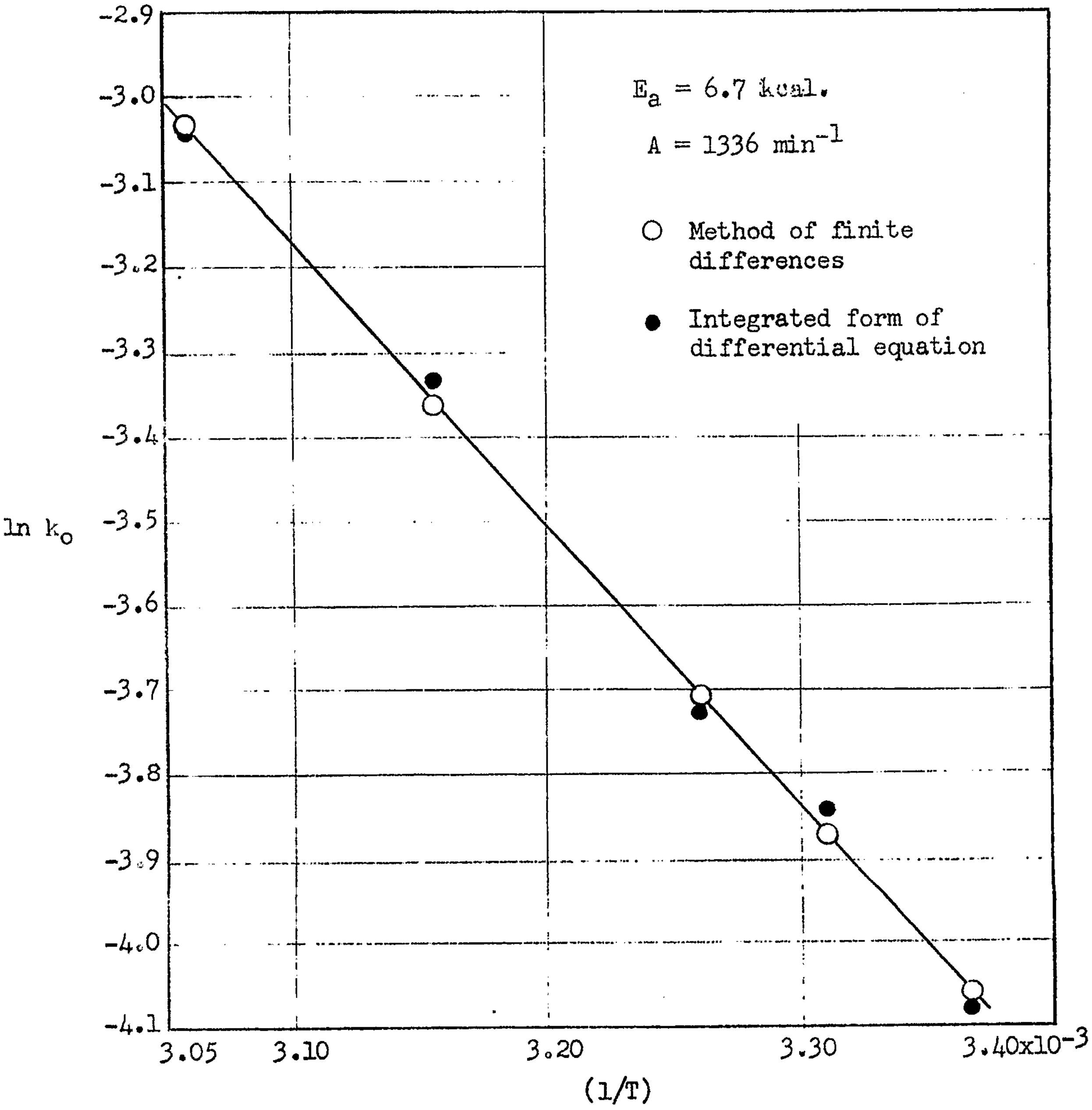


Fig. 13. Arrhenius plot for evaluation of the activation energy.

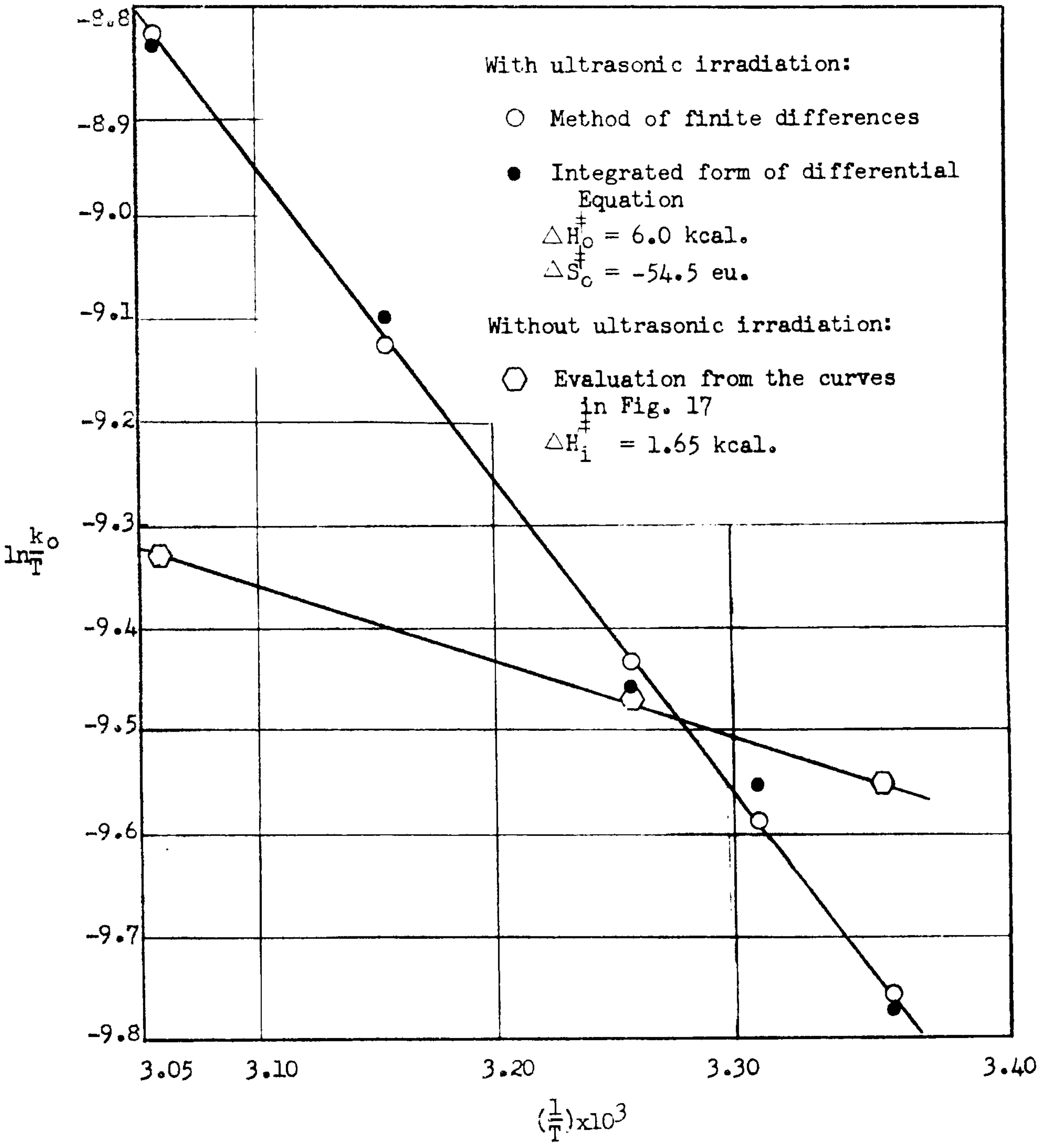


Fig. 14. Eyring's plot for evaluation of the activation enthalpy and entropy for coal extraction with and without ultrasonic irradiation.

Table 6. Variation of entropy of activation with fraction extracted.

		(x=0)		x=0.05	$-\frac{b}{R}x=0.3660$	x=0.1	$-\frac{b}{R}x=0.7319$
$T^{o}K$	$(\frac{1}{T})x10^3$	ln k_o	ln k_o/T	ln k	ln k/T	ln k	ln k/T
297	3.367	-4.0635	-9.7583	-4.4295	-10.1242	-4.7954	-10.4902
302	3.311	-3.874	-9.5855	-4.2399	- 9.9514	-4.6059	-10.3174
307	3.257	-3.705	-9.4329	-4.0710	- 9.7988	-4.4369	-10.1648
317	3.155	-3.366	-9.1259	-3.7320	- 9.4919	-4.0979	- 9.8579
327	3.058	-3.033	-8.8241	-3.3990	- 9.1900	-3.7649	- 9.5559

96<

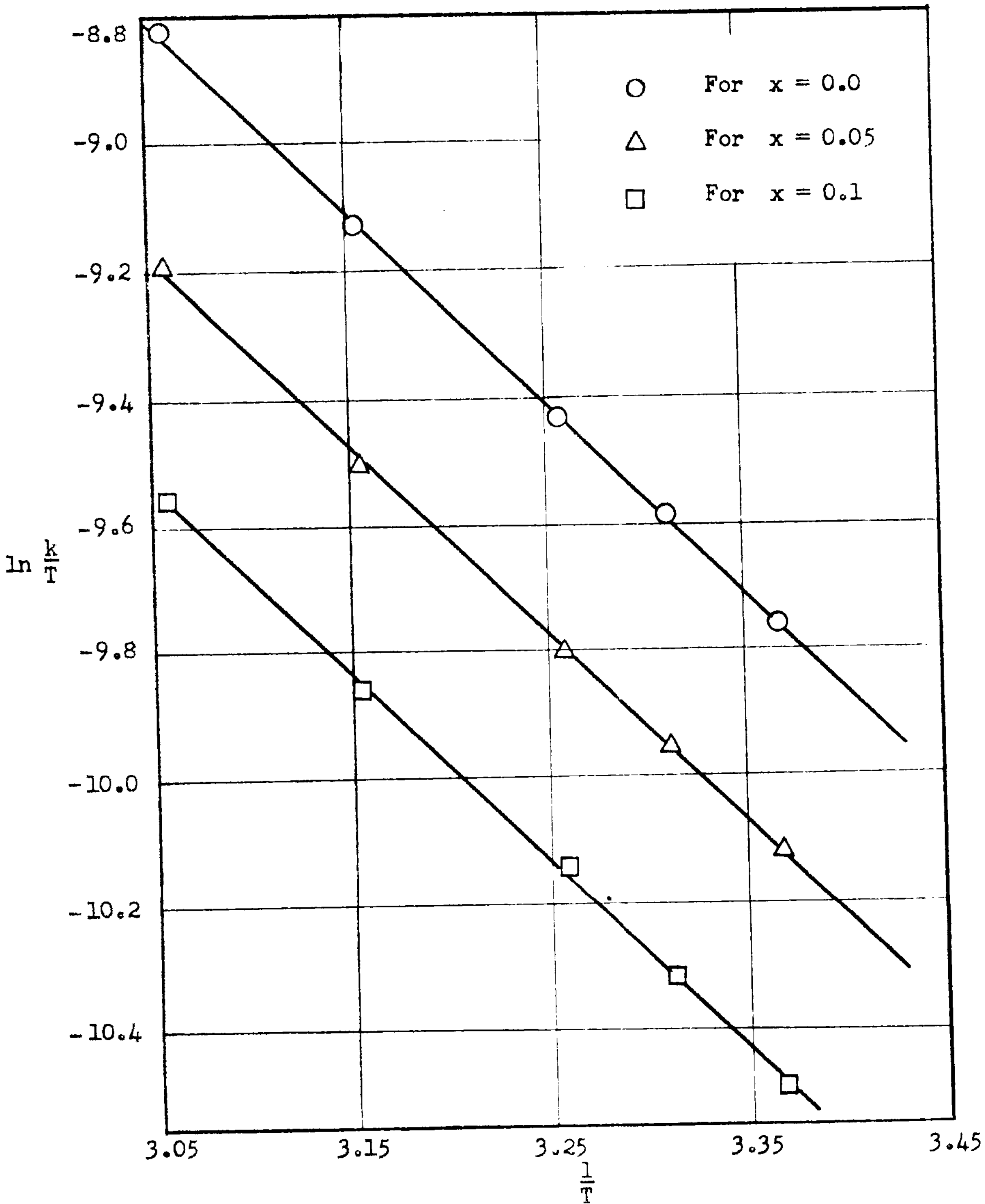


Fig. 15. A plot of ln $\frac{k}{T}$ versus $\frac{1}{T}$ for variation of activation entropies with fraction extracted.

Data showing the variation of entropy of activation with fraction extracted are listed in Table 6 and are plotted in Fig. 15.

The solution of the differential equation for the extraction process

$$\frac{dx}{dt} = k_o e^{-\frac{bx}{R}} (a-x) \tag{20}$$

integrated between the following boundary conditions; t=0 for x=0, and t=t for x=x, is

$$k_o t = -e^{\frac{ab}{R}} \Big[\ln(a-x) - \frac{b}{R}(a-x) + \frac{b^2}{4R^2}(a-x)^2 - \frac{b^3}{18R^3}(a-x)^3 + \ldots\ldots -\ln(a) + \frac{ba}{R} - \frac{b^2a^2}{4R^2} + \frac{b^3a^3}{18R^3} + \ldots\ldots\ldots\ldots \Big] \tag{21}$$

This can be simplified to:

$$k_o t = -e^{\frac{ab}{R}} \Big[\ln\frac{a-x}{a} + \frac{bx}{R} + \frac{b^2}{4R^2}(-2ax + x^2) - \frac{b^3}{18R^3}(-3a^2x + 3ax^2 - x^3) + \ldots\ldots\ldots\ldots \Big] \tag{22}$$

The fifth and subsequent terms can be neglected as calculations show that they are less than 1 percent of the first term.

From this kinetic study on solvent extraction of coal, the following model for extraction is proposed. In most reactions, the free energy of activation ($\Delta F^{\ddagger}$) remains constant throughout the entire reaction period.

However in the case of coal extraction by tetralin, an increase in free energy of activation with the time of reaction is observed. According to the absolute reaction rate theory, the data show that the increase in free energy of activation corresponds to a decrease in entropy of activation as the extraction process proceeds. This result is illustrated by Fig. 16 in which activation free energy is plotted against the reaction coordinate.

In interpreting the graph, the following physical model for coal is assumed. The coal structure is composed of a central nucleus of

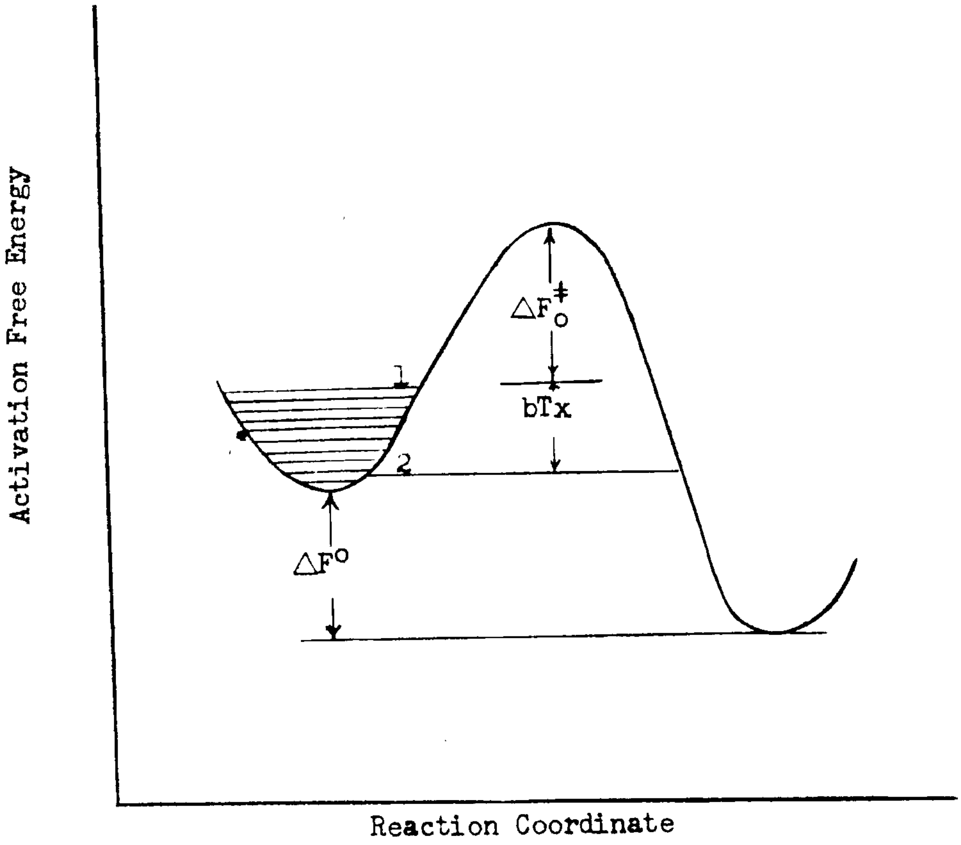


Fig. 16. A sketch of reaction coordinate versus activation free energy for extraction of coal.

coacervates in which the micelles form an ordered assembly and are surrounded by flocculates in a disordered mass. The micelles of the disordered mass become immobilized to different degrees. The stable ones form new aggregates which pack together uniformly. This model is basically supported by information given by Bangham et. al. (55).

With this model in mind, it can be assumed that the valley on the left hand in Fig. 16 represents various energy levels of coal in an unreacted state. Level 1 is the free energy level of coal that is

100<

extracted initially. As extraction goes on, it is harder for the soluble material in the coal to surmount the activation-energy barrier because the lower-lying energy levels correspond to a higher energy barrier. Level 2 is the lowest free energy level of coal that can be extracted at a given temperature. An increase in temperature is one of the factors which will further drop this lowest free-energy level. ΔF^o represents the standard free energy change for extraction of coal.

According to the foregoing physical model one readily sees that the first extract leaving the parent coal complex relieves the hindering van der Waal's bonds which bond the disordered <u>flocculates</u>. As more substances are extracted, more stably-packed coal constituents are left behind.

This produces an activation entropy decrease along with the extraction process. Obviously with the more ordered coal matrix left behind, the compounds remaining are less inclined to leave; in other words, the extraction becomes more difficult. To overcome this increasing tendency for the compounds to remain in the coal structure, a corresponding increase in activation free energy must be overcome.

In terms of a mathematical expression, the whole process can be described as follows:

$$\begin{array}{llll}
C_o & \xrightarrow{k_o} & C_1 & + E_1 \\
C_1 & \xrightarrow{k_1} & C_2 & + E_2 \\
C_2 & \xrightarrow{k_2} & C_3 & + E_3 \\
C_3 & \xrightarrow{k_3} & C_4 & + E_4 \\
\hline
C_n & \xrightarrow{k_n} & C_{n+1} & + E_{n+1}
\end{array}$$

where C_o is the initial coal, $C_1 \ldots\ldots\ldots C_n$ represent the steadily deactivated residual coal, $E_1 \ldots\ldots\ldots E_n$ represent the compounds extracted by tetralin, k_o is the initial rate constant, and $k_1 \ldots\ldots\ldots k_n$ represent the subsequent rate constants as the extraction proceeds. It is expected that $k_o > k_1 > k_2 \ldots\ldots\ldots > k_n$ because of decrease in entropy resulting in an increase in the required activation free energy.

Comparison of Experimental Results With and Without an Ultrasonic Irradiation

In order to understand the absolute effect of ultrasonic irradiation on the coal extraction process, a series of conventional extraction experiments were also carried out. In these experiments three temperatures, 24, 34, and 54°C, and five extraction periods, 2, 5, 10, 15, and 20 hours, were used. The experiment was conducted by simply placing the coal-tetralin mixture in a constant temperature bath for the desired time of extraction. During this period, the mixture was continuously stirred. The experimental data from these runs are in Tables 8, 9, and 10 in the Appendix and plotted in Fig. 17 together with the results for extraction of coal with ultrasonic energy. Comparison of experimental results with and without an ultrasonic effect will be discussed in two parts, the first part is the comparison of rate and yield of the extracts and the other is the comparison of infrared spectra.

