Arrhenius rate constant for the decomposition of the reactive volatile species [sec^{-1}]
k_g	mass transfer coefficient [m/sec]
k_{gas}	thermal conductivity of gas [$\text{J}/(\text{m sec } ^\circ\text{K})$]
k_s	thermal conductivity of the solid phase of the particle [$\text{J}/(\text{m sec } ^\circ\text{K})$]
M_R	typical molecular weight for a reactive species [g/g-mole]
M_{NR}	typical molecular weight for a nonreactive species [g/g-mole]
n_{iR}	effective mass flux of a reactive volatile species i in the particle [$\text{kg}/(\text{m}^2\text{sec})$]
$n_{i\text{NR}}$	effective mass flux of a nonreactive volatile species i in the particle [$\text{kg}/(\text{m}^2\text{sec})$]
n_R	total effective mass flux of all reactive volatile species i in the particle [$\text{kg}/(\text{m}^2\text{sec})$]
n_{NR}	total effective mass flux of all nonreactive volatile species i in the particle [$\text{kg}/(\text{m}^2\text{sec})$]
n_{RS}	total effective mass flux of all reactive volatile species at the surface of the particle [$\text{kg}/(\text{m}^2\text{sec})$]
n_{NRS}	total effective mass flux of all nonreactive volatile species at the surface of the particle [$\text{kg}/(\text{m}^2\text{sec})$]
p	number of particles
P_R	partial pressure of reactive volatiles in the gas phase of the particle [psia]
P_{NR}	partial pressure of nonreactive volatiles in the gas phase of the particle [psia]
P	total pressure of volatiles in the gas phase of the particle [psia]
q	heat flux at the surface of the particle [$\text{J}/(\text{m}^2\text{sec})$]
r_i	intrinsic rate of reaction for a devolatilization reaction i [$\text{kg}/(\text{m}^3\text{sec})$]
R_p	radius of the particle [m]

R_G	ideal gas constant
R	intrinsic rate of devolatilization [$\text{kg}/(\text{sec m}^3$ of solid phase)]
R_c	intrinsic rate of coking [$\text{kg}/(\text{sec m}^3$ of gas phase)]
S	surface area of a spherical particle [m^2]
t	time [sec]
T	uniform temperature of the particle [$^\circ\text{K}$]
T_0	initial temperature of the particle [298°K]
T_g	temperature of the sweep gas [$^\circ\text{K}$]
v_r	velocity of volatile species in the gas phase of the particle as they are convected out of the particle [m/sec]
$w(t)$	weight of reactive volatiles collected at time t [kg]
$W(t)$	weight of reactive and nonreactive volatiles collected at time t [kg]

Greek Letters

α	thermal diffusivity of solid [m^2/sec]
γ	fraction of C^* that represents the total reactive volatiles content
$(1 - \gamma)$	fraction of C^* that represents the total nonreactive volatiles content
ε	void space of the particle $\left[\frac{\text{m}^3 \text{ of gas phase in the particle}}{\text{m}^3 \text{ of particle}} \right]$
κ	Darcy permeability [m^2]
μ	characteristic viscosity of the nonreactive volatile species in the gas phase of the particle [$\text{kg}/\text{m sec}$]
π	3.1416....
ρ_s	density of the solid phase of the particle

σ standard deviation of the Gaussian distribution
of activation energies [cal/g-mole]

Ψ integrating factor

Dimensionless Groups

Da Damköhler number $\frac{R_p k''}{k_g}$

Nu Nusselt number $\frac{hD}{k_{\text{gas}}}$

Pr Prandtl number $\frac{C_p u}{k}$

Re Reynolds number $\frac{\rho u_m D}{\mu}$

where u_m is the superficial velocity of the sweep
gas

Sc Schmidt number $\frac{\mu}{\rho \mathcal{D}_{AB}}$

Sh Sherwood number $\frac{k_g 2R_p}{\mathcal{D}_{AB}}$

ϕ Thiele Modulus $\sqrt{\frac{k''}{\mathcal{D}_e}} R_p$

1. INTRODUCTION

In view of dwindling petroleum reserves and the ubiquitous nature of oil shale deposits, oil from oil shale is being considered once again as a source of chemical feedstock. Although more than one trillion barrels of oil exist in the eastern oil shale formations in Michigan (Katz and Goddard, 1964) and another 700 billion barrels of oil are present in the western formations of Colorado, Wyoming, and Utah (Lewis and Rothman, 1975), it is unclear whether significant fractions of this oil can be recovered.

Combustion and hot gas retorting are two methods currently being investigated as a means of recovering oil from oil shale. The proposed methods include both above ground and in situ processing (Jones, 1976; Lewis and Rothman, 1976). Mathematical simulations of these large scale commercial operations are presently being developed by Braun and Chin (1977) and Crowl and Piccirelli (1979) to study alternative operating strategies. These models necessarily require an understanding of the rate processes which occur in individual oil shale particles under pyrolysis conditions.

Devolatilization of shales has been modeled using simple kinetic schemes but, unfortunately, this strategy fails to predict the production of volatile products under a wide range of pyrolysis conditions. A satisfactory model has not been developed which incorporates the kinetics of devolatilization, a mechanism for intraparticle mass transport of volatile products, and the kinetics for intraparticle product degradation. Therefore, a prototype model will be developed in this study which describes all these rate processes during the pyrolysis of oil shale particles. The complex kinetics characteristic of oil shale devolatilization will be interpreted using the distribution of activation energies theory developed previously for coal pyrolysis (see, esp., Anthony and Howard, 1976). The kinetic model will be combined with material balances to describe the pyrolysis of large particles. For these larger particles, diffusion and bulk flow will affect the production of volatile products.

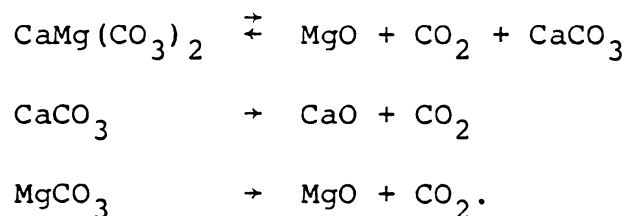
1.1. Physical Description of Oil Shale

Oil shale is a low porosity material which yields gaseous volatile products upon heating. Volatiles, other than water, which condense at temperatures above -78°C are classified as "oil." The noncondensable products are typically CO , CO_2 , H_2 , CH_4 , and C_2H_6 . The nominal void fraction of eastern oil shale particles is 0.05 (Crowl and Piccirelli, 1979); the western oil shales typically have

higher porosities on the order of 10% (Tisot and Murphy, 1965).

The solid phase of the particle is composed of inorganic and organic material. The solid organic phase contains kerogen, a complex polymeric material. The structure of kerogen is highly naphthenic with aromatic, nitrogen, and sulphur heterocyclic ring systems distributed throughout the kerogen molecule (Jones and Dickert, 1965). When an oil shale particle is heated, the volatile products are produced by devolatilization reactions which occur in the solid organic phase at temperatures between 475°K and 775°K.

The inorganic solid phase of western oil shales contains dolomite, $\text{CaMg}(\text{CO}_3)_2$; calcite, CaCO_3 ; and magnesium carbonate, MgCO_3 . At temperatures of 840°K or higher, Jukkola, et al. (1953) determined that these inorganic carbonates decomposed by the following endothermic reactions:



Allred's (1967) experiments also show that the inorganic carbonates do not decompose if the temperature is below 880°K. These endothermic reactions act as heat sinks in the retorting process and their presence could potentially limit the efficiency of a particular recovery strategy.

However, for the temperature range of the pyrolysis of kerogen (i.e., 473°K to 773°K) the decomposition reactions of the carbonates will not occur, so the heat sinks associated with these reactions should not limit the extent of pyrolysis.

1.2. Description of Oil Shale Pyrolysis

As an oil shale particle is heated the bonds of the kerogen molecule begin to break. Parts of the molecule are released as volatile species into the gas phase of the particle. These bond breaking processes are the devolatilization reactions which occur in the solid organic phase uniformly throughout the particle. Reactions producing certain classes of volatile species may be identified with a characteristic activation energy associated with the strength of the chemical bond being broken by thermal energy. Moreover, the volatiles released into the gas phase may be classified as either reactive or nonreactive, depending on their tendency to coke.

The reactive volatiles, associated with "oil" formation, are tarry, higher molecular weight species possibly existing as free radicals (Russell, et al., 1979). These reactive volatiles are subject to gas phase coking and cracking reactions and may deposit as inert char inside the particle instead of being released as "oil." The nonreactive volatiles are typically lower molecular weight species such as CO, CO₂, CH₄, C₂H₆, hydrogen, and water. Although these species are not subject to gas phase decomposition for

$T < 775^{\circ}\text{K}$, they do react at higher temperatures. The activation energies associated with the gas phase decomposition of the nonreactive species are of the order of 80-104 kcal/g-mole (Benson, 1968; Murphy, et al., 1958; Palmer, 1963); whereas, the activation energies for the gas phase decomposition of the reactive volatiles are of the order of 30-60 kcal/g-mole (Benson, 1968; Murphy, et al., 1958; Palmer, 1963). In typical cracking and coking reactions, additional nonreactive volatiles are produced when reactive volatiles decompose (Hirt and Palmer, 1963; Palmer and Cross, 1966; Hudson and Heicklen, 1968; Heicklen, et al., 1969); however, in this study it is assumed that the volatile species produced by the decomposition reactions are negligible.

Upon release from the solid, the volatiles are transported to the particle surface by convection and diffusion, but the reactive volatiles are subject to decomposition reactions. Therefore, the yield is limited by internal as well as external resistances to mass transfer. These limitations cause the buildup of reactive volatiles in the gas phase of the particle which increases the rate of gas phase decomposition.

For large particles the rate of volatiles production may be affected by mass transport processes. Anthony (1974) points out that very little experimental work has been conducted to find this limiting particle size for coal pyrolysis. It is noteworthy that no influence on the rate of coal devolatilization has been observed for particle diameters

up to 200 microns. Anthony (1974) states that the onset of mass transport limitations arises somewhere in the particle size range of 200-2000 microns. It will be assumed that the limiting particle size for oil shale devolatilization will also fall in this range.

Shih and Sohn (1978) have demonstrated that for large particles internal temperature gradients within the particle affect the retorting process; however, if the particle sizes are sufficiently small, the particle can be considered spatially isothermal. This assumption can be justified by estimating the time needed for a solid sphere of radius R and thermal diffusivity $\alpha (\equiv k_s / \rho_s C_p)$ to approach a uniform temperature when subjected to a step change at its boundary. According to Bird, et al. (1960), this occurs when $\alpha t / R^2 \simeq 0.4$. Granoff and Nuttall (1977) and Campbell, et al. (1977) have measured the following physical properties for Colorado oil shale:

$$C_p = 1.13 \times 10^3 \text{ J/kg } ^\circ\text{C}$$

$$\rho_s = 2.25 \times 10^3 \text{ kg/m}^3$$

$$k_s = 1.25 \text{ J/m sec } ^\circ\text{C}.$$

Thus, the thermal diffusivity, α , corresponding to these properties is $\sim 5 \times 10^{-7} \text{ m}^2/\text{sec}$. For particle radii ranging from hundreds of microns (i.e., 10^{-4} m) to tenths of a centimeter (i.e., 10^{-3} m), the real times corresponding to the dimensionless time 0.4 are approximately 10^{-2} sec and

1 sec, respectively. The time scale for devolatilization in most experiments is on the order of 10^5 sec; therefore, regardless of whether the environment of the particle is isothermal or nonisothermal, the particle will behave as though it is spatially isothermal. This will be true for particle diameters up to approximately one centimeter.

As the solid organic phase of the oil shale pyrolyzes, the void space within the particle will increase as volatiles leave the solid. For non-coking lignite coal, the particles maintain their porous structure throughout pyrolysis and leave behind a very porous structure of ash and char (see, Russell, et al., 1979). However, coking bituminous coal particles swell and soften during pyrolysis and volatiles escape as bubbles. Although the physical structure of oil shale is comparable to that of coking, bituminous coals, the prototype model developed hereinafter assumes that the shale particle maintains its geometric configuration and integrity throughout pyrolysis.

1.3. Kinetic Models for Pyrolysis

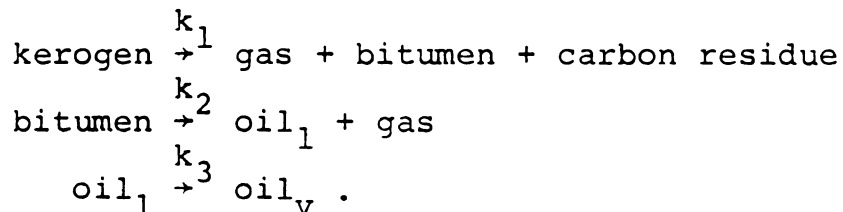
Hubbard and Robinson (1950) conducted isothermal experiments on samples of oil shale in the form of cylinders one centimeter in diameter and six centimeters in length. They determined the amount of kerogen reacted by measuring the amounts of oil, gas, and bitumen produced as a function of time and interpreted their data with a simple mechanism involving two consecutive first order reactions, viz.,



Their experiments showed that a carbonaceous residue was formed as a pyrolytic product. However, no measurements were made on the amounts of residue formed, and the residue does not appear in the reaction mechanism.

Allred (1967) was able to calculate the amount of residue directly from the data of Hubbard and Robinson (1950). He also conducted nonisothermal experiments in which the weight of volatiles collected were measured as a function of time and found that the production of oil and gas occurred over temperatures ranging from 477°K to 744°K. No further appreciable weight loss was observed until 880°K where inorganic carbonates began to decompose giving off additional volatile species.

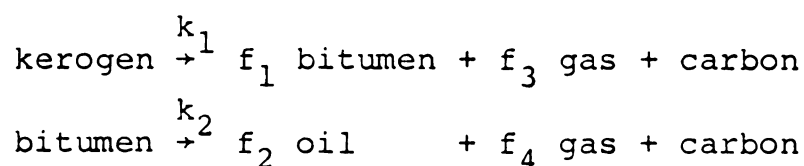
Allred tried to explain his data and that of Hubbard and Robinson using the kinetic mechanism proposed by Hubbard and Robinson. However, his measurements of the overall rate constant showed three distinct regions in which k vs. $1/T$ was linear. This observation led him to the following mechanism



At temperatures below 744°K, the decomposition of bitumen was observed to be rate limiting with an Arrhenius activation

energy of 40 kcal/g-mole. Above 744°K the vaporization of oily liquids became rate limiting with an activation energy of 15 kcal/g-mole. Jones and Dickert (1965) state that the activation energies of 45 kcal/g-mole reported for kerogen pyrolysis is to be expected for reactions involving carbon-carbon bond breaking.

Braun and Rothman (1975) observed that the experiments of Hubbard and Robinson were not true isothermal experiments because of the large particle size. They considered a kinetic scheme similar to that of Allred's but introduced a heating up period before retorting started. No devolatilization occurred until a certain thermal induction time was reached. Braun and Rothman observed that the duration of this initial stage decreases linearly with increasing temperature. The reaction scheme employed by Braun and Rothman is



where the stoichiometric coefficients f_1 , f_2 , f_3 , f_4 , and the initial concentration of kerogen are functions of the pyrolysis temperature. The rate constants k_1 and k_2 are

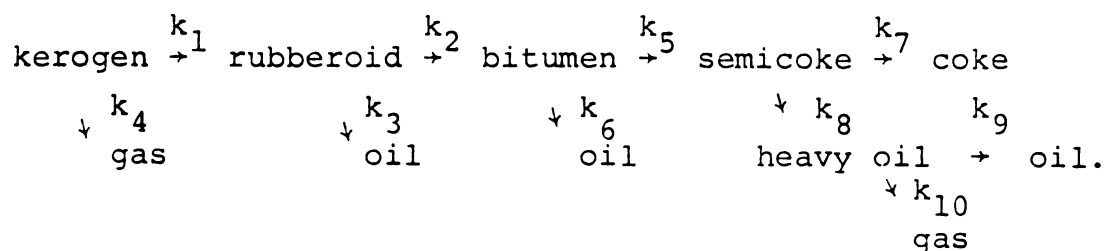
$$k_1 = 14.4 \exp \left(\frac{-10,650 \text{ cal/g-mole}}{R_G T} \right), \text{ sec}^{-1}$$

$$k_2 = 2.025 \times 10^{10} \exp \left(\frac{-42,443 \text{ cal/g-mole}}{R_G T} \right), \text{ sec}^{-1}.$$

Although these results are in general agreement with Allred's experiments in which the decomposition of bitumen is the rate limiting step at temperatures below 760°K, above 760°K kerogen decomposition is rate determining. Apparently, the decomposition of kerogen involves the breaking of relatively weak chemical bonds, while the decomposition of bitumen involves breaking much stronger bonds.

The data of Hubbard and Robinson (1950) and Cummins and Robinson (1972) show that the weight of volatiles collected as a function of time asymptotes to a value characteristic of a particular temperature. If the temperature is increased this asymptote also increases. The upper limit of this asymptote occurs around 773°K which Allred measured as the upper limit for oil and gas production. Braun and Rothman show that the limiting value of the fraction of kerogen converted to oil is 0.62 and occurs at temperatures over 748°K.

Because the molecular structure of oil shale is not well defined, Johnson, et al. (1975) concluded that it was unrealistic to describe the mechanism for each chemical species undergoing pyrolysis. By lumping groups of similar products, they were able to arrive at a more complicated kinetic scheme, viz.,



With this assumption they were able to interpret a wide range of isothermal and nonisothermal experiments conducted with various particle size shales. Their model contains no temperature dependent coefficients but contains twenty adjustable kinetic parameters. Such agreement between their model and experimental data is expected given the number of adjustable parameters. Furthermore, such a complex kinetic scheme may not be convenient for describing large scale retorts.

Campbell, et al. (1978) assumed that kinetic experiments could be interpreted as an average of many processes occurring simultaneously. They postulated that devolatilization of shale could be modeled as a single first order reaction with an effective activation energy of 52 kcal/g-mole. As with the two previous simple kinetic models, the initial concentration of reactive kerogen must be interpreted as a function of temperature to describe experiments at different temperatures. In another study Campbell, et al. (1977) observed that the heating rate in nonisothermal experiments also affected the final yield of volatiles. They postulated that the heating rate affected some intraparticle mechanism degrading the oil once it had been liberated from the solid phase.

The bond breakages that occur during pyrolysis include carbon-carbon, carbon-oxygen, and carbon-hydrogen bonds. The bond strengths of these three groups depend on neighboring functional groups but range from 80 kcal/g-mole to 104 kcal/g-mole. Anthony and Howard (1976) point out a

study by Jüntgen and Van Heek (1970) where it was demonstrated theoretically that a set of parallel first order reactions can be represented by a single first order expression having a lower activation energy. This phenomena can explain the lower activation energies, 40-60 kcal/g-mole, observed in kinetic experiments. This might also explain the low value of 19 kcal/g-mole obtained by Cummins and Robinson (1972) in their experimental study. Many of the qualitative features of oil shale kinetics have also been observed by researchers investigating coal devolatilization. Anthony and Howard (1976) give an extensive review of this work.

Pitt (1962) adapted Vand's (1943) treatment of a large number of simultaneous parallel rate processes with differing activation energies to interpret coal devolatilization experiments. In a refinement of Pitt's theory, Anthony and Howard (1975, 1976a, 1976b) described the devolatilization of the solid organic phase of coal as an infinite set of simultaneous, parallel, irreversible, first order reactions. The intrinsic rate of reaction for one of the reactions can be described by

$$r_i = -k_i C_{iB}.$$

These reactions are all first order in the mass concentration of unreacted material and have rate constants of the Arrhenius form

$$k_i = k_{oi} \exp\left(\frac{-E_i}{R_G T}\right).$$

The Arrhenius frequency factors, k_{oi} , for each reaction i can be estimated from transition state theory to have a value of 10^{13} sec^{-1} , provided the entropy of activation is close to zero (Anthony and Howard, 1976; Benson, 1968).

The activation energies for all the reactions represent a continuous distribution characterized by some distribution function. Anthony and Howard assumed a Gaussian distribution characterized by the parameters E_o , the mean activation energy, and σ , the variance of the distribution. If the frequency factor is the same for all the reactions, then only three, intrinsic, adjustable, kinetic parameters are introduced: E_o , σ , and k_o . If a more complex kinetic scheme is used, as in the Johnson, et al., model, two more adjustable parameters are required for each new reaction proposed. By using the distribution of activation energies approach and assuming a Gaussian distribution, only one additional parameter, σ , is introduced, although the number of reactions in the kinetic scheme is infinite. The distribution of activation energies model retains the complexity of many simultaneous first order reactions yet keeps the number of adjustable parameters to a minimum.

The theory is able to predict the weight loss at low temperatures since the reactions which produce volatiles at

these temperatures have characteristically low activation energies. As the temperature is increased, the additional yield of volatiles is again predicted. Volatiles released at higher temperatures are produced by reactions which have much higher activation energies than the mean, so these reactions occur extremely slow at low temperatures.

Hill, et al. (1967) observed that the density of the oil produced in pyrolysis experiments increased with temperature due to increasing amounts of higher molecular weight species produced at higher temperatures. This experimental evidence provides additional motivation to develop a theory of oil shale pyrolysis similar to the one already developed for coal. Basically, the idea is that higher molecular weight volatiles are bound more tightly to the solid and are liberated by reactions having high activation energies; whereas, the lower molecular weight volatiles are produced by reactions which have low activation energies. Because of the complex nature of kerogen, a continuous distribution of reactions characterized by different activation energies occurs.

The value for the initial concentration of volatiles in the distribution of activation energies theory represents the ultimate volatile content of the oil shale. This is in contrast to the initial concentrations in the simpler models which represent apparent volatile concentrations for a particular experiment. Anthony and Howard (1976a)

successfully used this approach to predict the weight of volatiles collected as a function of time for non-coking lignite coals.

1.4. Objectives of This Research

The kinetic model to be developed in this study uses the distribution of activation energies theory developed by Anthony and Howard and others. By comparing the kinetic model to experimental data for powdered oil shale samples where no mass transfer limitations exist, the parameters of the model can be determined for a particular shale. The kinetic model can then be used to predict weight loss as a function of time in cases where intraparticle and interparticle mass transfer limitations are important.

Simple kinetic approaches are not able to predict experimental data for a wide range of experimental conditions without the use of temperature dependent initial concentrations and stoichiometric coefficients. Anthony (1974) was able to overcome these problems in his coal devolatilization study by using the distribution of activation energies theory. Because the pyrolysis behavior of oil shale is similar to that of coal, it is natural to assume that this approach will also apply to oil shale.

Anthony (1974) did not extend his theory to situations where mass transfer limitations are important. Although Russell, et al. (1979) developed a model for coal pyrolysis which included intraparticle mass transfer as well

as gas phase decomposition, they did not employ the distribution of activation energy kinetics as developed hereinafter.

