

THE KINETICS OF THE THERMAL DECOMPOSITION OF MOROCCAN OIL  
SHALE BY THERMOGRAVIMETRY

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ABSTRACT

The kinetics of the thermal decomposition of Moroccan oil shale have been studied by isothermal and non-isothermal thermogravimetry. The effects of carrier gas flow rate and heating rate on kerogen decomposition have been examined. The weight-loss data obtained under non-isothermal conditions have been analyzed by the Coats-Redfern technique while the isothermal TG data have been correlated by using the integral method of kinetic analysis. A joint use of isothermal and non-isothermal TG measurements have shown that the oil shale decomposition involves two consecutive reactions with bitumen as an intermediate product. Kerogen decomposition into bitumen proceeds with an activation energy of 40 kJ/mole while the pyrolytic bitumen decomposes into products with an activation energy of 60 kJ/mole. A close agreement between the kinetic parameters, viz., activation energy and reaction order ( $n = 1$ ) etc., obtained under both isothermal and non-isothermal conditions substantiates the validity of the first order rate equation. The fact that the kinetic parameters remain unchanged with variations in heating rate (K/min) indicates that these parameters are probably insensitive to the efficiency of heat transfer between the sample and surroundings. However, the low activation energy for bitumen decomposition indicates certain mass transfer limitations such as diffusion of organic matter through the mineral carbonate matrix.

INTRODUCTION

Morocco has moderate deposits of oil shale which can be exploited using American processing technology. To date, U. S. processes are based on the thermal treatment of the shale to decompose kerogen into the desired oil product. The key step in the thermal treatment is the pyrolysis stage and involves the kinetic rate of kerogen decomposition and the corresponding formation of oil. Because oil shales have differing origins and are found in differing geological environments, it is not surprising that they behave differently when subjected to pyrolysis conditions. This study was initiated to investigate the pyrolysis kinetics of Moroccan oil shale. Thermogravimetric analysis (both iso- and non-isothermal) was used to determine the kinetic parameters for kerogen decomposition. The present results will be compared with the literature data on Jordan and Colorado oil shale.

Insoluble organic matter in oil shale is called kerogen. The thermal decomposition of the kerogen is by far the simplest method for extracting oil from shale. Numerous attempts [Hubbard and Robinson 1950; Allred, 1966; Dericco and Barrick, 1956] dealing with the mechanistic and kinetic points of view have been made to understand the processes occurring during oil shale pyrolysis. Hubbard and Robinson [1950] have employed an isothermal technique to obtain the pyrolysis rate data on powdered samples. One of the sources of error in isothermal methods is the time required for the sample to reach the reaction temperature. Braun and Rothman [1975] have shown that the oil-production kinetics can be explained more exactly by including a thermal induction period in the analysis of data obtained by Hubbard and Robinson [1950]. Non-isothermal thermogravimetric analysis has come into wide use in the last decade for studying pyrolysis. There are certain advantages of this method over the classical isothermal method. First, this method eliminates the errors introduced by the thermal induction period. Second, it permits a rapid scan of the whole temperature range of interest. Herll and Arnold [1976] have studied the decomposition of Chattanooga Black shale by non-isothermal TG while Haddadin, et al [1974, 1980], have employed TGA and DTA to investigate the kinetics of Jordan oil shale pyrolysis. The thermal decomposition of Colorado oil shale has been a subject of many studies [Granoff and Nuttall, 1977; Campbell et al 1978; Rajeshwar, 1981].

Recently, Behnisch, et al [1980], have pointed out that a combined kinetic analysis of isothermal and non-isothermal TG measurements is an effective method for determining the most probable kinetic mechanism of a decomposition process of a polymer. The kinetics of Moroccan oil shale decomposition has, therefore, been studied by isothermal and non-isothermal thermogravimetry. The weight-loss data analyzed by Coats-Redfern technique [1964] shows that the kerogen decomposition proceeds in two consecutive steps via bitumen as an intermediate. The kinetics of Moroccan oil shale decomposition will be compared with that of Jordan and Colorado oil shale decomposition.

#### EXPERIMENTAL SECTION

The oil shale used in the present study originated from Timhadit Site, Morocco. Chemical analysis of the oil shale is given in Table 1. The samples were crushed and sieved to pass through a 200 mesh screen; the samples were used without further treatment.