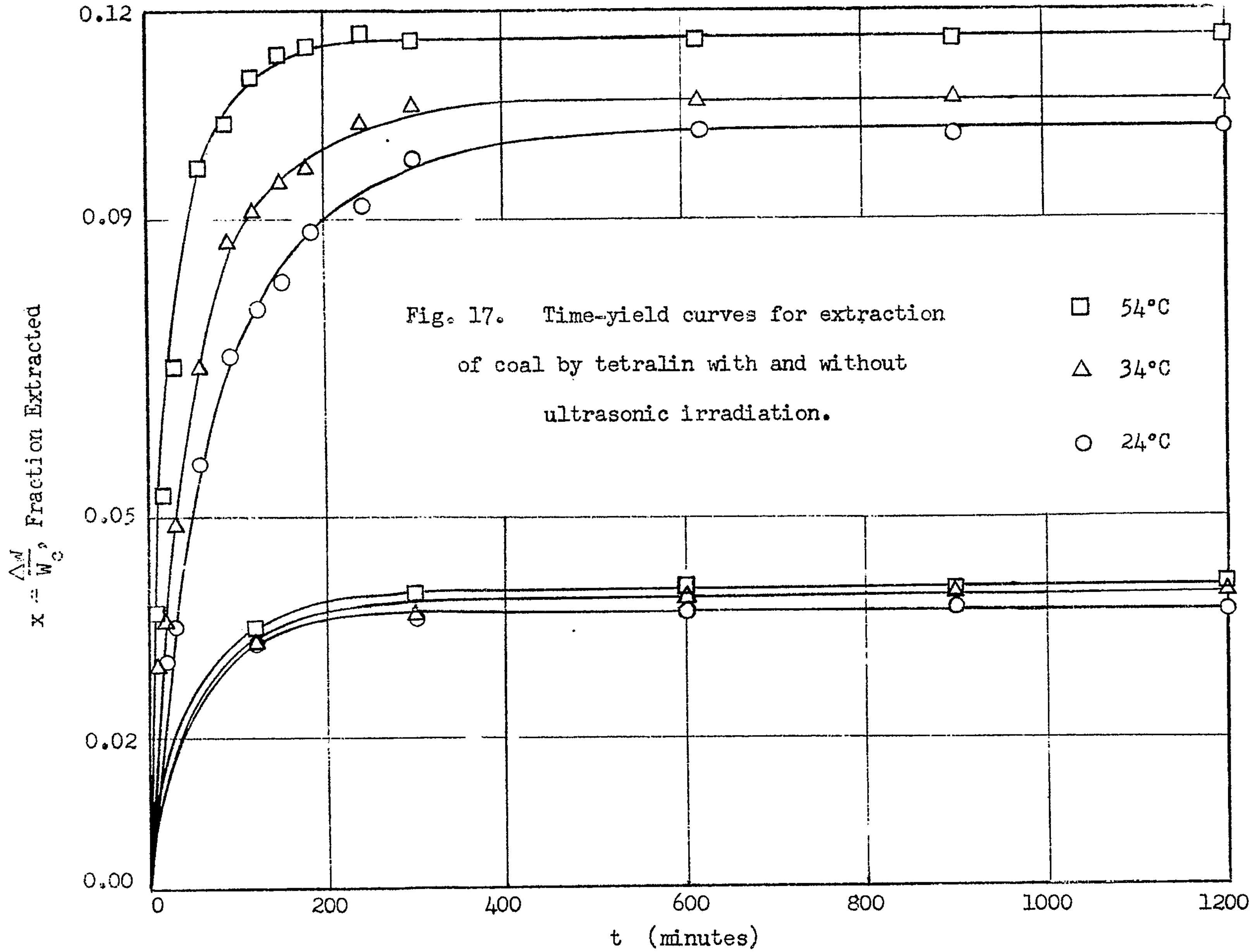


Fig. 17. Time-yield curves for extraction of coal by tetralin with and without ultrasonic irradiation.

Rate and yield Table 7 shows a comparison of yields after 20 hours of extraction with and without ultrasonic irradiation.

Table 7. Yields of extract after 20 hours in the presence and absence of ultrasonic energy.

Extraction Temp. (°C)	Yield (wt.%)	
	Without ultrasonic effect	With ultrasonic effect
24	3.70	10.21
34	3.97	10.61
54	4.10	11.41

The following observations can be made from an examination of the results of coal extraction in the presence and absence of ultrasonic field:

(1) A transient region was found to exist in both processes. The rate of extraction within this region, however, was found to be widely different. The difference can be seen from the different slopes during the first two hours of extraction (see Fig. 17). On the average the rate of yield under ultrasonic irradiation is 0.06%/min. as compared to 0.03%/min. without ultrasonic energy, a factor of two.

(2) A significant difference in the maximum yield of extract was also observed. On the average, the maximum yield of extract with the aid of ultrasonic irradiation is 10.7% as compared to

3.92% of the original coal without ultrasonic effect, a factor of 2.7. The increased amount of extract obtained with ultrasonic irradiation is presumably the result of the breaking of more bonds in the coal matrix.

It appears that affects of ultrasonic vibration on the coal extraction process are: (a) to increase the collision frequencies between the solvent and coal particles, resulting in an increase in the rate of extraction. In a sense this is equivalent to an increase of temperature of the extraction which raises the kinetic energy of both solvent and extractable molecules in the coal particle, and (b) to break bonds which, otherwise, stay intact in the coal structure. It is unlikely that the intensity of ultrasonic field used in this work (0.59 watt/cm^2) will break strong chemical bonds. However, the moderately bonded compounds (held with van der Waal bonds) are strong enough to resist dissolution by the conventional extraction process but seem to be affected by the ultrasonic energy. It is this action of the ultrasonic irradiation that increases the total yield of extract.

The extraction experiments on coal by tetralin without the aid of ultrasonic field were only carried out at three temperatures, i.e., 24°C, 34°C and 54°C. The initial enthalpy of activation, $\Delta H_1^{\ddagger}$, for this process was evaluated to be about 1.65 kcal/mole from an Eyring's plot of $\ln(k_o/T)$ versus $1/T$ (see Fig. 14). The initial rate constant, k_o, was evaluated from the average rate of extraction over the period of zero to fifteen minutes. The reason for choosing the zero to fifteen minutes extraction period was that in the case of extraction with the aid of ultrasonic field, the average k_o calculated over the first

15-minute period was found to be very close to the value obtained by extrapolating the data to zero extraction time (see Fig. 12). The activation enthalpy of 1.65 kcal/mole in this case is much lower than the value obtained for coal extraction with the ultrasonic field.

Apparently, without an ultrasonic effect the material available for extraction by tetralin is limited to those very weakly bonded substances. Since the bonding energy for the materials extracted is small, the temperature has little effect on the rate of extraction. Therefore, one obtains a low activation enthalpy. These weakly bonded substances are not abundant in the coal, consequently the maximum amount of extraction is only a few percent.

Infrared spectra Some effort has been spent trying to characterize the extraction products by use of gas chromatography. The analysis showed little significant differences. A reason for these results setback is because the tetralin used contains about 2% impurity, also the benzene and trichloroethylene used are not pure reagents, however, the maximum concentration of extracted materials in the solvent mixture is only about 0.01%. As a result, no new peaks corresponding to the extracted substances could be found. There is, of course, one alternative; that is, to concentrate the extracts before they are analyzed by a gas chromatograph. However by doing so, the concentration of impurities are also relatively increased and little significant gain can be obtained by this procedure.

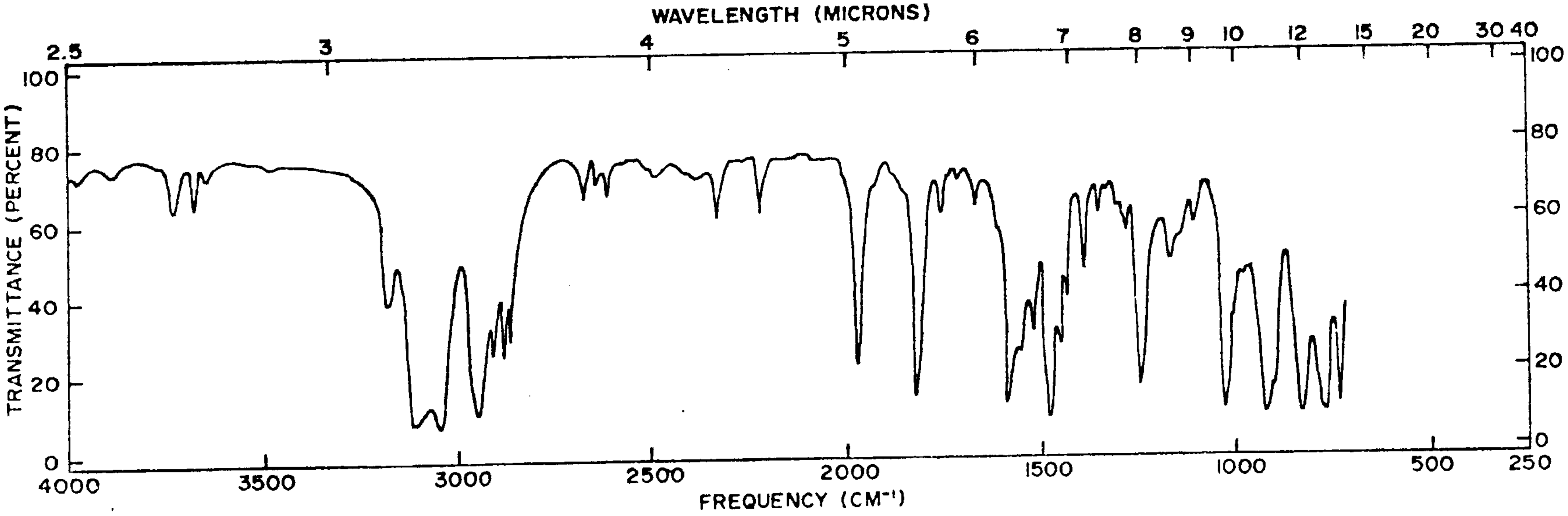
In this case, there is, however, a sensitive method which can be employed to help understand at least qualitatively the characteristic of extracted materials. The employed method is infrared spectroscopy.

Five types of materials have been analyzed by this method. They are (a) the mixture of tetralin, benzene and trichloroethylene in a ratio corresponding to the actual content of these three solvents in the extracts; the ratio is 1 : 10 : 10 by volume; (b) the extracts from the extraction without the aid of ultrasonic field at 54°C for 10 hours; (c) the extracts from the extraction with the aid of ultrasonic field at 54°C for 10 hours; (d) the concentrated extracts from samples in (b); and (e) the concentrated extracts from samples in (c). The further concentration of extracts was done by use of a micro-distillation unit. This unit is operating in vacuum. The distillation temperature was 60°C. The concentrated samples were collected when three quarters of solution had evaporated. The spectra of these five materials are shown in Figs. 18, 19, and 20.

Comparing Fig. 19(a) and Fig. 19(b), we find that the spectra of extracts without and with ultrasonic effect show a striking similarity. There is, however, a slight difference in absorption intensity which occurs in two absorption regions, wave numbers from 1435 cm^{-1} to 1450 cm^{-1} and wave numbers from 2851 cm^{-1} to 2890 cm^{-1}. For these two absorption regions the extracts with the aid of ultrasonic field exhibit a slightly higher absorption intensity than those without the aid of ultrasonic effect. Since there is no difference in the position of peaks between the spectra of these two extracts, the extracts from both extraction processes presumably contain the same materials but in different quantities.

Comparing the spectra of concentrated and original extracts, we see that only the two absorption regions already mentioned above change

Fig. 18. Infrared spectrum of tetralin, benzene, and trichloroethylene solvent mixture.



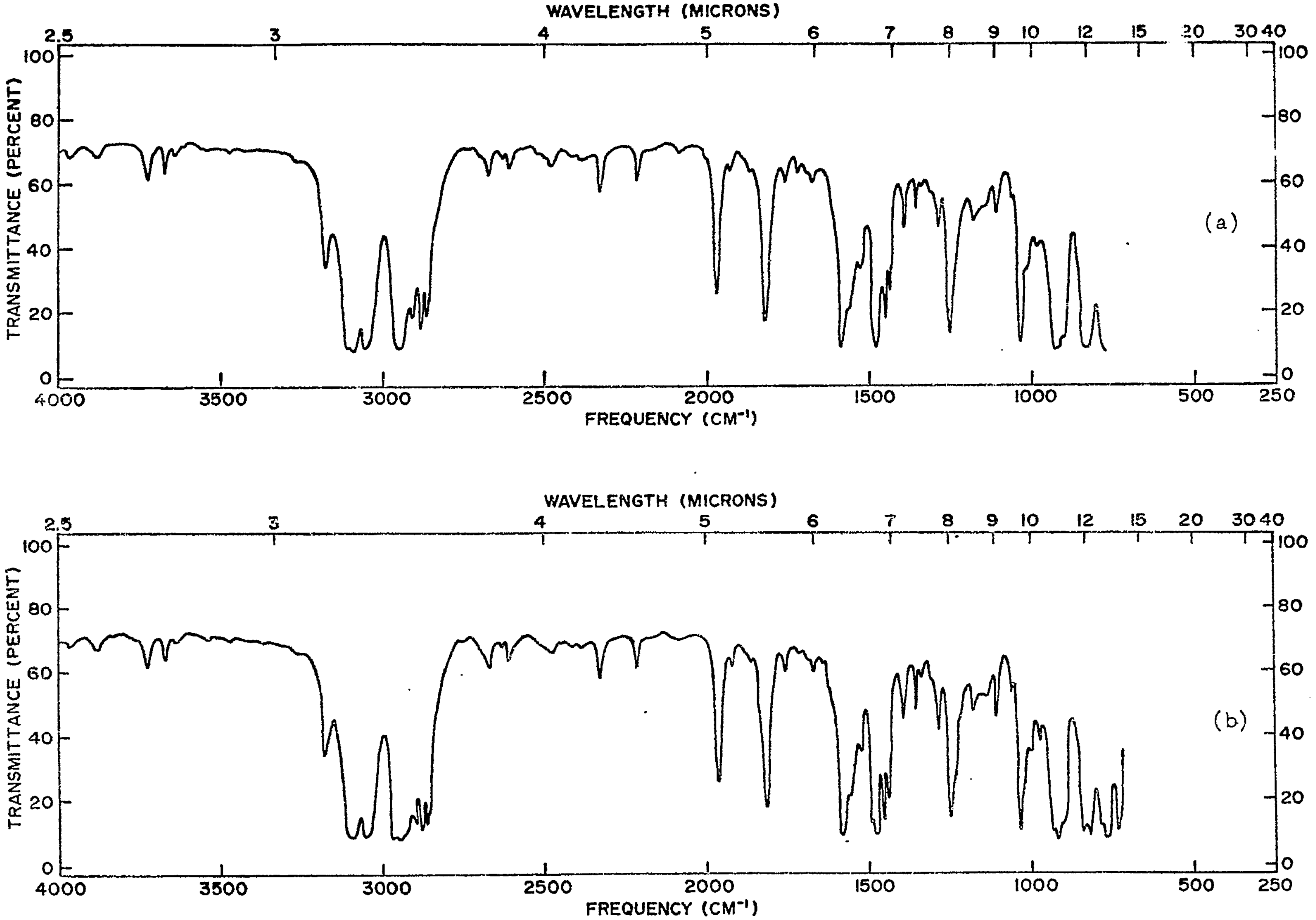


Fig. 19. Infrared spectra of the extracts from coal extraction by tetralin (a) without the aid of ultrasonic irradiation, (b) with the aid of ultrasonic irradiation.

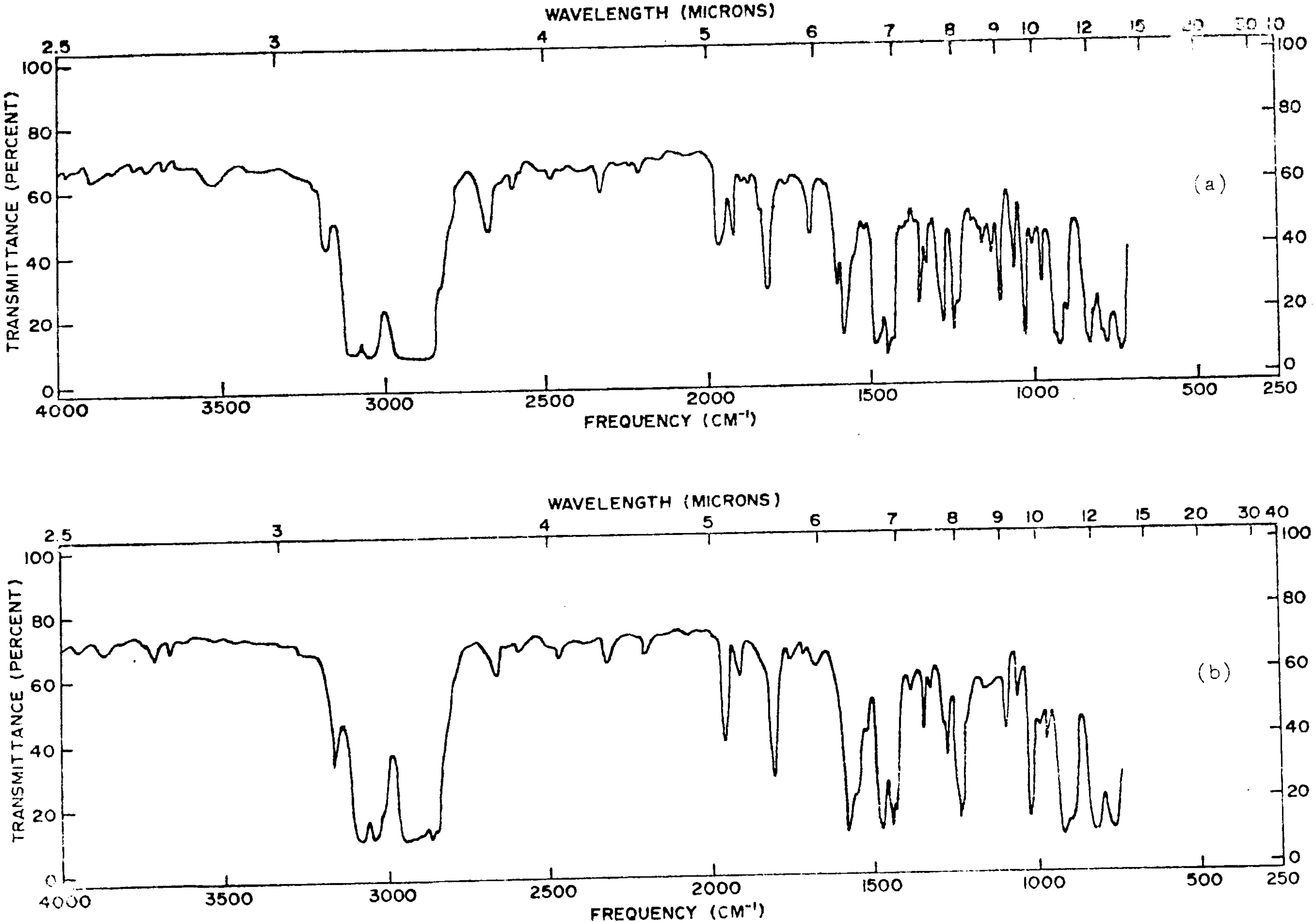


Fig. 20. Infrared spectra of the concentrated extracts from coal extraction by tetralin (a) without the aid of ultrasonic irradiation, (b) with the aid of ultrasonic irradiation.

their absorption intensities. Other peaks remain nearly the same. Of course, there are some relative change of intensity for some peaks, which is obviously due to the effect of being concentrated. Since no significant new peaks are produced because of the change of concentration, the concentrated and original extracts are considered to be essentially the same. There is, however, one rather weak new peak, at 3510 cm^{-1} appeared in the spectrum of concentrated extracts without the aid of ultrasonic wave, (Fig. 20 a), but not in the spectrum of the original extracts, (Fig. 19 a). There is no way to explain whether this is due to an increase in concentration or due to the contamination during the distillation process. Since the peak is rather weak it is considered insignificant.

A comparison of the spectra of solvent mixture and the spectra of extracts show changes at a number of places. Stronger absorption intensity is recorded for the extracts than the solvent mixture at wave numbers, 1352 cm^{-1}, 1435 cm^{-1}, 1450 cm^{-1}, 2851 cm^{-1}, 2874 cm^{-1}, and 2890 cm^{-1}. There is no new peak found in the extracts. Apparently the extracted compounds have at least the same chemical groups as the solvents. The first three frequencies are the bending and scissoring vibrations of C-H and $-CH_2-$. The other three frequencies are stretching vibrations of C-H in chemical groups like $-CH_2-$, $C-CH_3$ and tertiary C-H. According to the structure-frequency correlation, the functional groups CH, CH_2, and CH_3 in these absorption bands are from aliphatic compounds. Since aliphatic compounds are mostly found as side chains in the coal matrix, this result suggests that in the solvent extraction of coal at moderate temperatures only the side chains of coal matrix are affected.

For extraction process with ultrasonic irradiation more side chains are extracted as compared with the process without ultrasonic irradiation.

CONCLUSIONS

An experimental method has been developed for the solvent extraction of coal under the influence of ultrasonic irradiation. The rate of extraction of bituminous coals with tetralin is accelerated because the ultrasonic field hastens the dispersal of the coal micelles without inducing decomposition of the large extractable molecules.

This investigation shows that the extraction process is essentially complete after 10 hours of extraction, although the largest portion of the possible extract yield for a given test condition is obtained in two and a half hours.

For coal extraction at or near room temperature, a modified first-order series reaction was found to represent the experimental data. The data show that the coal structure is held together by bonds of various strengths. The dissolution of the weakly-bonded compounds in the coal requires an activation free energy of about 24.5 kcal/mole to 25.1 kcal/mole. The extraction process ends when all the weakly bonded materials have been extracted.

The activation entropy for the initial phase of the extraction process was calculated to be -54.5 e.u. This value is considerably lower than the value calculated by assuming tetralin as a gas molecule absorbed on a solid site of coal to form an activated complex. In the formation of the activated complex the tetralin molecule loses three translational degree of freedom (-112.8 e.u.) and one rotational degree of freedom (-3.4 e.u.), a total of -116.2 e.u. The method used for the calculation of entropy is that described by Glasstone, et. al., (56). Although tetralin is a liquid and the value of each translational and rotational degree of freedom is less than that for a gas, the activation entropy calculated for this process is still of the right order of magnitude and is quite reasonable.

The rate of extraction is very fast initially and then decreases with time. The rate constants for extraction at 24°C were found to be 0.0172 min^{-1} in the initial phase of the extraction process and 0.0082 min^{-1} near the end of extraction, and at 54°C, were found to be 0.0482 min^{-1} for the former and 0.0211 min^{-1} for the latter.

Extraction experiments were also performed without the aid of ultrasonic irradiation. The rate and yield of extracts were both found to be much smaller compared with those under the aid of ultrasonic irradiation. At 24°C the average rate and the maximum yield without ultrasonic effect are 0.025%/min. and 3.71% as compared with 0.064%/min. and 10.2% with the aid of ultrasonic effect. At 54° for the former are 0.029%/min. and 4.1% and for the latter are 0.091%/min. and 11.4%.