In the approach developed here, the heating rate enters the problem explicitly through the boundary condition for the temperature. This is in contrast to the approach of Campbell, et al. (1977) where the heating rate appears implicitly in the kinetic rate parameters. It is anticipated that the appearance of the heating rate in the boundary condition will allow for more accurate model predictions over a wider range of experimental conditions.

2. A MATHEMATICAL MODEL FOR THE PYROLYSIS OF OIL SHALE

The porous oil shale particle will be treated as an effective homogeneous mixture of organic and inorganic compounds. Each devolatilization reaction which liberates a volatile species i occurs homogeneously throughout the particle. Because the porosity of the particle is very small and the rate of devolatilization is slow compared to the intraparticle mass transport, the pseudo-steady state assumption will be applied to the gas phase material balances.

The mechanism for intraparticle mass transfer includes both diffusion and convection. The diffusive flux will be described by Fick's law of diffusion characterized by an effective diffusion coefficient, and the convective flux will be described by Darcy's law. A resistance to mass transfer will also occur between the gas surrounding the particle and the surface of the particle. This resistance occurs across an imaginary film surrounding the particle and is characterized by a convective mass transfer coefficient. For very small particles, intraparticle mass transport occurs extremely fast, so the concentration of

species i will be the same everywhere in the particle. Therefore, the only resistance to mass transfer will occur across the imaginary film surrounding the particle.

A finite resistance to heat transfer will also occur across this imaginary film. This resistance is characterized by a convective heat transfer coefficient, which will be estimated from correlations found in Bennett and Myers (1962) for a sphere suspended in a gas stream. An estimate of the mass transfer coefficient will be made using the Colburn analogy (i.e., $j_m = j_h$).

The temperature of the particle is approximately uniform (see, Section 1.2) for particle diameters less than one centimeter. However, the endothermic heats of reaction for the devolatilization reactions will act to lower the temperature of the particle relative to the surroundings. Hence, the temperature of the particle will be determined by the amount of heat transferred between the particle and its surroundings and the heat removed by the pyrolysis reactions.

2.1. Devolatilization Kinetics

The intrinsic rate of reaction for species i undergoing devolatilization can be described by

$$r_i = k_i C_{iB} \quad (1)$$

where

$$k_i = k_o \exp\left(\frac{-E_i}{R_G T}\right). \quad (2)$$

C_{iB} is the mass concentration of species i bound to the solid (i.e., mass of species i per unit volume of solid phase).

Eqs. (1) and (2) can be combined to give

$$r_i = k_o \exp\left(\frac{-E_i}{R_G T}\right) g(E_i, t) C_{iB}^o \quad (3)$$

where

$$g(E_i, t) \equiv \frac{C_{iB}}{C_{iB}^o}. \quad (4)$$

The ratio in Eq. (4) will be determined later by a material balance over the solid phase of the particle.

The constant C_{iB}^o represents the initial mass concentration of species i which decomposes by a reaction having an activation energy between E_i and $E_i + \Delta E_i$. The probability that a reaction, which produces species i , has a certain activation energy is represented by $f(E_i)\Delta E_i$.

Thus,

$$C_{iB}^o = C^* f(E_i) \Delta E_i \quad (5)$$

where C^* is the total initial mass concentration of volatile species that decompose. Because $\sum_i C_{iB}^o = C^*$, the density function must satisfy

$$\sum_i f(E_i) \Delta E_i = 1. \quad (6)$$

The total intrinsic rate of reaction is obtained by summing the contributions from all species i . Eqs. (3) and (5) imply that

$$\sum_i r_i = k_O C^* \sum_i \exp\left(\frac{-E_i}{R_G T}\right) g(E_i, t) f(E_i) \Delta E_i. \quad (7)$$

If the number of different activation energies in the reaction set is very large, then the sum appearing in Eq. (7) can be calculated as an integral with the result that

$$\sum_i r_i \equiv R = k_O C^* \int_a^b \exp\left(\frac{-E}{R_G T}\right) g(E, t) f(E) dE \quad (8)$$

where the limits of the integral in Eq. (8) define the interval over which $f(E)$ is defined.

Eq. (8) is the total intrinsic rate of devolatilization for all volatile species. To describe the intrinsic rate of devolatilization for the reactive volatile species, Eq. (8) is multiplied by γ , the fraction of C^* which yields reactive volatiles. Similarly, the intrinsic rate of reaction for the nonreactive species is given by Eq. (8) multiplied by $(1-\gamma)$.

The density function $f(E)$ for the activation energies is unknown. In this study it is assumed that $E_0 \gg 0$ and that $\sigma \ll E_0$ so a Gaussian density can be used:

$$f(E) = \frac{\exp\left(\frac{-(E-E_0)^2}{2\sigma^2}\right)}{\sqrt{2\pi} \sigma}. \quad (9)$$

Anthony (1974) was successful in using Eq. (9) to interpret coal devolatilization experiments. It is noteworthy that this model requires only one more parameter than the simple lumped first order kinetic model, yet the number of reactions being considered is infinite. The devolatilization parameters, which do not depend on the temperature, include a mean activation energy E_0 , the variance σ , and a frequency factor k_0 . The parameter γ may be viewed as a stoichiometric coefficient. One of the objectives of this thesis will be to estimate these parameters from pyrolysis data on western oil shale.

2.2. Coking Kinetics

The intrinsic rate of decomposition of a reactive species i in the interstices of the particle can be described by a single first order irreversible reaction

$$r_{ci} = k'' C_{iR}. \quad (10)$$

C_{iR} is the mass concentration of reactive volatile species (i.e., mass per unit volume of gas phase). This type of expression is consistent with the studies of Murphy, et al. (1958); Palmer and Cross (1966); and Hirt and Palmer (1963). The coking constant k'' is assumed to be the same for each species i . This rate constant was determined by Campbell, et al. (1977) as

$$k'' = 3.1 \times 10^7 \exp\left(\frac{-35 \text{ kcal/g-mole}}{R_G T}\right), \text{ sec}^{-1}. \quad (11)$$

The summation of all reactive species i in Eq. (10) gives the total decomposition rate,

$$R_C = k'' C_R \quad (12)$$

where C_R is the total mass concentration of reactive species.

2.3. Material and Energy Balances

2.3.1. Material Balance for the Reactive Volatile Species in the Gas Phase of the Particle

A mass balance for a reactive volatile species i in the gas phase of a shale particle is

$$\frac{\partial}{\partial t} (C_{iR} \varepsilon) + \varepsilon (\nabla \cdot \underline{n}_{ir}) = \gamma r_i (1 - \varepsilon) - r_{ci} \varepsilon. \quad (13)$$

$\underline{n}_{ir}$ is the intraparticle mass flux of reactive volatile species i and ε is the void fraction of the particle.

Figure 1 gives a schematic of the physical situation and helps to define some of the notation.

If Eq. (13) is summed over all species i , then for pseudo-steady state

$$\nabla \cdot \underline{n}_R = \left(\frac{1 - \varepsilon}{\varepsilon} \right) \gamma R - R_C. \quad (14)$$

Using spherical coordinates with $\underline{n}_R$ varying in the radial direction only, Eq. (14) becomes

$$\frac{1}{r^2} \frac{d}{dr} (r^2 n_R) = \frac{(1 - \varepsilon)}{\varepsilon} \gamma R - R_C \quad (15)$$

where n_R denotes the radial component of $\underline{n}_R$.

The mass flux of reactive volatiles with respect to stationary coordinates is defined by Bird, et al. (1960) as

$$n_R = -\rho \mathcal{D}_e \frac{dx_R}{dr} + x_R (n_R + n_{NR}). \quad (16)$$

n_{NR} is the radial component of the flux of nonreactive species. With $x_R = \frac{C_R}{\rho}$, Eq. (16) becomes for $\rho \approx \text{constant}$

$$n_R = -\mathcal{D}_e \frac{dC_R}{dr} + \frac{C_R}{\rho} (n_R + n_{NR}) \quad (17)$$

Substituting $\rho v_r = n_R + n_{NR}$, Eq. (17) becomes

$$n_R = -\mathcal{D}_e \frac{dC_R}{dr} + C_R v_r. \quad (18)$$

$\mathcal{D}_e$ is an effective diffusion coefficient and v_r can be related to the pressure by Darcy's law

$$v_r = - \frac{\kappa}{\mu} \frac{dP}{dr}. \quad (19)$$

Eq. (19) is a constitutive equation which describes the velocity of a fluid flowing through a porous media. κ is the permeability of the porous media, μ is the viscosity of the fluid, and the gradient of the total pressure is the driving force for flow. The total pressure is equal to the sum of the partial pressures of the nonreactive and reactive species, that is, $P = P_{NR} + P_R$. Assuming ideal gas behavior, the total pressure is related to the concentrations by

$$P = R_G T \left(\frac{C_R}{M_R} + \frac{C_{NR}}{M_{NR}} \right). \quad (20)$$

Direct substitution of Eqs. (20), (19), and (18) into Eq. (15) results in a nonlinear differential equation for C_R . However, if a nonreactive species is typically of lower molecular weight than the reactive species, then $\frac{C_{NR}}{M_{NR}} \gg \frac{C_R}{M_R}$, and the total pressure is independent of C_R . Therefore,

$$P \approx \frac{R_G T C_{NR}}{M_{NR}} \quad (21)$$

This simplification uncouples the material balances for C_R and C_{NR} .

The boundary conditions for Eq. (15) are

$$\left. \frac{dC_R}{dr} \right|_{r=0} = 0 \quad (22a)$$

$$n_R|_{r=R_p} = k_g (C_R|_{r=R_p} - C_{R\infty}). \quad (22b)$$

C_R is the mass concentration of reactive species far from the particle and k_g is a convective mass transfer coefficient. For situations where a sweep gas flows past the particle, $C_{R\infty} \approx 0$.

The first boundary condition specifies symmetry for the concentration profile at the center of the particle. The second boundary condition requires continuity of mass flux at the surface of the particle. The mass transfer coefficient will be taken to be a constant independent of concentration and temperature. k_g will be calculated by using the Colburn analogy (see, p. 646 in Bird, et al., 1960)

$$j_H = Nu Re^{-1} Pr^{-1/3} = j_m = Sh Re^{-1} Sc^{-1/3}.$$

An estimate of Nu can be made using the following correlation (see, p. 386 in Bennett and Myers, 1962)

$$Nu = 2 + 0.6 (Pr)^{1/3} (Re)^{1/2}.$$

This correlation was developed for a sphere suspended in a gas stream. The sweep gas will be assumed to be nitrogen. As an approximation, the diffusivity of methane in nitrogen is used to calculate Sh and Sc . The transport properties of the nonreactive volatile species appearing in Eqs. (19) and (21) will also be assumed to be those of methane. For powdered shale particles, $Nu \approx 2$ will be employed.

2.3.2. Material Balance for the Nonreactive Volatile Species in the Gas Phase of the Particle

A mass balance for a nonreactive volatile species i in the interstices of the particle is

$$\frac{\partial (C_{iNR} \epsilon)}{\partial t} + \epsilon (\nabla \cdot \underline{n}_{iNR}) = (1 - \gamma) (1 - \epsilon) r_i \quad (23)$$

where $\underline{n}_{iNR}$ is the intraparticle mass flux of nonreactive volatiles. Once again, if Eq. (23) is summed over all nonreactive species, then

$$\nabla \cdot \underline{n}_{NR} = \frac{(1 - \epsilon)}{\epsilon} (1 - \gamma) R, \quad (24)$$

provided pseudo-steady state applies. In spherical coordinates, Eq. (24) is

$$\frac{1}{r^2} \frac{d}{dr} (r^2 n_{NR}) = \frac{(1 - \epsilon)}{\epsilon} (1 - \gamma) R. \quad (25)$$

The intraparticle mass flux of nonreactive species includes both diffusion and convection

$$n_{NR} = -D_e \frac{dC_{NR}}{dr} + C_{NR} v_r. \quad (26)$$

v_r is given by Eqs. (19) and (21) as before.

The boundary conditions for Eq. (25) are

$$\left. \frac{dC_{NR}}{dr} \right|_{r=0} = 0 \quad (27a)$$

$$n_{NR} \big|_{r=R_p} = k_g (C_{NR} \big|_{r=R_p} - C_{NR\infty}). \quad (27b)$$

The mass transfer coefficient for the nonreactive species is estimated in the same way as for the reactive species. $C_{NR\infty}$ is approximately zero, if a sweep gas flows past the particle.

2.3.3. A Material Balance for the Volatile Species Bound to the Solid Phase

A material balance for species i bound to the solid phase of the particle is

$$\frac{d(C_{iB} V_p (1 - \epsilon))}{dt} = -k_o \exp\left(\frac{-E_i}{R_G T}\right) C_{iB} V_p (1 - \epsilon). \quad (28)$$

If the volume of the particle and the void fraction are constant, then Eq. (28) is

$$\frac{dC_{iB}}{dt} = -k_o \exp\left(\frac{-E_i}{R_G T}\right) C_{iB}. \quad (29)$$

Thus,

$$\frac{C_{iB}}{C_{iB}^o} = \exp\left[-k_o \int_0^t \exp\left(\frac{-E_i}{R_G T}\right) dt\right] \quad (30)$$

which defines $g(E_i, t)$ appearing in Eq. (4).

2.3.4. Material Balance for the Weight of Volatiles Collected

The weight of volatiles collected as a function of time from an arbitrary sample of oil shale particles can be described by performing an overall material balance around all the particles. This yields

$$\frac{dW}{dt} = Sp\epsilon(n_{RS} + n_{NRS}). \quad (31)$$

The surface area of a particle is S (i.e., $4\pi R_p^2$), p is the number of particles, n_{RS} and n_{NRS} are the mass fluxes of reactive and nonreactive species at the surface of the particle, and W is the total weight of volatiles collected.

2.3.5. Energy Balance

The energy balance for the particle is

$$\frac{d(V_p \rho_s C_p T)}{dt} = qS - R|\Delta H|V_p(1 - \epsilon) \quad (32)$$

where V_p is the volume of the particle, C_p is the heat capacity of the solid phase, ρ_s is the density of the solid

phase, T is the uniform temperature of the particle, and $|\Delta H|$ is the endothermic heat of reaction. The heat flux at the surface of the spherical particle is q and equals

$$q = h(T_g - T) \quad (33)$$

where h is a convective heat transfer coefficient and T_g is the temperature in the gas far from the particle. The heat transfer coefficient in Eq. (33) is assumed to be independent of concentration and temperature.

For pseudo-steady state, Eqs. (32) and (33) imply that

$$h(T_g - T)S = R|\Delta H|V_p(1 - \epsilon), \quad (34)$$

which yields

$$T = T_g - \frac{R|\Delta H|R_p(1 - \epsilon)}{3h} \quad (35)$$

where R_p is the radius of the particle. Eq. (35) shows that the temperature of the particle will differ from that of the gas depending upon R_p and h . The magnitude of this difference can be investigated by calculating the second term on the right hand side of Eq. (35) for large and small particles.

The heat of pyrolysis for Colorado oil shale is 335 kJ/kg (see, Campbell, et al., 1977), and the porosity is 10%. With $Nu = 2$ and $k_{gas} \approx 0.03 \text{ J/(m sec } ^\circ\text{K)}$, $h = 65 \text{ J/(m}^2 \text{ sec } ^\circ\text{K)}$ for $D = 8 \times 10^{-4} \text{ m}$; and, $h = 4 \text{ J/(m sec } ^\circ\text{K)}$ for $D = 0.0127 \text{ m}$.

These particle diameters were used in experiments to be investigated later, so the values of $\frac{R_p |\Delta H|}{3h}$ are 0.7 ($\text{m}^3 \text{ sec } ^\circ\text{K})/\text{kg}$ and 17 ($\text{m}^3 \text{ sec } ^\circ\text{K})/\text{kg}$.

For isothermal experiments, R is a maximum at $t = 0$ and decreases as the reaction progresses. In nonisothermal experiments, R increases to a maximum and then decreases to zero. It will be assumed as a first approximation that the values of $\frac{R_p |\Delta H| (1-\epsilon)}{3h}$ in Eq. (35) are small compared to T_g . If this is the case, then the temperatures of the particle and the sweep gas will be approximately the same. This assumption will be verified a posteriori when the values of E_o , σ , k_o , and C^* are determined and values for R are calculated.

For nonisothermal experiments the heating rate of the particle enters the problem through T_g . The heating rate does not affect the intrinsic kinetic rate parameters as postulated by Campbell, et al. (1977) but enters the rate expression through the explicit temperature dependence of k_i .

3. SPECIAL CASES TO BE STUDIED

3.1. Chemical Kinetics Controlling Regime--Isothermal

The equations developed in the previous section can be solved for the situation where intraparticle mass transport occurs much faster than chemical kinetics. These cases are typical of small particles, and the concentration of volatile species in the gas phase of the particle will be the same everywhere in the particle.

3.1.1. Reactive Species

Integrating Eq. (15) and applying the boundary conditions (22a) and (22b) yields

$$R_p^2 k_g (C_R - C_{R\infty}) = \frac{(1 - \epsilon)}{\epsilon} \frac{\gamma R_p^3}{3} - \frac{R_c R_p^3}{3} . \quad (36)$$

Solving Eq. (36) for C_R gives

$$C_R = \frac{\frac{R_p}{3} \gamma \frac{(1 - \epsilon)}{\epsilon} R + k_g C_{R\infty}}{k_g + \frac{R_p}{3} k''} . \quad (37)$$

Substituting Eq. (37) into Eq. (22b) gives the flux of reactive species out of the particle

$$n_{RS} = \left[\frac{R_p \frac{\gamma(1-\epsilon)}{\epsilon} R - R_p k'' C_{R\infty}}{3 + Da} \right] \quad (38)$$

where Da is the Damköhler number

$$Da \equiv \frac{R_p k''}{k_g} . \quad (39)$$

The Damköhler number is the ratio of the rate of gas phase decomposition to the rate of interphase mass transfer.

3.1.2. Nonreactive Species

Integrating Eq. (25) and applying the boundary conditions (27a) and (27b), results in

$$R_p^2 k_g (C_{NR} - C_{NR\infty}) = \frac{(1-\epsilon)(1-\gamma) R R_p^3}{3\epsilon} \quad (40)$$

Thus,

$$C_{NR} = \frac{(1-\epsilon)}{3\epsilon} \frac{(1-\gamma)}{k_g} R R_p + C_{NR\infty} \quad (41)$$

Substituting Eq. (41) into Eq. (27b) gives the flux of nonreactive species out of the particle

$$n_{NRS} = \left[\frac{(1-\epsilon)(1-\gamma) R R_p}{3\epsilon} \right]. \quad (42)$$

Note that the flux does not depend on the external resistance to mass transfer. This is a consequence of the pseudo-steady state assumption and the absence of coking reactions. As

the external resistance to mass transfer becomes very small (i.e., $k_g \rightarrow \infty$, $Da \rightarrow 0$), $C_R \rightarrow C_{R\infty}$ and $C_{NR} \rightarrow C_{NR\infty}$. As the external resistance increases (i.e., $k_g \rightarrow 0$, $Da \rightarrow \infty$), $C_R \rightarrow 0$ since R goes to zero at long times. This indicates that all reactive volatiles will eventually go to coke if not transported out of the particle. If $k''=0$, then Eqs. (37) and (38) reduce to Eqs. (41) and (42), respectively.

3.1.3. Weight of Volatiles Collected

Substituting Eqs. (38) and (42) into Eq. (31) gives

$$\frac{dw}{dt} = V_p p (1 - \epsilon) \left[\frac{\gamma}{(1 + \frac{Da}{3})} + (1 - \gamma) \right] R + \frac{V_p p \epsilon k'' C_{R\infty}}{(1 + \frac{Da}{3})}. \quad (43)$$

Eq. (43) describes the rate of volatiles collected as a function of time and is applicable in both isothermal and nonisothermal situations. The only difference will be the form of $g(E, t)$ as given by Eqs. (4) and (30).

Substituting Eqs. (30), (9), and (4) into Eq. (8) gives for the isothermal case

$$R = \frac{k_o C^*}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} \exp\left(\frac{-E}{R_G T}\right) \exp[-k_o t \exp\left(\frac{-E}{R_G T}\right)] \times \exp\left[\frac{-(E - E_o)^2}{2\sigma^2}\right] dE. \quad (44)$$

When $C_{R\infty} = 0$, Eqs. (44) and (43) yield

$$\frac{dw}{dt} = \frac{V_p p (1 - \varepsilon) k_o C^*}{\sqrt{2\pi} \sigma} \left[\frac{\gamma}{(1 + \frac{Da}{3})} + (1 - \gamma) \right] \times$$

$$\int_{-\infty}^{+\infty} \exp\left(\frac{-E}{R_G T}\right) \exp[-k_o t \exp\left(\frac{-E}{R_G T}\right)] \exp\left[-\frac{(E - E_o)^2}{2\sigma^2}\right] dE. \quad (45)$$

Integration of Eq. (45) over time gives

$$w(t) = V_p p (1 - \varepsilon) C^* \left[\frac{\gamma}{(1 + \frac{Da}{3})} + (1 - \gamma) \right] \times$$

$$\left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t \exp\left(\frac{-E}{R_G T}\right)] \exp\left[-\frac{(E - E_o)^2}{2\sigma^2}\right] dE \right] \quad (46)$$

Eq. (46) describes the total weight of volatiles collected as a function of time for isothermal situations where chemical kinetics controls the production of volatiles. The weight of "oil" collected is given by Eq. (46) without the term $(1 - \gamma)$ and will be represented by the variable $w(t)$.