A DuPont 951 thermogravimetric balance interfaced with a DuPont 990 thermal analyzer was used to obtain the weight-loss data as a function of time and temperature. Two kinds of experiments were performed. The first was to obtain non-isothermal kinetics of oil shale decomposition while the second one was performed under isothermal conditions.

In the first set, a known weight of sample (about 25 mg) was subjected to a linear heating rate in a dry stream of nitrogen. Decomposition was carried out by heating the sample from ambient temperature to 900°C. The heating rates of 1, 2, 5, 10, 20 and 50°C/min were employed. The weight-loss data and DTG curves were obtained in each case. In the second set of experiments, the sample was introduced into the furnace maintained isothermally at a desired temperature. End effects were considered negligible as the furnace was about ten times longer than the sample pan. The isothermal kerogen decomposition was carried out at 325, 375, 410, 425, 450, and 475°C.

The fraction of kerogen pyrolyzed,  $\alpha$  was defined by the expression:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (1)$$

where  $W_0$  = initial weight of the sample (mg),

$W_t$  = weight of the sample at "t" min (mg),

$W_\infty$  = weight of the sample after complete pyrolysis of kerogen (mg).

Each run was duplicated in order to minimize the error.

#### Kinetic Expressions:

The general expression for the decomposition of a solid [Blazek, A. 1973] is given by

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (2)$$

where  $\alpha$  = fractional conversion at time t,

k = specific rate constant,

$f(\alpha) = (1 - \alpha)$  in first order reactions.

Equation (2) can be written as follows by substituting k in terms of activation energy and frequency factor.

$$\frac{d\alpha}{dt} = Z \cdot \exp(-E/RT) \cdot (1 - \alpha), \quad (3)$$

where Z = frequency factor ( $\text{min}^{-1}$ ),

E = activation energy (J/g mole),

R = gas constant (J/g mole K),

T = temperature (K).

For non-isothermal decomposition of solids, Equation (3) can be modified by introducing heating rate as follows

$$\frac{d\alpha}{dT} \cdot \frac{dT}{dt} = Z \cdot \exp(-E/RT) \cdot (1 - \alpha) \quad (4)$$

or

$$\frac{d\alpha}{dT} = \frac{Z}{\beta} \cdot \exp(-E/RT) \cdot (1 - \alpha), \quad (5)$$

where  $\beta = dT/dt$ .

In the present study, two procedures were followed to evaluate the activation energy. The first was a graphical method while the second involved regression analysis.

The graphical method developed by Coats and Redfern [1964] was used here. The kerogen decomposition was considered to be first order in kerogen concentration [Rajeshwar, 1981; Campbell, et al 1978]. In this case, a plot of

$$\left[ - \ln \left( - \frac{\ln(1 - \alpha)}{T^2} \right) \right]$$

against  $1/T$  should result in a straight line of slope  $E/R$ .

In the second method, Equation (5) was rearranged and integrated to give

$$1 - \alpha = \exp - \frac{Z}{\beta} \int_0^T \exp(-E/RT) dT \quad (6)$$

or

$$= \exp - \left[ \frac{Z}{\beta} \left( \frac{RT^2}{E + 2RT} \cdot \exp(-E/RT) \right) \right]. \quad (7)$$

Equation (7) can be written as follows

$$\ln \left( \frac{E + 2RT}{T^2} \cdot \ln \frac{1}{1 - \alpha} \right) = \ln \frac{ZR}{\beta} - \frac{E}{RT}. \quad (8)$$

Equation (8) is of the form

$$y = a + bx, \quad (9)$$

where

$$y = \ln \left( \frac{E + 2RT}{T^2} \cdot \ln \frac{1}{1 - \alpha} \right), \quad (10)$$

$$a = \ln \frac{ZR}{\beta}, \quad (11)$$

$$b = -E/R, \quad (12)$$

and

$$x = 1/T \quad (13)$$

With the aid of repeated regression analysis, the values of slope and intercept can be computed. In the first step, an initial guess of  $E$  was made to calculate  $y$  (Equation (10)). Next,  $y$  was corrected for calculated values of  $E$  from Equation (12), and  $a$  and  $b$  were redetermined from the regression. The iteration was continued until the accuracy of  $E$  and  $Z$  was satisfied.

For the isothermal decomposition of kerogen, Equation (2) was integrated to give

$$- \ln(1 - \alpha) = k \cdot t. \quad (14)$$

A plot of  $[-\ln(1 - \alpha)]$  against  $t$  yields a straight line with slope equal to  $k$ . The values of  $t$  used here include the induction period  $t_0$  as suggested by Braun and Rothman [1975].