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NOMENCLATURE

Symbols	Definition
a	The maximum change in weight of original coal (ash free).
a_i	Initial concentration of the coal, g.cc^{-1}.
b	Constant.
b'	Constant equivalent to b or bT.
b_T	Initial concentration of tetralin, g cc^{-1}.
C_o	Initial coal.
$C_1 \ldots\ldots C_n$	The steadily deactivated residual coals.
d	Constant equivalent to $(x_{max})^{-\frac{1}{2}}$.
E_a	Activation energy, Kcal mole^{-1}.
$E_1 \ldots\ldots E_n$	Compounds extracted by tetralin.
$\Delta F_o^{\ddagger}$	Initial free energy of activation, Kcal mole^{-1}.
$\Delta F^{\ddagger}$	Free energy of activation, Kcal mole^{-1}.
ΔF^{o}	Standard activation free energy.
$G_o \ldots\ldots G_{n-1}$	Gases, g.
h	Planck's constant, 6.62×10^{-27} erg sec.
$\Delta H^{\ddagger}$	Enthalpy of activation, Kcal mole^{-1}.
$\Delta H_1^{\ddagger}$	Initial enthalpy of activation of the conventional extraction of coal.
$\Delta H_o^{\ddagger}$	Initial enthalpy of activation, Kcal mole^{-1}.
k	Boltzmann constant, 1.3803×10^{-16} erg deg^{-1} molecule^{-1}.
k'	First order reaction rate constant.
k_2	Second order reaction rate constant.
k_a	Phase boundary extraction rate constant.
k_b	The rate constant for the backward reaction.

k_d	Diffusion extraction rate constant.
k_f	The rate constant for the forward reaction.
k_o	Initial rate constant.
k_o'	Initial rate constant of second order reaction.
$k_o \ldots\ldots k_{n-1}$	Rate constants.
$L_o \ldots\ldots L_{n-1}$	Liquid, g.
P_i	Internal pressure of solvent.
R	Gas constant, 1.987 cal mole^{-1}deg^{-1}.
$R_o \ldots\ldots R_{n-1}$	Solid coal, g.
$\Delta S^{\ddagger}$	Entropy of activation, cal mole^{-1}deg^{-1}.
$\Delta S_o^{\ddagger}$	Initial entropy of activation, cal mole^{-1}deg^{-1}.
s	Constant equivalent to $(x_{max})^{-1}$.
t	Time, minutes.
T	Absolute temperature, ^{o}K.
W_c	Initial weight of coal on ash free basis, g.
W_f	Final weight of coal, g.
W_i	Initial weight of coal, g.
ΔW	Weight of coal extracted, g.
$x = \frac{\Delta W}{W_c}$	Fraction of coal extracted.
x_{eq}	Fraction of coal extracted at equilibrium.
x_m	The maximum fraction of coal extracted.
α	Temperature dependent constant.
β	Temperature dependent constant
ε	Dielectric constant.
μ	Dipole moment, esu cm.
κ	Transmission coefficient, assumed to be approximately 1.

APPENDIX

Table 8. Experimental data for extraction of coal with tetralin at 24°C using a conventional extraction process.

Sample no.	t (hours)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{ave}
1	2	0.2262	0.2186	7.462	0.2126	0.0351	0.0328
2	2	0.2698	0.2623	7.535	0.2537	0.0297	
3	2	0.2888	0.2803	8.416	0.2715	0.0310	
4	2	0.2479	0.2396	8.252	0.2331	0.0354	
5	5	0.1952	0.1890	6.297	0.1836	0.0343	0.0362
6	5	0.2131	0.2059	7.091	0.2003	0.0354	
7	5	0.2699	0.2597	9.937	0.2535	0.0392	
8	5	0.2103	0.2033	7.101	0.1978	0.0359	
9	10	0.2306	0.2216	8.772	0.2166	0.0405	0.0371
10	10	0.3138	0.3022	11.20	0.2947	0.0380	
11	10	0.3300	0.3190	10.92	0.3102	0.0352	
12	10	0.3004	0.2906	9.803	0.2825	0.0347	
13	15	0.2252	0.2179	7.371	0.2118	0.0348	0.0375
14	15	0.2755	0.2657	9.500	0.2588	0.0367	
15	15	0.2781	0.2674	10.48	0.2613	0.0401	
16	15	0.2712	0.2613	9.788	0.2549	0.0384	
17	20	0.3239	0.3114	12.42	0.3045	0.0408	0.0370
18	20	0.3046	0.2940	10.24	0.2861	0.0358	
19	20	0.2388	0.2301	8.411	0.2243	0.0375	
20	20	0.2721	0.2736	9.007	0.2657	0.0339	

Table 9. Experimental data for extraction of coal with tetralin at 34°C using a conventional extraction process.

Sample no.	t (hours)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{avg}
1	2	0.2120	0.2052	6.756	0.1993	0.0339	0.0331
2	2	0.2928	0.2845	8.345	0.2754	0.0303	
3	2	0.2498	0.2418	7.792	0.2347	0.0332	
4	2	0.2244	0.2168	7.378	0.2108	0.0350	
5	5	0.2111	0.2031	7.980	0.1985	0.0402	0.0370
6	5	0.2568	0.2483	8.573	0.2415	0.0355	
7	5	0.2512	0.2453	8.669	0.2362	0.0367	
8	5	0.3097	0.2992	10.36	0.2911	0.0356	
9	10	0.2012	0.1940	7.091	0.1891	0.0375	0.0382
10	10	0.2220	0.2153	8.567	0.2105	0.0407	
11	10	0.2460	0.2378	8.307	0.2314	0.0359	
12	10	0.2861	0.2734	10.33	0.2668	0.0387	
13	15	0.2752	0.2642	10.78	0.2586	0.0417	0.0398
14	15	0.2567	0.2475	9.370	0.2415	0.0388	
15	15	0.2348	0.2261	8.357	0.2205	0.0379	
16	15	0.2698	0.2696	10.755	0.2636	0.0408	
17	20	0.2312	0.2234	8.029	0.2176	0.0369	0.0397
18	20	0.2103	0.2022	8.070	0.1978	0.0408	
19	20	0.2502	0.2499	10.15	0.2445	0.0415	
20	20	0.2536	0.2439	9.433	0.2382	0.0396	

Table 10. Experimental data for extraction of coal with tetralin at 54°C using a conventional extraction process.

Sample no.	t (hours)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{avg}
1	2	0.2400	0.2313	8.453	0.2254	0.0375	0.0352
2	2	0.2772	0.2681	8.909	0.2605	0.0342	
3	2	0.2999	0.2906	9.246	0.2819	0.0328	
4	2	0.2607	0.25	8.897	0.2451	0.0363	
5	5	0.2907	0.2806	10.08	0.2733	0.0369	0.0398
6	5	0.2299	0.2206	9.072	0.2160	0.0420	
7	5	0.2632	0.2541	9.235	0.2476	0.0373	
8	5	0.2519	0.2413	10.17	0.2365	0.0430	
9	10	0.2308	0.2211	9.431	0.2168	0.0435	0.0403
10	10	0.2182	0.2102	8.003	0.2052	0.0390	
11	10	0.2520	0.2429	9.025	0.2369	0.0381	
12	10	0.2559	0.2460	9.764	0.2405	0.0406	
13	15	0.3076	0.2969	10.64	0.2892	0.0368	0.0400
14	15	0.2955	0.2838	11.61	0.2778	0.0418	
15	15	0.3124	0.2988	11.53	0.2918	0.0395	
16	15	0.2498	0.2398	9.834	0.2347	0.0419	
17	20	0.2648	0.2550	10.04	0.2492	0.0403	0.0410
18	20	0.2740	0.2638	10.20	0.2576	0.0396	
19	20	0.2778	0.2657	11.49	0.2606	0.0441	
20	20	0.2918	0.2805	10.96	0.2741	0.0400	

Table 11a. Experimental data
for extraction of coal at 24°C
with the aid of ultrasonic irradiation.

Sample no.	t (min)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{avg}
1	10	0.1606	0.1563	4.288	0.1510	0.0284	0.0296
2	10	0.1681	0.1635	4.583	0.1580	0.0290	
3	10	0.2124	0.2061	6.311	0.1997	0.0316	
4	10	0.1921	0.1870	5.131	0.1807	0.0284	
5	20	0.2101	0.2039	6.202	0.1976	0.0314	0.0305
6	20	0.2280	0.2215	6.470	0.2142	0.0302	
7	20	0.2492	0.2423	6.900	0.2438	0.0283	
8	20	0.2688	0.2607	8.118	0.2526	0.0321	
9	25	0.1914	0.1862	5.200	0.1799	0.0289	0.0311
10	25	0.2168	0.2110	5.811	0.2039	0.0285	
11	25	0.3194	0.3092	10.21	0.3003	0.0340	
12	25	0.2676	0.2593	8.303	0.2516	0.0330	
13	30	0.2240	0.2167	7.203	0.2106	0.0342	0.0352
14	30	0.1952	0.1885	6.813	0.1836	0.0371	
15	30	0.1905	0.1843	6.234	0.1791	0.0348	
16	30	0.2883	0.2789	9.407	0.2711	0.0347	
17	60	0.1779	0.1681	9.771	0.1673	0.0584	0.0573
18	60	0.1753	0.1659	9.413	0.1649	0.0571	
19	60	0.1631	0.1546	8.514	0.1534	0.0555	
20	60	0.2439	0.2306	13.35	0.2294	0.0582	
21	90	0.2481	0.2320	16.14	0.2333	0.0692	0.0717
22	90	0.2449	0.2285	16.37	0.2302	0.0711	
23	90	0.2151	0.2002	14.97	0.2023	0.0740	
24	90	0.2815	0.2624	19.11	0.2647	0.0722	
25	120	0.3438	0.3180	25.73	0.3232	0.0796	0.0782
26	120	0.3057	0.2844	21.33	0.2875	0.0742	
27	120	0.2592	0.2398	19.45	0.2437	0.0798	
28	120	0.3314	0.3067	24.68	0.3116	0.0792	

Table 11a (continued)

Sample no.	t (min)	W_i	W_f	$\Delta W \text{x} 10^3$	W_c	x	x_{ave}
29	150	0.3082	0.2830	25.21	0.2898	0.0870	0.0818
30	150	0.3252	0.2999	25.35	0.3058	0.0829	
31	150	0.3270	0.3023	24.69	0.3075	0.0803	
32	150	0.2965	0.2751	21.47	0.2788	0.0770	
33	180	0.2866	0.2629	23.69	0.2695	0.0879	0.0888
34	180	0.2777	0.2533	24.36	0.2610	0.0933	
35	180	0.2836	0.2598	23.76	0.2666	0.0891	
36	180	0.2925	0.2691	23.35	0.2750	0.0849	
37	240	0.2761	0.2517	24.38	0.2596	0.0939	0.0919
38	240	0.2833	0.2596	23.68	0.2664	0.0889	
39	240	0.2947	0.2696	25.05	0.2771	0.0904	
40	240	0.2610	0.2379	23.17	0.2454	0.0944	
41	300	0.2663	0.2404	25.89	0.2504	0.1034	0.0980
42	300	0.2873	0.2604	26.91	0.2702	0.0996	
43	300	0.2811	0.2553	25.88	0.2644	0.0979	
44	300	0.2873	0.2627	24.61	0.2701	0.0911	
45	600	0.2701	0.2462	23.87	0.2539	0.0940	0.1020
46	600	0.2634	0.2387	24.77	0.2477	0.1001	
47	600	0.2458	0.2205	25.31	0.2311	0.1094	
48	600	0.2728	0.2460	26.81	0.2566	0.1045	
49	900	0.2467	0.2223	24.38	0.2319	0.1051	0.1013
50	900	0.2542	0.2281	26.13	0.2391	0.1093	
51	900	0.2811	0.2560	25.11	0.2643	0.0950	
52	900	0.2441	0.2221	21.99	0.2295	0.0958	
53	1200	0.2305	0.2086	21.89	0.2167	0.1010	0.1021
54	1200	0.2212	0.2012	20.03	0.2080	0.0963	
55	1200	0.2069	0.1859	21.03	0.1945	0.1081	
56	1200	0.2394	0.2163	23.19	0.2251	0.1030	

Table 11b. Variation of rate constant, k, with fraction extracted, x, at 24°C a=0.102 by the method of finite differences.

t(min.)	x	$\frac{\Delta x}{\Delta t}$	x	a-x	$k=\frac{\Delta x/\Delta t}{(a-x)}$	ln k
0	0					
15	0.0236	0.00127	0.01905	0.08295	0.01531	-4.17999
30	0.0381	0.000853	0.0364	0.0656	0.0130	-4.34359
45	0.0492	0.000663	0.04805	0.05395	0.01229	-4.39977
60	0.0580	0.000523	0.05705	0.04495	0.01164	-4.45412
75	0.0649	0.000416	0.06425	0.03775	0.01102	-4.50886
90	0.0705	0.00034	0.070	0.032	0.01063	-4.54490
105	0.0751	0.00028	0.0747	0.0273	0.01026	-4.58032
120	0.0789	0.00023	0.0786	0.0234	0.00983	-4.65206
135	0.0821	0.000193	0.0818	0.0202	0.00955	-4.67428
150	0.0847	0.000163	0.08455	0.01745	0.00934	-4.66364
165	0.0870	0.000143	0.08685	0.01515	0.00944	-4.70033
180	0.0890	0.00012	0.0888	0.0132	0.0091	-4.74528
195	0.0906					

Table 12a. Experimental data
for extraction of coal at 29°C
with the aid of ultrasonic irradiation.

Sample no.	t (min)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{avg}
1	10	0.2805	0.2728	7.675	0.2638	0.0291	0.0307
2	10	0.2067	0.2005	6.155	0.1942	0.0317	
3	10	0.2387	0.2317	7.000	0.2242	0.0312	
4	10	0.2511	0.2438	7.273	0.2361	0.0308	
5	15	0.2008	0.2002	6.130	0.1887	0.0325	0.0310
6	15	0.2186	0.2123	6.226	0.2054	0.0303	
7	15	0.2380	0.2314	6.585	0.2238	0.0294	
8	15	0.3073	0.2981	9.198	0.2891	0.0318	
9	20	0.1795	0.1744	5.183	0.1688	0.0307	0.0314
10	20	0.1613	0.1563	5.005	0.1517	0.0330	
11	20	0.2814	0.2740	7.409	0.2646	0.0280	
12	20	0.2321	0.2250	7.092	0.2182	0.0325	
13	25	0.1666	0.1609	5.718	0.1567	0.0365	0.0351
14	25	0.1833	0.1774	5.895	0.1724	0.0342	
15	25	0.1806	0.1747	5.911	0.1699	0.0348	
16	25	0.1749	0.1691	5.739	0.1644	0.0349	
17	30	0.1501	0.1433	6.819	0.1412	0.0483	0.0461
18	30	0.1781	0.1703	7.821	0.1675	0.0467	
19	30	0.2230	0.2138	9.120	0.2097	0.0435	
20	30	0.2171	0.2078	9.371	0.2042	0.0459	
21	60	0.1931	0.1817	11.42	0.1816	0.0629	0.0659
22	60	0.2228	0.2214	13.28	0.2095	0.0634	
23	60	0.2273	0.2127	14.62	0.2137	0.0684	
24	60	0.2359	0.2206	15.28	0.2218	0.0689	
25	90	0.2231	0.2061	16.99	0.2098	0.0810	0.0763
26	90	0.2335	0.2163	16.71	0.2196	0.0761	
27	90	0.2396	0.2223	17.30	0.2253	0.0768	
28	90	0.2667	0.2487	17.88	0.2508	0.0713	

Table 12b. Variation of rate constant, k, with fraction extracted, x, at 29°C a=0.105 by the method of finite differences.

t	x	$\frac{\Delta x}{\Delta t}$	x	a–x	$k=\frac{\Delta x/\Delta t}{(a-x)}$	ln k
0	0					
15	0.02785	0.001476	0.02215	0.08285	0.01782	-4.02815
30	0.0443	0.000955	0.042175	0.062825	0.01520	-4.1872
45	0.0565	0.00071	0.05495	0.05005	0.01418	-4.2797
60	0.0656	0.00053	0.0645	0.0405	0.01309	-4.33669
75	0.0725	0.000416	0.07185	0.03315	0.01255	-4.37883
90	0.0781	0.00033	0.0775	0.0275	0.0120	-4.42365
105	0.0825	0.0000266	0.0821	0.0229	0.00116	-4.4575
120	0.0861	0.00022	0.0858	0.0192	0.01145	-4.47056
135	0.0891	0.00018	0.0888	0.0162	0.01111	-4.50073
150	0.0915	0.00015	0.09135	0.01365	0.01099	-4.53461
165	0.0936	0.00012	0.09335	0.01165	0.01030	-4.57643
180	0.0952					

Table 13a. Experimental data
for extraction of coal at 34°C
with the aid of ultrasonic irradiation.

Sample no.	t (min)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{avg}
1	10	0.2675	0.2603	7.225	0.2516	0.0287	0.0310
2	10	0.2118	0.2054	6.418	0.1992	0.0322	
3	10	0.2513	0.2438	7.450	0.2365	0.0315	
4	10	0.2640	0.2561	7.850	0.2482	0.0316	
5	15	0.2548	0.2468	7.861	0.2397	0.0328	0.0315
6	15	0.2247	0.2185	6.172	0.2113	0.0292	
7	15	0.1994	0.1907	8.685	0.1875	0.0303	
8	15	0.2644	0.2560	8.374	0.2485	0.0337	
9	20	0.1731	0.1673	5.828	0.1628	0.0358	0.0361
10	20	0.1675	0.1620	5.497	0.1575	0.0349	
11	20	0.1816	0.1752	6.438	0.1708	0.0377	
12	20	0.1995	0.1927	6.753	0.1876	0.0360	
13	25	0.1671	0.1597	7.431	0.1571	0.0473	0.0446
14	25	0.2267	0.2178	8.912	0.2132	0.0418	
15	25	0.2272	0.2181	9.123	0.2137	0.0427	
16	25	0.2110	0.2018	9.248	0.1985	0.0466	
17	30	0.3411	0.3263	14.72	0.3207	0.0459	0.0489
18	30	0.2699	0.2573	12.64	0.2538	0.0498	
19	30	0.2835	0.2821	13.62	0.2665	0.0511	
20	30	0.3105	0.2963	14.25	0.2920	0.0488	
21	60	0.2998	0.2815	18.27	0.2819	0.0648	0.0700
22	60	0.2522	0.2348	17.26	0.2371	0.0728	
23	60	0.3084	0.2898	18.56	0.2900	0.0640	
24	60	0.2352	0.2179	17.34	0.2212	0.0784	
25	90	0.2392	0.2198	19.34	0.2249	0.0860	0.0868
26	90	0.2779	0.2548	23.10	0.2613	0.0884	
27	90	0.2818	0.2577	24.17	0.2650	0.0912	
28	90	0.3207	0.2961	24.61	0.3016	0.0816	
29	120	0.2919	0.2666	25.28	0.2745	0.0921	0.0909
30	120	0.2940	0.2691	24.91	0.2765	0.0901	
31	120	0.2894	0.2655	23.89	0.2721	0.0878	
32	120	0.2739	0.2498	24.11	0.2576	0.0936	

Table 13a (continued)

Sample no.	t (min)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{ave}
33	150	0.2811	0.2574	23.68	0.2643	0.0896	0.0951
34	150	0.1573	0.1409	16.42	0.1479	0.1110	
35	150	0.3001	0.2743	25.79	0.2822	0.0914	
36	150	0.2178	0.2402	21.78	0.2464	0.0884	
37	180	0.2534	0.2318	21.59	0.2383	0.0906	0.0988
38	180	0.273	0.2479	25.16	0.2567	0.0980	
39	180	0.2515	0.2265	24.97	0.2365	0.1056	
40	180	0.2726	0.2467	25.89	0.2563	0.1010	
41	240	0.2387	0.2137	24.98	0.2244	0.1113	0.1028
42	240	0.2704	0.2459	24.54	0.2704	0.0965	
43	240	0.2675	0.2436	23.95	0.2516	0.0952	
44	240	0.2516	0.2221	25.16	0.2325	0.1082	
45	300	0.2678	0.2429	24.98	0.2518	0.0992	0.1052
46	300	0.2543	0.2277	26.54	0.2391	0.1110	
47	300	0.2832	0.2568	26.39	0.2662	0.0991	
48	300	0.2286	0.2554	26.78	0.2402	0.1115	
49	600	0.2777	0.3067	29.01	0.2884	0.1006	0.1056
50	600	0.2964	0.3265	30.15	0.3070	0.0982	
51	600	0.2536	0.2834	29.82	0.2665	0.1119	
52	600	0.297	0.257	31.19	0.2792	0.1117	
53	900	0.2939	0.2626	31.28	0.2763	0.1132	0.1060
54	900	0.3364	0.3049	31.47	0.3163	0.0995	
55	900	0.3249	0.2937	31.26	0.3056	0.1023	
56	900	0.2935	0.2634	30.08	0.2760	0.1090	
57	1200	0.3386	0.3070	31.62	0.3184	0.0993	0.1061
58	1200	0.2802	0.2513	28.96	0.2635	0.1099	
59	1200	0.2673	0.2389	28.46	0.2514	0.1132	
60	1200	0.3042	0.275	29.18	0.2861	0.1020	

Table 13b. Variation of rate constant, k,
with fraction extracted, x, at 34°C
a=0.106 by the method of finite differences.

t(min.)	x	$\frac{\Delta x}{\Delta t}$	x	a-x	$k=\frac{\Delta x/\Delta t}{(a-x)}$	ln k
0	0					
15	0.0314	0.001676	0.02515	0.08085	0.02073	-3.87687
30	0.0503	0.001056	0.04725	0.05875	0.01797	-4.01977
45	0.0631	0.00073	0.06125	0.04475	0.01631	-4.11673
60	0.0722	0.000553	0.0714	0.0346	0.01598	-4.13716
75	0.0797	0.000403	0.07825	0.02775	0.01452	-4.23298
90	0.0843	0.00029	0.08405	0.02195	0.00132	-4.32833
105	0.0884	0.00024	0.08795	0.01805	0.01321	-4.32757
120	0.0916	0.000193	0.0913	0.0147	0.01313	-4.33365
135	0.0942	0.000156	0.09395	0.01205	0.01295	-4.34744
150	0.0963	0.000126	0.0961	0.0099	0.01273	-4.36458
165	0.0980	0.000103	0.09785	0.00815	0.01264	-4.37167
180	0.0994					

Table 14a. Experimental data

for extraction of coal at 44°C

with the aid of ultrasonic irradiation.