3.2. Chemical Kinetics Controlling Regime--Nonisothermal

Many experiments are designed so the temperature far from the particle increases linearly with time, i.e., $T = T_o + bt$. The parameter b is a constant heating rate. Substituting Eqs. (30), (9), and (4) into Eq. (8) gives

$$R = \frac{k_o C^*}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} \exp\left[\frac{-E}{R_G(T_o + bt)}\right] \exp\left(-k_o \int_o^t \exp\left[\frac{-E}{R_G(T_o + bt)}\right] dt\right) \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE. \quad (47)$$

If $\frac{-E}{R_G(T_o + bt)} = x$, then

$$R = \frac{k_o C^*}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} \exp\left[\frac{-E}{R_G(T_o + bt)}\right] \exp\left[\frac{-k_o E}{R_G b} \int_{\frac{-E}{R_G T_o}}^{\frac{-E}{R_G(T_o + bt)}} \frac{\exp(x)}{x^2} dx\right] \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE. \quad (48)$$

Recognizing that $T_o + bt = T$

$$R = \frac{k_o C^*}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} \exp\left(\frac{-E}{R_G T}\right) \exp\left[\frac{-k_o E}{R_G b} \int_{\frac{-E}{R_G T_o}}^{\frac{-E}{R_G T}} \frac{\exp(x)}{x^2} dx\right] \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE. \quad (49)$$

Integrating over x gives

$$R = \frac{k_o C^*}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} \exp\left(\frac{-E}{R_G T}\right) \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] \times$$

$$\exp\left[\frac{-k_o E}{R_G b} \left[Ei\left(\frac{-E}{R_G T}\right) - Ei\left(\frac{-E}{R_G T_o}\right) - \frac{\exp\left(\frac{-E}{R_G T}\right)}{\left(\frac{-E}{R_G T}\right)} + \frac{\exp\left(\frac{-E}{R_G T_o}\right)}{\left(\frac{-E}{R_G T_o}\right)}\right]\right] dE. \quad (50)$$

where $Ei(\cdot)$ is the exponential integral function and T_o is the initial temperature of the particle. Substitution of Eq. (50) into Eq. (43) with $C_{R\infty}=0$ yields

$$\frac{dW}{dT} = V_p p (1 - \epsilon) \left[\frac{\gamma}{(1 + \frac{Da}{3})} + (1 - \gamma) \right] \frac{R}{b} \quad (51)$$

where R is defined by Eq. (50). Eq. (51) can be integrated numerically to obtain the weight of volatiles collected as a function of temperature for nonisothermal situations where chemical kinetics controls the rate of volatiles production. The weight of "oil" collected ($\equiv w(t)$) is Eq. (51) without the term $(1 - \gamma)$.

3.3. Diffusional Limitations for Pyrolysis--Isothermal

For very short times or for very low pyrolysis temperatures, the concentration of reactive and nonreactive volatiles in the interstices of the particle will be relatively small. If the mass concentration of nonreactive volatiles is small, the total pressure given by Eq. (21) will be small. If this pressure is low enough so that $C_R v_r$ and $C_{NR} v_r$ in Eqs. (18) and (26) are small relative to $D_e \frac{dC_r}{dr}$ and $D_e \frac{dC_{NR}}{dr}$, then the dominant mechanism for intraparticle mass transport of volatiles will be diffusion.

3.3.1. Reactive Species

For intraparticle diffusional limitations, Eqs. (15) and (18) can be combined to give

$$-\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dC_R}{dr} \right) = \frac{(1 - \epsilon)}{\epsilon} \gamma R - R_C. \quad (52)$$

the general solution of Eq. (52) is

$$C_R = \frac{C_1}{r} \cosh \sqrt{\frac{k''}{D_e}} r + \frac{C_2}{r} \sinh \sqrt{\frac{k''}{D_e}} r + \frac{(1 - \varepsilon)}{\varepsilon} \frac{\gamma}{k''} R. \quad (53)$$

Applying the boundary conditions Eqs. (22a) and (22b) results in

$$C_R = \left[\frac{\gamma k_p R_p^2 (1 - \varepsilon) R}{k'' \varepsilon} - R_p^2 k_g C_{R\infty} \right] \frac{\sinh \sqrt{\frac{k''}{D_e}} r}{r} + \frac{\gamma (1 - \varepsilon)}{k'' \varepsilon} R \quad (54)$$

where

$$\phi \equiv \sqrt{\frac{k''}{D_e}} R_p. \quad (55)$$

Substitution of Eq. (54) into Eq. (22b) gives the flux of reactive volatile species out of the particle.

$$n_{RS} = \left[\frac{\left(\frac{\gamma (1 - \varepsilon)}{\varepsilon} R - k'' C_{R\infty} \right) R_p}{Da - \left[\frac{\phi^2}{1 - \phi \coth \phi} \right]} \right] \quad (56)$$

For $\phi \rightarrow 0$ (i.e., $D_e \rightarrow \infty$), Eq. (56) reduces to Eq. (38) for the case of no intraparticle mass transfer limitations. By applying L'Hospital's rule, it is simple to show that

$$\lim_{\phi \rightarrow 0} \frac{\phi^2}{(1 - \phi \coth \phi)} = -3$$

3.3.2. Nonreactive Species

For intraparticle diffusional limitations, Eqs. (25) and (26) can be combined to give

$$\frac{-1}{r^2} \frac{d}{dr} (r^2 D_e \frac{dC_{NR}}{dr}) = \frac{(1 - \gamma)(1 - \varepsilon)}{\varepsilon} R. \quad (57)$$

The solution of Eq. (54) subject to the boundary conditions, Eqs. (27a) and (27b), is

$$C_{NR} = \left[\frac{(1 - \gamma)(R_p^2 - r^2)}{6D_e} + \frac{(1 - \gamma)R_p}{3k_g} \right] \frac{(1 - \varepsilon)}{\varepsilon} R + C_{NR\infty}. \quad (58)$$

Substitution of Eq. (58) into Eq. (27b) gives the flux of nonreactive volatile species

$$n_{NRS} = \frac{(1 - \gamma)(1 - \varepsilon)R_p}{3\varepsilon} R. \quad (59)$$

Eq. (58) shows that the concentration profile is affected by diffusional limitations; however, Eq. (59) is identical to Eq. (42) owing to the pseudo-steady state assumption. As $k'' \rightarrow 0$ (i.e., $\phi \rightarrow 0$ and $Da \rightarrow 0$), Eq. (56) and Eq. (59) are the same except for the parameter γ . Thus,

$$n_S = n_{RS} + n_{NRS} \rightarrow (1 - \varepsilon)R_p R / 3\varepsilon.$$

3.3.3. Weight of Volatiles Collected

Eqs. (56) and (59) can be substituted into Eq. (31) with the result that

$$\frac{dW}{dt} = V_p (1 - \varepsilon) \left[\frac{3\gamma}{Da - \left(\frac{\phi^2}{1 - \phi \coth \phi}\right)} + (1 - \gamma) \right] R + \frac{3V_p \varepsilon k'' C_{R\infty}}{Da - \left(\frac{\phi^2}{1 - \phi \coth \phi}\right)}. \quad (60)$$

Eq. (60) describes the rate of volatiles collected as a function of time for both isothermal and nonisothermal situations where diffusional mass transfer limitations exist. For isothermal cases the total intrinsic rate of devolatilization is given by Eq. (44). Substitution of Eq. (44) into Eq. (60) and assuming $C_{R\infty}=0$ yields

$$\frac{dW}{dt} = \frac{V_p p(1 - \varepsilon) k_o C^*}{\sqrt{2\pi} \sigma} \left[\frac{3\gamma}{Da - \left(\frac{\phi^2}{1 - \phi \coth \phi}\right)} + (1 - \gamma) \right] \times \int_{-\infty}^{+\infty} \exp\left(\frac{-E}{R_G T}\right) \exp[-k_o t \exp\left(\frac{-E}{R_G T}\right)] \exp\left[-\frac{(E - E_o)^2}{2\sigma^2}\right] dE. \quad (61)$$

Integrating Eq. (61) over time gives

$$W(t) = V_p p(1 - \varepsilon) C^* \left[\frac{3\gamma}{Da - \left(\frac{\phi^2}{1 - \phi \coth \phi}\right)} + (1 - \gamma) \right] \times \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t \exp\left(\frac{-E}{R_G T}\right)] \exp\left(\frac{-(E - E_o)^2}{2\sigma^2}\right) dE \right]. \quad (62)$$

Eq. (62) describes the total weight of volatiles collected as a function of time for isothermal situations where diffusional limitations affect the production of volatiles. Note that the only difference in this result and Eq. (46), which describes the situation of no intraparticle mass transfer limitations, is the constant multiplicative factor containing ϕ . The weight of "oil" collected is Eq. (62)

w

a

3

r

p

w

b

a

p

c

3

a

S.

gr

wh

Ag

without the term $(1 - \gamma)$ and will be represented once again as $w(t)$.

3.4. Convection Limitations for Pyrolysis--Isothermal

For high pyrolysis temperatures, the concentration of reactive and nonreactive volatiles in the interstices of the particle will be large. Therefore, the total pressure within the shale particle relative to the surroundings may be high enough to cause the convective terms in Eqs. (18) and (26) to dominate the diffusive terms. Thus, intraparticle mass transport of volatiles will be controlled by convective processes.

3.4.1. Nonreactive Species

For intraparticle convection limitations, Eqs. (25) and (26) can be combined to give

$$\frac{1}{r^2} \frac{d}{dr} (r^2 C_{NR} v_r) = \frac{(1 - \varepsilon)(1 - \gamma)R}{\varepsilon}. \quad (63)$$

Substituting Eqs. (19) and (21) into Eq. (63) and integrating the result yields

$$C_{NR} = \left[A_1 - \frac{\mu M_{NR}(1 - \gamma)(1 - \varepsilon)Rr^2}{3\varepsilon R_G T} - \frac{A_2}{r} \right]^{\frac{1}{2}} \quad (64)$$

where A_1 and A_2 are arbitrary constants of integration.

Applying the boundary conditions to Eq. (64) gives

$$C_{NR} = \left[\frac{(1 - \gamma)(1 - \varepsilon)R_p R}{3\varepsilon k_g} + C_{NR\infty} \right]^2 +$$

$$\left[\frac{\mu M_{NR} (1 - \gamma) (1 - \epsilon) (R_p^2 - r^2) R}{3\kappa \epsilon R_G T} \right]^{\frac{1}{2}}. \quad (65)$$

Substituting Eq. (65) into Eq. (27b) gives the flux of nonreactive species out of the particle

$$n_{NRS} = \frac{(1 - \gamma) (1 - \epsilon) R_p R}{3\epsilon}. \quad (66)$$

Eq. (66) is the same as Eqs. (42) and (59), because coking is ignored and pseudo-steady state is employed.

Substitution of Eq. (66) into Eqs. (19) and (21) gives the velocity profile within the shale particle

$$v_r = \frac{(1 - \gamma) (1 - \epsilon) r R}{3\epsilon} \left[\left[\frac{(1 - \gamma) (1 - \epsilon) R_p R}{3\epsilon k_g} + C_{NR\infty} \right]^2 + \frac{\mu M_{NR} (1 - \epsilon) (1 - \gamma) (R_p^2 - r^2) R}{3\kappa \epsilon R_G T} \right]^{-\frac{1}{2}}. \quad (67)$$

Note that at the surface of the particle, if $C_{NR\infty}$ is zero, $v_r = k_g$.

3.4.2. Reactive Species

For intraparticle convection limitation, Eqs. (15) and (18) can be combined to give

$$\frac{1}{r^2} \frac{d}{dr} (r^2 C_R v_r) = \gamma \frac{(1 - \epsilon) R}{\epsilon} - R_c. \quad (68)$$

By introducing the variable, $f(r) \equiv r^2 v_r C_R$, Eq. (68) becomes

$$\frac{df(r)}{dr} + \frac{k''}{v_r} f(r) = \frac{\gamma(1-\varepsilon)Rr^2}{\varepsilon}. \quad (69)$$

Eq. (69) can be solved by using the integrating factor

$$\Psi \equiv \exp\left[\int_a^r \frac{k''}{v_r} dr\right]. \quad (70)$$

The lower limit on the integral in Eq. (70) is arbitrary and does not have to be specified.

Substituting Eq. (67) into Eq. (70) results in

$$\Psi(r) = \exp[H(r) - H(a)] \quad (71)$$

where

$$H(r) \equiv \frac{3k''\varepsilon\sqrt{z+yr^2}}{(1-\gamma)(1-\varepsilon)R} + \frac{3}{2} \frac{k''\varepsilon\sqrt{z}}{(1-\gamma)(1-\varepsilon)R} \ln \left[\frac{\sqrt{z+yr^2} - \sqrt{z}}{\sqrt{z+yr^2} + \sqrt{z}} \right], \quad (72)$$

$$z \equiv \left[\frac{(1-\gamma)(1-\varepsilon)R_p R}{3\varepsilon k_g} + C_{NR\infty} \right]^2 + \frac{\mu M_{NR}(1-\gamma)(1-\varepsilon)R_p^2 R}{3\kappa\varepsilon R_G T}, \quad (73)$$

and

$$Y \equiv \frac{-\mu M_{NR}(1-\gamma)(1-\varepsilon)R}{3\kappa\varepsilon R_G T}. \quad (74)$$

If $C_{NR\infty}=0$ and $k_g \rightarrow \infty$, Eq. (73) becomes

$$z \equiv \frac{\mu M_{NR}(1-\gamma)(1-\varepsilon)R_p^2 R}{3\kappa\varepsilon R_G T}. \quad (75)$$

Now, if Eq. (69) is multiplied by Ψ and integrated, then

$$C_R = \frac{\gamma(1 - \varepsilon) R e^{-H(r)}}{r^2 v_r \varepsilon} \int_0^r e^{H(\hat{r})} \hat{r}^2 d\hat{r}. \quad (76)$$

The boundary condition at the surface of the particle is

$$n_R|_{r=R_p} = v_r C_R|_{r=R_p} \quad (77)$$

Substituting Eq. (76) into Eq. (77) gives the flux of volatile species out of the particle.

$$n_{RS} = \frac{\gamma(1 - \varepsilon) R}{R_p^2 \varepsilon} \int_0^{R_p} e^{H(\hat{r})} \hat{r}^2 d\hat{r}. \quad (78)$$

Note that at $r = R_p$, $e^{H(R_p)} = 1$, and

$$e^{H(r)} = \exp\left[\frac{3k''\varepsilon(z+yr^2)^{\frac{1}{2}}}{(1-\gamma)(1-\varepsilon)R}\right] \times$$

$$\left[\frac{(z+yr^2)^{\frac{1}{2}} - (z)^{\frac{1}{2}}}{(z+yr^2)^{\frac{1}{2}} + (z)^{\frac{1}{2}}}\right] \frac{3}{2} \frac{k''\varepsilon(z)^{\frac{1}{2}}}{(1-\gamma)(1-\varepsilon)R} \quad (79)$$

3.4.3. Weight of Volatiles Collected

Eqs. (66) and (78) can be substituted into Eq. (31) to give

$$\frac{dW}{dt} = 4\pi R_p^2 \varepsilon p \left[\frac{(1-\gamma)(1-\varepsilon)R_p R}{3\varepsilon} + \frac{\gamma(1-\varepsilon)R}{R_p^2 \varepsilon} \times \int_0^{R_p} e^{H(\hat{r})} \hat{r}^2 d\hat{r} \right] \quad (80)$$

Substituting Eqs. (74), (75), and (79) into Eq. (80) and making the change of variable $\bar{r} \equiv \hat{r}/R_p$, Eq. (80) becomes

$$\frac{dW}{dt} = V_p p (1 - \varepsilon) (1 - \gamma) R + 3\gamma V_p p (1 - \varepsilon) R \int_0^1 \exp \left[\frac{B\varepsilon}{(1 - \varepsilon)R} \times \right. \\ \left. (1 - \bar{r}^2) \right]^{\frac{1}{2}} \times \left[\frac{(AR[1 - \bar{r}^2])^{\frac{1}{2}} - (AR)^{\frac{1}{2}}}{(AR[1 - \bar{r}^2])^{\frac{1}{2}} + (AR)^{\frac{1}{2}}} \right]^2 \frac{1}{4} \left[\frac{B\varepsilon}{(1 - \varepsilon)R} \right]^{\frac{1}{2}} \bar{r}^2 d\bar{r} \quad (81)$$

where

$$A \equiv \frac{\mu M_{NR} (1 - \gamma) R_p^2}{3\kappa R_G T} \quad (82)$$

$$B \equiv \frac{3k''^2 \mu M_{NR} R_p^2}{\kappa R_G T (1 - \gamma)}. \quad (83)$$

For isothermal cases, the total intrinsic rate of devolatilization is given by Eq. (44).

Eq. (81) can be integrated numerically to obtain the total weight of volatiles collected as a function of time for isothermal situations where convection limitations affect the production of volatiles. Eq. (81) gives the rate at which oil is collected provided the term containing $(1 - \gamma)$ is deleted.

Table 1 lists the expected range of kinetic parameters for Colorado Oil Shale and Table 2 gives the values of certain physical and transport properties used in subsequent model calculations. Table 3 lists typical physical and transport properties for eastern oil shales.

Table 1.--Expected Values for the Kinetic Parameters in the Distribution Model.

Parameter	Expected Range
Arrhenius frequency factor, k_0	$10^{13} - 10^{14}$, sec^{-1}
Mean activation energy, E_0	40 - 60 kcal/g-mole
Variance of the mean, σ	0 - 20 kcal/g-mole

Table 2.--Physical and Transport Properties for Western Oil Shale.

Parameter	Nominal Value	Reference
Physical Properties		
Specific heat, C_p	$1.13 \times 10^3 \text{ J/(kg } ^\circ\text{C)}$	Granoff and Nuttall (1977)
Density of solid phase, ρ_s	$2.25 \times 10^3 \text{ kg/m}^3$	Campbell, et al. (1977)
Porosity, ϵ	0.10	Tisot and Murphy (1965)
Permeability, κ (Eastern Shale)	$1.234 \times 10^{-15} \text{ m}^2$	Crowl and Piccirelli (1979)
Heat of reaction, ΔH	335 kJ/kg	Campbell, et al. (1977)
Fraction of kerogen converted to oil, γ	0.62	Braun and Rothman (1975)
Ultimate volatile content, C^*	338 kg/m^3	Granoff and Nuttall (1977)
Transport Properties		
Thermal conductivity of solid phase, k_s	$1.25 \text{ J/(m}^2\text{-s-}^\circ\text{C)}$	Granoff and Nuttall (1977)
Effective diffusion coefficient, D_e	$1 \times 10^{-10} \text{ m}^2/\text{sec}$	Satterfield (1970)
Heat transfer coefficient, h	$4 - 60 \text{ J/(m}^2\text{-s)}$	
Mass transfer coefficient, k_g	.05 - .3 m/sec	

Table 3.--Physical and Transport Properties for Eastern Oil Shales.

Parameter	Nominal Value	Reference
Physical Properties		
Specific heat, C_p	$1.013 \times 10^3 \text{ J/(kg-}^\circ\text{K)}$	Crowl and Piccirelli (1979)
Density of solid phase, ρ_s	$2.44 \times 10^3 \text{ kg/m}^3$	" "
Porosity, ϵ	0.05	" "
Permeability, κ	$1.234 \times 10^{-15} \text{ m}^2$	" "
Heat of reaction, ΔH	335 kJ/kg	Campbell, et al. (1977)
Fraction of kerogen converted to oil, γ	.18	Crowl and Piccirelli (1979)
Ultimate volatile content, C^*	377 kg/m^3	" "
Transport Properties		
Thermal conductivity of solid phase, k_s	$0.628 \text{ J/m-s-}^\circ\text{K)}$	Crowl and Piccirelli (1979)
Effective diffusion coefficient, D_e	$1 \times 10^{-10} \text{ m}^2/\text{sec}$	Satterfield (1970)
Heat transfer coefficient, h	4 - 60 $\text{J/m}^2 \text{ sec}$	
Mass transfer coefficient, k_g	.05 - .03 m/sec	

4. THE EFFECT OF KINETIC PARAMETERS ON "OIL" YIELD

For very small particles, the weight of "oil" produced will be limited by chemical kinetics. The effect of the kinetic parameters on the weight of "oil" collected for small particles can be calculated using Eq. (46) with the term containing $(1 - \gamma)$ deleted. In what follows, the fraction of the total possible oil yield will be calculated for different values of k_o , E_o , and σ . The base case for these calculations will be $k_o = 6.95 \times 10^{13} \text{sec}^{-1}$, $E_o = 55,333 \text{ cal/g-mole}$, and $\sigma = 2000 \text{ cal/g-mole}$. For this set of calculations the Damköhler number will be set equal to zero. The effect of the heating rate on the weight of oil collected for small particles can be calculated using Eqs. (50) and (51).

The integration of E over the interval $(-\infty, +\infty)$ was approximated by integrating over the finite interval $[E_o - 2\sigma, E_o + 2\sigma]$. Even with this truncation, 95.45% of the reactions are still included in the reaction set. The error introduced by the truncation will be small since the probability that a reaction has an activation energy in the truncated region is very small. The integral was calculated

using Simpson's rule (see, p. 79 of Carnahan, et al., 1969). It was determined that thirty applications of Simpson's rule were necessary to obtain an error of less than 10^{-6} in the evaluation of the integral.

4.1. The Effect of σ on "Oil" Yield

Figure 2 is a plot of the dimensionless oil weight collected versus time at 648°K for three values of σ . The sigma values of 2 and 10 kcal/g-mole represent narrow and broad distributions. At 648°K, the curve representing $\sigma = 10$ kcal/g-mole displays the greatest "oil" yield during the time represented. This behavior is a consequence of the higher probability that a reaction has an activation energy much lower and much higher than E_0 . For these reactions, the rate constants will be relatively large despite the low temperature, and a significant production of volatiles will occur.

For large and small values of σ , the ultimate "oil" yield is the same. However, σ influences the time required for pyrolysis significantly. Note that for $\sigma = 2$ kcal/g-mole the probability that a reaction has an activation energy less than or greater than E_0 is much smaller than the case with $\sigma = 10$ kcal/g-mole. Thus, with $2R_G T < E_0$, the rate of devolatilization is extremely slow--esp. if $2R_G T < E_0 - 2\sigma$. For $T = 648$ K, $\sigma = 2$ kcal/g-mole, and $E_0 = 55,333$ cal/g-mole, $2R_G T = 2.6$ kcal/g-mole $< E_0 - 2\sigma = 51,333$ kcal/g-mole. Thus, for the time scale shown on Figure 2, the effect of σ on

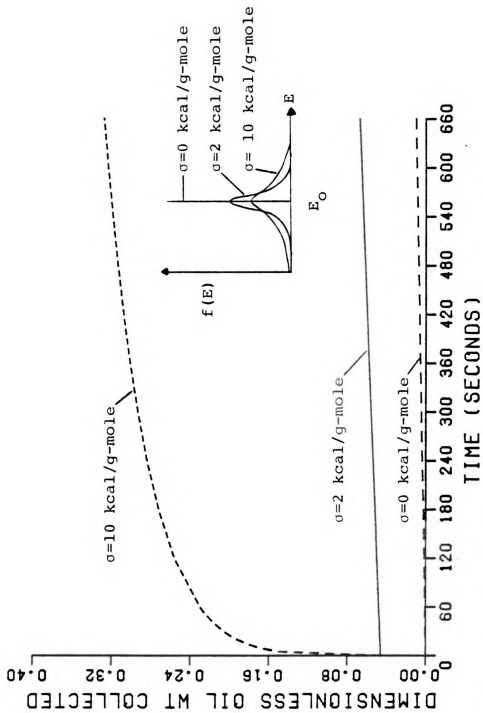


Figure 2. The effect of σ on the "oil" yield at 648°K .

$E_O = 55,333$ kcal/g-mole, $k = 6.95 \times 10^{13} \text{ sec}^{-1}$, $2R_G T = 2600$ kcal/g-mole.

the "oil" yield is dramatic. Note, however, that $\sigma = 10$ kcal/g-mole gives $E_0 - 2\sigma \approx 35$ kcal/g-mole.