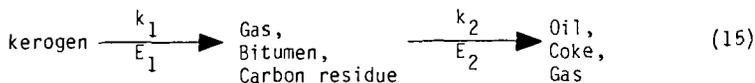
## RESULTS AND DISCUSSION

### Thermogravimetric Data

The weight loss data were obtained on powdered oil shale samples under non-isothermal and isothermal conditions. The oil shale decomposition was carried out using a small sample size and a thin platinum foil boat in order to obtain a steady state condition in a short time. In non-isothermal TGA, the sample was heated from ambient temperature to 900°C with heating rates ranging from 1 to 50°C/min. The isothermal TGA was carried out in the temperature range of 325 to 475°C. The results obtained under non-isothermal and isothermal conditions are comparable and they suggest that the kerogen decomposition proceeds via bitumen as an intermediate. First, the non-isothermal TG results are presented followed by the results obtained under isothermal conditions.

Figure 1 presents the weight-loss data for Moroccan oil shale as a function of temperature at various heating rates. The important features of this figure, which are worth mentioning here, are as follows: First, the total kerogen content in Moroccan oil shale was found to be about 9 percent (wt) of the total shale weight. Below 200°C, approximately 0.5 to 0.75 percent weight-loss was observed, which represented the moisture content of the shale. The carbonate decomposition commenced at temperatures above 525°C depending upon the heating rate and gave a weight-loss of about 25 to 26 percent. Second, and a more important observation, was regarding the effect of heating rate on total weight-loss. A complete decomposition of kerogen was effected at 500°C with a heating rate of 1 K/min while only 50 percent of the total kerogen was found to decompose at 500°C when a rate of 50°C/min was used. In the latter case, a temperature of 600°C was required to achieve the complete decomposition of kerogen into oil. This difference can be explained by the fact that the higher the heating rate the shorter is the exposure of sample to a particular temperature. However, as will be shown in the later part of this section, the variation in heating rate did not alter the kinetic parameters.

Figure 2 illustrates typical DTG curves corresponding to the data shown in Figure 1 for heating rates of 2, 5, 10 and 50 K/min. Three salient features of this figure are to be noted. First, there is a shift in rate maxima toward higher temperatures as the heating rate is increased from 5 to 50 K/min. These results are complementary to the above-mentioned findings on the effect of heating rates (Figure 1). These results are strikingly similar to those obtained by Herrell and Arnold [1976], and Chen and Nuttall [1979]. Second, the presence of two clearly defined rate maxima in the temperature range of 300 to 600°C indicate that the two reactions or processes occur consecutively in this temperature range. Actually, Allred [1966] had proposed the following mechanism for the pyrolysis of oil shale:



The present results are in accordance with his model, and they lead us to believe that the first peak at lower temperature corresponds to the decomposition of kerogen to bitumen while the second peak represents the decomposition of pyrolytic bitumen into oil and gas. Recently, Rajeshwar [1981] also reported similar results on Colorado oil shale. Third, the rate of weight-loss increased by a factor of three with an increase in heat rate from 2 to 5 K/min. However, a further increase in heating rate (5 to 50 K/min) did not accelerate kerogen decomposition rate appreciably.

### Kinetic Analysis

The data presented in Figure 1 was used to determine the kinetic parameters of kerogen decomposition. A plot of

$$- \ln \left[ 1 - \frac{\ln(1 - \alpha)}{T^2} \right]$$

against  $1/T$  shown in Figure 3 was used to evaluate the activation energy. The kerogen decomposition was assumed to be first order to kerogen concentration. Two sets of straight lines with different slopes (Figure 3) clearly demonstrate that the two consecutive reactions occur in the temperature range of 300 to 600°C. The first reaction occurring at lower temperature (kerogen + bitumen) proceeds with an activation energy of about 40.2 kJ/mole. The second reaction which occurs beyond 350°C has an average activation energy of 58.1 kJ/mole. The kinetic parameters are presented in Table II. The fact that the variation in heating rate does not alter the slope of the straight line plots presented in Figure 3 suggests that the kinetic parameters determined in the present study are probably not sensitive to the efficiency of heat transfer between the sample and surroundings. These results corroborate very well with those observed by Rajeshwar [1981].