Sample no.	t (min)	W_i	W_f	$\Delta W \times 10^3$	W_c	x	x_{avg}
1	10	0.2163	0.2097	6.569	0.2034	0.0323	0.0298
2	10	0.2656	0.2584	7.193	0.2498	0.0288	
3	10	0.2727	0.2652	7.461	0.2564	0.0291	
4	10	0.2987	0.2905	8.145	0.2809	0.0290	
5	15	0.2720	0.2628	9.156	0.2558	0.0358	0.0389
6	15	0.2657	0.2564	9.269	0.2498	0.0371	
7	15	0.2821	0.2711	11.01	0.2653	0.0415	
8	15	0.3203	0.3079	12.41	0.3012	0.0412	
9	20	0.3302	0.3169	13.32	0.3105	0.0429	0.0490
10	20	0.2049	0.1947	10.23	0.1927	0.0531	
11	20	0.2497	0.2380	11.74	0.2348	0.0500	
12	20	0.2580	0.2459	12.13	0.2426	0.0500	
13	25	0.2494	0.2359	13.58	0.2345	0.0579	0.0546
14	25	0.3127	0.2975	15.23	0.2940	0.0518	
15	25	0.2983	0.2836	14.67	0.2805	0.0523	
16	25	0.2619	0.2480	13.89	0.2463	0.0564	
17	30	0.2072	0.1937	13.48	0.1948	0.0692	0.0648
18	30	0.2745	0.2586	15.82	0.2581	0.0613	
19	30	0.2790	0.2628	16.16	0.2623	0.0616	
20	30	0.2729	0.2557	17.22	0.2566	0.0671	
21	60	0.2264	0.2079	18.48	0.2129	0.0868	0.0827
22	60	0.2595	0.2400	19.42	0.2440	0.0796	
23	60	0.2762	0.2541	22.10	0.2597	0.0851	
24	60	0.3110	0.2878	23.19	0.2924	0.0793	
25	90	0.2575	0.2333	24.16	0.2421	0.0998	0.0969
26	90	0.2732	0.2485	24.69	0.2569	0.0961	
27	90	0.2972	0.2718	25.43	0.2795	0.0910	
28	90	0.2793	0.2529	26.45	0.2627	0.1007	

Table 14a (continued)

Sample no.	t (min)	W_i	W_f	$\Delta W \times 10^3$	W_c	x	x_{ave}
29	120	0.2543	0.2277	26.588	0.2391	0.1112	0.1020
30	120	0.2657	0.2401	25.529	0.2498	0.1022	
31	120	0.2745	0.2496	24.881	0.2581	0.0964	
32	120	0.3202	0.2906	29.568	0.3011	0.0982	
33	150	0.2579	0.2333	24.638	0.2425	0.1016	0.1062
34	150	0.2473	0.2242	23.14	0.2326	0.0995	
35	150	0.2402	0.2150	25.16	0.2259	0.1114	
36	150	0.2480	0.2218	26.19	0.2332	0.1123	
37	180	0.2555	0.2316	23.83	0.2402	0.0992	0.1070
38	180	0.2583	0.2325	25.83	0.2312	0.1117	
39	180	0.2581	0.2333	24.83	0.2427	0.1023	
40	180	0.2423	0.2162	26.16	0.2279	0.1148	
41	240	0.2757	0.2488	26.91	0.2592	0.1038	0.1109
42	240	0.2417	0.2153	26.39	0.2273	0.1161	
43	240	0.2711	0.2464	24.73	0.2549	0.0970	
44	240	0.2030	0.1789	24.19	0.1909	0.1267	
45	300	0.2123	0.1883	23.99	0.1996	0.1202	0.1120
46	300	0.2090	0.1874	21.64	0.1964	0.1101	
47	300	0.2354	0.2123	23.13	0.2213	0.1045	
48	300	0.2066	0.1846	21.99	0.1943	0.1132	
49	600	0.1906	0.1695	21.17	0.1793	0.1181	0.1120
50	600	0.2209	0.1982	22.66	0.2077	0.1091	
51	600	0.2328	0.2087	24.12	0.2189	0.1102	
52	600	0.2980	0.2670	30.99	0.2802	0.1106	
53	900	0.2484	0.2234	25.02	0.2336	0.1071	0.1111
54	900	0.2175	0.1936	23.89	0.2045	0.1168	
55	900	0.2583	0.2325	25.79	0.2428	0.1062	
56	900	0.2324	0.2074	24.98	0.2185	0.1143	
57	1200	0.2345	0.2084	26.13	0.2205	0.1185	0.1118
58	1200	0.2725	0.2466	25.93	0.2562	0.1012	
59	1200	0.2464	0.2218	24.56	0.2317	0.1060	
60	1200	0.2243	0.1987	25.63	0.2109	0.1215	

Table 14b. Variation of rate constant, k, with fraction extracted, x, at 44°C a=0.111 by the method of finite differences.

t (min.)	x	$\frac{\Delta x}{\Delta t}$	x	$a-x$	$k=\frac{\Delta x/\Delta t}{(a-x)}$	ln k
0	0					
15	0.0400	0.002083	0.03125	0.07975	0.02612	-3.6457
30	0.0625	0.001197	0.05795	0.05305	0.02256	-3.7923
45	0.0759	0.00075	0.07375	0.03725	0.02013	-3.9063
60	0.0850	0.000513	0.0836	0.0274	0.0187	-3.97995
75	0.0913	0.0003667	0.0905	0.0205	0.01789	-4.0242
90	0.0960	0.00027	0.09535	0.01565	0.01725	-4.06067
105	0.0994	0.00020	0.099	0.012	0.01667	-4.09487
120	0.1020	0.000153	0.1017	0.0093	0.01645	-4.10816
135	0.1040	0.0001167	0.10375	0.00725	0.01609	-4.1303
150	0.1055	0.00009	0.1053	0.00565	0.0159	-4.1422
165	0.1067	0.00007	0.10655	0.00445	0.0157	-4.1548
180	0.1076					

Table 15a Experimental data

for extraction of coal at 54°C

with the aid of ultrasonic irradiation.

Sample no.	t (min)	W_i	W_f	$\Delta W \times 10^3$	W_c	x	x_{avg}
1	10	0.2633	0.2534	9.877	0.2475	0.0399	0.0369
2	10	0.2837	0.2738	9.925	0.2668	0.0372	
3	10	0.2062	0.1994	6.787	0.1939	0.0350	
4	10	0.3068	0.2965	10.30	0.2885	0.0357	
5	15	0.2665	0.2539	12.58	0.2506	0.0502	0.0460
6	15	0.3332	0.3198	13.41	0.3133	0.0428	
7	15	0.3060	0.2933	12.69	0.2878	0.0441	
8	15	0.2889	0.2761	12.74	0.2716	0.0469	
9	20	0.2838	0.2707	13.13	0.2569	0.0492	0.0539
10	20	0.2954	0.2812	14.25	0.2778	0.0513	
11	20	0.3094	0.2933	16.12	0.2910	0.0554	
12	20	0.2831	0.2672	15.89	0.2662	0.0597	
13	25	0.2551	0.2389	16.24	0.2399	0.0677	0.0645
14	25	0.2740	0.2559	18.11	0.2576	0.0703	
15	25	0.3194	0.3014	17.96	0.3003	0.0598	
16	25	0.3394	0.3202	19.21	0.3191	0.0602	
17	30	0.2736	0.2543	19.27	0.2573	0.0749	0.0701
18	30	0.2765	0.2583	18.23	0.2601	0.0701	
19	30	0.2806	0.2627	17.93	0.2639	0.0681	
20	30	0.2982	0.2793	18.87	0.2804	0.0673	
21	60	0.1926	0.1747	17.93	0.1811	0.0990	0.0968
22	60	0.2222	0.2029	19.26	0.2039	0.0922	
23	60	0.2255	0.2052	20.31	0.2120	0.0958	
24	60	0.2244	0.2032	21.14	0.2110	0.1002	
25	90	0.2051	0.1835	21.56	0.1928	0.1118	0.1029
26	90	0.2525	0.2306	21.89	0.2374	0.0922	
27	90	0.2333	0.2121	21.12	0.2194	0.0965	
28	90	0.2023	0.1811	21.13	0.1902	0.1111	

Table 15a (continued)

Sample no.	t (min)	W_i	W_f	$\Delta W x 10^3$	W_c	x	x_{ave}
29	120	0.28077	0.2543	26.48	0.2640	0.1003	0.1092
30	120	0.2526	0.2252	27.46	0.2375	0.1175	
31	120	0.2491	0.2210	28.13	0.2342	0.1123	
32	120	0.2645	0.2345	29.94	0.2487	0.1067	
33	150	0.2889	0.2576	31.33	0.2717	0.1003	0.1121
34	150	0.2526	0.2252	27.46	0.2375	0.1156	
35	150	0.2491	0.2210	28.13	0.2342	0.1201	
36	150	0.2945	0.2634	31.11	0.2769	0.1124	
37	180	0.2645	0.2345	29.94	0.2487	0.1204	0.1132
38	180	0.2890	0.2576	31.33	0.2717	0.1153	
39	180	0.3019	0.2688	33.16	0.2839	0.1168	
40	180	0.2564	0.2322	24.18	0.2411	0.1003	
41	240	0.3194	0.2833	36.10	0.3003	0.1202	0.1151
42	240	0.2911	0.2583	32.79	0.2737	0.1198	
43	240	0.2925	0.2623	30.20	0.2750	0.1098	
44	240	0.2447	0.2193	25.45	0.2301	0.1106	
45	300	0.2543	0.2275	26.73	0.2391	0.1118	0.1140
46	300	0.2435	0.2186	24.91	0.2290	0.1088	
47	300	0.256	0.2275	28.53	0.2408	0.1185	
48	300	0.2369	0.2109	26.05	0.2228	0.1169	
49	600	0.2796	0.2489	30.65	0.2629	0.1166	0.1138
50	600	0.3052	0.2735	31.71	0.2870	0.1105	
51	600	0.2898	0.2604	29.46	0.2725	0.1081	
52	600	0.3098	0.2748	34.96	0.2913	0.1200	
53	900	0.2583	0.2288	29.46	0.2429	0.1213	0.1140
54	900	0.3124	0.2802	32.19	0.2937	0.1096	
55	900	0.3095	0.2780	31.46	0.2910	0.1081	
56	900	0.2736	0.2345	30.10	0.2573	0.1170	
57	1200	0.2885	0.2559	32.64	0.2713	0.1203	0.1141
58	1200	0.2594	0.2310	28.39	0.2439	0.1164	
59	1200	0.2491	0.2235	25.60	0.2342	0.1093	
60	1200	0.2972	0.2683	28.95	0.2722	0.1092	

Table 15b. Variation of rate constant, k,
with fraction extracted, x, at 54°C
$a=0.114$ by the method of finite differences.

t(min.)	x	$\frac{\Delta x}{\Delta t}$	x	a-x	$k=\frac{\Delta x/\Delta t}{(a-x)}$	ln k
0	0					
		0.00333	0.0251	0.0889	0.037638	-3.2803
15	0.0502					
		0.00153	0.0617	0.0523	0.029317	-3.5302
30	0.0732					
		0.00088	0.0798	0.0342	0.025731	-3.6607
45	0.0864					
		0.00056	0.0906	0.0234	0.023932	-3.7332
60	0.0948					
		0.000373	0.0976	0.0164	0.022764	-3.7832
75	0.1004					
		0.000253	0.1023	0.0117	0.021652	-3.8333
90	0.1042					
		0.00018	0.10555	0.00845	0.021302	-3.8496
105	0.1069					
		0.000126	0.10785	0.00615	0.020595	-3.8834
120	0.1088					
		0.000093	0.1095	0.0045	0.020733	-3.8767
135	0.1102					

Table 16. Determination of k_o

by using the integrated form of proposed model.

$$k_o = \frac{-1}{t} e^{\frac{ab}{R}} \left(\ln \frac{a-x}{a} + \frac{bx}{R} + \frac{b^2}{4R^2}(-2ax + x^2) - \frac{b^3}{18R^3}(-3a^2x + 3ax^2 - x^3) \right)$$

Time (min)	T = 24°C		T = 29°C		T = 34°	
	x	k_o	x	k_o	x	k_o
10	0.0145	0.0159	0.0171	0.0186	0.0120	0.0123
25	0.0311	0.0163	0.0351	0.0185	0.0446	0.0249
30	0.0353	0.0161	0.0461	0.0231	0.0489	0.0240
60	0.0573	0.0175	0.0659	0.0219	0.0700	0.0244
90	0.0717	0.0186	0.0763	0.0204	0.0868	0.0277
120	0.0782	0.0174	0.0845	0.0203	0.0909	0.0244
150	0.0818	0.0159	0.0909	0.0210	0.0951	0.0236
180	0.0888	0.0177	0.0978	0.0250	0.0988	0.0242
240	0.0919	0.0154	0.0991	0.0204	0.1028	0.0249
300	0.0980	0.0185	0.1034	0.0255	0.1052	0.0297
		ave 0.01694		ave 0.02147		ave 0.02402

Table 16 (continued)

Determination of k_o by using

the integrated form of proposed model.

$$k_o = \frac{-1}{t} e^{\frac{ab}{R}} \left(\ln \frac{a-x}{a} + \frac{bx}{R} + \frac{b^2}{4R^2} (-2ax + x^2) - \frac{b^3}{18R^3} (-3a^2x + 3ax^2 - x^3) \right)$$

Time (min)	T = 44°C		T = 54°	
	x	k_o	x	k_o
10	0.0298	0.0345	0.0369	0.0445
25	0.0546	0.0337	0.0645	0.0436
30	0.0648	0.0384	0.0701	0.0429
60	0.0827	0.0333	0.0968	0.0507
90	0.0969	0.0373	0.1029	0.0439
120	0.1020	0.0356	0.1092	0.0481
150	0.1062	0.0375	0.1121	0.0524
180	0.1070	0.0335	0.1132	0.0547
		ave 0.03548		ave 0.04763

Table 17.

Variation of contribution activation entropy, $\Delta S_c^{\ddagger}$, with fraction extracted, x.

		$\Delta S_c^{\ddagger} = bx$				
x	Temp.	24°C	29°C	34°C	44°C	54°C
	b	14.51	14.18	13.91	14.57	15.56
0.0		0.00	0.00	0.00	0.00	0.00
0.01		0.15	0.14	0.14	0.15	0.16
0.02		0.29	0.28	0.28	0.29	0.31
0.03		0.44	0.43	0.42	0.44	0.47
0.04		0.58	0.57	0.57	0.58	0.62
0.05		0.73	0.71	0.69	0.73	0.78
0.06		0.87	0.85	0.83	0.87	0.93
0.07		1.02	0.99	0.97	1.02	1.09
0.08		1.16	1.13	1.11	1.17	1.24
0.09		1.31	1.28	1.25	1.31	1.40
0.10		1.45	1.42	1.39	1.46	1.56
0.102		1.48	1.45	1.42	1.49	1.59
0.105			1.49	1.46	1.53	1.63
0.106				1.47	1.54	1.65
0.111					1.62	1.73
0.114						1.77

A KINETIC COMPARISON OF COAL PYROLYSIS AND COAL DISSOLUTION

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ABSTRACT

A comparison is presented of coal pyrolysis at temperatures ranging from 409° to $497^\circ C$ and thermal dissolution of coal in tetralin at temperatures ranging from 350° to $450^\circ C$, both utilizing a Utah high-volatile bituminous coal. The initial coal pyrolysis reactions are second order with an enthalpy of activation of 35.6 kcal per mole. The fraction of total product yield produced under second order conditions ranges from 67% at $409^\circ C$ to 96% at $497^\circ C$. The process then gradually deteriorates to a first order reaction in the later stages with enthalpy of activation of 4.1 kcal per mole. The initial reactions of solution of coal in tetralin are second order with an enthalpy of activation of 28.8 kcal per mole. The fraction of total product produced under second order conditions ranges from 63% at $350^\circ C$ to 94% at $450^\circ C$. The dissolution process then gradually changes to first order in the later stages with enthalpy of activation of 15.6 kcal per mole. A model is presented which relates the two processes and explains the significance of the above similarities.

Introduction

In recent years efforts to understand the basic structure of coal and the nature of its reactions have been intensified. These studies have been prompted in part by a realization that natural reserves of petroleum and natural gas are limited, at least in an economic sense, and that we must be prepared to supply a major proportion of our fuels market from our vast coal reserves. Considering the fact that our society is geared to the utilization of liquid and gaseous fuels, the necessity for economical conversion of coal to liquid and gaseous fuels is obvious, if it is to supply our energy needs.

As part of a program designed to lead to basic understanding of possible coal conversion processes, studies are in progress in this laboratory in the areas of pyrolysis, thermal dissolution in solvents, hydrogenation, interaction with intense fields of radiation and other related processes. Each process has yielded information concerning the structure of coal and possibilties for its conversion to liquid or gaseous fuels. Some very interesting similarities were noted between coal pyrolysis and thermal dissolution of coal in tetralin. The discussion of these similarities and their significance forms the basis for this presentation.

Coal Pyrolysis

In a typical coal pyrolysis study[9], samples of a Utah high-volatile bituminous coal of 77.5% carbon on a moisture and ash free basis (47.46% volatile matter on a dry basis) were sized to -40 +60 mesh, and one-gram samples pyrolyzed under conditions of constant temperature. The loss in weight of the sample as a function of time was measured at each of several temperatures ranging from 409° to 497°C, these data being the basis for a kinetic analysis of the process.

Typical fractional weight loss - time curves from this study are shown in Figure 1.

The data of the first 60 minutes, accounting for most of the product evolution, produced slight curvature at some temperatures when applied in a second order rate expression. A rate equation of general form was applied:

$$\frac{dx}{dt} = k_n(a-x)^n \qquad (1)$$

where $n \neq 1$ and denotes the order of the reaction, "x" is the observed weight loss at time "t", as a fraction of the initial sample weight, and "a" is the maximum weight loss obtainable at the temperature concerned. Integrating and evaluating the integration constant with $x = 0$ when $t = 0$ yields

$$\frac{a^{1-n} - (a-x)^{1-n}}{1-n} = k_n t \qquad (2)$$

At each temperature a value of n was selected which produced a straight line over the 60 - minute period on a plot of Equation 2. It was noted that the reaction order varied from 1.8 at 409°C to 2.2 at 497°C. These results are shown in Figure 2.

The fraction of the total product yield produced under conditions of approximately second order ranges from 67% at 409°C to 96% at 497°C, thereby accounting for most of the pyrolysis product. This is illustrated in Table I.

TABLE I

EXTENT OF SECOND ORDER REACTION IN COAL PYROLYSIS

Temp. °C	Time at End of 2nd Order	Maximum Potential Yield "a"	"x" at end of 2nd Order	% of prod. during 2nd Order, $\frac{x}{a}$
409	60 min.	0.1543	0.1042	67%
418	55 min.	0.2072	0.1518	73%
428	45 min.	0.2310	0.1709	74%
433	60 min.	0.2320	0.1858	80%
447	50 min.	0.2565	0.2209	86%
457	55 min.	0.2760	0.2476	90%
459	55 min.	0.2780	0.2519	91%
469	60 min.	0.2920	0.2725	93%
481	60 min.	0.3175	0.3048	96%
485	60 min.	0.3165	0.3029	96%
497	60 min.	0.3330	0.3212	96%

For the data obtained at times longer than 60 minutes, a first order rate expression was applied:

$$\frac{dx}{dt} = k_1(a-x) \qquad (3)$$

Integrating and evaluating the constant of integration with $x = 0$ when $t = 0$ yields:

$$\ln \frac{a}{a-x} = k_1 t \qquad (4)$$

Figure 3 represents a plot of Equation 4, indicating that the reactions are first order at times greater than approximately 90 minutes. A gradual decay from second order to first order is noted.

Applying the Absolute Reaction Rate Theory of Eyring[1] as presented and discussed previously[9]:

$$\ln \left(\frac{h}{\kappa k}\frac{k'}{T}\right) = -\frac{\Delta H^*}{R}\frac{1}{T} + \frac{\Delta S^*}{R} + \ln \alpha \qquad (5)$$

Where h is Planck's constant, k is Boltzmann's constant, k' is the reaction velocity constant, T is the absolute temperature, κ is a transmission coefficient, assumed equal to 1, ΔH^* and ΔS^* are enthalpy and entropy of activation, respectively, and α is the molar concentration of reacting sites per gram of coal. A plot of Equation 5 for the approximately second order region is shown in Figure 4, using a value of 2.1 for the average reaction order, yielding an enthalpy of activation of 35.6 kcal per mole for that region. A similar plot for the first order region yields a value of 4.1 kcal per mole for that region.

A plot of a first order expression of the form of Equation 4 reveals that the reactions are first order in the later stages of the coal dissolution process. This is shown in Figure 7.