Figure 3 shows the effect of σ on the oil yield for a higher temperature, viz., 775°K. For this case, $2R_G T$ is closer to $E_0 - 2\sigma$ than previously, so the temperature is high enough to cause reactions with activation energies around E_0 to contribute significantly. This is a direct result of the dependence of the Arrhenius rate constant on the temperature. Note that the behavior for very short times (i.e., $t < 30$ sec) is similar to the results shown in Figure 2, but that the long time behavior is opposite. Once again, for $t \rightarrow \infty$, all of these curves will approach unity.

It is interesting that the case where $\sigma = 10$ kcal/g-mole shows the smallest "oil" yield for $t > 60$ sec. This occurs because $2R_G T < E_0 + 2\sigma$, so the rate constants for the reactions with activation energies much higher than E_0 are very small. Therefore, these reactions cannot contribute significantly to the weight of "oil" collected during the time scale displayed by Figure 3. This type of behavior may explain differences between oil shale resources having different organic compositions. A simple lumping strategy equivalent to setting $\sigma = 0$ for all shales would not have the flexibility exhibited by Figures 2 and 3.

4.2. The Effect of E_0 on "Oil" Yield

Figure 4 is a plot of the dimensionless weight of "oil" collected versus time at 775°K for three values of

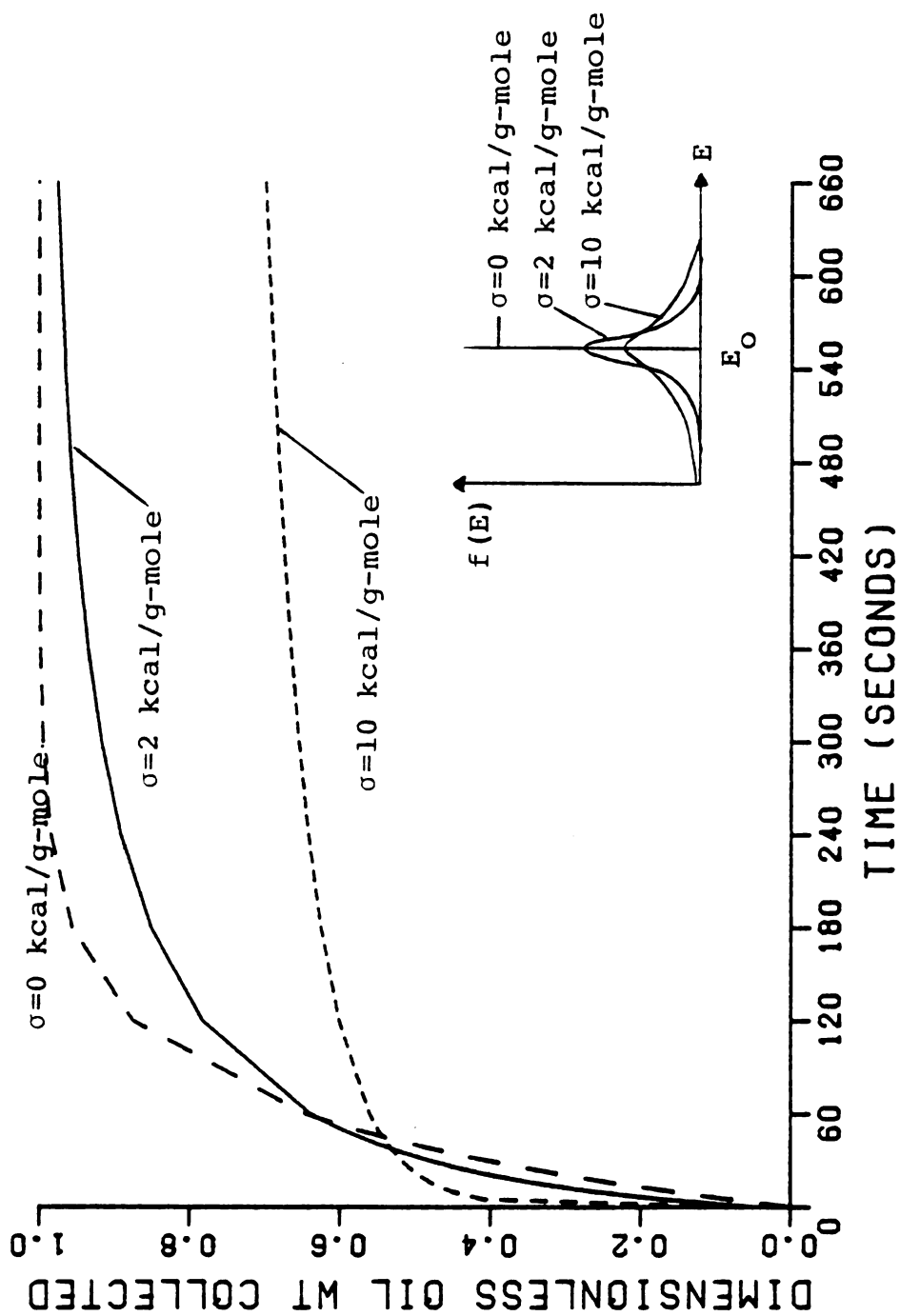


Figure 3. The effect of σ on the "oil" yield at 775°K .
 $E_0 = 55,333$ cal/g-mole, $k_0 = 6.95 \times 10^{13} \text{ sec}^{-1}$, $2R_G T = 3100$ cal/g-mole.

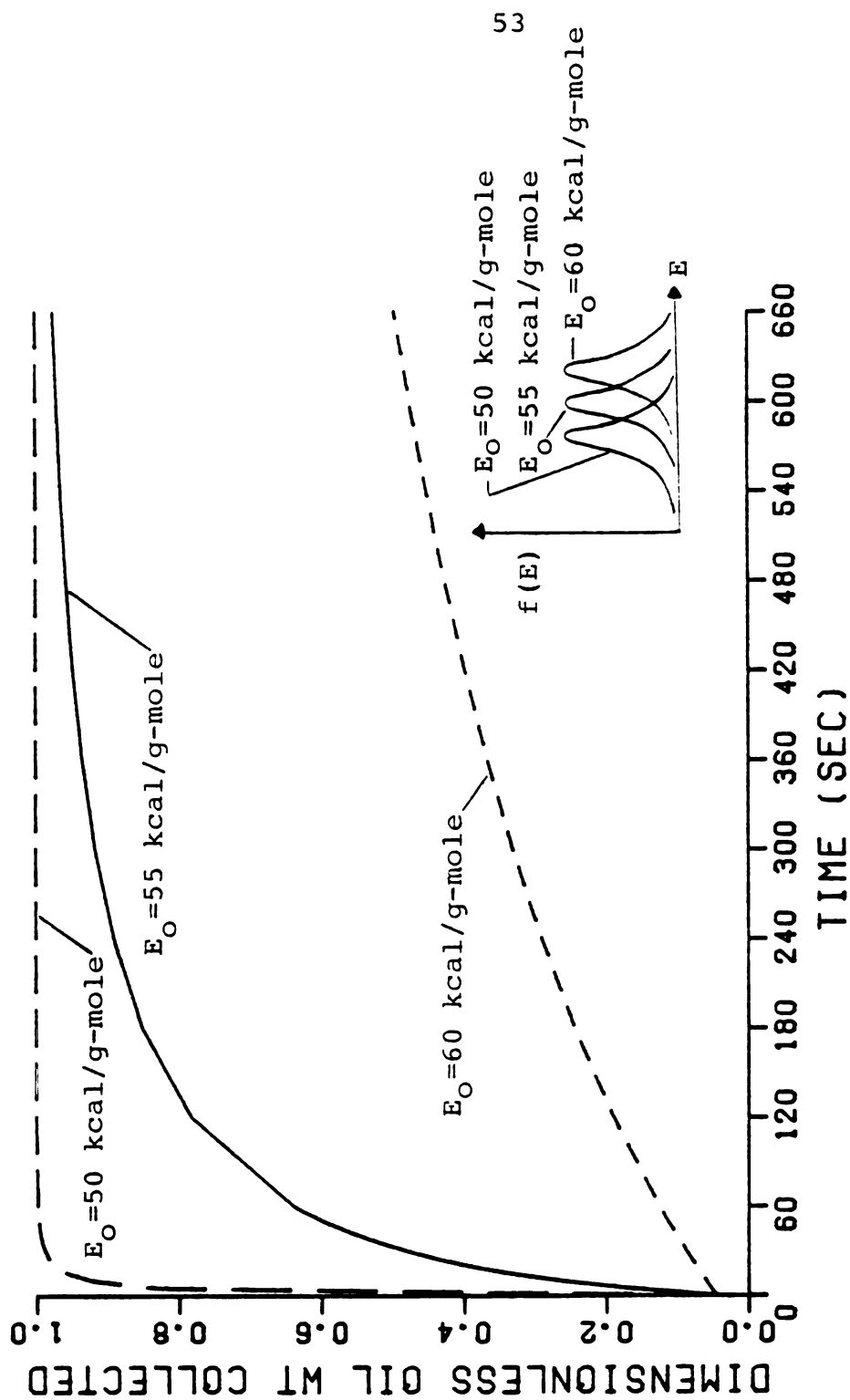


Figure 4. The effect of E_O on the "oil" yield at 775°K.
 $k_O = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 2000 \text{ cal/g-mole}$, $2R_G T = 1300 \text{ cal/g-mole}$.

E_0 . As expected, the rate of "oil" production is greatest for the short time behavior for the case of $E_0 = 50,000$ cal/g-mole. This is a direct consequence of the dependence of the Arrhenius rate constant on E . As E_0 is lowered, reactions with lower activation energies are included in the reaction set. Therefore, the rate constants for all the reactions are increased and consequently the production of "oil" increases.

As E_0 is increased, reactions with higher activation energies are included in the reaction set. Consequently, the rate constants are much smaller and the rate of "oil" production is lower. Once again, for $t \rightarrow \infty$, all of these curves will approach unity. It is also apparent that the weight of oil collected is extremely sensitive to E_0 , since a 10% increase in E_0 drastically reduces the weight of "oil" collected during the short time behavior.

4.3. The Effect of k_0 on Oil Yield

Figure 5 is a plot of the dimensionless weight of oil collected as a function of time at 775°K for three values of k_0 . In Eq. (46) k_0 appears in the argument of an exponential term. As k_0 increases, the value of this exponential term decreases, resulting in an increase in the weight of oil collected. This behavior is shown in Figure 5. In Section 4.2. it was shown that if E_0 is increased or decreased by only 10%, the weight of "oil" collected was affected dramatically. A similar effect is seen in Figure 5,

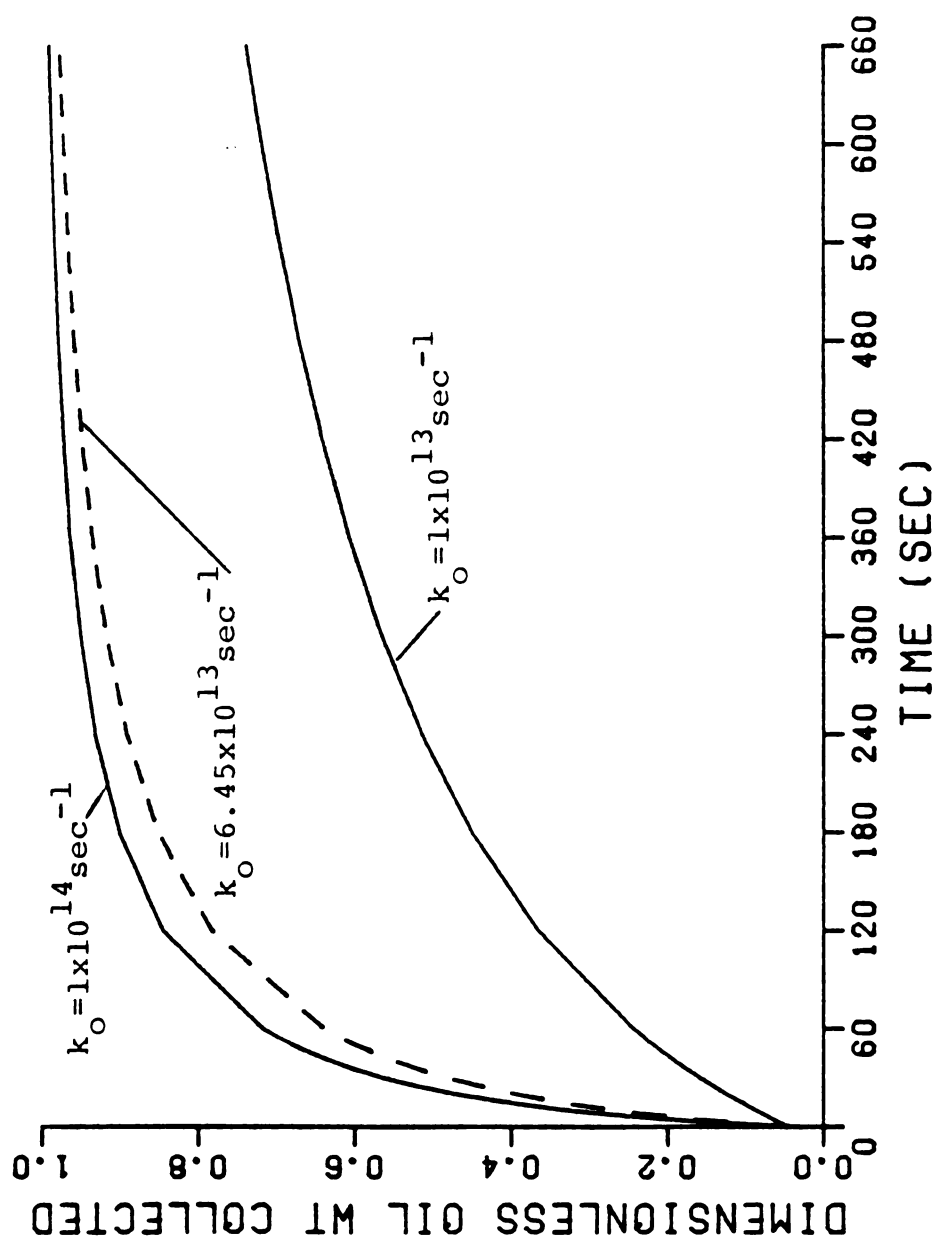


Figure 5. The effect of k_O on the "oil" yield at 775°K .
 $E_O = 55,333 \text{ cal/g-mole}$, $\sigma = 2000 \text{ cal/g-mole}$, $2R_G T = 3100 \text{ cal/g-mole}$.

if k_o is decreased by an order of magnitude. Therefore, the distribution model is much more insensitive to k_o than E_o . As before, for $t \rightarrow \infty$, all the curves approach unity.

4.4. The Effect of the Heating Rate on Oil Yield

Eq. (51) was integrated using a fourth order Runge-Kutta technique (see, p 363 Carnahan, et al., 1969). A step size of 1°C was used in order to minimize the truncation error. For these calculations a value for $C^*(1 - \epsilon)V_{pp}$ corresponding to 10 ml of potential oil was used. The program used in this calculation can be found in Appendix E. Figure 6 is a plot of the volume of oil collected as a function of temperature for five values of the heating rate. The volume of oil collected at the lower heating rates appears to approach an asymptote, but because $Da = 0$, the volume of oil collected will ultimately approach 10 ml as $t \rightarrow \infty$.

It is evident in Figure 6 that as the heating rate is lowered, the volume of oil collected is decreased. This model prediction is consistent with the experimental observations of Campbell, et al. (1977). They explained this observation in terms of greater self-generated gas sweep rates in the particle at the higher heating rates. However, this mechanism is not present in the model discussed here, so an alternative explanation is desirable. But, at this time it is not clear what the mechanism is that causes this behavior. The fact that the distribution model

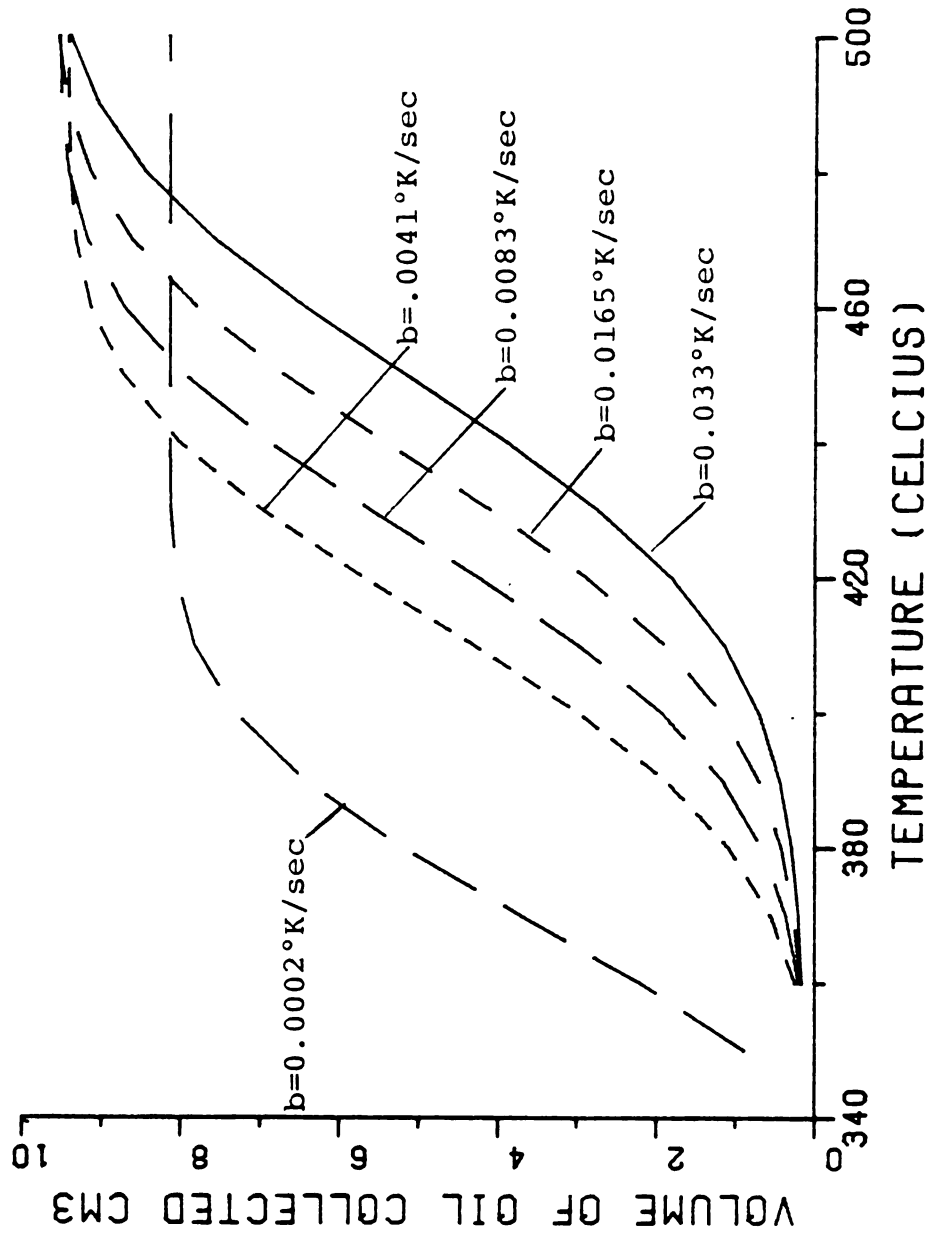


Figure 6. The effect of the heating rate on oil yield.

$E_o = 55,333$ cal/g-mole, $k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 2000$ cal/g-mole

qualitatively and nearly quantitatively follows observed experimental behavior even with $Da = 0$ lends support for this approach. It is anticipated that the model will also give satisfactory predictions for cases where the heating rate is nonlinear.

5. PARAMETER ESTIMATES USING DATA FOR WESTERN OIL SHALE

Campbell, et al. (1978) conducted several isothermal and nonisothermal experiments on powdered samples of Colorado oil shale. The diameter of the particles used in the experiments was 800 microns, and the oil content of the shale was 22 gal/ton as measured by the Fisher Assay. In one isothermal experiment, the weight of oil collected as a function of time at 648°K was measured. From this experiment it was possible to determine the parameters k_o , E_o , σ , and $C^*(1 - \epsilon)$ for the distribution of activation energies model. For this experiment $Da/3 = 3 \times 10^{-8}$, which implies that very little degradation of the liberated "oil" is expected to occur. This is a consequence of the small particle size and the low temperature of pyrolysis.

5.1. Estimates of Parameters for the Distribution of Activation Energy Model

Values for E_o , σ , k_o , and $(1 - \epsilon)C^*$ were obtained by curvefitting $w(t)$ given by Eq. (46) to the experimental data using a direct search optimization scheme (see, Hooke and Jeeves, 1961). Details of the procedure can be found

in Appendix A. The results of the optimization gave the following values for the four parameters:

$$k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$$

$$E_o = 55,333 \text{ cal/g-mole}$$

$$\sigma = 1740 \text{ cal/g-mole}$$

$$\gamma C^*(1 - \epsilon) \approx 223 \text{ kg/m}^3$$

The results of the estimating procedure can be seen in Figure 7. Because the first nine data points were used in the optimization scheme, the model accurately predicts the data for the first 40 ks. However, the long time response of the model deviates from the data.