The regression method was also used in this study to determine the kinetic parameters. The activation energies and frequency factors evaluated by this iteration method are listed in Table II. They compare fairly well with those obtained by the graphical method.

Results obtained under isothermal conditions will be discussed at this stage. Figure 4 shows the kerogen decomposition as a function of time at various temperatures. During the initial period of these isothermal runs less than 1 minute was required to attain steady state values of temperature. As explained earlier, the use of small sample size (~25 mg) small diameter furnace and thin platinum foil boat aided in obtaining steady-state conditions in short time. During the temperature-induced time lag period, very small weight losses were recorded; at temperatures higher than 450°C it amounted to about 12 to 14 percent of total weight-loss. Several workers [Campbell, et al 1978; Granoff and Nuttall, 1977; and Haddadin and Mizyet, 1974] have developed the kinetic expressions similar to Equation (14), assuming the shale particle temperature to be uniform and mass transfer rate to be high. In the present study, Equation (14) was used to evaluate the specific rate constant (Figure 5).

Table III compares the  $k$  values (computed from Figure 5) with the literature values for the decomposition of Jordan and Colorado oil shale. This comparison shows that at temperatures lower than 425°C, the decomposition rate of Moroccan shale is twice as fast as that of Jordan shale, and about three to four times as fast as that of Colorado shale. At 475°C the  $k$  values for

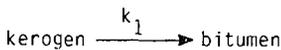
decomposition of Moroccan shale is about four times higher than that reported for the pyrolysis of Jordan shale, but it is almost identical to the  $k$  value for Colorado shale decomposition.

The Arrhenius plot shown in Figure 6 was used to determine activation energy and frequency factor. Figure 6 also shows two distinct reactions. Their kinetic parameters,  $E_1 = 38.4 \text{ kJ mole}^{-1}$  and  $E_2 = 62.3 \text{ kJ mole}^{-1}$ , listed in Table II, are in good agreement with those obtained under non-isothermal conditions. Activation energy ( $E_a$ ) for kerogen decomposition to bitumen compares fairly well with that reported by Braun and Rothman [1975]. The low activation energy ( $-40 \text{ kJ/mole}$ ) indicates that the decomposition of kerogen to bitumen involves the breaking of relatively weak chemical bonds [Braun and Rothman, 1975].

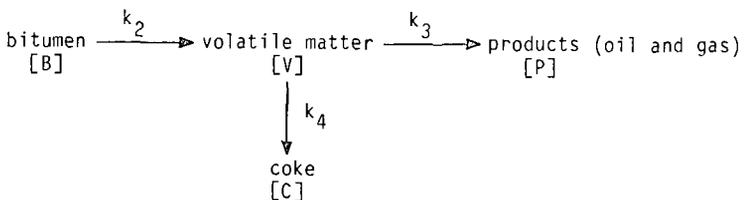
The low activation energy obtained in the present study under both the isothermal and non-isothermal experiments suggest certain physical processes controlling the reaction. The rate expressions used to determine the kinetic parameters in this investigation were developed assuming that there are no heat and mass transfer limitations and that the reaction kinetics controls the rate of weight-loss. The fact that the variation of heating rates (Figure 3) did not affect the activation energy value substantiates the validity of the assumption that there are no heat transfer limitations. Rejeshwar [1981] pointed out that the heating rate variations can be used as a diagnostic probe to obtain information on mechanistic aspects. Haddadin, et al [1974, 1980] also obtained low activation energy during the pyrolysis of Jordan oil shale. They postulated a mechanism in which the diffusion of organic matter through the carbonate matrix controls the rate process. Several diffusion-controlling models [Levenspiel, 1972; Blazek, 1973; Ginstling and Brounshtein, 1956] have been developed to analyze the fluid-solid reactions and solid decomposition. According to the method suggested by Levenspiel [1972], experimental curves obtained by plotting  $(1 - \alpha)$  versus  $t/\tau$  ( $\tau$  is the time required for complete decomposition) are compared with the predicted curves for various mechanisms, e.g., chemical reaction, film diffusion and ash layer diffusion. The data obtained under isothermal conditions was used for this plot between  $(1 - \alpha)$  and  $t/\tau$ . It was deduced from this plot that the ash layer diffusion controls the reaction rate.

According to Haddadin and Mizyet [1974], Equation (15) can then be written as:

First Step:



Second Step:



where [B], [V], [P] and [C] denote the weight fractions of bitumen, volatile matter, products (oil and gas) and coke, respectively.