A plot of the Eyring Reaction Rate equation, as shown in Figure 8, yields an enthalpy of activation of 28.8 kcal per mole for the second order region. A similar plot for the first order region yields a value for ΔH^{*} of 15.1 kcal per mole for that region.

Discussion

A plot of the time-yield curves for both processes, at corresponding temperatures and utilizing the same scale, emphasizes the similarity as well as the differences in the two processes. Such a plot is shown in Figure 9. These observed similarities may be of particular value inasmuch as the basic reacting material in both cases is coal of very similar properties. A comparison of pyrolysis at 409°C with dissolution at 410°C, as a fraction of the maximum yield at the temperature concerned (Figure 10), reveals a similar rate of approach toward completion. The experimental observation that in both processes the major proportion of the product yield occurs under second order conditions, as shown in Tables I and II, is of particular interest. The further similarity in enthalpies of activation for the second order regions, being 35.6 kcal per mole for pyrolysis and 28.8 kcal per mole for dissolution, suggests the possibility of similar rate-controlling reactions.

In determining the reaction order for a given process, an expression is written describing the proportionality between the observed rate of decrease in quantity of a reactant and the quantities of the various reactants which are unused at any particular time. The sum of the exponents of the concentrations (or more precisely the activities) of the various reactants which are required to account for the experimentally observed reaction rates constitutes the order of the reaction, by definition. Equation 1 is an example of such an expression of general form, k_n thus being a constant of proportionality.

It would be expected that in a complex system such as coal many steps may occur in the reaction sequence between the initial coal and the final products as they are released from the char. For consecutive reactions the overall rate of product yield is determined essentially by the slowest steps in the sequence. Hence the data presented herein relate to the slowest steps in the reaction sequence, and the reactions involved in these slow steps are second order over most of the range of reaction at these temperatures.

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It has been observed in connection with thermal cracking of hydrocarbons in the petroleum industry that purely thermal decomposition reactions become appreciable at 350°C.[6] Thus considering the fact that coal is basically hydrocarbon in nature, thermal rupture of bonds throughout the coal mass would become extensive at temperatures above 350°C, irrespective of whether other reactants were present in the system. In fact the appearance of the plastic state when a bituminous coal is heated to this temperature range is considered to be the result of thermal decomposition reactions. In this temperature range the rate of decomposition reactions has been observed to double for each 10°C temperature rise.

The rupture of a covalent bond would leave an unpaired electron on the fragment on either side of the bond, resulting in two free radicals. Since free radicals are unstable and highly reactive they would seek stabilization. This could conceivably occur by a rearrangement of atoms within the fragment, by a polymerization of fragments, or by the addition of an atom or other radical group to the fragment. The path followed in achieving stabilization of a particular fragment would depend upon the existing combination of the following factors:

(1) whether the fragment is aromatic, hydroaromatic, or aliphatic in nature (a fully aromatic fragment could provide no possibility for stabilization through rearrangement of atoms);

(2) the availability of atoms or small radicals in the immediate vicinity of the fragment seeking stabilization;

(3) the relative energies and reaction rates of the competing stabilization reactions.

Since the formation of stabilized molecules is essential to the process (free radicals in significant quantities are not observed in the product of either of these processes at these temperatures) the availability of stabilization opportunities is important.

Let us first consider the solution of coal in tetralin. The tetralin molecule (1,2,3,4-tetrahydronaphthalene) yields four hydrogen atoms in formation of the naphthalene molecule. It was observed[8] that whereas the formation of naphthalene and hydrogen from tetralin was essentially negligible at these temperatures in the absence of coal, appreciable quantities of naphthalene and hydrogen were produced when the tetralin and coal were heated together. The analyses of the dissolution data led to the following conclusions:

(1) that the dissolution process was first order with respect to unreacted but potentially reactive coal and first order with respect to unreacted tetralin;

(2) that the process involved the release of hydrogen atoms by the tetralin in the immediate vicinity of the

thermally ruptured bonds in the coal;

(3) that the greater portion of the stabilization process was accomplished by the hydrogen atoms supplied by the tetralin;

(4) that these reactions involving the transfer of hydrogen atoms were the rate-controlling steps in the reaction sequence.

It may be observed from coal hydrogenation studies that molecular hydrogen is ineffective, in the absence of an appropriate catalyst, in appreciably increasing the volatile product yield above that of simple coal pyrolysis, indicating that atoms or free radicals, not molecules, are required for stabilization at these temperatures. This might well be expected from energy considerations.

It may further be suggested that interactions between a solvent such as tetralin and the coal may appreciably reduce the activation energies associated with thermal rupture of bonds within the coal structure, thus permitting more extensive bond rupture leading to much higher yields of soluble product. However there appears to be little or no rupture of carbon-carbon bonds within fused aromatic structures at these temperatures.

Although phenanthrene is a fully aromatic molecule, and the process of dissolving bituminous coal in phenanthrene does not result in a net transfer of hydrogen, nevertheless extraction yields as high as 90-95% at 350°C have been reported by Orchin and coworkers[2,7]. Heredy and Fugassi[3] studied the mechanism of dissolution of bituminous coal in phenanthrene utilizing a special preparation wherein the hydrogen on the phenanthrene was replaced by tritium. They found that the dissolution process involved hydrogen disproportionation with extensive transfer of tritium to the coal extract and subsequent transfer of comparable amounts of hydrogen from the coal to the phenanthrene.

Infrared analysis of the coal and of the extracts revealed an appreciable increase in aromaticity in the products as compared with the original coal. This was interpreted by these authors to represent an aromatization of the hydroaromatic structure present in the original coal.

Lahiri and coworkers[4,5] observed a direct and quantitative relationship between the hydroaromatic content of coal and the yield of tar when pyrolysed at temperatures below 600°C. They observed that dehydrogenation of coal (e.g., with a halogen) resulted in a corresponding decrease in tar yield, a fully dehydrogenated coal yielding no tar at all. They observed further that the conversion of aromatic structures in coal to hydroaromatics through hydrogenation produced a corresponding increase in tar yield, the relationship being quantitative. These authors concluded that the aromatic carbon in coal is quantitatively converted to char during low temperature pyrolysis, and that the hydroaromatic carbon is quantitatively converted into primary tar.

It appears reasonable to conclude that the thermal rupture of bonds initiated by heating the coal to temperatures in the range of 350°C. and higher produces free radical fragments which then react in a manner dependent upon the species present in the system. Purely aromatic fragments will polymerize into large "molecules" which are non-volatile or insoluble, if other means of stabilization are not available. Hydroaromatic fragments will stabilize by rearrangement of atoms, becoming more aromatic in the process. Addition of a hydroaromatic solvent provides a source of hydrogen atoms which can stabilize the aromatic fragments, inhibit polymerization and produce a soluble product. Even an aromatic solvent such as phenanthrene, if energy conditions permit, can act as an agent in "transferring" hydrogen atoms to the aromatic structures thus increasing the quantity of soluble product, the net effect being a transfer of hydrogen from the hydroaromatic to the aromatic fragments.

It has been consistently observed that large molecules are inherently less stable at elevated temperatures than smaller molecules of similar composition. Thus hydrogenation studies have demonstrated that hydrogen in the presence of an appropriate catalyst can inhibit polymerization of hydrocarbon fragments during thermal cracking processes, yielding small molecules in preference to very large molecules. Hence the energy considerations in a coal system at elevated temperatures in the range considered here would favor stabilization of fragments by addition of atoms or small radicals, if such are available in the vicinity of the fragment.

Conclusions

The following conclusions may be derived from the observations presented above:

(1) When bituminous coal is heated to temperatures between 350° and 500°C, thermal rupture of bonds within the coal structure becomes extensive, the higher the temperature the more extensive the bond rupture.

(2) The fragments thus produced, being very reactive, will seek stabilization through reaction with available reactive species. Energy considerations

favor reaction with another free radical, rather than a molecule, in the absence of an appropriate catalyst.

(3) A hydroaromatic fragment may conveniently achieve stabilization by transferring a hydrogen atom from the saturated portion of the fragment to the area of the ruptured bond, a manifestation of atomic rearrangement.

(4) Small aliphatic side chains, probably present primarily on the hydroaromatic structures, may achieve stabilization by hydrogen transfer from the hydroaromatic structure.

(5) In the absence of a stabilization opportunity involving atoms or small radicals, adjacent aromatic fragments polymerize, thus achieving stabilization.

(6) Addition of a hydroaromatic solvent (e.g. tetralin) provides a source of hydrogen atoms which become the principal means of stabilization of the aromatic fragments.

(7) Addition of an aromatic solvent may contribute to stabilization by transferring hydrogen atoms to the aromatic fragments, and receiving hydrogen atoms from the hydroaromatic portions of the coal, if energy considerations permit such transfer.

(8) In pyrolysis in the absence of a solvent, the vapor pressure of the fragment following stabilization determines whether it escapes as volatile product or remains in the char. In dissolution, solubility of the stabilized fragment determines its final status.

Thus coal pyrolysis and coal dissolution are visualized as processes of similar nature, the slow or rate-determining steps involving the stabilization of the fragments produced by thermal decomposition at the temperature of the system. The types and quantities of reactive species in the system, available in the immediate vicinity of the thermally ruptured bonds, determine the extent of formation of volatile or soluble products. These processes at these temperatures do not appreciably rupture the bonds within the fused aromatic nuclei. Hence the general size distribution of "molecules" in the volatile or soluble product is characteristic of the parent coal from which it is derived, subject to the effects of temperature upon degree of bond rupture and upon vapor pressure and solubility.

Acknowledgment

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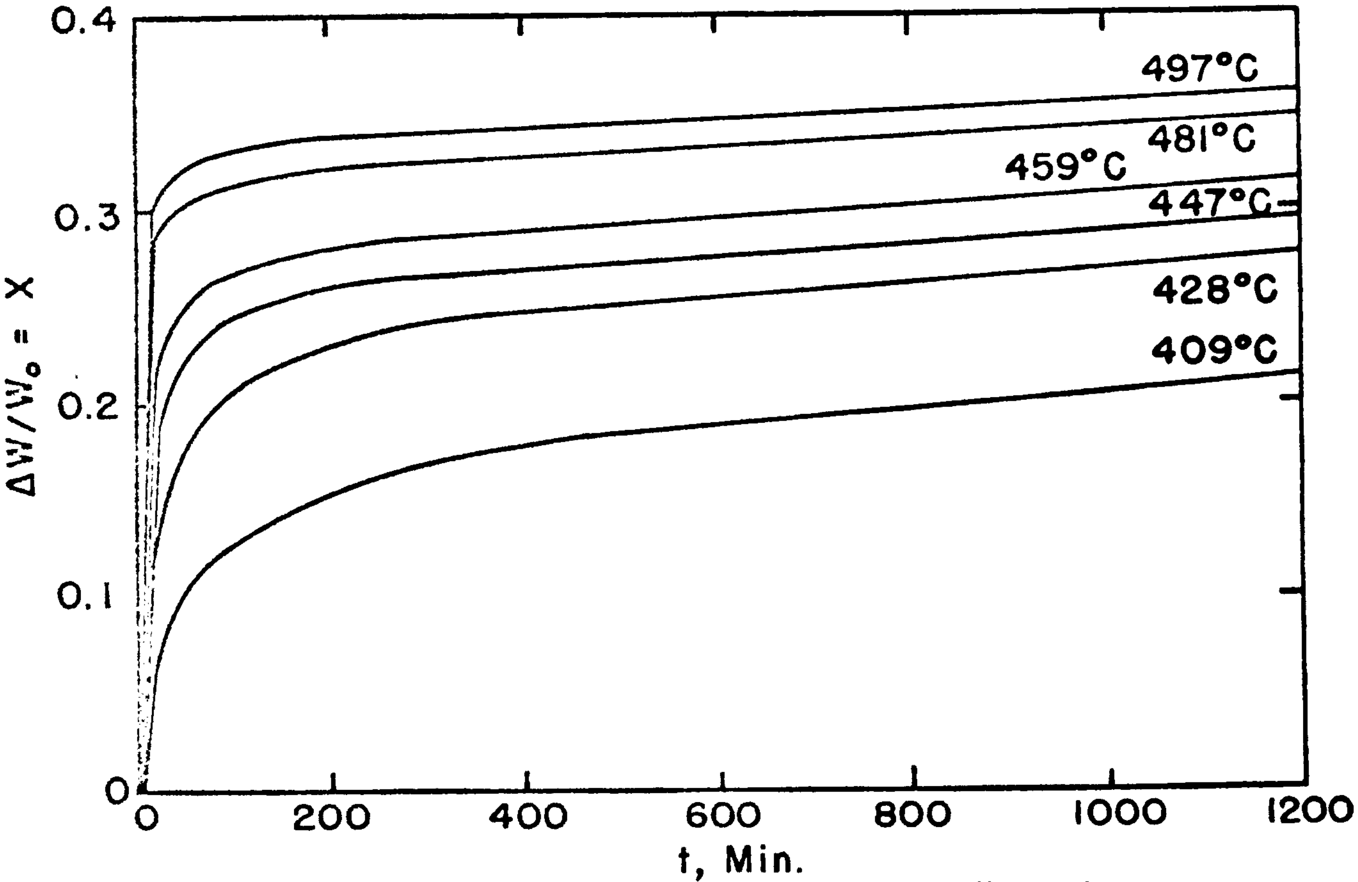

Figure I. Fractional Weight Loss-Time Curves, Coal Pyrolysis

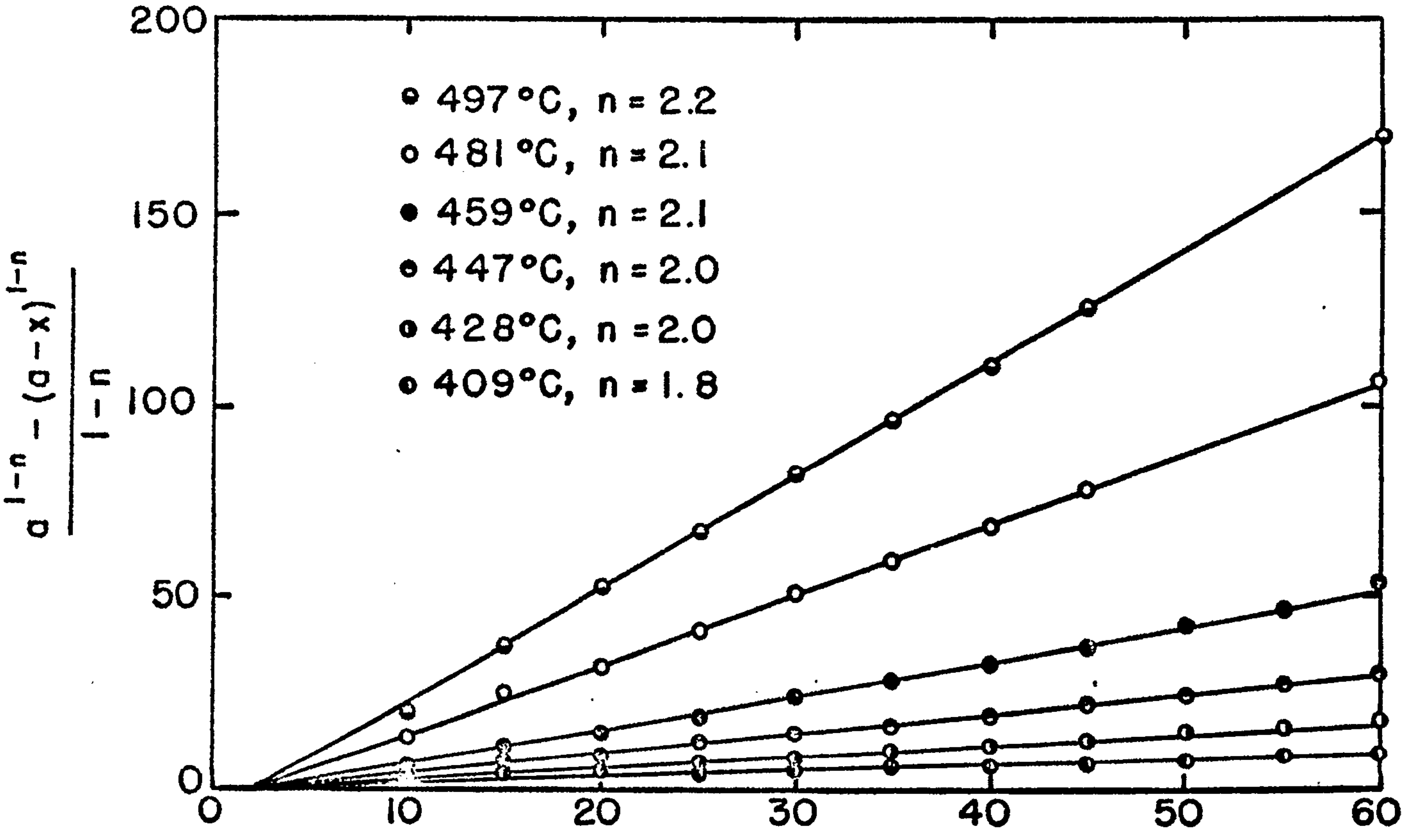

Figure 2. Plot of "n^th^" Order Equation, Coal Pyrolysis

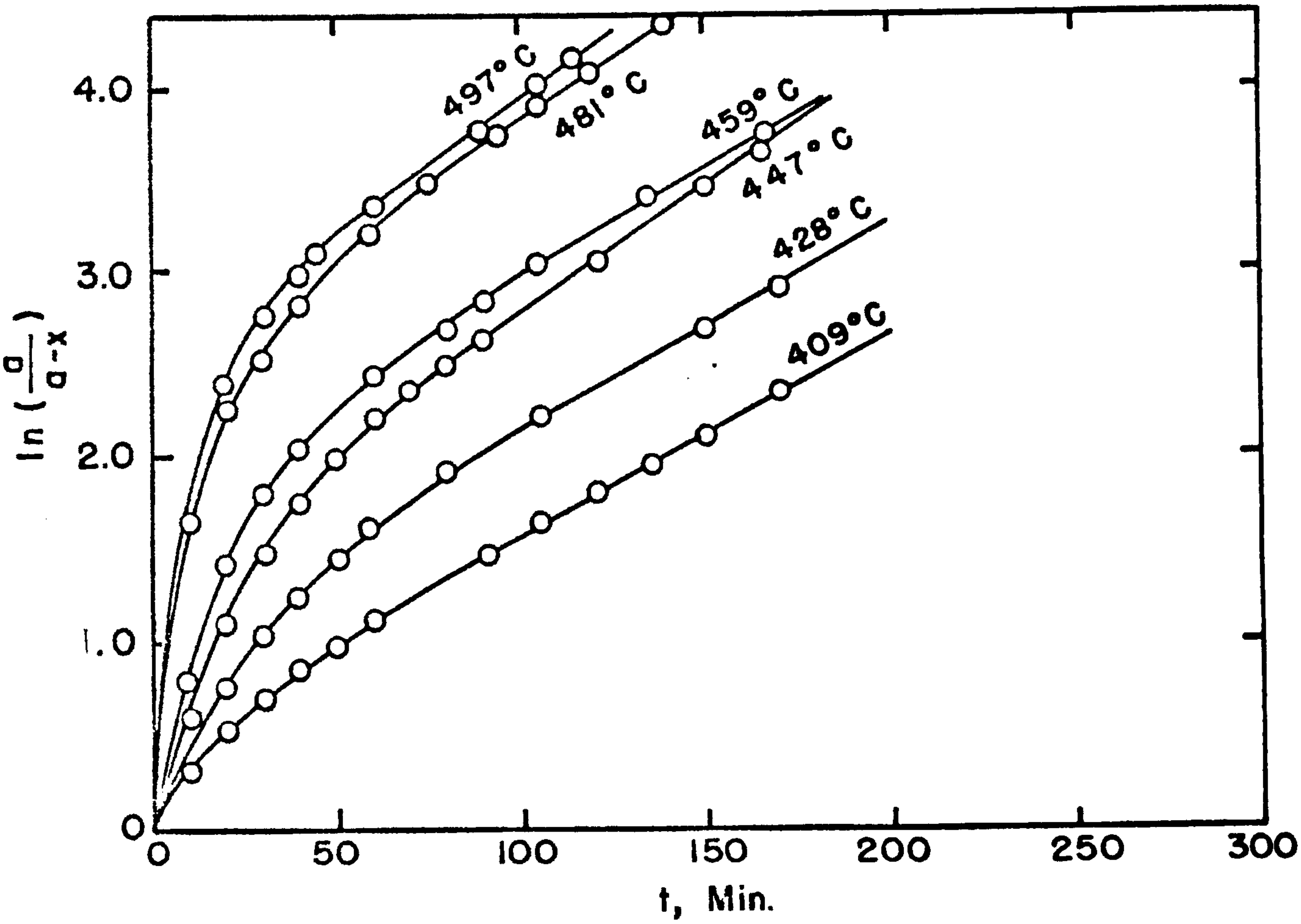

Figure. 3. First Order Plot of Data, Coal Pyrolysis

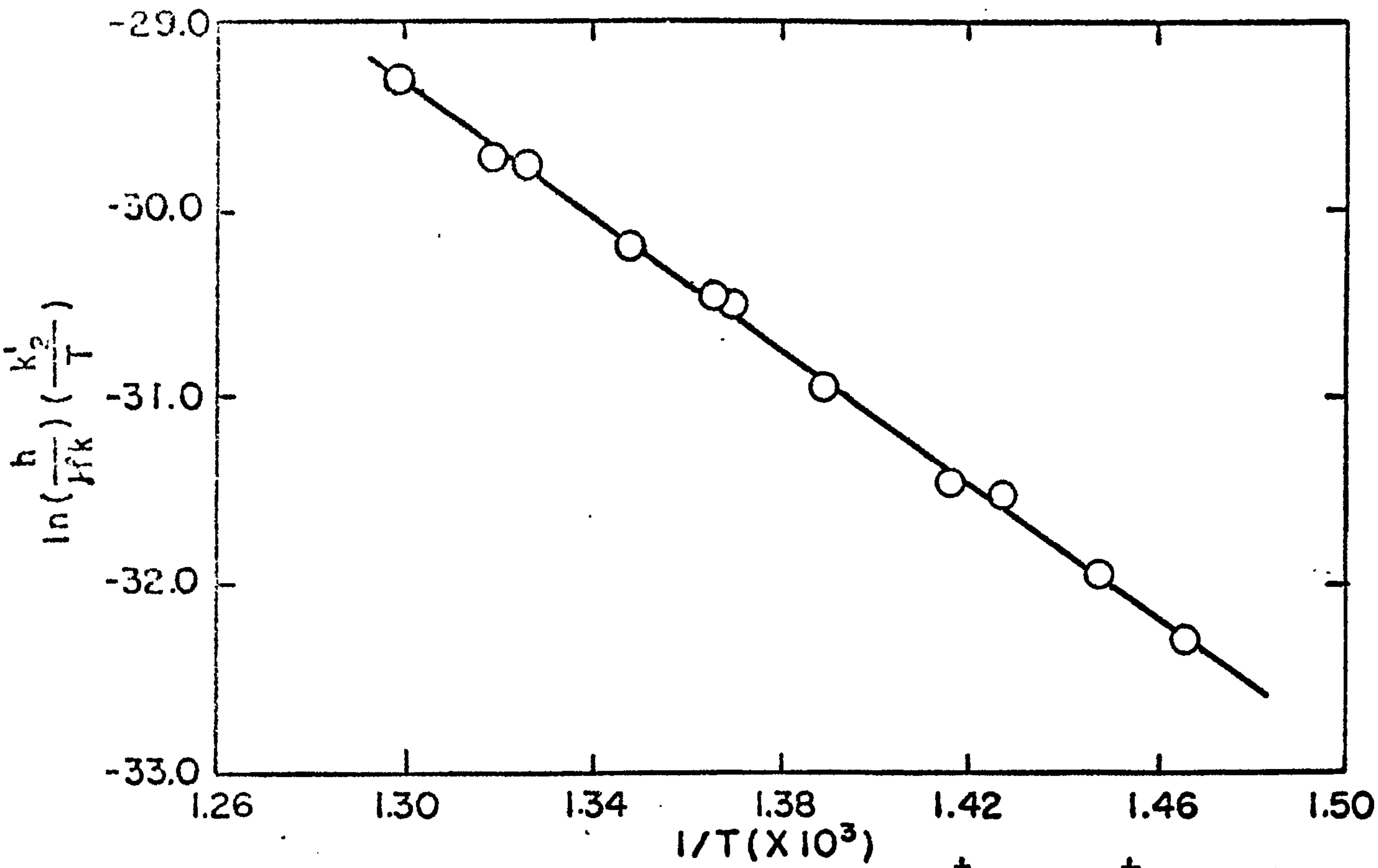

Figure 4. Eyring Plot for Evaluating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, First 60 Min, Coal Pyrolysis