In a second isothermal experiment, Campbell, et al. (1978) measured the total weight loss as a function of time at 673°K. For this experiment, $Da/3 = 8 \times 10^{-8}$, indicating once again that "oil" degradation will be negligible. The values of γ and $(1 - \epsilon)C^*$ were obtained by fitting Eq. (46) for the total weight collected to the experimental data using the values for k_o , E_o , and σ obtained previously. Details of this procedure can be found in Appendix C. The values for γ and $(1 - \epsilon)C^*$ are:

$$\gamma \approx 0.65$$

$$(1 - \epsilon)C^* = 344 \text{ kg/(m}^3 \text{ of particle)}$$

The total initial mass concentration of volatiles as indicated by $(1 - \epsilon)C^*$ represents 15 wt% of the initial weight of the particle. This corresponds favorably with the 15 wt% of organic material as measured by Jukkola, et al. (1953) for 28 gal/ton Colorado oil shale. It also compares

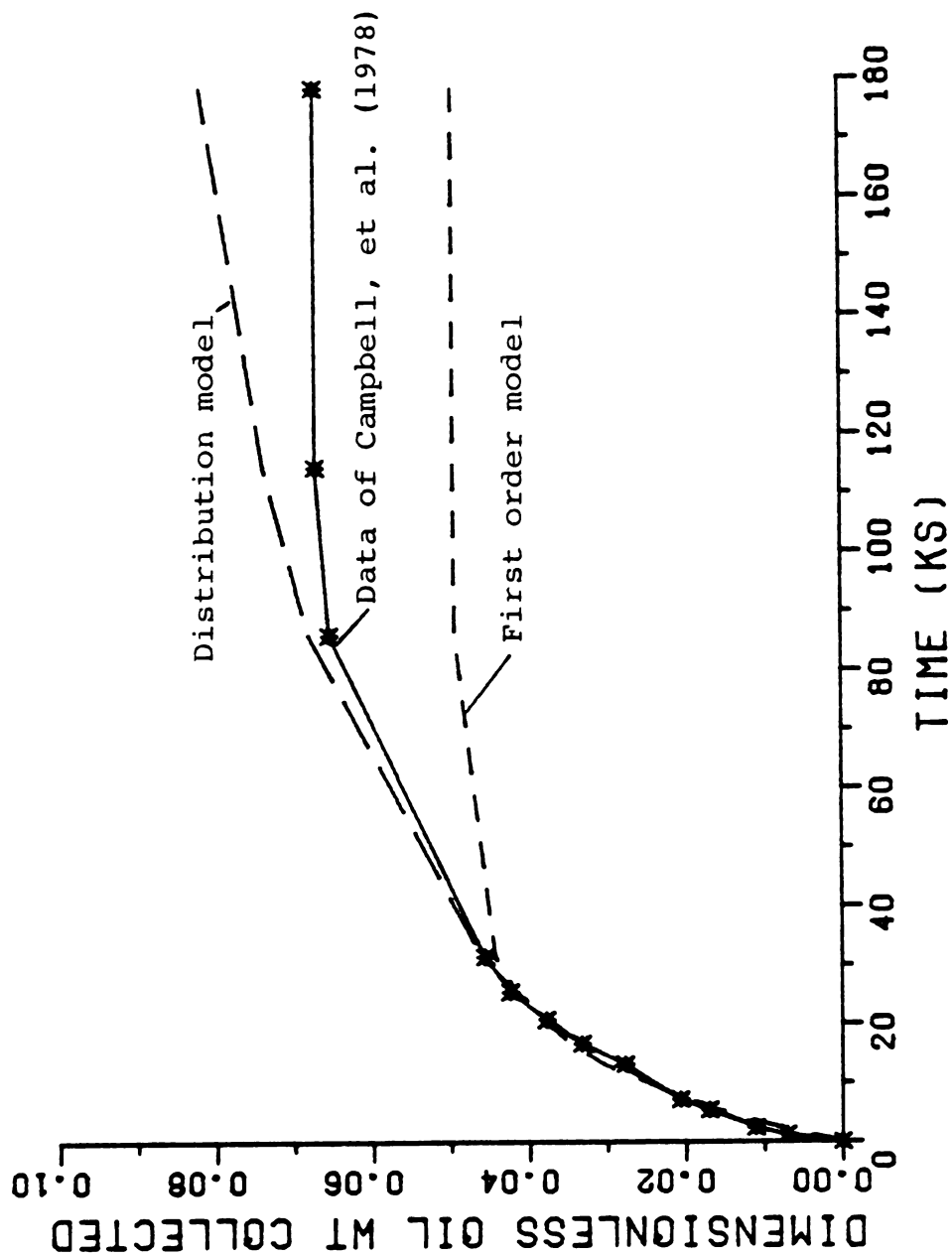


Figure 7. Results of parameter estimation at 648°K for the distribution and first order models.

$$E_O = 55,333 \text{ cal/g-mole}, k_O = 6.95 \times 10^{13} \text{ sec}^{-1}, \sigma = 1740 \text{ cal/g-mole}, \\ \gamma C^*(1 - \epsilon) = 223 \text{ kg/m}^3$$

well with the initial concentration of kerogen (i.e., 377.3 kg/m³) for Michigan oil shale (see, Cowl and Piccirelli, 1979). The experiments of Granoff and Nuttall (1977) also showed that the total weight loss at 793°K for 22 gal/ton Colorado oil shale was 15 wt% of the initial weight of the shale. Braun and Rothman (1975) determined that the fraction of kerogen converted to oil was 0.62. The value for γ is consistent with this value. The value for the mean activation energy E_0 is typical of what has been observed previously for oil shale pyrolysis (see, Section 1.3). The variance of the distribution is much smaller than 9,380 cal/g-mole obtained by Anthony (1974) for lignite coal. This smaller value of σ apparently indicates that the bonds which make up the kerogen molecule may be more uniform than those of a coal molecule.

The results of the last estimating procedure are shown in Figure 8. The total weight of volatiles collected is made dimensionless with the initial weight of the particles. It is apparent from Figure 8 that the distribution model does not predict a sharp plateau at long times. The absence of a distinct plateau could be explained by the shape of the distribution function. For instance, the Gaussian distribution of activation energies requires that the activation energies for all the reactions producing volatile species occur in the interval $[E_0 - 2\sigma, E_0 + 2\sigma]$. The experiments of Allred (1967) have shown that the reactions producing gaseous nonreactive species nominally occur at

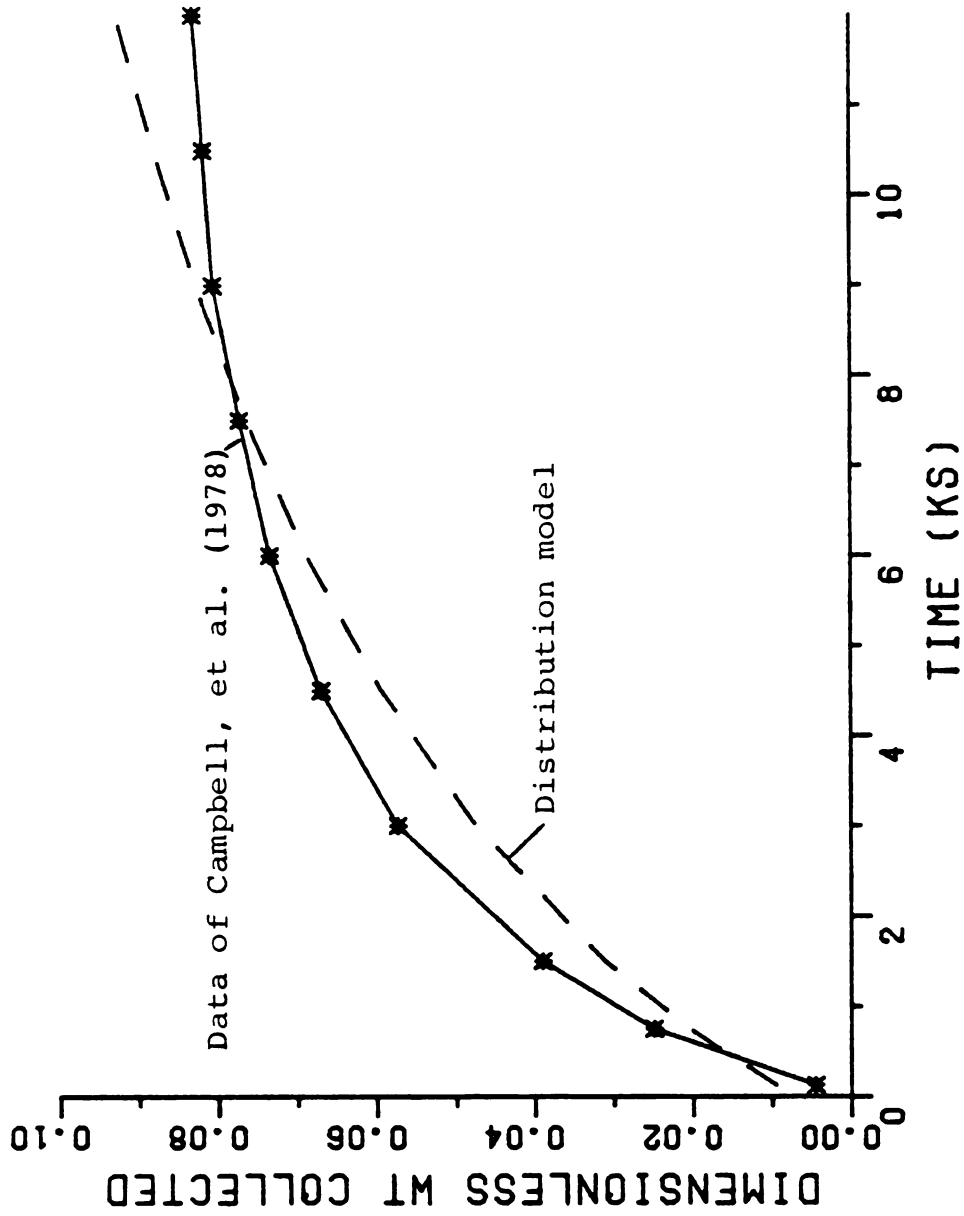


Figure 8. Results of parameter estimation at 673°K to obtain γ and $C^*(1 - \epsilon)$.

$E_O = 55,333$ cal/g-mole, $k_O = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 1740$ cal/g-mole,

$\gamma = 0.65$, $C^*(1 - \epsilon) = 344 \text{ kg/m}^3$

lower temperatures than those reactions producing reactive species (i.e., "oil"). Given the low value of σ , the lower limit of the distribution function $[E_0 - 2\sigma]$ might not be expected to include the activation energies for those reactions producing nonreactive species. Thus, the distribution function might better be described by a bimodal distribution. One peak of this bimodal distribution would be characterized by σ_1 and E_{01} and would be centered around the mean activation energy of the reactions producing nonreactive species. The second peak of this bimodal distribution would be characterized by E_{02} and σ_2 and would be centered around the mean activation energy of the reactions producing reactive species. A bimodal distribution would improve the model prediction in Figure 8 if E_{01} and E_{02} differed significantly and if $\sigma_1 \ll E_{01}$ and $\sigma_2 \ll E_{02}$. First, the short time response will be more rapid since reactions with lower activation energies are included in the reaction set (see, Section 4.2). Secondly, the probability that a reaction has an activation energy in the interval $[E_{01} + 2\sigma_1, E_{02} - 2\sigma_2]$ will be small. Therefore, the long time response will be improved since reactions having activation energies in the interval mentioned above will not contribute to the weight loss unless $2R_G T \approx E_{02}$.

For these two isothermal experiments the maximum value of R occurs at $t=0$. At 648°K and 673°K , the values of R at $t=0$ are 0.01 and $0.06 \text{ kg/m}^3\text{sec}$, respectively. Corresponding values of $\frac{R_p |\Delta H| (1 - \epsilon) R}{3h}$ in Eq. (35) are 0.01°K

and 0.04°K respectively. This indicates that the temperature of the particle is constant for the duration of the experiments.

5.2. Estimates of Parameters for a Lumped First Order Model

A comparison study was made by fitting the "oil" weight loss data of Campbell, et al. (1978) to a single, first order, irreversible reaction (i.e., $\sigma \equiv 0$). The method for determining the parameters k_o , E_o , and $C^*(1 - \epsilon)$ was similar to the one used previously (see, Section 5.1 and Appendix D). The parameters for this model are:

$$k_o = 4.2063 \times 10^{13} \text{ sec}^{-1}$$

$$E_o = 52,667 \text{ cal/g-mole}$$

$$\gamma C^*(1 - \epsilon) = 111.09 \text{ kg/m}^3$$

Figure 7 shows a comparison of the first order model and the distribution model. Because the first nine data points were used in the optimization scheme, both models accurately predict the data for the first 40 ks. However, the first order model does not accurately predict the data at long times because of the low value of $C^*(1 - \epsilon)$. Although the distribution model is more accurate in this respect, it also deviates from the data at long times because of the higher value of $C^*(1 - \epsilon)$. The previous discussion suggested a means to correct this for the distribution model, but for the simple lumped approach the strategy employed by Campbell, et al. (1978) as discussed in the Introduction, may be the only alternative available.

5.3. Prediction of Nonisothermal Pyrolysis Using Kinetic Parameters Estimated from Isothermal Data

In a nonisothermal experiment, Campbell, et al. (1978) measured the volume of oil collected as a function of time as the temperature of the sample was heated at $0.033^{\circ}\text{K/sec}$. Eq. (51) was integrated using a fourth order Runge-Kutta technique (see, p 363 Carnahan, et al., 1969) to obtain the volume of oil collected versus temperature for the distribution model. A step size of 1°K was used in order to minimize the truncation error. The program that was used in making this calculation is discussed in Appendix E. Eq. (D.2) in Appendix D was used to calculate the volume of oil collected versus temperature for the first order model.

The data of Campbell, et al. (1978) is compared in Figure 9 with predictions made by the distribution model and the first order model. With no further adjustable parameters the distribution model is more representative of the data than the first order model. The initial concentration of kerogen must be adjusted in the first order model if it is to predict the data at long times. Such a requirement is typical of approaches using simple kinetic schemes. In an attempt to explain differences between the data and the distribution model, the sensitivity of Eq. (51) to the parameters E_0 and the heating rate was investigated (see Chapter 4). It was pointed out in Chapter 4 that the two most sensitive parameters in the distribution model were

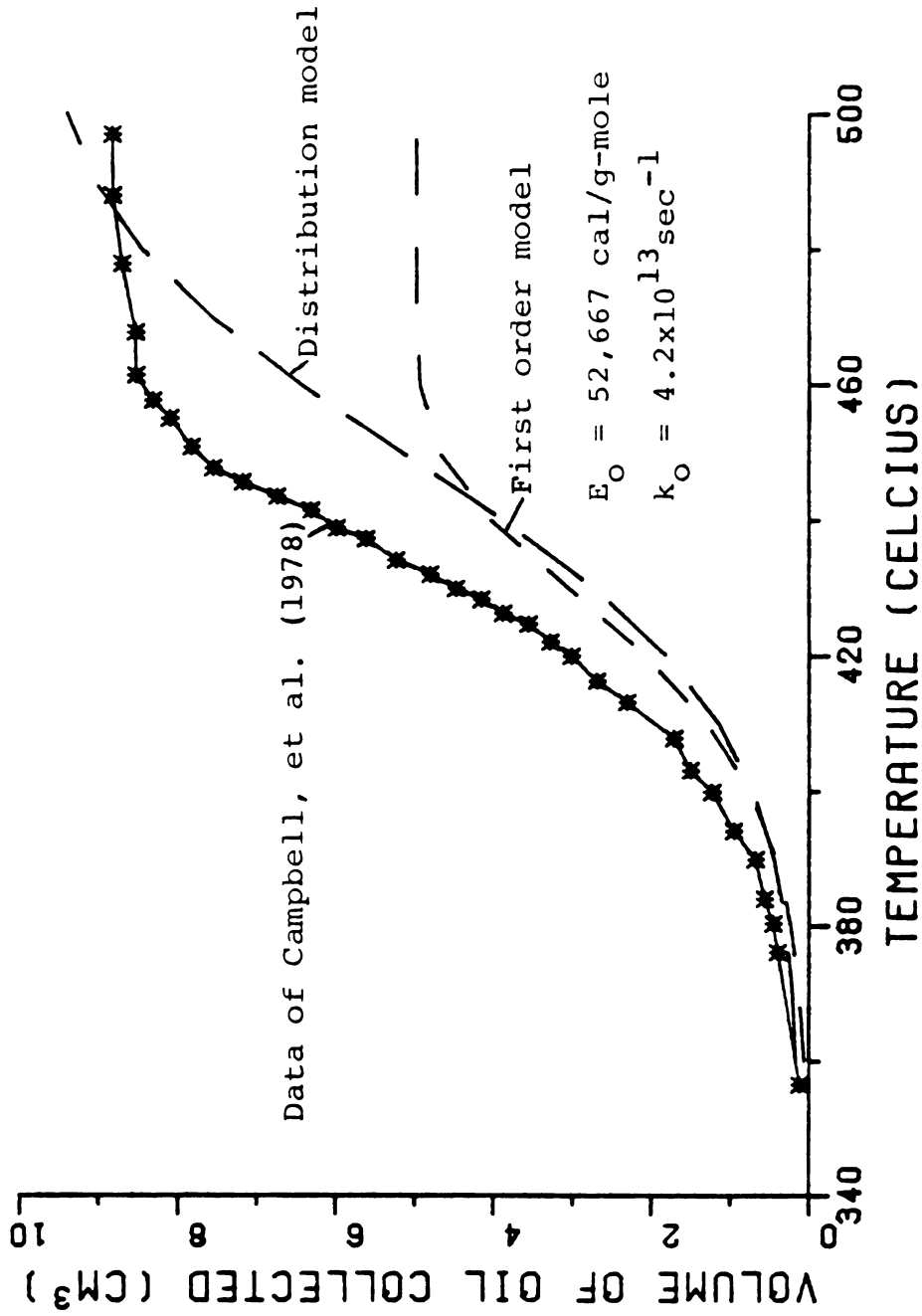


Figure 9. The distribution and first order models for a heating rate of 0.033°K/sec.

$$E_O = 55,333 \text{ cal/g-mole}, k_O = 6.95 \times 10^{13} \text{ sec}^{-1}, \sigma = 1740 \text{ cal/g-mole}, \gamma C^*(1 - \epsilon) = 223 \text{ kg/m}^3$$

E_0 and the heating rate. The effect of varying σ will be negligible since such a small value of σ was found by the optimization scheme. However, in general, the effect of σ in the distribution model is not negligible as discussed in Section 4.1.

The effect of E_0 on the "oil" yield is shown in Figure 4. By reducing E_0 by 5% and 10%, the response is altered significantly. Even an error of 1% in the determination of E_0 would affect the response. Such an error is possible since the optimization procedure identified several local minima very close to each other. The least of all the local minima was chosen as the global minimum. If the optimization process had continued, possibly one of the other local minima could have been identified as the global minimum. This procedure would have required excessive computer time, and the global minimum that was arrived at was considered satisfactory.

Figure 10 shows the experimental data along with the predictions given by the distribution model for four different heating rates. The data can be represented quite well if the heating rate of the experiment were $0.0165^\circ\text{K}/\text{sec}$. However, this would have required that the heating rate be lower than reported by a factor of two.

For this nonisothermal experiment the maximum value of R occurs at 723°K and equals $0.16 \text{ kg}/\text{m}^3\text{sec}$. The corresponding value of $\frac{R_p |\Delta H| (1 - \varepsilon) R}{3h}$ in Eq. (35) is 0.10°K .

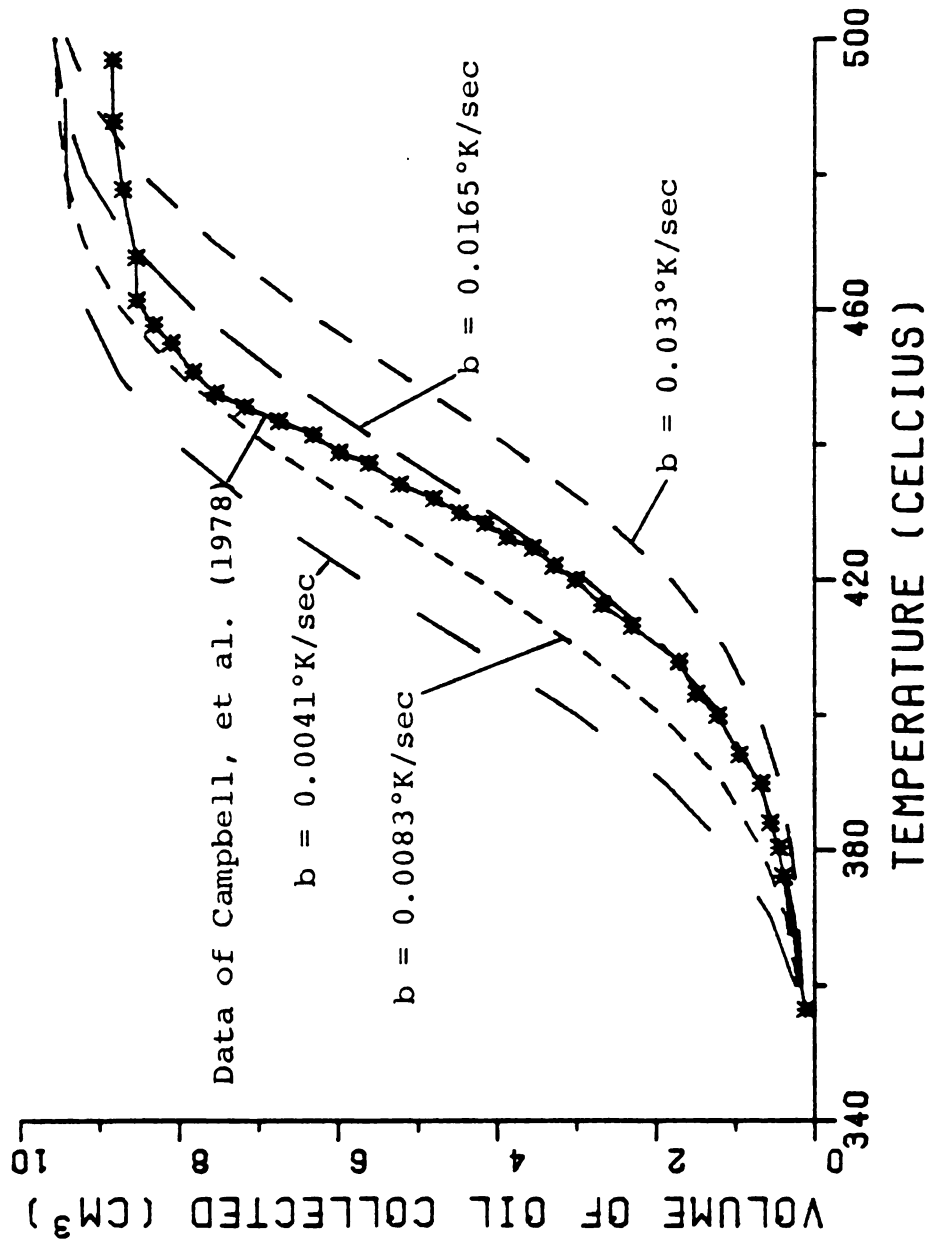


Figure 10. The effect of the heating rate.
 $E_o = 55,333 \text{ cal/g-mole}$, $k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 1740 \text{ cal/g-mole}$,
 $\gamma C^*(1 - \epsilon) = 223 \text{ kg/m}^3$

Therefore, for the duration of the experiment the temperatures of the particles and the sweep gas will be approximately the same.

5.4. Prediction of Isothermal Pyrolysis for Large Particles

Granoff and Nuttall (1977) conducted an isothermal experiment at 703°K with a 12.7 mm diameter sphere and measured the total weight loss as a function of time. The oil shale that was used in the experiment contained the same oil content as that used by Campbell, et al. (1978). Therefore, the parameters that were determined from the data of Campbell, et al. (1978) will be used in this set of calculations. For this large particle size, the mechanisms for intraparticle mass transfer are expected to be diffusion for the short time data and convection for the long time data. However, $Da = 8 \times 10^{-5}$, which indicates that degradation of the liberated "oil" will be negligible. Eq. (62) is used to calculate the total weight of volatiles collected in the presence of diffusion limitations.