The first step involving the decomposition of kerogen to bitumen is relatively rapid [Haddadin and Mizyet, 1974] and can thus be omitted from consideration in the controlling kinetics. The second step which involves transport of oil vapor and gas to the atmosphere is the rate controlling step. The overall rate for this step is

$$\frac{d[P]}{dt} = k_3 [V] . \quad (16)$$

Assuming steady state concentration of volatiles during the process, we have

$$\frac{d[V]}{dt} = 0 = k_2[B] - k_3[V] - k_4[V] . \quad (17)$$

Solving for [V],

$$[V] = \frac{k_2}{k_3 + k_4} \cdot [B] \quad (18)$$

and substituting in Equation (18), we have

$$\frac{d[P]}{dt} = \frac{k_2 \cdot k_3}{k_3 + k_4} [B] . \quad (19)$$

If diffusion of volatile matter controls the reaction rate, we have

$$k_2 \gg k_3 ; \quad - \frac{d[B]}{dt} = \frac{k_2 k_3}{k_4} \cdot [B] = k[B] , \quad (20)$$

where k is the overall rate constant of the weight change. Equation (20) applies to a situation where the carbonate matrix acts as a porous diffusion barrier.

#### CONCLUSIONS

The combined use of non-isothermal and isothermal TG measurements has shown that the thermal decomposition of Moroccan oil shale involves two consecutive reactions, with bitumen as intermediate.



Both the reactions follow a first order kinetics.

Activation energy of 40 kJ/mole for the decomposition of kerogen to bitumen suggests that this step involves the breaking of a relatively weak chemical bond.

The rate of bitumen decomposition is controlled by the volatile matter transport through the inorganic matrix. Low value of activation energy obtained for this reaction are complementary to such a mechanism.

The decomposition rate of Moroccan oil shale is about 2-4 times higher than that of Jordan shale in the temperature range of 300 to 500°C.

A comparison of decomposition rates for Moroccan and Colorado Oil shales shows that at temperatures lower than 400°C, the Moroccan shale decomposes more rapidly than the Colorado shale; at 475°C the decomposition rates for both shales become almost identical.

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TABLE I. CHEMICAL ANALYSIS OF MORROCCAN OIL SHALE

1. Fischer Oil Assay	71 k/tonne
2. Density	2.25 q/ml
3. Chemical composition of raw shale compound	
A. Keragen	9.5 wt%
C - 69.7% (wt)	
H - 6.7	
S - 9.1	
N - 2.3	
O - 12.2	
B. Dolomite	14.4
C. Calcite	37.7
D. Quartz	17.2
E. Argiles (Illite-Kaolinite)	12.2
F. Pyrites	1.6
G. $FeCO_3 + Fe_2O_3$	1.6
H. $TiO_2 + Phosphate$	2.2
I. Other constituents	3.4

TABLE II. KINETIC PARAMETERS FOR THE NON-ISOTHERMAL AND ISOTHERMAL DECOMPOSITION OF MORROCCAN OIL SHALE

Method	Activation Energy (kJ/mole)		Frequency Factor (s/min)	
	$E_1$	$E_2$	$Z_1$	$Z_2$
Non-Isenthal Mode, Graphical Method	40.2	58.1	$6.9 \times 10^4$	$2.8 \times 10^5$
Non-Isenthal Mode, Regression Method	43.0	64.8	$7.2 \times 10^4$	$3.2 \times 10^5$
Isothermal Mode	38.4	62.3	$4.6 \times 10^4$	$4.8 \times 10^5$

TABLE III. A COMPARISON OF FIRST ORDER RATE CONSTANTS FOR OIL SHALE DECOMPOSITION

Temp. (°C)	First Order Rate Constants (min <sup>-1</sup> )			
	Moroccan Shale	Jordan Shale	Colorado Shale	
	Present Study	[Haddadin and Mizyret, 1974]	[Braun and Rothman, 1975]	[Campbell et al., 1978]
325	0.05	-	-	-
330	-	0.024	-	-
360	-	0.037	-	-
375	0.09	-	-	-
400	-	-	0.02	0.025
405	-	0.057	-	-
410	0.18	-	-	-
425	0.20	-	-	0.090
440	-	0.078	-	-
450	0.31	-	0.18	-
475	0.41	0.113	0.48	-