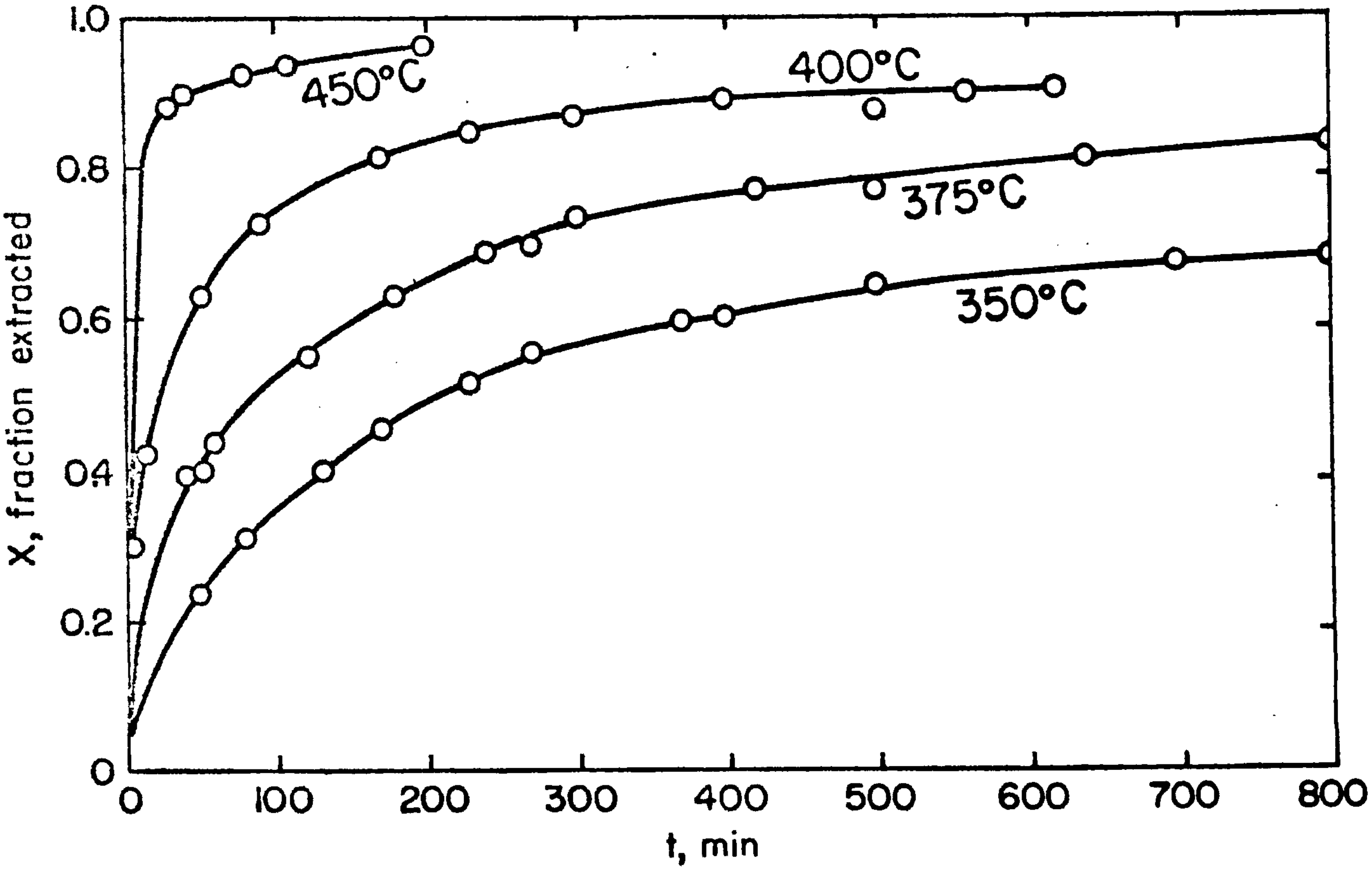

Figure 5. Time - Yield Curves in Coal Dissolution

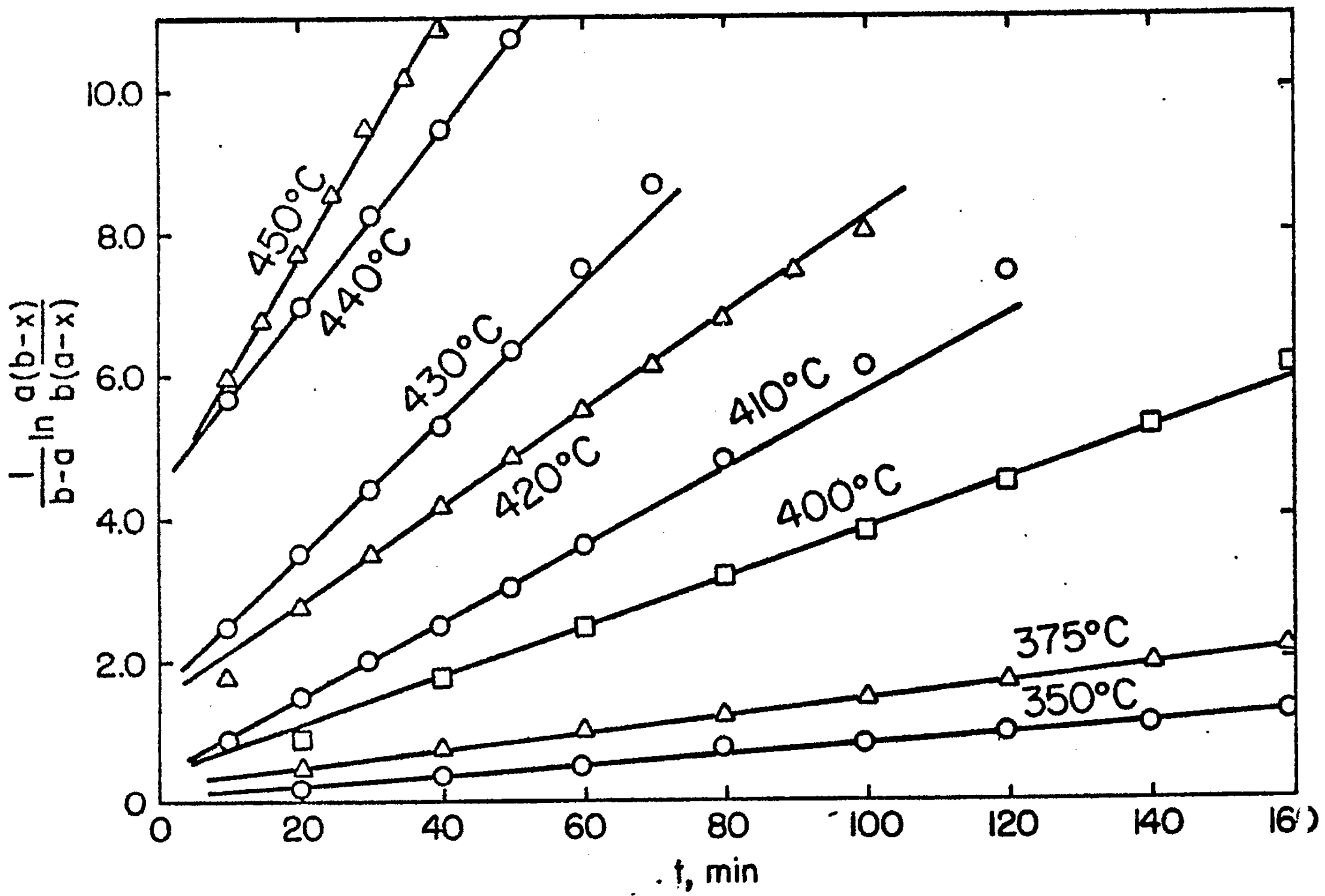

Figure 6. Plot of Second Order Equation in Coal Dissolution

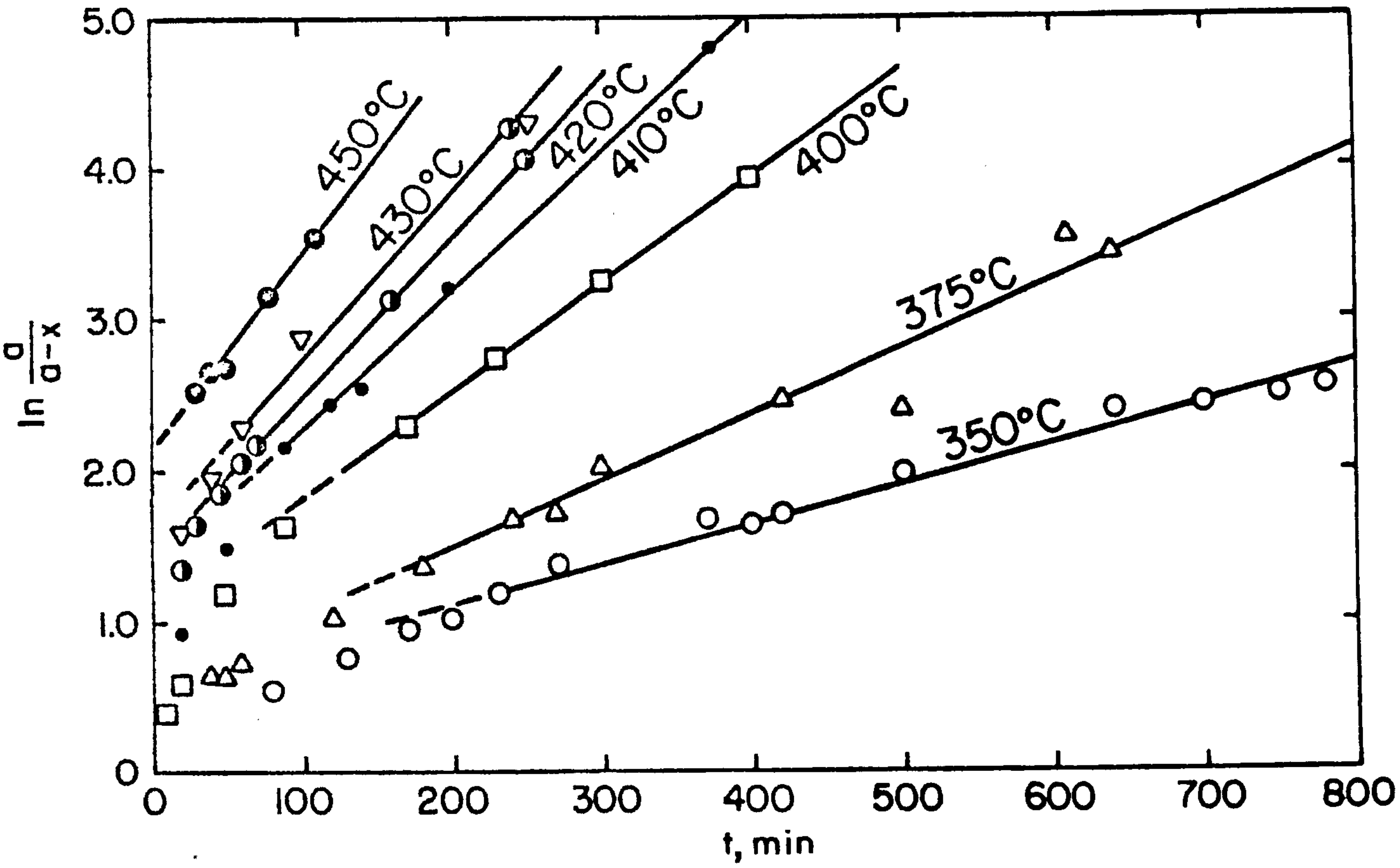

Figure 7. Plot of First Order Equation in Coal Dissolution

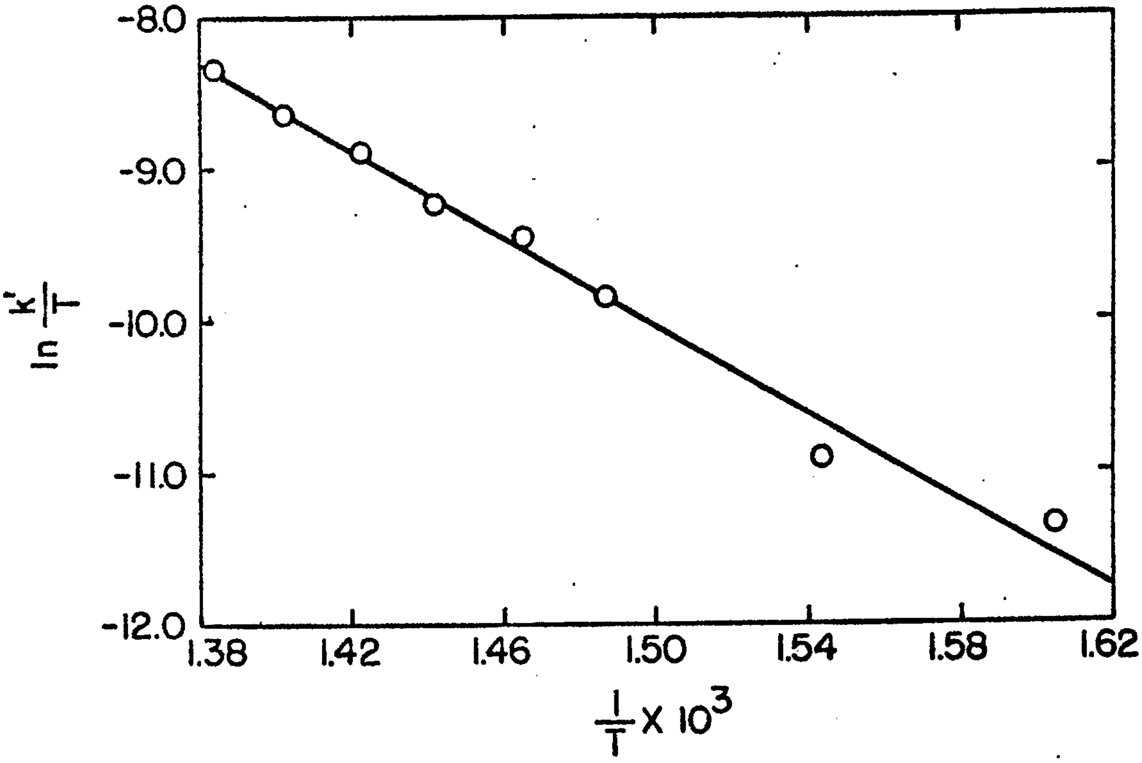

Figure 8. Absolute Reaction Rate Plot for Evaluating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, Second Order Region, in Coal Dissolution