Figure 11 is a comparison of the data with the distribution model for the total weight loss using three values of ϕ . Up to 300 seconds, the cases where $\phi=20$ and $\phi=40$ represent the data quite well. The values of the effective diffusion coefficients corresponding to $\phi=20$ and $\phi=40$ are $4 \times 10^{-11} \text{ m}^2/\text{sec}$ and $10^{-11} \text{ m}^2/\text{sec}$, respectively. The case where $\phi=0$ represents no intraparticle mass transfer

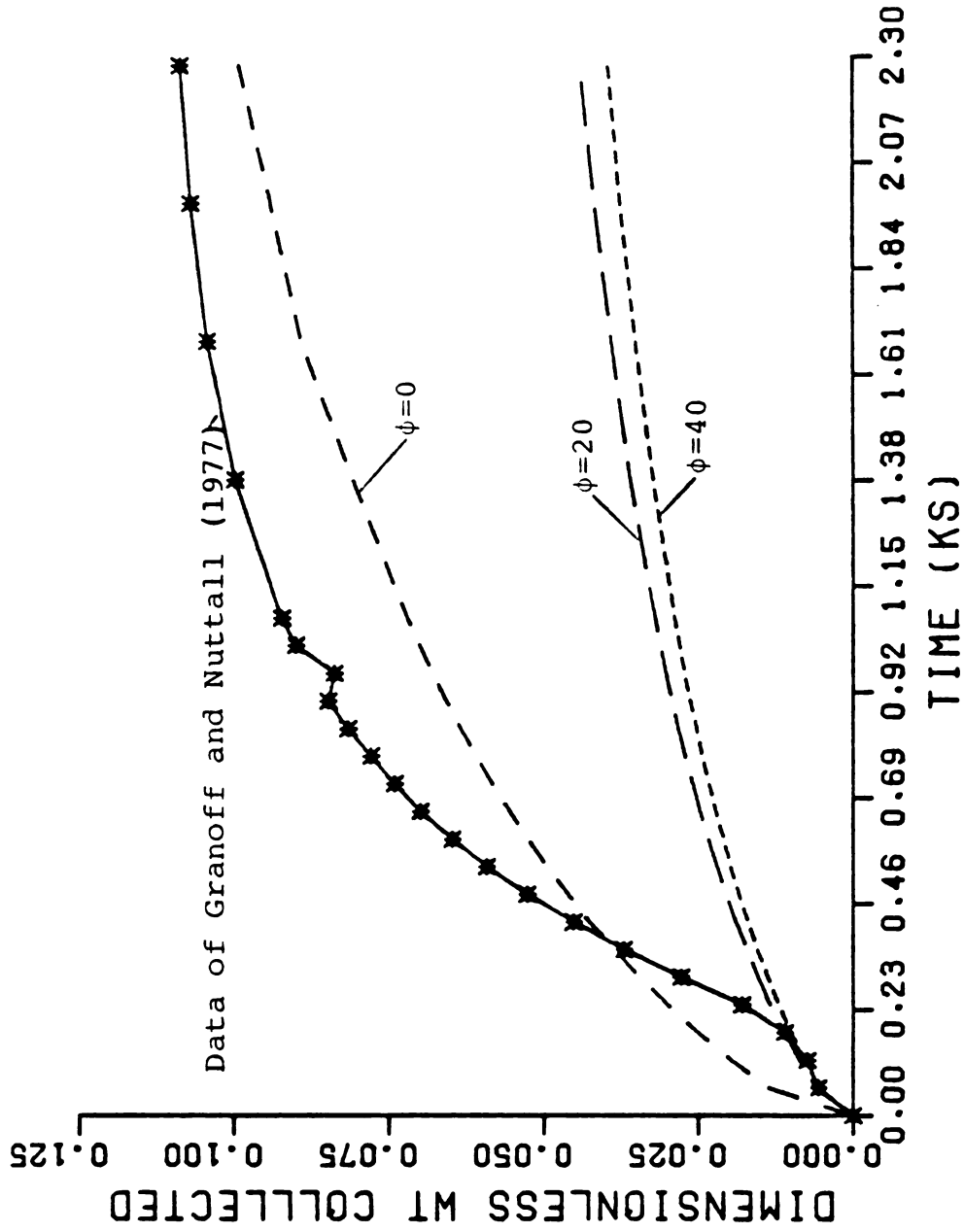


Figure 11. Distribution model with diffusional limitations at 703°K.
 $E_o = 55,333$ cal/g-mole, $k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 1740$ cal/g-mole,
 $C^*(1 - \epsilon) = 344 \text{ kg/m}^3$

limitations. Apparently, at short times there are diffusional limitations present as hypothesized in Section 3.3.

To calculate the total weight of volatiles collected versus time for convection limitations, Eq. (81) was integrated. A fourth order Runge-Kutta technique (see, p 363 of Carnahan, et al., 1969) was used with a step size of ten seconds. The program that was used in making this calculation is presented in Appendix F. Figure 12 is a comparison of the data with the convection case and the case where $\phi=0$. Both cases lag behind the data after 360 seconds but begin to approach the data at longer times. This lag in the weight loss at short times for both the case where $\phi=0$ and the convection case gives further support for a bimodal distribution. As was pointed out in Section 4.2, if reactions with lower activation energies are included in the reaction set, the rate of volatiles production increases. An increase in the production of volatiles would increase the initial time response of the model. Depending on the magnitude of this increase, the convection case may be expected to represent the data more accurately. It is noteworthy that previous attempts to interpret this data with other models (cf., Granoff and Nuttall, 1977; Shih and Sohn, 1978) were also relatively unsuccessful and gave similar predictions as those given by the distribution model.

For this isothermal experiment the maximum value of R occurs at $t=0$ and equals $0.35 \text{ kg/m}^3\text{sec}$. The corresponding value of $\frac{R_p |\Delta H| (1 - \epsilon) R}{3h}$ in Eq. (35) is 5.50°K .

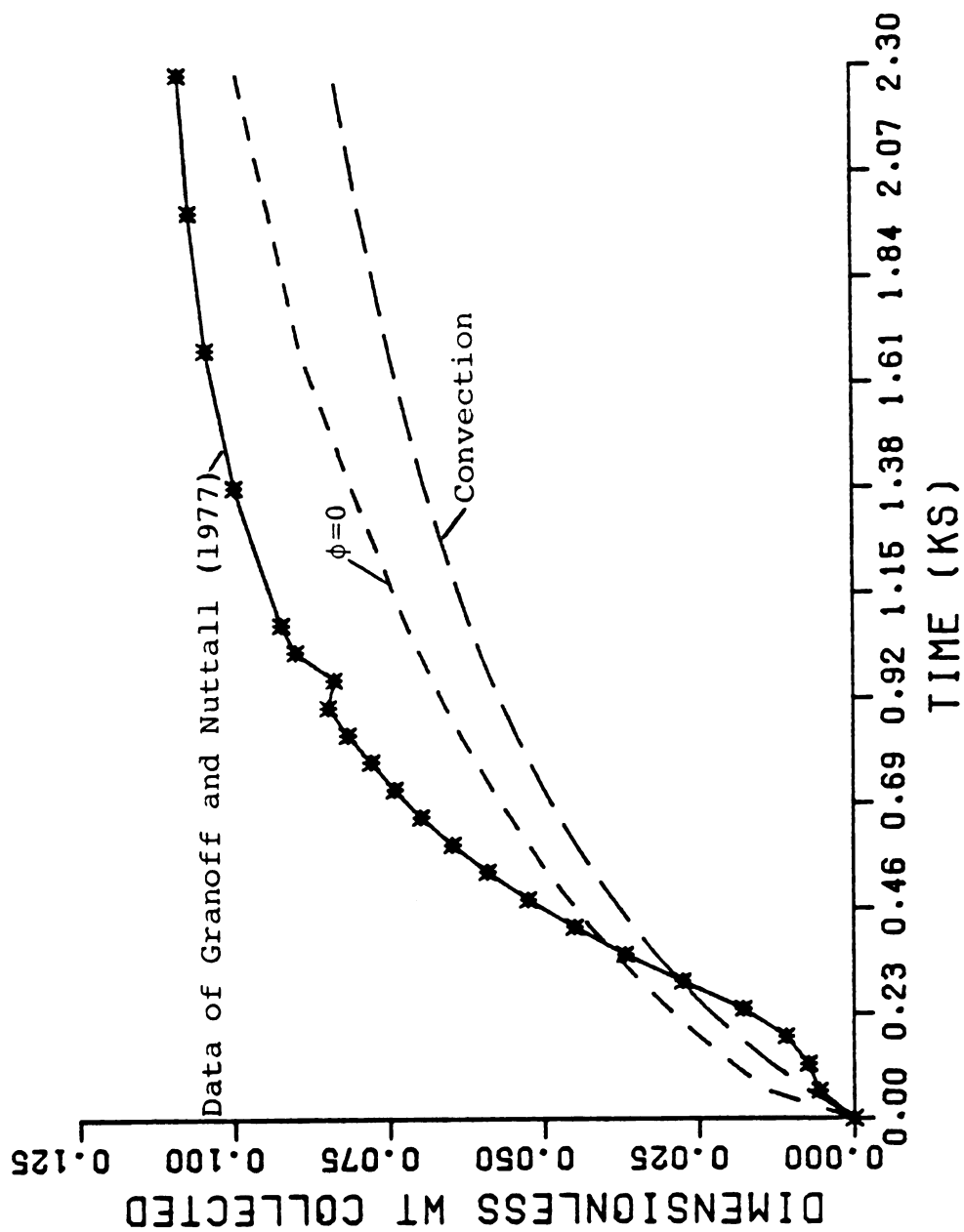


Figure 12. Distribution model with convection limitations at 703°K.
 $E_o = 55,333$ cal/g-mole, $k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$, $\sigma = 1740$ cal/g-mole,
 $C^*(1 - \epsilon) = 344 \text{ kg/m}^3$

This term is approximately equal to one after 23 minutes into the experiment. Because of the large particle size, the temperature of the particle will be cooler relative to the surroundings. This small difference is not expected to affect the diffusion, convection, and kinetic responses significantly.

6. MODEL PREDICTIONS FOR EASTERN OIL SHALE

The kinetics of devolatilization of eastern oil shales has been modeled as a single, second-order, irreversible reaction (Crowl and Piccerelli, 1979). The rate expression for this reaction is

$$R_{cp} = 2.4868 \times 10^{13} \exp \left(\frac{-30,337^\circ\text{K}}{T} \right) \rho_K^2 \frac{\text{kg}}{\text{m}^3 \text{sec}} \quad (84)$$

where ρ_K is the concentration of unreacted kerogen. The initial concentration of kerogen was measured to be 377.3 kg/m³ or 15.26 wt % of the initial weight of the shale. Crowl and Piccirelli (1979) used this second order expression in an intraparticle mass transport model to predict the pyrolytic behavior of a semi-infinite slab of oil shale.

In order to make comparisons between the intraparticle mass transfer models using second order kinetics versus using the distribution of activation energy kinetics, it was necessary to obtain values of E_o , σ , and k_o typical of eastern oil shale. The determination of these parameters requires weight loss versus time data for the devolatilization of eastern oil shale. Since no experimental data are presently available in the literature for eastern oil

shales, hypothetical isothermal oil loss data at 775°K for powdered oil shale were generated using the second-order kinetic model. Eq. (46) for the weight of oil collected was curvefitted to the initial time data as before with $\gamma C^*(1 - \epsilon) = 377.3 \text{ kg/m}^3$. The results of this parameter determination are

$$k_o = 5.88 \times 10^{13} \text{ m}^3/\text{kg sec}$$

$$E_o = 53,333 \text{ cal/g-mole}$$

$$\sigma = 1563 \text{ cal/g-mole.}$$

With these parameters Eqs. (46), (62), and (81), can be used to calculate the weight of oil collected as a function of time at different temperatures. These equations are made dimensionless with the maximum possible weight of oil which can be produced (i.e., $V_p \gamma C^*(1 - \epsilon)$). To obtain predictions for the second order model, Eqs. (46), (62), and (81) will differ only in the form of R . For the second order model

$$R_{cp} = k_o \exp\left(\frac{-E}{R_G T}\right) \left[\frac{\rho_K^o}{1 + k_o \exp\left(\frac{-E}{R_G T}\right) \rho_K^o} \right]^2 \quad (85)$$

where $\rho_K^o = 377.3 \text{ kg/m}^3$ and k_o and E are the kinetic parameters appearing in Eq. (84).

The isothermal, dimensionless oil weight collected versus time was calculated for each model for the chemical kinetics controlling regime, diffusional limitations, and convection limitations using a hypothetical 5 cm in diameter sphere of eastern oil shale. The calculations were made

at temperatures of 648°K, 703°K, and 775°K. Internal temperature gradients were ignored since the main purpose of this study was to compare the differences between second order and distribution of activation energy kinetics. The values for Da at 648°K, 703°K, and 775°K corresponding to a particle size of 5 cm are 4×10^{-4} , 3×10^{-3} , and 2×10^{-2} , respectively.

6.1. Chemical Kinetics Controlling Regime

For the chemical kinetics controlling regime the dimensionless weight of oil collected under isothermal conditions according to the second order model is

$$\bar{w}(t) = \frac{1}{(1 + \frac{Da}{3})} \left[1 - \frac{1}{(1 + k_o \exp(\frac{-E}{R_G T}) \rho_K^o t)} \right]. \quad (86)$$

Figure 13 shows the response of the distribution model and the second order model. The close agreement between the models is expected at 775°K since this was the temperature at which the parameter determination was made. It is noteworthy that a single first order expression (i.e., $\sigma = 0$ kcal/g-mole) will not represent "data" from the second order model. However, the distribution model represents the "data" quite well because of the flexibility introduced by the parameter σ . The model predictions at the other temperatures are also very close.

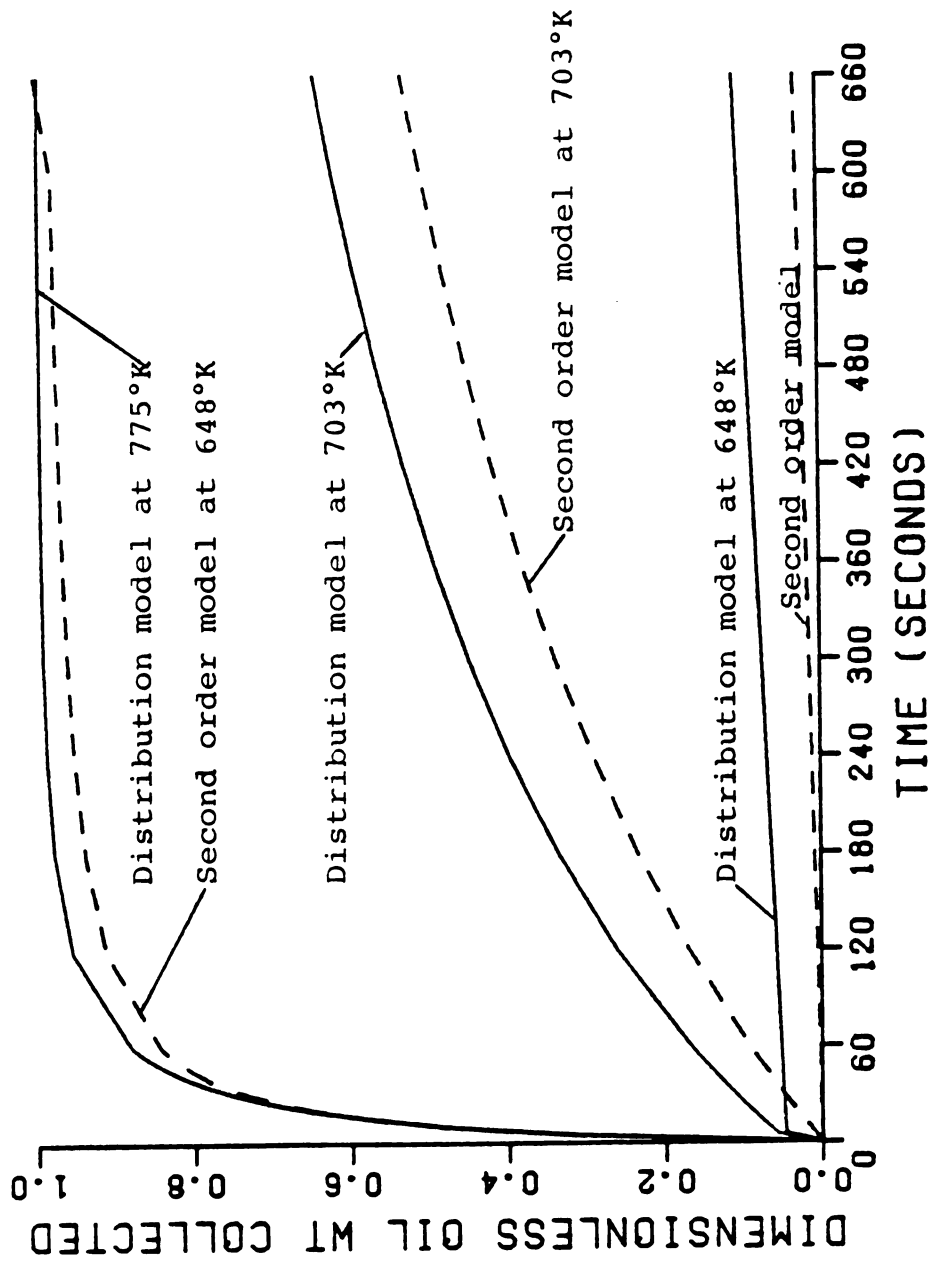


Figure 13. Distribution and second order models for the chemical kinetics controlling regime.

6.2. Diffusional Limitations for Pyrolysis

With diffusional limitations, the dimensionless weight of oil collected for the second order model under isothermal conditions is

$$\bar{w}(t) = \frac{3\gamma}{Da - (\frac{\phi^2}{1 - \phi \coth \phi})} \left[1 - \frac{1}{(1 + k_o \exp(\frac{-E}{R_G T}) \rho_k^o t)} \right] \quad (87)$$

Figure 14 shows the response of the distribution model and the second order model for $\phi=40$. Close agreement is again seen at 775°K. The weight loss occurs over a much longer time scale but all the curves will eventually attain the final value of $\frac{3\gamma}{Da - (\frac{\phi^2}{1 - \phi \coth \phi})}$. Once again, close agreement is seen at all temperatures.

6.3. Convection Limitations for Pyrolysis

For convection limitations, the isothermal, dimensionless weight of oil collected is

$$\frac{d\bar{w}(t)}{dt} = \frac{3R}{\rho_K^o} \int_0^1 \exp \left[\left[\frac{B}{R} (1 - r^{-2}) \right]^{\frac{1}{2}} \right] \times$$

$$\left[\frac{(AR[1 - \bar{r}^2]^{\frac{1}{2}} - (AR)^{\frac{1}{2}})}{(AR[1 - \bar{r}^2]^{\frac{1}{2}} + (AR)^{\frac{1}{2}})} \right]^2 \frac{1}{2} \left[\frac{B}{R} \right]^{\frac{1}{2}} \bar{r}^2 d\bar{r} \quad (88)$$

where A and B are defined by Eqs. (82) and (83). Eqs. (81) and (88) were integrated using a fourth order Runge-Kutta technique. It was determined that a step size of 10 seconds

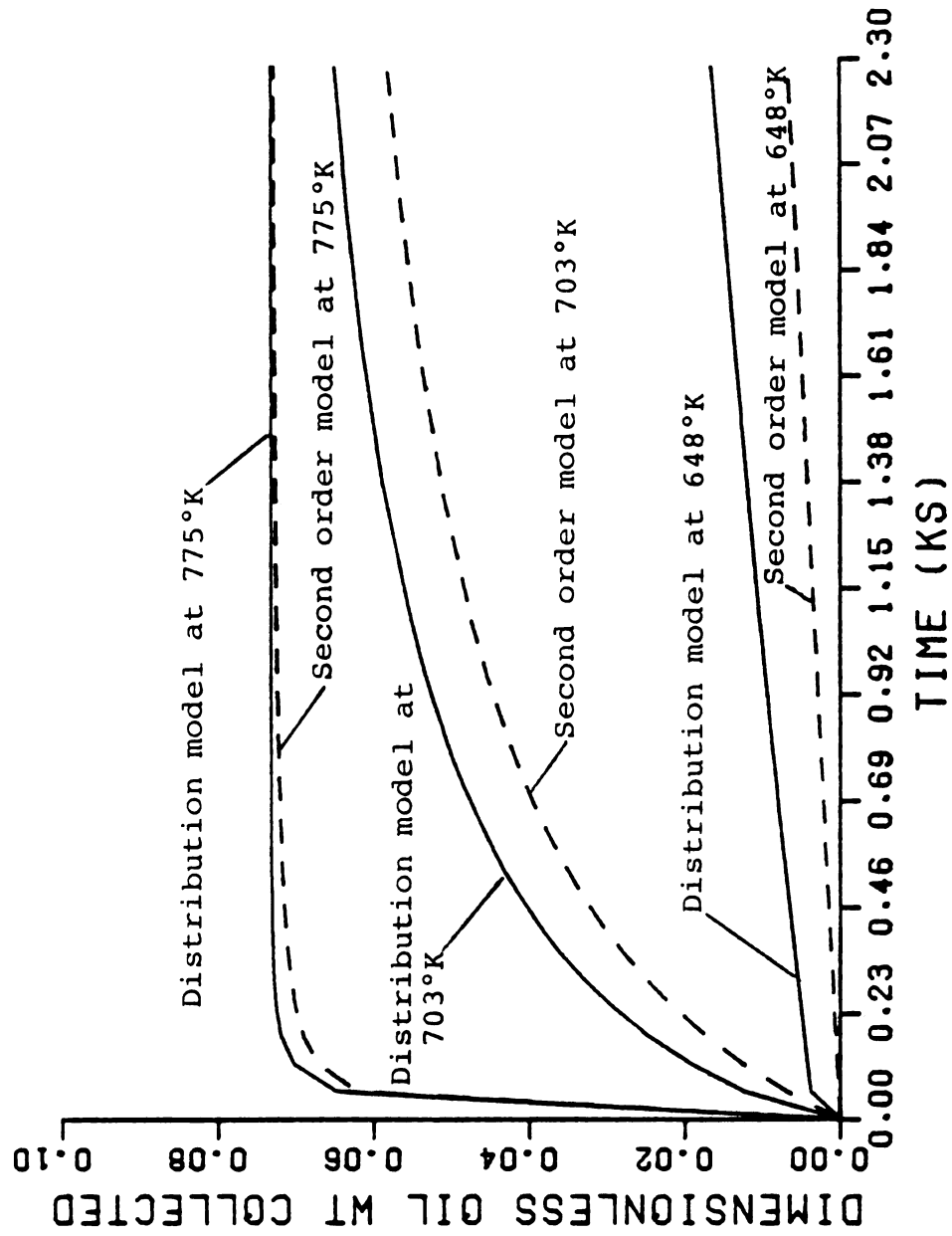


Figure 14. Distribution and second order models for diffusional limitations. $\phi=40$.

was necessary to avoid truncation error. Figure 15 shows the response of the distribution model and the second order model. Once again close agreement is seen at 775°K. The weight loss occurs over the same time scale as the diffusion case. The final value for the dimensionless weight collected are 0.83 for the second order model and 0.82 for the distribution model showing that a yield loss has occurred. This yield loss was caused by the buildup of reactive species in the gas phase of the particle because of intraparticle convection limitations. This buildup increased the rate of coking, and consequently, a yield loss occurred, characterized by the asymptote at 0.83. It appears that the curves for the other two temperatures will eventually approach this asymptote. Close agreement at all three temperatures is seen again.