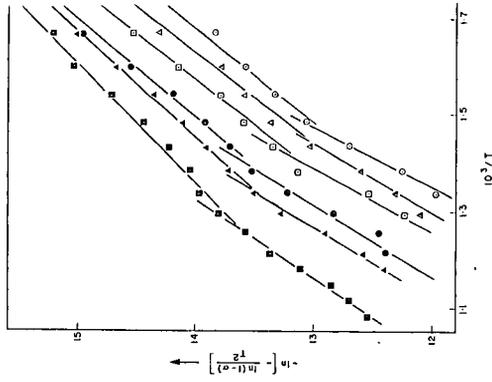


Figure 3. Analysis of the TG data for Moroccan oil shale by the Coats-Redfern method. Heating rates: (○) 1 K/min, (△) 2 K/min, (□) 5 K/min, (●) 10 K/min, (▲) 20 K/min, and (■) 30 K/min.

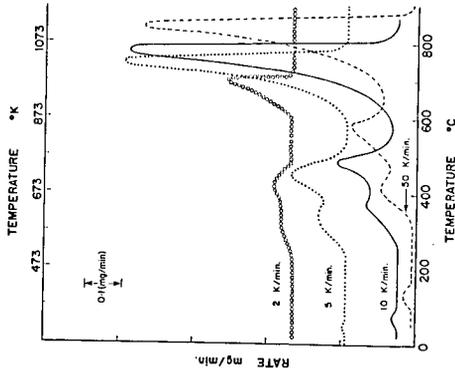


Figure 2. DTG curves for Moroccan oil shale at 2 K/min, 5 K/min, 10 K/min, 20 K/min, and 50 K/min.

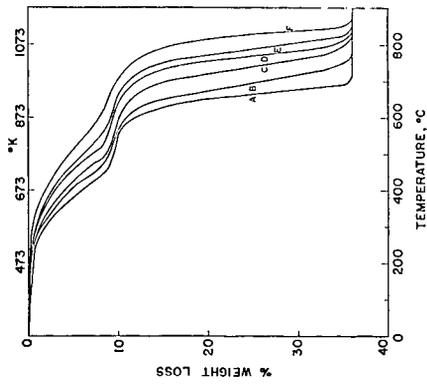


Figure 1. Non-isothermal TG curves for Moroccan oil shale at various heating rates: [A] 1 K/min, [B] 2 K/min, [C] 5 K/min, [D] 10 K/min, [E] 20 K/min, and [F] 50 K/min.

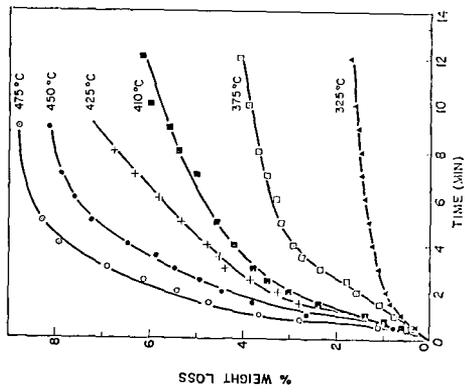


Figure 4. Percent weight loss for Mexican oil shale at various temperatures (isothermal TG curves).

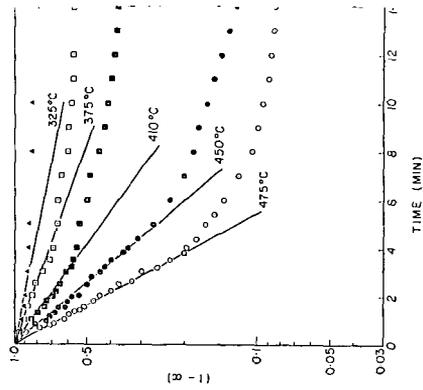


Figure 5. Analysis of isothermal TG data (from Figure 4).

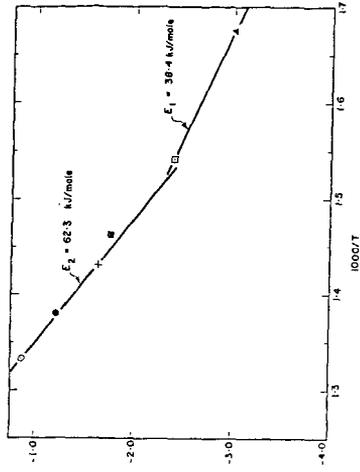


Figure 6. Arrhenius plot of  $\ln k$  versus  $1000/T$  using isothermal TG data.