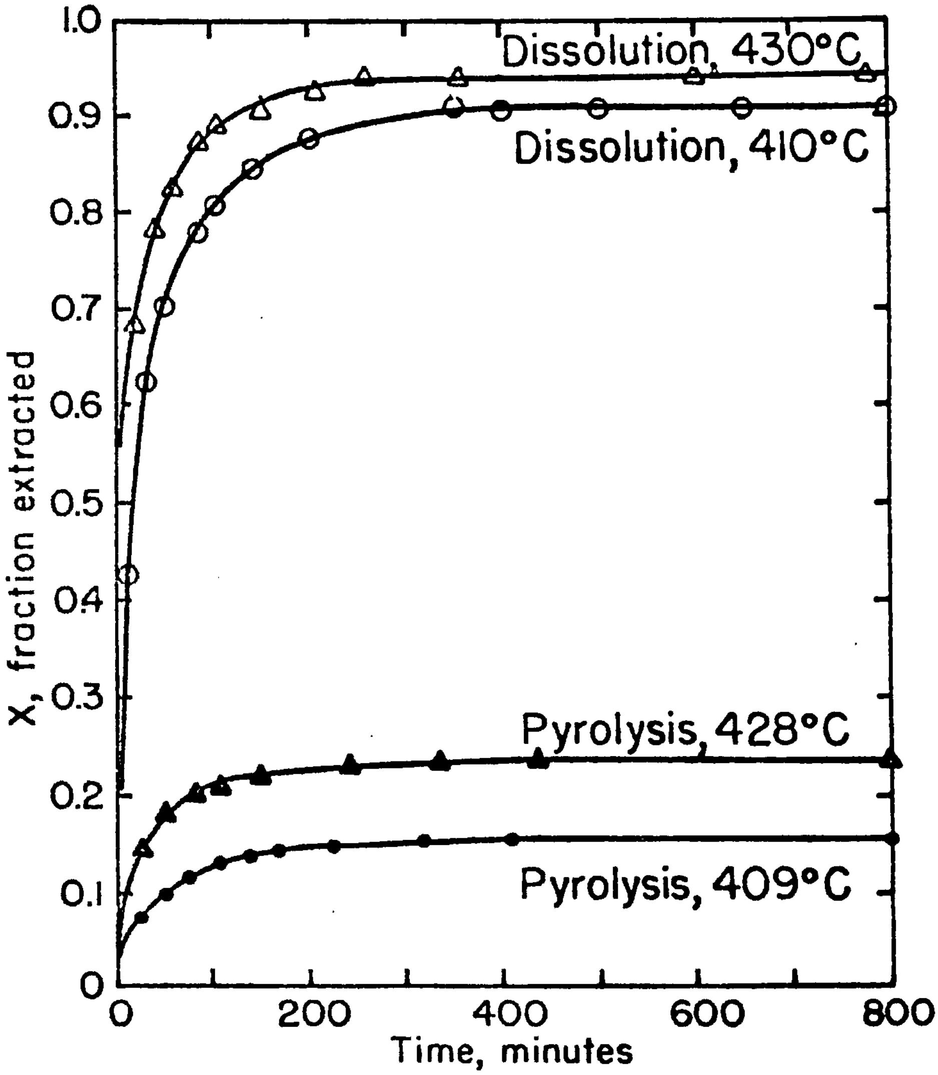

Figure 9. Comparison of Time-Yield Curves for Coal Pyrolysis and Dissolution

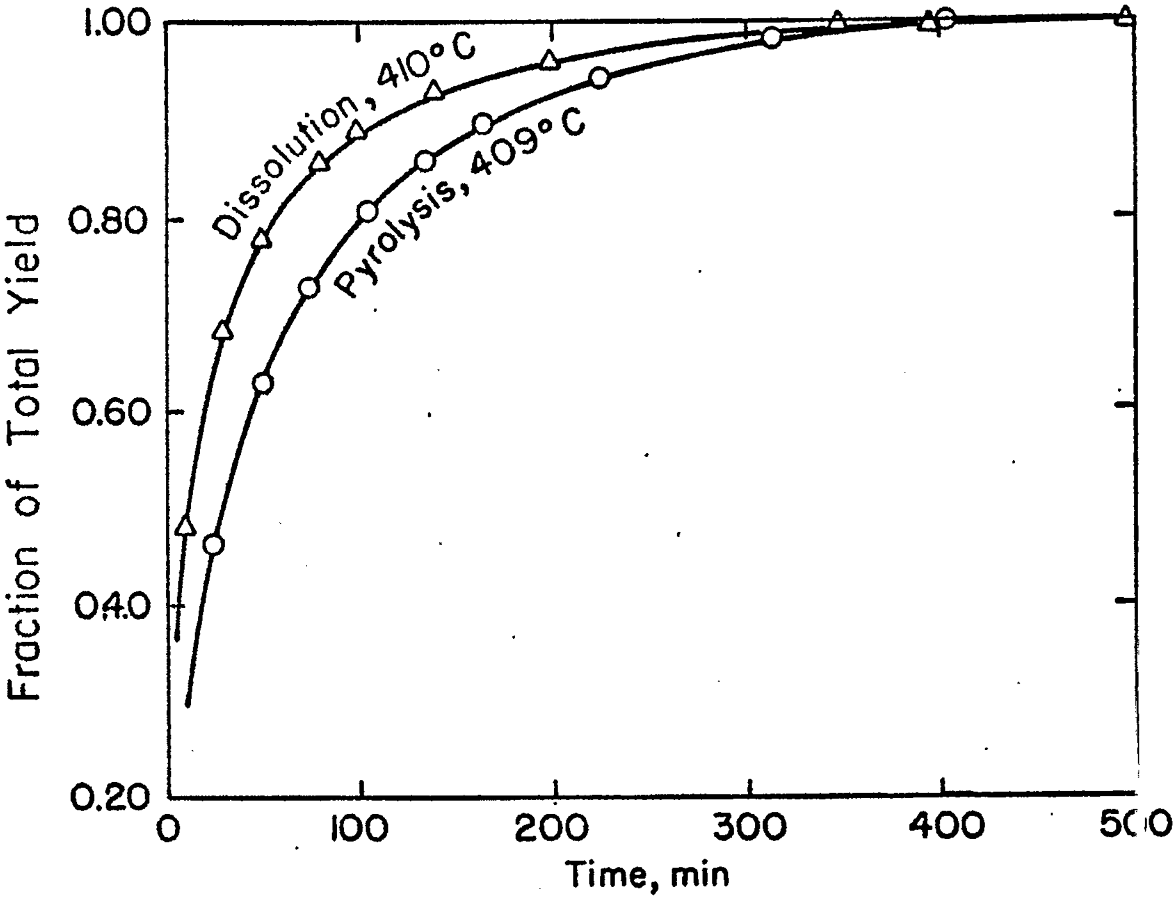

Figure 10. Comparison of Fraction Yield vs. Time

KINETICS OF THE HYDRO-REMOVAL OF SULPHUR, OXYGEN AND NITROGEN FROM A LOW TEMPERATURE COAL TAR*

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ABSTRACT

The results of the batch hydrogenolysis of S, O, and N compounds of a low temperature tar in the presence of a WS_2 catalyst indicate that all the hetero-atoms can be completely removed at 500°C and a pressure of 1500 psi. Cracking, aromatization, and possibly dehydrogenation reactions start taking place at temperatures above 375°C. The hydrogenation of aromatic hydrocarbons starts at a pressure of 1250 psi. The hydro-removal reactions of S, O, and N are all first order with respect to the heterocyclic molecules. Sulphur removal follows a true Arrhenius temperature dependence but the removal of O and N shows slight curvatures in the Arrhenius plot which can be resolved into two parts, each approaching linearity with a break at 400°C and having different activation energies. The magnitude of energies of activation and enthalpies of activation obtained suggest that chemical reactions, but not physical processes, are rate controlling. The surface reaction involving the rupture of the C-S, C-O, and C-N bonds of the heterocyclic molecules appears to be the rate-determining step.

Introduction

Hydro-refining of coal tars has been the subject of many papers and patents all over the world during the last two decades. Most of the work reported was carried out in batch or continuous systems and the effect of operating variables on the removal of S, O, and N compounds present in coal tars was investigated.[1,3,5,8,9,11] Very little data are so far published on the kinetics of the removal of S, O, and N present in tars, though some work has been reported on the kinetics of the hydrogenation of pure heterocyclic compounds containing S, O, and N. Wilson, et al.,[13] studied the kinetics of the hydrogenation of a dilute solution of dibenzothiophene and 3-methyl isoquinoline in a virgin naphtha over a commercial cobalt-molybdate catalyst. The reactions of S and N removal were found to be of first order with activation energies of 3.8 and 20 k.cal/mol, respectively. Owens and Amberg[10] reported the activation energy for hydro-desulphurization of thiophene over a sulphided mixed oxide catalyst as 24-25 k.cal/mol and either

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hydrogen adsorption or the surface reaction as the rate-controlling step. Tarama, et al.,[12] studied the hydrogenolysis of thiophene in benzene over a V_2O_3-+Co O_3 catalyst and found the reaction to be of first order with respect to thiophene and 0.5 order with respect to hydrogen. The authors proposed that the surface reaction between adsorbed hydrogen atoms and the sulphur compound is the rate-determining step. Gunther[4] hydrogenated pure cresol and a 3 percent solution of cresol in a hydrogenated oil over a WS_2-NiS catalyst. The reactions were reported to be of first order with activation energies of 56.2 and 19.4 k.cal/mole, respectively. Cox and Berg[2] studied the kinetics of the hydrogenolysis of five and six-membered heterocyclic nitrogen compounds and the reactions were found to be of second order for five-member rings and first order for six-member rings. In the present communication, the results of the investigation on the kinetics of the removal of sulphur, oxygen, and nitrogen present in a low temperature coal tar over a WS_2 catalyst are reported.

Experimental

Materials

Tar - A low temperature tar fraction from a high volatile bituminous coal. The properties of the tar are given in table 1.

Catalyst - Unsupported Tungsten Sulphide (WS_2,-200 mesh).

Hydrogen - 100 percent pure hydrogen.

Equipment

A one litre high pressure Autoclave with a magnetic drive stirrer, pressure and temperature control devices, liquid and gas sampling lines, and water quenching system as shown in figure 1.

Procedure for Hydrogenation Experiments

In each experiment 250 gm of tar and 25 gm of the catalyst were used. The equipment was evacuated to remove air, filled with hydrogen and heated to the desired temperature. The time for heating the reaction mixture to the desired temperature varied between 15 and 20 minutes. About 2 gm of the product was drawn from the autoclave at different time intervals. The samples were dried, filtered, and analyzed for S, O, and N contents by micromethods. Sulphur was determined by the bomb method, oxygen by the "Coleman Model 36," oxygen analyzer and nitrogen by the "F. M. Model 185" C-H-N Chromatographic Analyzer. The hydrogen pressure in the system was almost maintained constant throughout. Experiments were carried out at temperatures ranging from 300° to 500° C and pressures from 500 to 2000 psi.

Results and Discussion

Effect of operating conditions

Low temperature tars contain considerable amounts of sulphur, oxygen, and nitrogen compounds, the nature and quantity of each group depending upon the type of parent coal and carbonization conditions. Each of the above groups contains compounds of different structures occurring throughout the boiling range of the tar. The fundamental structures of the different groups of heterocompounds present in tars are given in table 2.[7] The hydro-removal of S, O, and N from these compounds depends upon the extent of cleavage of the C-S, C-O, and C-N bonds and the addition of hydrogen to the residual fragments in the presence of a suitable catalyst Some of the typical reactions of the heterocompounds under hydrogenation conditions are shown in figures 2 to 4.[6] The degree of removal of S, O, and N mainly depends upon the reaction temperature, pressure, time, and type of catalyst used. The effects of temperature and pressure on conversion are shown in figures 5 to 8. It can be seen from figure 5 that the extent of desulphurization, deoxygenation, and denitrogenation increased fast up to a temperature of 400°C and later was slowed down. At 500°C and a pressure of 1500 psi, almost all the S, O, and N was removed. There was no change in the content of aromatic hydrocarbons up to a temperature of 375°C, but at higher temperatures the aromatics in the product increased. It appears that cracking, aromatization, and possibly dehydrogenation reactions start taking place above 375°C resulting in an increase of aromatic hydrocarbons. It is also likely that some of the aromatic hydrocarbons might have been formed from the hydrogenolysis reactions of heterocyclic compounds. The olefins in the product decreased up to a temperature of 450°C but at higher temperatures there was an increase in the olefin content. This may possibly be due to excessive cracking and dehydrogenation reactions taking place at temperatures above 450°C. Figure 6 shows that the total conversion and conversion to gasoline (liquid boiling below the I.B.P. of feed) increased up to a temperature of 450°C and later reduced. On the other hand, the dry gas formation slowly increased up to 450°C and later there was a rapid increase. It appears that the cracking of the original tar molecules takes place with the formation of gasoline and gas up to a temperature of 450°C. At higher temperatures, excessive cracking takes place throughout the boiling range leading to the formation of coke and dry gas. The fall in hydrogen consumption over 450°C indicates the presence of dehydrogenation reactions at higher temperatures.

There was a rapid increase in the hydro-removal of S, O, and N (figure 7) up to a pressure of 1500 psi, but the increase is small at higher pressures. The aromatic content of the product remained almost constant up to a pressure of 1250 psi but reduced considerably at higher pressures. Aromatic hydrocarbons present in the feed material seem to be getting hydrogenated at pressures above 1250 psi. The olefin hydrogenation increased linearly with pressure. The total conversion and conversion to gasoline increased slowly up to a pressure of 1250 psi but the increase was rapid at higher pressures. There was only a slight increase in hydrogen consumption and conversion to gas as the pressure increased (figure 8). The results indicate that condensation, dehydrogenation, and other side reactions are very much suppressed at pressures higher than 1500 psi, thus leading to higher total conversion and conversion to gasoline.

Kinetics

The time-conversion curves (figures 9 to 11) for hydro-removal of S, O, and N at different temperatures have the same characteristic shapes with a sharp rise in conversion in the initial stages. The conversion was almost quantitative at equilibrium and, therefore, the reactions are not subject to any thermodynamic limitations but appear to be limited only by kinetic factors.

Figures 12 to 14 contain plots of $\text{Log}\,\frac{a}{a-x}$ versus time at different temperatures where "a" is the initial concentration of the hetero-atoms and "x" is the conversion. The linearity of these figures shows that the hydro-removal reactions of S, O, and N are all first order with respect to the heterocyclic molecules. The rate of removal can therefore be represented by the following equations.

1. $\frac{-d(S)}{dt} = k_s\ (S)$

2. $\frac{-d\ (O)}{dt} = k_o\ (O)$

3. $\frac{-d\ (N)}{dt} = k_n\ (N)$

where k_s, k_o, and k_n are the rate constants for the hydro-removal of S, O, and N, respectively. The concentration of hydrogen under the experimental conditions was large and almost constant throughout the course of the reaction, the amount of consumption being negligibly small. Even if hydrogen atoms are involved in the rate-determining step, the hydrogen concentration may not show up in the rate equation but would be one of the constant factors that are contained in the rate constant term. However, since hydrogen is actually taking part in the hydro-removal of S, O, and N, the reactions may be considered as pseudo first order reactions.

Figures 15 to 17 illustrate the temperature dependence of the first order rate constants at temperatures between 300°C and

500°C. Sulphur removal follows a true Arrhenius temperature dependence but in case of O and N, the plots showed slight curvatures which can be resolved into two parts, each approaching linearity with a break at 400°C and having different activation energies. The rate constants which represent the rates of hydroremoval of S, O, and N in the temperature range 300°-500°C can be represented by the following equations:

1. $k_s = 2 \times 10^2 \, e^{-11,000/RT}$ Min.$^{-1}$

2(a). $k_{o_1} = 6 \times 10^6 \, e^{-12,000/RT}$ Min.$^{-1}$ (300°-400°C range)

2(b). $K_{o_2} = 3 \times 10^5 \, e^{-8,000/RT}$ Min.$^{-1}$ (400°-500°C range)

3(a). $k_{n_1} = 1 \times 10^6 \, e^{-10,000/RT}$ Min.$^{-1}$ (300°-400°C range)

3(b). $k_{n_2} = 3 \times 10^{11} \, e^{-14,000/RT}$ Min.$^{-1}$ (400°-500°C range)

Figures 18 to 20 represent the Eyring plots where Log $\frac{k^1}{T}$ was plotted versus the reciprocal of the absolute temperature. The following values were obtained for the enthalpies and entropies of activation:

$\Delta H_s = 9,000$ Cal/mol., $\Delta S_s = -50$ e.u.

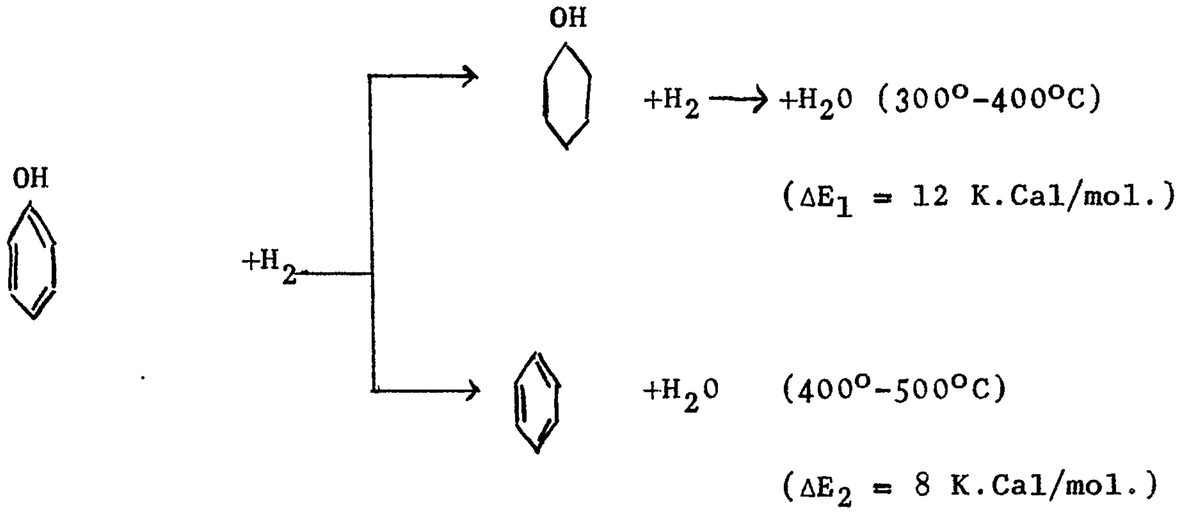
$\Delta H_{o_1} = 11,000$ Cal/mol., $\Delta S_{o_1} = -40$ e.u.

$\Delta H_{o_2} = 6,000$ Cal/mol., $\Delta S_{o_2} = -42$ e.u.

$\Delta H_{n_1} = 8,000$ Cal/mol., $\Delta S_{n_1} = -45$ e.u.

$\Delta H_{n_2} = 12,000$ Cal/mol., $\Delta S_{n_2} = -41$ e.u.

In the temperature range studied in the present investigation, mixed phase conditions might exist and the reactions might predominately be taking place in liquid and vapor phases in the ranges 300°-400° and 400°-500°C, respectively, requiring different activation energies. It is also possible that competing reactions with different activation energies might be taking place. This sort of heterogeneity and the existence of competing reactions seem to be responsible for the observed breaks in the Arrhenius plots of O and N removal reactions. In case of oxygen compounds, the liquid phase reactions seem to be having higher activation energies than the vapor phase reactions, whereas the reverse is true in case of nitrogen. The following type of competing reactions might possibly be taking place in case of phenols under the present experimental conditions.



The conversion of phenols to cyclohexanols may perhaps be favored at lower temperatures (300°-400°C) but at higher temperatures (400°-500°C) these reactions may not be favored because of the dehydrogenation reactions which are likely to take place in this temperature range. There is no likelihood of the presence of competing reactions during the hydro-removal of nitrogen. It appears that mainly the nonbasic nitrogen compounds are getting hydrogenated in the 300°-400°C range whereas the basic compounds are predominately getting converted in the range 400°-500°C, the latter having higher activation energies.

The magnitude of the energies of activation and enthalpies of activation of the hydro-removal reactions indicates that chemical reactions but not physical processes are rate controlling. The only possible chemical reactions that can be considered during the hydrolytic splitting of the heterocyclic molecules are the rupture of the C-S, C-O, and C-N bonds and the addition of hydrogen atoms to the fragments of heterocyclic molecules on the surface of the catalyst as represented below.

1. $\text{Heteromolecule} \xrightarrow{\text{Slow}} \text{Hydrocarbon fragment} + \text{Hetero-atom fragment}$

2. $\text{Hydrocarbon fragment} + H^o \xrightarrow{\text{Fast}} \text{Hydrocarbon}$

3. $\text{Heteroatom fragment} + H^o \xrightarrow{\text{Fast}} H_2S,\ H_2O,\ \text{or}\ NH_3$

The last two steps are expected to be fast because of their free radical nature. Therefore, the first step involving the cleavage of hetero-molecules appears to be rate determining.

Acknowledgment

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Table 1

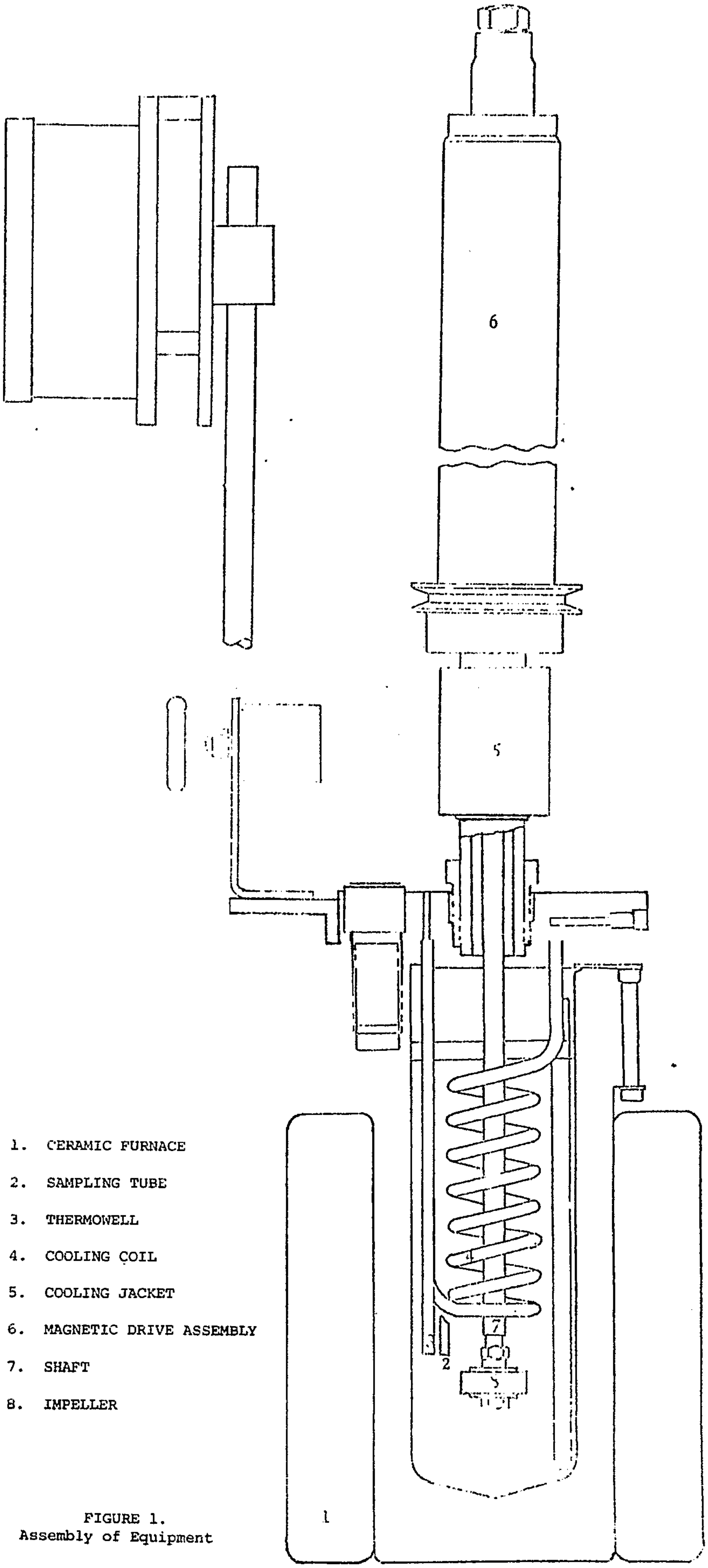
Properties of tar

Spi. gr	0.9686
Tar acids (vol. %)	30.2
Tar bases (vol. %)	2.5
Sulphur (wt. %)	0.8342
Nitrogen (wt. %)	0.3985
Oxygen (wt. %)	6.3145
Boiling range	200-325°C
Hydrocarbon types (vol. %)	
Saturates	28.32
Olefins	18.42
Aromatics	53.26

Table 2

Fundamental heterocyclic structures present in L. T. tar

Sulphur compounds	Oxygen compounds	Nitrogen compounds
Sulphides	Phenols	Pyridines
Disulphides	Indenols	Cyclopentanopyridines
Mercaptans	Phenyl Phenols	Phenyl Pyridines
Thiophenes	Naphthols	Quinolines
Benzo Thiophenes	Fluorenols	Benzoquinolines
Dibenzo Thiophenes	Indanones	Anilines
	Carborylic acids	Benzylanilines
	Asphaltic and resinous bodies	Naphthylamines
		Pyrroles
		Indoles
		Carbazoles