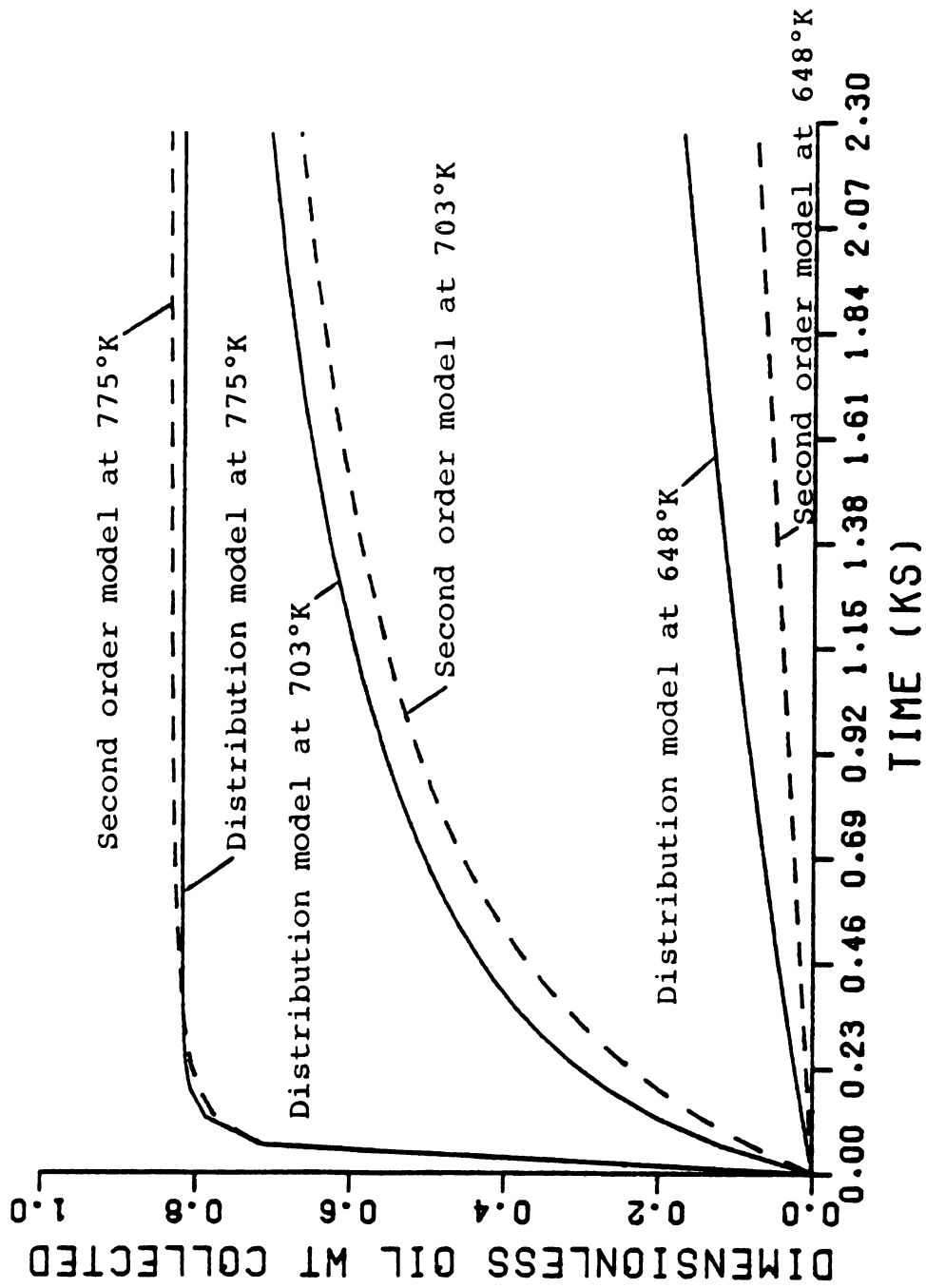


Figure 15. Distribution and second order model for convection limitations.

7. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

The low value of σ that was determined for western oil shale indicated that the bonds of the kerogen molecule are very uniform. The predictions given by the second order and distribution models for eastern oil shale were very similar. This implies that perhaps these simpler kinetic expressions are adequate in describing the kinetics of devolatilization. However, the failure of the first order model and the success of the distribution model in non-isothermal situations indicates that the distribution model is required. The need for the more complicated distribution model to describe the kinetics of devolatilization remains unknown until additional data from isothermal experiments conducted with powdered oil shale particles over a wide range of temperatures are available.

The determination of the parameters k_o , E_o , σ , γ , and C^* requires a set of data from an isothermal experiment measuring both the weight of reactive and nonreactive volatiles collected versus time for powdered oil shale

particles. Ideally, the temperature of this experiment should be 775°K, the data from such an experiment would not be expected to show an apparent weight loss plateau. In the isothermal experiment which was used to determine the parameters in this study, only the weight of oil collected as a function of time at 648°K was measured. The data from this experiment show that the weight of oil collected as a function of time approaches an asymptote characteristic of 648°K. Steps were taken in the parameter determination scheme so that this apparent weight loss plateau would not be imposed on the model. However, it is anticipated that the parameters could be determined more accurately if data from isothermal experiments at the highest temperature of pyrolysis were used.

The experimental observation that nonreactive and reactive volatiles are produced at different temperatures led to the suggestion that a bimodal distribution might be more appropriate than a Gaussian in characterizing the activation energies of the devolatilization reactions. This suggestion was given further support since model predictions for the total weight loss lagged behind the data at short times (see, Section 5.4). This lag suggested that reactions with lower activation energies should be included in the reaction set in order to speed up the short time response (see, Section 4.2). If a bimodal distribution is indeed the case, the parameters E_{o1} and σ_1 which characterize one peak of the bimodal distribution could be determined by the

weight of nonreactive volatiles collected versus time in an isothermal experiment. The parameters E_{O_2} and σ_2 which characterize the second mode could be determined by the weight of reactive species (i.e., "oil") collected versus time. If the distribution is actually bimodal, then the parameters E_O , σ , γ , and C^* which were estimated in this thesis characterized only the peak representing the activation energies of the reactions producing reactive species.

The value of $C^*(1 - \epsilon)$, the ultimate volatile content of the oil shale, was determined to be 15.26 wt % of the initial weight of the particle and corresponded to values from other experimental investigations. E_O was determined to be 55,333 cal/g-mole and is typical of activation energies represented in other studies. The fraction of kerogen converted to oil, γ , was determined to be 0.65. This value was nearly identical with the value of 0.62 obtained by Braun and Rothman (1975).

The model predictions for nonisothermal experiments where the temperature of the sample increased linearly with time were consistent with experimental data. These model predictions were made using no further adjustable parameters and the heating rate entered the calculation explicitly through the boundary condition for the temperature. Although favorable predictions were obtained using linear heating rates, it is anticipated that the distribution model will also predict situations where nonlinear heating rates are used.

For experiments with 12.7 mm particles it was not clear if the production of volatiles was affected by intraparticle convection limitation (see, Figure 12). However, Figure 11 suggests that the production of volatiles at short times may be affected by diffusion with an effective diffusion coefficient of 10^{-11} m²/sec. The calculations comparing the convection response for second order and distribution of activation energy kinetics for a 5 cm in diameter sphere (see, Section 6.3) show that the production of volatiles is limited by intraparticle convection. The limitations cause a buildup of reactive volatiles in the particle and consequently an increase in the rate of gas phase decomposition. Further experiments need to be conducted to define the limiting particle size where the rate of production of volatile species is no longer controlled by chemical kinetics but by intraparticle mass transfer.

APPENDICES

APPENDIX A

PROCEDURE FOR ESTIMATING THE DEVOLATILIZATION PARAMETERS

APPENDIX A

PROCEDURE FOR ESTIMATING THE DEVOLATILIZATION PARAMETERS

The parameters in the distribution of activation energies kinetic model can be determined using the weight of oil collected versus time isothermal data at 648°K. The weight of oil collected given by Eq. (46) can be made dimensionless by dividing by the initial weight of the particle. Thus,

$$\frac{w(t)}{V_p \rho_s} = \frac{\gamma C^* (1 - \varepsilon)}{\rho_s} \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t \exp(\frac{-E}{R_G T})] \right. \\ \left. \times \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE \right]. \quad (A.1)$$

The estimating procedure seeks to find a minimum in the sum of the squares of the differences between the data and the model. For this strategy, the objective function is

$$J(A_o, k_o, E_o, \sigma) \equiv \sum_{i=1}^n \left[y_i - A_o \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t_i \exp(\frac{-E}{R_G T})] \right. \right. \times$$

$$\left[\exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE \right]^2 \quad (A.2)$$

where $A_o \equiv \frac{\gamma C^*(1 - \epsilon)}{\rho_s}$ and y_i are the data points at 648°K.

In order to begin the optimization it was necessary to choose starting values for the parameters k_o , E_o , σ , and A_o . The starting points were determined using the Michigan State University IMSL subroutine ZSRCH. ZSRCH generates a specified number of points in an n-dimensional space for use as starting points in nonlinear optimization routines.

For each set of starting values, a direct search optimization scheme was used to find the best values for the parameters that minimized the objective function Eq. (A.2) (see, Hooke and Jeeves, 1961; Beveridge and Schechter, 1970; and Walsh, 1975). The objective function is highly nonlinear and has many local minima. Because many sets of starting values will converge to different local minima, several sets of starting values were tried. It was found that twenty starting sets of parameters were sufficient to identify the various local minima.

The Hooke and Jeeves method and ZSRCH require that constraints be placed on the parameters. The following constraints were imposed:

$$1.0 \times 10^{13} \leq k_o \leq 1.0 \times 10^{14} \text{ sec}^{-1}$$

$$40,000 \leq E_o \leq 60,000 \text{ cal/g-mole}$$

$$0 \leq \sigma \leq 10,000 \text{ cal/g-mole}$$

$$0 \leq A_o \leq 0.15 .$$

The global minimum of the objective function was used to define the parameter estimates. For the data of Campbell, et al. (1978), the devolatilization parameters were found to be

$$k_o = 6.95 \times 10^{13} \text{ sec}^{-1}$$

$$E_o = 55,333 \text{ cal/g-mole}$$

$$\sigma = 1740 \text{ cal/g-mole}$$

$$A_o = 0.09906 .$$

The step sizes and the number of times the step sizes were halved were chosen to economize the computing time without sacrificing accuracy. Several combinations of step sizes and number of halvings were tried. It was determined that the starting step sizes should be

$$\Delta k_o = 0.1 \times 10^{13} \text{ sec}^{-1}$$

$$\Delta E_o = 2000 \text{ cal/g-mole}$$

$$\Delta \sigma = 1000 \text{ cal/g-mole}$$

$$\Delta A_o = 0.01.$$

It was also determined that halving five times gave sufficient results. Further halving did not decrease the least squares error appreciably and only led to excessive computing costs.

Campbell, et al. (1978) show twelve data points in their experiment measuring the weight of oil collected as a function of time. The data show the weight of oil collected varying nearly linearly with time and then leveling off to

a plateau characteristic of 648°K. If all data points were used in the estimating routine, it was felt that the value for $\gamma C^*(1 - \epsilon)$ characteristic of 648°K would be imposed upon the model and not the true $\gamma C^*(1 - \epsilon)$. Therefore, only the first nine data points were used since none of these were in the plateau region. Hence, in Eq. (A.2), $n=9$. In terms of experimental accuracy, these first nine data points are probably the most accurate. Ideally, an isothermal experiment should be conducted at 775°K where the total weight loss would be realized. The data from this type of experiment would not impose an apparent $\gamma C^*(1 - \epsilon)$ on the model provided no degradation of the liberated oil takes place. Appendix B contains the program as well as sample outputs of the curve-fitting strategy.

APPENDIX B

COMPUTER PROGRAM FOR ESTIMATING THE DEVOLATILIZATION PARAMETERS

APPENDIX B

COMPUTER PROGRAM FOR ESTIMATING THE

DEVOLATILIZATION PARAMETERS

```

100 PROGRAM MAGIC(OUTPUT)
    REAL A(4),B(4),S(4),BASE(4),H(4),P(4),TIME(120),LEAST
    INTEGER N,K,IP,M(4),IW(9),IER,J,FLAG,L
    FORMAT(*--*,30X,*K=*,17X,*EA*,16X,*SIGMA*,14X,*CSTAR*,9X,*FUNCTION
    +VALUE*)
    101 FORMAT(*0*,*STARTING POINT      =*,5X,E14.8,5X,E14.8,5X,E14.8,5X,E14
    +*,8,5X,E14.8)
    102 FORMAT(*0*,*FINAL POINT        =*,5X,E14.8,5X,E14.8,5X,E14.8,5X,E14
    +*,8,5X,E14.8)
    103 FORMAT(*0*,*FINAL STEP SIZES   =*,5X,E14.8,5X,E14.8,5X,E14.8,5X,E14
    +*,8)
    104 FORMAT(*0*,*INTERMEDIATE POINT=*,5X,E14.8,5X,E14.8,5X,E14.8,5X,E14
    +*,8,5X,E14.8)

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INITIALIZATION OF ARGUMENTS FOR ZSRCH

```

C
C
C
A(1)=1.0E13 $ A(2)=40000.0 $ A(3)=0.0 $ A(4)=0.0
B(1)=1.0E14 $ B(2)=60000.0 $ B(3)=10000. $ B(4)=0.15
N=4 $ K=20 $ IP=0

```

INITIALIZATION OF TIME DATA

```

C
C
C
DATA (TIME(I),I=1,9)/1194.,2388.,5373.,7164.,13134.,16716.,20741.,
+25481.,31407.

```

THE OPTIMIZATION PROCESS NOW BEGINS. PROGRAM MAGIC IS USING THE IMSL SUBROUTINE ZSRCH TO FIND STARTING VALUES TO BE USED IN A HOOKE AND JEEVES DIRECT SEARCH OPTIMIZATION SCHEME. HOOKE AND JEEVES TIME DATA ARE OBTAINED FROM CAMPBELL, ET AL.(FUEL, WEIGHT LOSS VS. P.373) FOR COLORADO OIL SHALE. 57, NO. 6, 1978. PROGRAM MAGIC WILL THEN FIT THE DATA TO THE DISTRIBUTION OF ACTIVATION ENERGIES MODEL DEVELOPED BY MARLATT AND PETTY AT MICHIGAN STATE UNIVERSITY FOR OIL SHALE DEVOLATILIZATION. MAGIC WILL DETERMINE THE ADJUSTABLE PARAMETERS K, EO, SIGMA, AND CSTAR BY FINDING THE LEAST SQUARES ERROR. THE HOOKE AND JEEVES METHOD WILL BE USED TO FIND THESE MINIMUM USING THE STARTING POINTS PROVIDED BY ZSRCH.

```

C C C      DO 5 J=1,K
C C C      H(1)=0.1E13 $ H(2)=2000.0 $ H(3)=1000.0 $ H(4)=0.01
C C C      T=64K. $ FLAG=0
C C C      ZSRCH FINDS A STARTING POINT
C C C      CALL ZSRCH(A,R,N,K,IP,S,N,IW,IER)
C C C      HOOKF AND JEEVES IS NOW EMPLOYED.
C C C      FRASE=LEAST(TIME,S(1),S(2),S(3),S(4),T)
60    DO 50 L=1,M
C C C      BASE(L)=S(L)
C C C      PRINT 100
C C C      PRINT 101,S,FBASE
C C C      THIS DO LOOP CONTROLS THE NUMBER OF TIMES,I-1, THAT THE STEP
C C C      SIZES ARE HALVED.
C C C      DO 10 I=1,6
C C C      EXPLORATORY MOVES AROUND BASE POINT
C C C      DO 80 L=1,N
30    OLDRA(S(L))=FRASF(L)
80    CALL EXPLOR(H,BASE,TIME,T,FRASE,FLAG)
C C C      MAGIC CHECKS TO SEE IF IMPROVEMENT WAS MADE, IF NOT, HALVE STEP
C C C      SIZES.
C C C      IF(FLAG.EQ.0) GO TO 50
C C C      MAGIC MAKES A PATTERN MOVE.
C C C      DO 90 L=1,N
40    P(L)=2.*BASE(L)-OLDRA(S(L))
90    CHECK THE CONSTRAINTS ON THE PARAMETERS
C C C      IF(P(1).LT.1.0E13.OR.P(1).GT.1.0E14) GO TO 30
C C C      IF(P(2).LT.4.0E04.OR.P(2).GT.6.0E04) GO TO 30
C C C      IF(P(3).LE.0..OR.P(3).GT.1.0E04) GO TO 30
C C C      IF(P(4).LT.0.0.OR.P(4).GT.0.15) GO TO 30
C C C      EXPLORATORY MOVES AFTER PATTERN MOVE
C C C      CALL EXPLOR(H,P,TIME,T,FRASE,FLAG)

```



```

C
C
C
C
      IF NO IMPROVEMENT WAS MADE BY THE PATTERN MOVE, STAY WITH OLD
      BASE POINT.

      IF (FLAG.EQ.1) GO TO 20
      GO TO 30
      DO 95 L=1,N
      OLD BAS(L)=BASE(L)
      BASE(L)=P(L)
      GO TO 40
      IF (I.EQ.6) GO TO 10
      DO 95 L=1,N
      H(L)=H(L)/2.
      PRINT 104, BASE, FBASE
      CONTINUE
      PRINT 102, BASE, FBASE
      PRINT 103, H
      CONTINUE
      STOP
      END
      SUBROUTINE EXPLOR(H,BASE,TIME,I,FBASE,FLAG)
      REAL TIME(120),BASE(4),H(4),FUNCT,FBASE,LEAST
      INTEGER FLAG
      FLAG=0

      CHANGE THE FIRST PARAMETER

      S1=BASE(1)+H(1)
      IF (S1.LT.1.0E13.OR.S1.GT.1.0E14) GO TO 6
      FUNCT=LEAST(TIME,S1,BASE(2),BASE(3),BASE(4),T)
      IF (FUNCT.LT.FBASE) GO TO 1
      S1=BASE(1)-H(1)
      IF (S1.LE.1.0E13.OR.S1.GT.1.0E14) GO TO 2
      FUNCT=LEAST(TIME,S1,BASE(2),BASE(3),BASE(4),T)
      IF (FUNCT.LT.FBASE) GO TO 1
      GO TO 2
      1 BASE(1)=S1
      FBASE=FUNCT
      FLAG=1

      CHANGE THE SECOND PARAMETER

      S2=BASE(2)+H(2)
      IF (S2.LT.4.0E04.OR.S2.GT.6.0E04) GO TO 7
      FUNCT=LEAST(TIME,FBASE(1),S2,BASE(3),BASE(4),T)
      IF (FUNCT.LT.FBASE) GO TO 3
      S2=BASE(2)-H(2)
      IF (S2.LT.4.0E04.OR.S2.GT.6.0E04) GO TO 4
      FUNCT=LEAST(TIME,FBASE(1),S2,BASE(3),BASE(4),T)
      IF (FUNCT.LT.FBASE) GO TO 3
      GO TO 4
      3 BASE(2)=S2
      FBASE=FUNCT
      FLAG=1

```

```

C
C
C
      CHANGE THE THIRD PARAMETER
4      S3=BASE(3)+H(3)
      IF(S3.LE.U..OR.S3.GT.1.UE04) GO TO 8
      FUNCT=LEAST(TIME,BASF(1),BASE(2),S3,BASF(4),1)
      IF(FUNCT.LT.FBASE) GO TO 5
8      S7=BASE(3)-H(3)
      IF(S3.LE.U..OR.S3.GT.1.UE04) GO TO 9
      FUNCT=LEAST(TIME,BASF(1),BASE(2),S3,BASF(4),1)
      IF(FUNCT.LT.FBASE) GO TO 5
      GO TO 9
5      BASE(3)=S3
      FBASE=FUNCT
      FLAG=1
C
C
C
      CHANGE THE FOURTH PARAMETER
9      S4=BASE(4)+H(4)
      IF(S4.LT.0..OR.S4.GT.0.15) GO TO 10
      FUNCT=LEAST(TIME,BASE(1),BASE(2),BASE(3),S4,1)
      IF(FUNCT.LT.FBASE) GO TO 11
10     S4=BASE(4)-H(4)
      IF(S4.LT.0..OR.S4.GT.0.15) RETURN
      FUNCT=LEAST(TIME,BASE(1),BASE(2),BASE(3),S4,1)
      IF(FUNCT.LT.FBASE) GO TO 11
      RETURN
11     BASE(4)=S4
      FBASE=FUNCT
      FLAG=1
      RETURN
END
REAL FUNCTION LFAST(TIME,KOAR,EACT,SIGMA,CSTAR,T)
REAL TIME(120),MODEL,ODDSUM,KOAR
DIMENSION WT(120)
LEAST=0.
C
C
C
      THE DATA ARE FROM CAMPBELL, ET AL. (1978).
      DAYA (WT(1),1=1,9)/.0071,.0111,.0170,.0207,.0277,.0333,.0375,.0424
      +,.0456/
      A=EACT-2.*SIGMA
      B=EACT+2.*SIGMA
      PARM2=1.987.*T
      PARM3=2.*SIGMA**2.

```

```

C C C C C C
DO 10 I=1,N
  PARM1=-K0/R*TIME(I)
  DOFA=DISI(A,EACT,PARM1,PARM2,PARM3)
  DOFB=DISI(B,EACT,PARM1,PARM2,PARM3)
  THE MODEL IS THE ISOTHERMAL INTEGRATION OF THE DISTRIBUTION OF
  ACTIVATION ENERGIES MODEL. THIRTY APPLICATIONS OF SIMPSON'S RULE
  EVALUATES THE INTEGRAL.
  SUM EVEN TERMS
  SUM=0.
  PARM4=(R-A)/30.
  DO 20 L=1,29
    E=PARM4*L+A
    SUM=SUM+DISI(E,EACT,PARM1,PARM2,PARM3)
  CONTINUE
  SUM=2.*SUM
  SUM ODD TERMS.
  ODDSUM=0.
  PARM5=(R-A)/60.
  DO 30 J=1,59,2
    E=A+PARM5*J
    ODDSUM=ODDSUM+DISI(E,EACT,PARM1,PARM2,PARM3)
  CONTINUE
  ODDSUM=4.*ODDSUM
  TOTSUM=((R-A)/160.)*((DOFA+DOFB+SUM+ODDSUM)
  MODEL=CSTAR*(1.-(TOTSUM/(2.5068*SIGMA)))
  THE ERROR IS THE LEAST SQUARES ERROR.
  ERROR=(WT(I)-MODEL)**2
  LEAST=LEAST+ERROR
  CONTINUE
  RTURN
END
FUNCTION DIST(E,EACT,PARM1,PARM2,PARM3)
  FIRST=EXP(PARM1*EXP(-E/PAKM2))
  SECOND=EXP(-(E-EACT)**2/PAKM3)
  DIST=FIRST*SECOND
  RTURN
END

```

STARTING POINT =	RO	EA	SIGMA	CSTAR	FUNCTION VALUE
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
FINAL POINT =					
FINAL STEP SIZE =					
STARTING POINT =	RO	EA	SIGMA	CSTAR	FUNCTION VALUE
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
FINAL POINT =					
FINAL STEP SIZE =					
STARTING POINT =	RO	EA	SIGMA	CSTAR	FUNCTION VALUE
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
FINAL POINT =					
FINAL STEP SIZE =					
STARTING POINT =	RO	EA	SIGMA	CSTAR	FUNCTION VALUE
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
INTERMEDIATE POINT =					
FINAL POINT =					
FINAL STEP SIZE =					

APPENDIX C

PROCEDURE FOR ESTIMATING γ AND $C^*(1 - \varepsilon)$

APPENDIX C

PROCEDURE FOR ESTIMATING γ AND $C^*(1 - \epsilon)$

The values of γ and $C^*(1 - \epsilon)$ can be obtained from the total weight collected versus time isothermal data at 673°K. The total weight of volatiles collected, given by Eq. (46), can be made dimensionless by dividing by the initial weight of the particle. Thus,

$$\frac{W(t)}{V_p p \rho_s} = \frac{C^*(1 - \epsilon)}{\rho_s} \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t \exp(\frac{-E}{R_G T})] \times \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE \right]. \quad (C.1)$$

As in Appendix A, the following objective function is defined

$$J(B_o) = \sum_{i=1}^n \left[y_i - B_o \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t_i \exp(\frac{-E}{R_G T})] \times \exp\left[-\frac{(E-E_o)^2}{2\sigma^2}\right] dE \right] \right]^2 \quad (C.2)$$

where $B_o = C^*(\frac{1 - \epsilon}{\rho_s})$ and y_i are the data points at 673°K. In the estimating strategy ten data points were used; thus, $n=10$ in Eq. (C.2).

Since the values of k_o , E_o , and σ were determined previously the only undetermined parameter is B_o . The minimum in $J(B_o)$ can be found by setting the first derivative with respect to B_o equal to zero and solving for B_o . The result is,

$$B_o = \frac{\sum_{i=1}^{10} y_i \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t_i \exp(\frac{-E}{R_G T})] \exp[\frac{-(E-E_o)^2}{2\sigma^2}] dE \right]}{\sum_{i=1}^{10} \left[1 - \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} \exp[-k_o t_i \exp(\frac{-E}{R_G T})] \exp[\frac{-(E-E_o)^2}{2\sigma^2}] dE \right]^2} \quad (C.3)$$

Thus, the value of B_o or $\frac{C^*(1-\epsilon)}{\rho_s}$ can be calculated directly from the data. γ can be calculated by dividing A_o from the estimating procedure in Appendix A by B_o . The program which calculates γ and $C^*(1-\epsilon)$ is included on the pages which follow.


```

20      SUM = 0.0
21      DO 30 I=1,NR
22      F=1+(E-A)*1/2
23      TOTSUM = TOTSUM + DIST(F,KOAF,EACT,SIGMA,TIME(I),T)
24      ODDSUM = 4.*DECSUM
25      TOTSUM = ((E-A)/14.*)*(DOFA+DOFB+SUM+ODDSUM)
26      CAL*T(I) = 1.-(TOTSUM/(2.*EER*SIGMA))
27      F = F + T(I)*CAL*T(I)
28      DECF = F + CAL*T(I)**2
29      OCTA = SUM + 2.*EER/3/DECF
30      DIST = 1.*OCTA
31      F = 1.1
32      CAL*T(I) = (CAL*T(I) + OCTA)/2.*EER/3
33      DIST = 1.1*TIME(I)*T(I)*CAL*T(I)
34      F = 1.1
35      FOUNTION = DIST(F,KOAF,EACT,SIGMA,TAU,T)
36      F = 1.1
37      FI = STEEP*(-KOAF+TAU)*EXP(-E/(1.4872*T))
38      SECC = EXP(-(E-EACT)**2/(2.*SIGMA**2))
39      DIST = FI*STE*SECC
40      F = 1.1
41      F = 1.1

```

APPENDIX D

PROCEDURE FOR ESTIMATING THE KINETIC PARAMETERS IN THE LUMPED FIRST ORDER MODEL

APPENDIX D

PROCEDURE FOR ESTIMATING THE KINETIC PARAMETERS IN THE LUMPED FIRST ORDER MODEL

The weight of reactive volatiles collected as a function of time can be described by an overall material balance around all the particles.

$$w(t) = \gamma C_B^0 V_p - \gamma C_B V_p \quad (D.1)$$

where $C_B = C_B^0 \exp[-k_o \int_0^t \exp(\frac{-E}{R_G T}) dt]$ for first order kinetics. This balance assumes no intraparticle mass transfer limitations and no gas phase decomposition reactions.

Thus,

$$w(t) = V_p \gamma C_B^0 \left[1 - \exp[-k_o \int_0^t (\frac{-E}{R_G T}) dt] \right] \quad (D.2)$$

The weight of reactive volatiles collected can be made dimensionless by dividing by the initial weight of the particle. Therefore,

$$\bar{w}(t) = \frac{\gamma C_B^0}{\rho_s} \left[1 - \exp[-k_o \int_0^t (\frac{-E}{R_G T}) dt] \right] \quad (D.3)$$

For isothermal experiments

$$\bar{w}(t) = \frac{\gamma C_B^O}{\rho_s} \left[1 - \exp[-k_O t \exp(\frac{-E}{R_G T})] \right] \quad (D.4)$$

As in Appendix A the following objective function can be defined

$$J(C_O, k_O, E) = \sum_{i=1}^n \left[y_i - C_O [1 - \exp(-k_O t_i \exp(\frac{-E}{R_G T}))] \right]^2 \quad (D.5)$$

where $C_O = \frac{\gamma C_B^O}{\rho_s}$ and y_i are the data points at 648°K.

The three parameters C_O , k_O , and E which minimized J were determined using the Hooke and Jeeves direct search scheme described in Appendix A. Starting values for the parameters were again obtained from ZSRCH. Once again, nine data points were used in this estimating procedure; therefore, $n=9$ in Eq. (D.5).

The starting steps sizes were

$$\Delta C_O = 0.01$$

$$\Delta E_O = 2000 \text{ cal/g-mole}$$

$$\Delta k_O = 0.1 \times 10^{13} \text{ sec}^{-1}$$

and the parameter constraints were

$$0 \leq C_O \leq 0.15$$

$$40,000 \leq E_O \leq 60,000 \text{ cal/g-mole}$$

$$1.0 \times 10^{13} \leq k_O \leq 1.0 \times 10^{14} \text{ sec}^{-1}.$$

The step sizes were halved five times as before.

APPENDIX E

COMPUTER PROGRAM FOR CALCULATING THE VOLUME OF OIL
COLLECTED FOR NONISOTHERMAL CONDITIONS FOR THE
CHEMICAL KINETICS CONTROLLING REGIME

APPENDIX E

COMPUTER PROGRAM FOR CALCULATING THE VOLUME OF OIL COLLECTED FOR NONISOTHERMAL CONDITIONS FOR THE CHEMICAL KINETICS CONTROLLING REGIME

Eq. (51) was integrated using a fourth order Runge-Kutta technique (see, p. 363 Carnahan, et al., 1969). A step size of 1°K was used to minimize the truncation error. To calculate the volume of oil, Eq. (51) was divided by the average density of the oil produced $\rho_{oil} = 0.91 \times 10^{-3} \text{ kg/cm}^3$ (see, Campbell, et al., 1978). The initial condition which was used is: volume of oil collected = 0.15 cm^3 at $T=628^\circ\text{K}$. Eq. (50) is the intrinsic rate of reaction for a linear increase in the temperature with time and involves the exponential integral function. The Michigan State University IMSL library subroutine MMDEI was used to calculate the exponential integral. The computer program which was used to integrate Eq. (51) is given on the pages that follow. Subroutine CALOK calculates the Runge-Kutta parameters. Function DIST calculates the integrand of the integral over E appearing in Eq. (50).


```

SUPROUTINE CALOK(H)
REAL KOAP,K(3),NUR
COMMON A,P,EACT,KOAK,FARM,FARM1,FARM2,FARM3,FARM4,K,N2,FARM7,PARMS,FARM
+9,CSTAK,SIGMA,T,HP,SINTEG
DO 1 J=1,3
DCFA=DIST(A,EACT,KOAK,PARM1,PARF2,PARM3,PARM4)
DCFB=DIST(B,EACT,KOAK,PARM1,PARM2,PARM3,PARM4)
SUM EVEN TERMS.
SUV=0.
DO 20 L=1,29
E=A+PARM7*L
SUM=SUM+DIST(E,EACT,KOAK,PARM1,PARM2,PARM3,PARM4)
CONTINUE
SUP=2.*SUM
SUM ODD TERMS.
ODDSUM=0.
DO 30 L=1,59,2
E=A+PARM7*L
ODDSUM=ODDSUM+DIST(E,EACT,KOAK,PARM1,PARM2,PARM3,PARM4)
CONTINUE
ODDSUM=4.*ODDSUM
SINTEG=PARM8+(DOF4+DOFB+SUM+ODDSUM)
DA=1.+7.6040504*EXP(-75.00/FA2PM4)
NUM=CSTAF+4.7667E-05*KOAK*SINTEG
DENO=DA*9.1E-04*2.5065*SIGMA*HP
K(J)=NUM/DENO
IF(J.EQ.3) GO TO 1
T=T+H/2.
PARM4=1.9872*T
CONTINUE
RETURN
END

```

CC C

2

CC C

3

1


```

FUNCTION DISTC(E,EACT,KDAR,PAR*1,PARM2,PARM3,PARM4)
  REAL KDA0,NMDEI
  FIRST=EXP(-(E-EACT)*3./PARM4)
  SLCC=CEXP(-(E-EACT)*3./PARM3)
  THE MONOISOTHERMAL INTEGRATION OF THE APORETIUS RATE OF GROWTH IS
  EVALUATED HERE. IF A LINEAR TEMPERATURE HISTORY IS ASSUMED FOR
  THE PARTICLE, THE INTEGRATION IS ANALYTIC INVOLVING THE FOLLOVING-
  INITIAL INTEGRAL FUNCTION. THE INSL ROUTINE MODEL CALCULATES THE
  EXPERIMENTAL INTEGRAL.
  SUME=0
  I=0
  I=0
  PARM5=-E/PARM1
  PARM6=-E/PARM4
  PARCE=PARM5
  SUME=SUM-NMDEI(I*OPT,APC,IER)
  APC=PARM6
  SUME=SUM+NMDEI(I*OPT,APC,IER)
  SUME=SUM+EXP(PARM5)/PARM5
  SUME=SUM-APC(I*PARM5)/PARM5
  SUM=-KDA0*F*SUM/PARM4
  TH=THD+EXP(SUM)
  DISTC=FIRST*SECOND*THIRD
  RETURN
END

```

APPENDIX F

COMPUTER PROGRAM FOR CALCULATING THE WEIGHT OF
VOLATILES COLLECTED AS A FUNCTION OF TIME FOR
ISOTHERMAL CONVECTION LIMITATIONS

APPENDIX F

COMPUTER PROGRAM FOR CALCULATING THE WEIGHT OF VOLATILES COLLECTED AS A FUNCTION OF TIME FOR ISOTHERMAL CONVECTION LIMITATIONS

Eq. (81) was integrated using a fourth order Runge-Kutta technique (see, p. 363 Carnahan, et al., 1969). A step size of 10 seconds was used to minimize the truncation error. The intrinsic rate of reaction for isothermal cases is given by Eq. (44). The computer program which was used to integrate Eq. (81) is given on the pages that follow. Subroutine CALOK calculates the Runge-Kutta parameters. Function DIST calculates the integrand of the integral over E appearing in Eq. (44). Function DIST2 calculates the integrand of the integral over $\bar{r}$ in Eq. (81).

4

```

SUPROUTINE CALCK
REAL KOAR,K(3),T(500)
COMMON KOAR,EACT,SIGMA,VOID,T,TIME,PARM1,PARM2,PARM3,PARM4,PARM5,P
+ARM6,PARM7,PARM8,PRON,K,H,WT,AA,BB,A,B
DO 1 L=1,3
DOFA=DIST(A,EACT,KOAR,SIGMA,T,TIME)
DOFB=DIST(B,EACT,KOAR,SIGMA,T,TIME)
SUME=0
DO 2 M=1,20
E=A+PARM1*M
SUM=SUM+DIST(E,EACT,KOAR,SIGMA,T,TIME)
CONTINUE
SUME2=.5*SUM
CDSUM=1.0
DO 3 W=1,50*2
E=A+PARM2*W
ODDSUM=ODDSUM+DIST(E,EACT,KOAR,SIGMA,T,TIME)
CONTINUE
CDSUM=4.0*ODDSUM
SINTEG=APM3*(DOFA+DOFB+SUM+CDSUM)
PRON=SINTEG*PARM4
E0F=DIST2(C,AA,BB,PRON)
E0F1=DIST2(1.0,AA,BB,PRON)
SUM=0
DO 4 W=1,20
R=PARM5*W
SUM=SUM+DIST2(R,AA,BB,PRON)
CONTINUE
ODDSUM=1.0
DO 5 W=1,50*2
R=PARM6*W
ODDSUM=ODDSUM+DIST2(R,AA,BB,PRON)
CONTINUE
ODDSUM=4.0*ODDSUM
SINTEG=APM7*(E0F+E0F1+SUM+CDSUM)
FIRST=PRON+CINTEG+FIRST
SECOND=VGIN+PRON*.13333333333333333
X(L)=FIRST+SECOND
IF(L.EQ.3) GO TO 1
TIME=TIME+W/2.
CONTINUE
RETURN
END

```

```

FUNCTION DIST(E,LACT,KOAR,SIGMA,T,TAU)
REAL KOAR
FIRST=EXP(-E/(1.3672*T))
SECOND=EXP(-KOAR*TAU*EXP(-E/(1.3672*T)))
THIRD=EXP(-(E-LACT)**2/(2.*SIGMA**2.))
DIST=FIRST*SECOND*THIRD
RETURN
END

```

```

FUNCTION GISTO(R,AA,PC,PRCD)
ARG=SQRT(PC*(1.-R**2.)/PRCD)
FIRST=EXP(ARG)
ARG=SQRT(AA*PRCD*(1.-R**2.))
ARG1=SQRT(AA*PRCD)
SECOND=((ARG-ARG1)/(ARG+ARG1))**2.
C=SQRT(PC/PRCD)/4.
THIRD=SECOND**C
DIST=FIRST*THIRD*R**2.
RETURN
END

```

LIST OF REFERENCES

LIST OF REFERENCES

- Allred, V. D. 1967. "Shale Oil Developments: Kinetics of Oil Shale Pyrolysis." Proceedings of the Fourth Oil Shale Symposium, Quarterly of the Colorado School of Mines, 67, 657.
- Anthony, D. B. 1974. "Rapid Devolatilization and Hydrogasification of Pulverized Coal." ScD. Thesis, Department of Chemical Engineering, Mass. Instit. Techol., Cambridge.
- Anthony, D. B. and Howard, J. B. 1976. "Coal Devolatilization and Hydrogasification." AICHE Jl., 22, 625.
- Anthony, D. B., Howard, J. B., Hottel, H. C. and Meissner, H. P. 1976. "Rapid Devolatilization and Hydrogasification of Bituminous Coal." Fuel, 55, 121.
- Anthony, D. B., Howard, J. B., Hottel, H. C., and Meissner, H. P. 1975. "Rapid Devolatilization of Pulverized Coal." Fifteenth Symposium (International) on Combustion, 1303, The Combustion Institute, Pittsburgh, PA.
- Bennett, C. O. and Myers, J. C. 1962. Momentum, Heat, and Mass Transfer. New York: McGraw-Hill.
- Benson, S. 1968. Thermochemical Kinetics. New York: Wiley.
- Beveridge, G. S. and Schechter, R. S. 1970. Optimization: Theory and Practice. New York: McGraw-Hill.
- Bird, R. B., Stewart, W. E., and Lightfoot, E. N. 1960. Transport Phenomena. New York: Wiley.
- Braun, R. L. and Chin, R. C. Y. 1977. Progress Report on Computer Model for In Situ Oil Shale Retorting. Report UCRL-52292, Lawrence Livermore Laboratory, Livermore, Cal.

- Campbell, J. H., Koskinas, G. H., Coburn, T. T., and Stout, N. D. 1977. Oil Shale Retorting: Part 1, The Effects of Particle Size and Heating Rate on Oil Evolution and Intraparticle Oil Degradation. Report UCRL-52256, Lawrence Livermore Laboratory, Livermore, Cal.
- Campbell, J. H., Koskinas, G. H., and Stout, N. D. 1978. "Kinetics of Oil Generation from Colorado Oil Shale." Fuel, 57, 372.
- Carnahan, B., Luther, H. A., and Wilkes, J. O. 1969. Applied Numerical Methods. New York: Wiley.
- Crowl, D. A. and Piccirelli, R. A. 1979. Transport Processes in Pyrolysis of Antrim Oil Shale. College of Engineering Energy Center, Wayne State University, Detroit, Mi.
- Cummins, J. J. and Robinson, W. E. 1972. "Thermal Degradation of Green River Kerogen at 150° to 350°C: Rate of Production Formation." Bureau of Mines Report of Investigations, 7620.
- Granoff, B. and Nuttall, H. E. 1977. "Pyrolysis Kinetics for Oil Shale Particles." Fuel, 56, 234.
- Heicklen, J., Hudson, J. L., and Armi, L. 1969. "Theory of Carbon Formation in Vapor Phase Pyrolysis--II. Variable Concentration of Active Species." Carbon, 7, 365.
- Hill, G. R., Johnson, D. J., Miller, L., and Dougan, J. L. 1967. "Direct Production of Low Pour Point High Gravity Shale Oil." Ind. Eng. Chem. Prod. Res. and Dev., 6, 52.
- Hirt, T. J. and Palmer, H. B. 1963. "Kinetics of Deposition of Pyrolytic Carbon Films from Methane and Carbon Suboxide." Carbon, 1, 65.
- Hooke, R. and Jeeves, T. A. 1961. "'Direct Search' Solution of Numerical and Statistical Problems." Association for Computing Machinery Journal, 8, 212.
- Hubbard, A. B. and Robinson, W. E. 1950. "A Thermal Decomposition Study of Oil Shale." Bureau of Mines Report of Investigations, 4744.
- Hudson, J. L. and Heichlen, J. 1968. "Theory of Carbon Formation in Vapor-Phase Pyrolysis--I. Constant Concentration of Active Species." Carbon, 6.

- Johnson, W. F., Walton, D. K., Keller, H. H., and Couch, E. J. 1975. "In Situ Retorting of Oil Shale Rubble: A Model of Heat Transfer and Product Formation in Oil Shale Particles." Proceedings of the 8th Oil Symposium, Quarterly of the Colorado School of Mines, 71, 237.
- Jones, J. B. "Paraho Oil Shale Retort." Proceedings of the Ninth Oil Shale Symposium, Quarterly of the Colorado School of Mines, 71, 120.
- Jones, D. G. and Dickers, J. J. 1965. "Composition and Reactions of Oil Shale of the Green River Formation." AICHE Chem. Engin. Symp. Ser., 61, 33.
- Jukkola, E. E., Denilauler, A. J., Jensen, H. B., Barnet, W. I., and Murphy, W. I. 1953. "Thermal Decomposition Rates of Carbonates in Oil Shale." Ind. and Eng. Chem., 45, 2711.
- Jüntgen, H. and Van Heek, K. H. 1970. "Reaktionabläufe unter Nichtisothermen Bedingungen." Fortschritte der Chemischen Forschung, 13, 601.
- Katz, D. L. and Goddard, J. D. 1964. A Study of the Dow Oil Recovery Process. Report 06061-1-F, The Dow Chemical Company, Midland, Mi.
- Lewis, A. E. and Rothman, A. J. 1976. Rubble In Situ Extraction (RISE): A Proposed Program for Recovery of Oil from Oil Shale. Report UCRL-51768, Lawrence Livermore Laboratory, Livermore, Cal.
- Murphy, D. B., Palmer, H. B., and Kinney, C. R. 1958. "A Kinetic Study of the Deposition of Pyrolic Carbon Films." Industrial Carbon and Graphite, 77, Society of Chemical Industry, London.
- Palmer, H. B. 1963. "An Analysis of Carbon Deposition Kinetics In Isothermal Flow Systems." Carbon, 1, 55.
- Palmer, H. B. and Cross, W. D. 1966. "Carbon Films from Carbon Suboxide Decomposition. Inhibition by Carbon Monoxide and the Heat of Formation of C_{20} ." Carbon, 3, 475.
- Pitt, G. J. 1962. "The Kinetics of the Evolution of Volatile Products from Coal." Fuel, 41, 267.
- Russell, W. B., Saville, D. A., and Greene, M. I. 1979. "A Model for Short Residence Time Hydropyrolysis of Single Coal Particles." AICHE J1. 25, 65.

Satterfield, C. N. 1970. Mass Transfer in Heterogeneous Catalysis. M.I.T. Press, Cambridge, Mass.

Shih, Shin-Min and Sohn, S. Y. 1978. "A Mathematical Model for the Retorting of a Large Block of Oil Shale: Effect of the Internal Temperature Gradient." Fuel, 57.

Tisot, P. R. and Murphy, W. R. 1965. "Physical Structure of Green River Oil Shale." AICHE Symp. Ser., 61, 25.

Vand, V. 1943. "A Theory of the Irreversible Electrical Resistance Charges of Metallic Films Evaporated in Vacuum." Proceedings of the Physical Society (London), A55, 222.

Walsh, G. R. 1975. Methods of Optimization. New York: Wiley.