1. CERAMIC FURNACE
2. SAMPLING TUBE
3. THERMOWELL
4. COOLING COIL
5. COOLING JACKET
6. MAGNETIC DRIVE ASSEMBLY
7. SHAFT
8. IMPELLER

FIGURE 1.
Assembly of Equipment

MERCAPTANS

$$RSH + H_2 \longrightarrow RH + H_2S$$

DISULFIDES

$$RSSR' + 3H_2 \longrightarrow RH + R'H + 2H_2S$$

SULFIDES

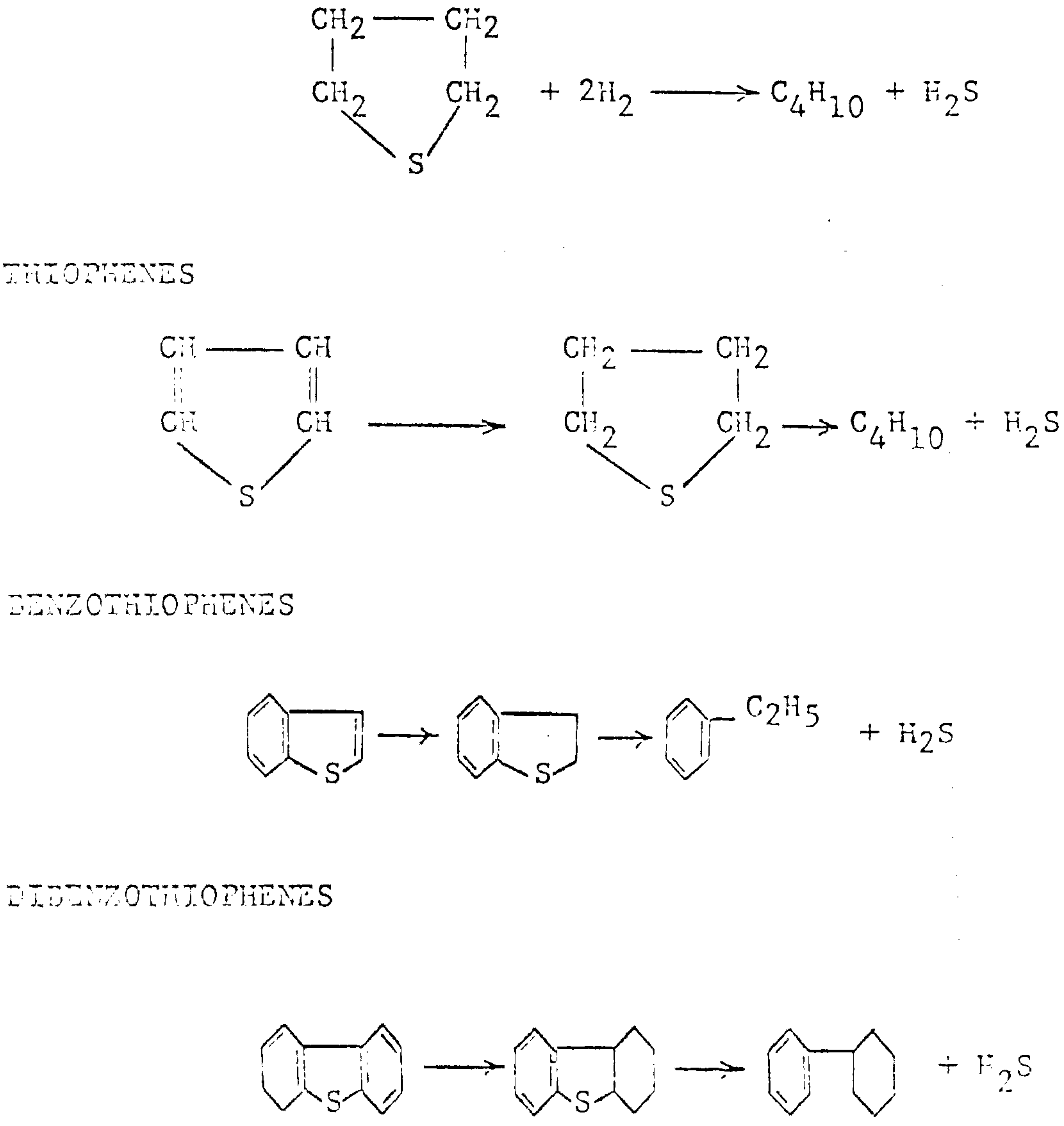
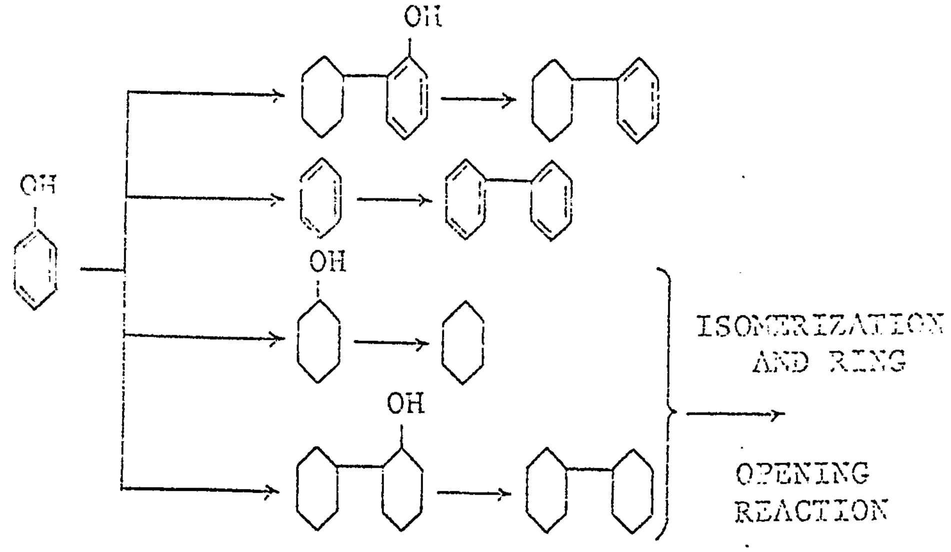
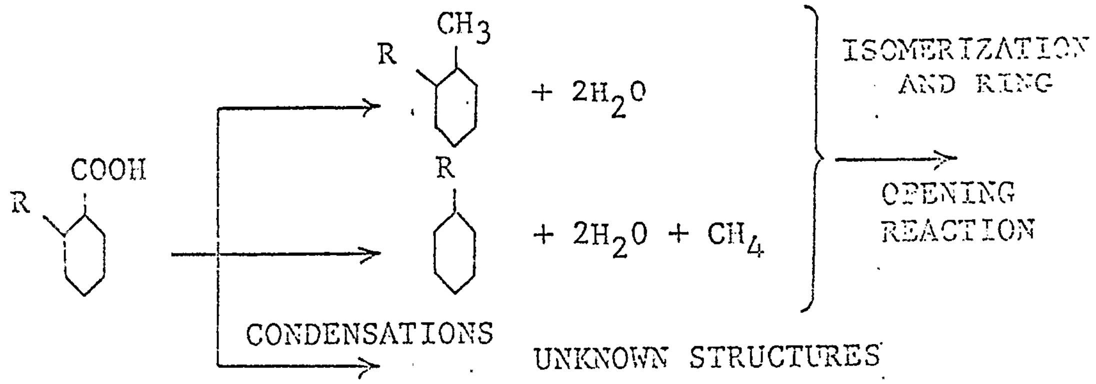


FIG. 2. TYPICAL SULFUR COMPOUND REACTIONS

PHENOLS



NAPHTHENIC ACIDS

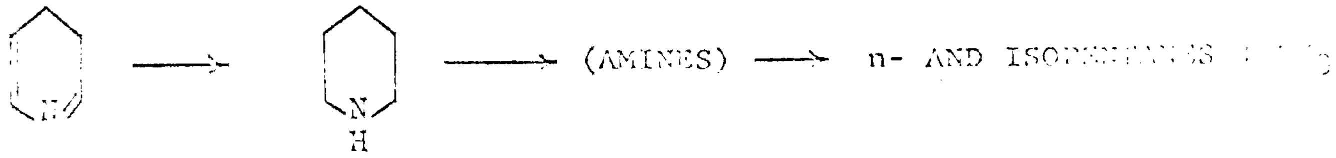


ASPHALTS AND RESINS

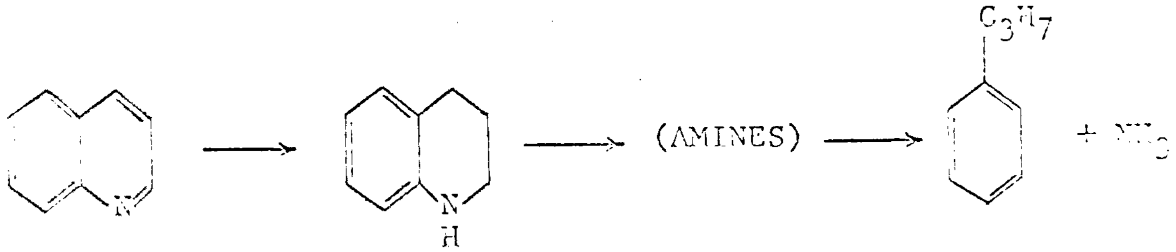
COMPLEX MOLECULES $\longrightarrow$ LOWER MOLECULAR WEIGHT HYDROCARBONS + H_2O

FIG. 3. TYPICAL OXYGEN COMPOUND REACTIONS

PYRIDINES



QUINOLINES



ISOQUINOLINES

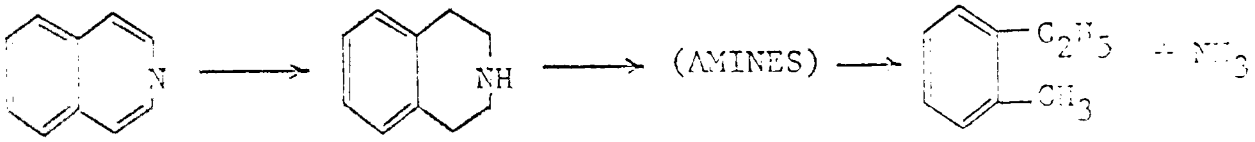


FIG. 4A. TYPICAL NITROGEN COMPOUND REACTIONS

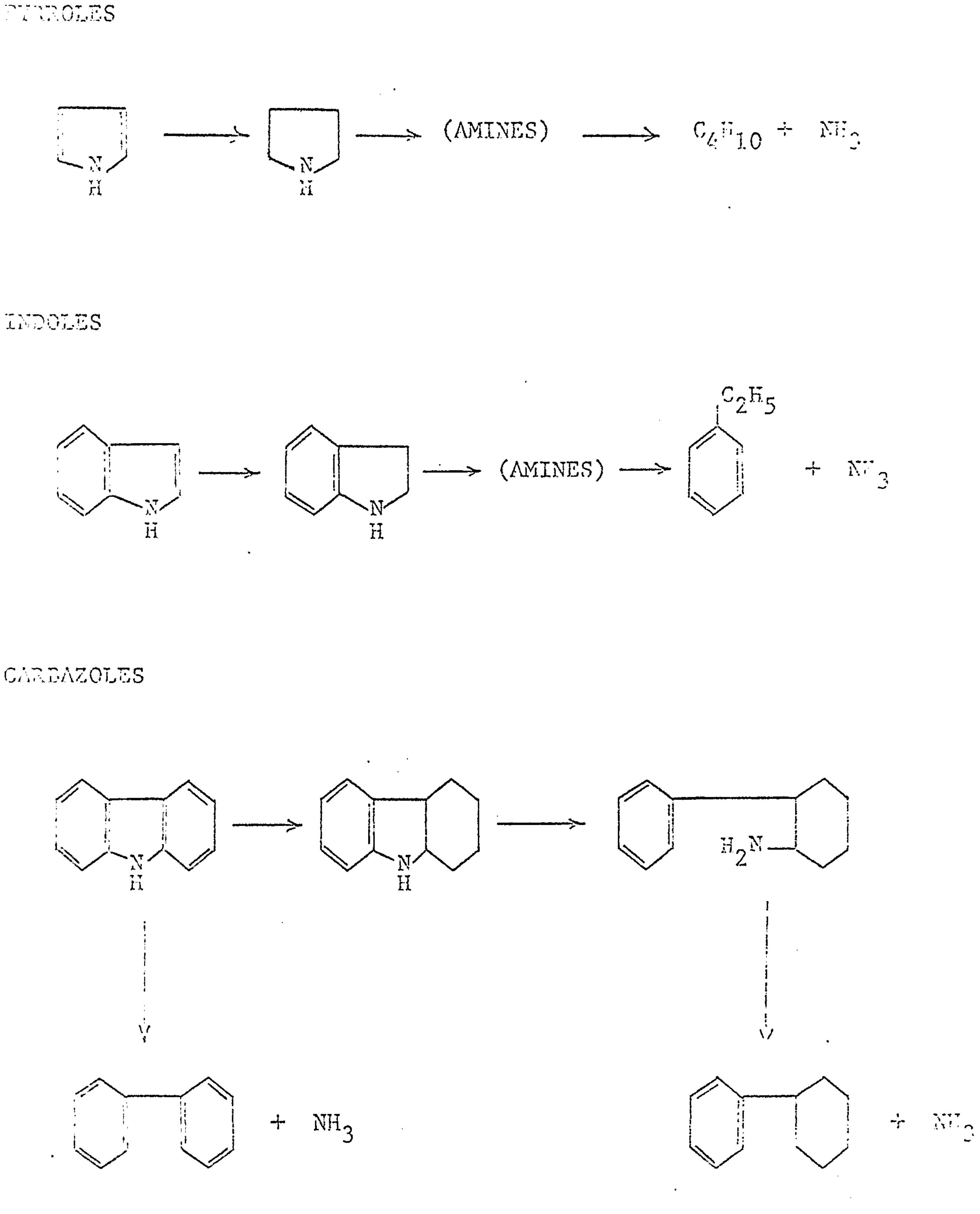


FIG. 4B. TYPICAL NITROGEN COMPOUND REACTIONS

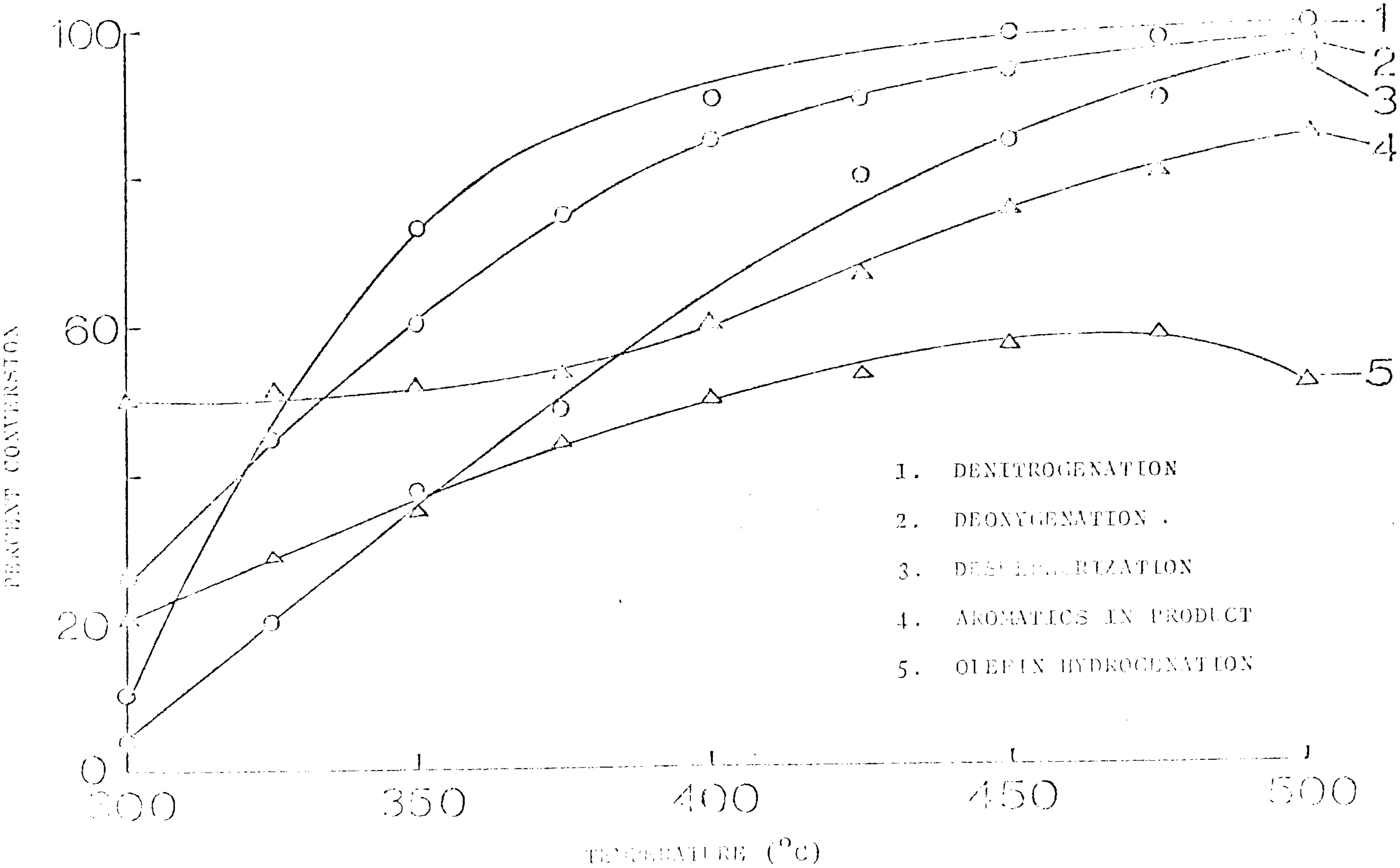


FIG. 5. EFFECT OF TEMPERATURE ON CONVERSION

[illegible] ([illegible]) [illegible]

[illegible]

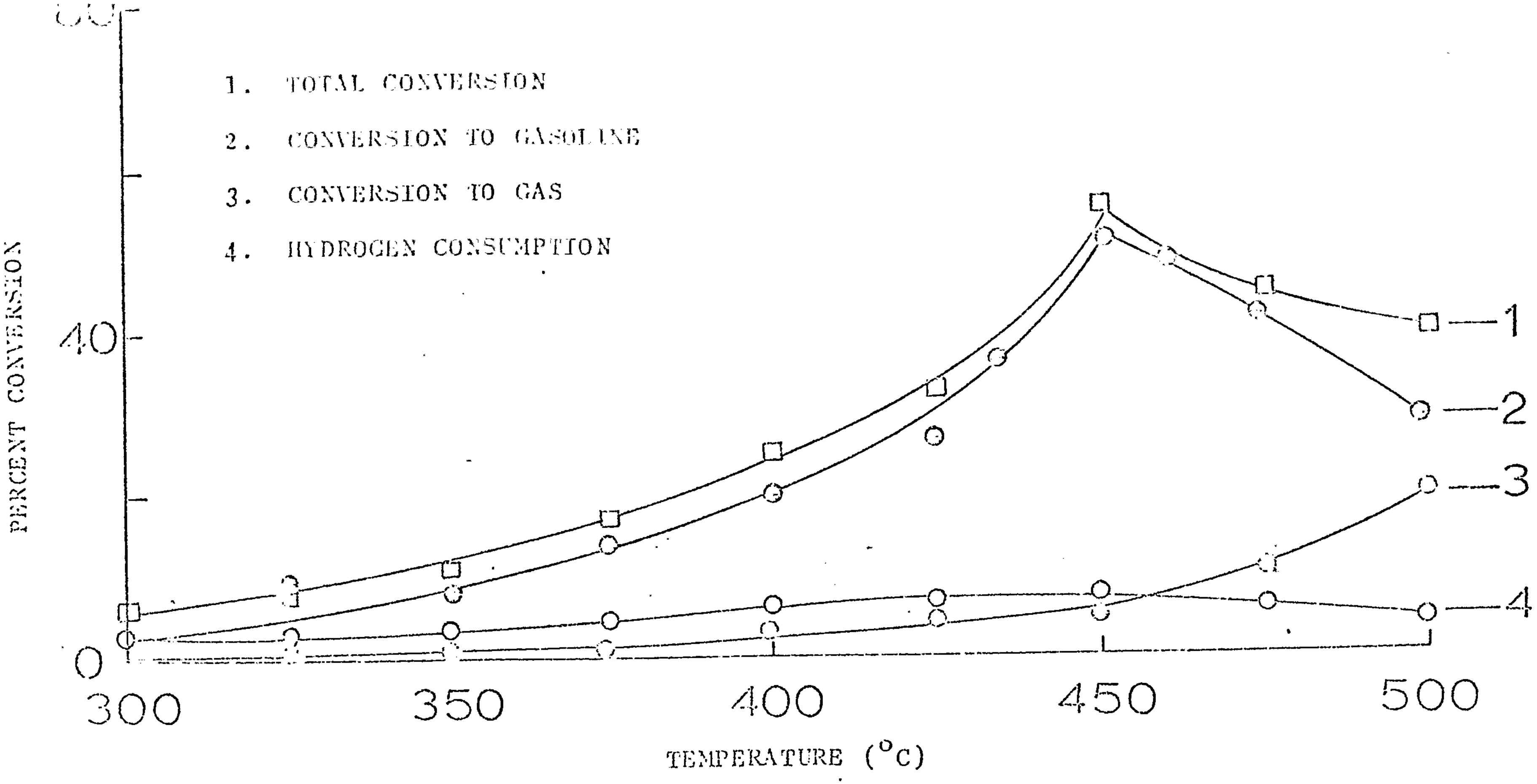


FIG. 6. EFFECT OF TEMPERATURE ON CONVERSION

PRESSURE (PSI) = 1500

REACTION TIME = 2 hrs.

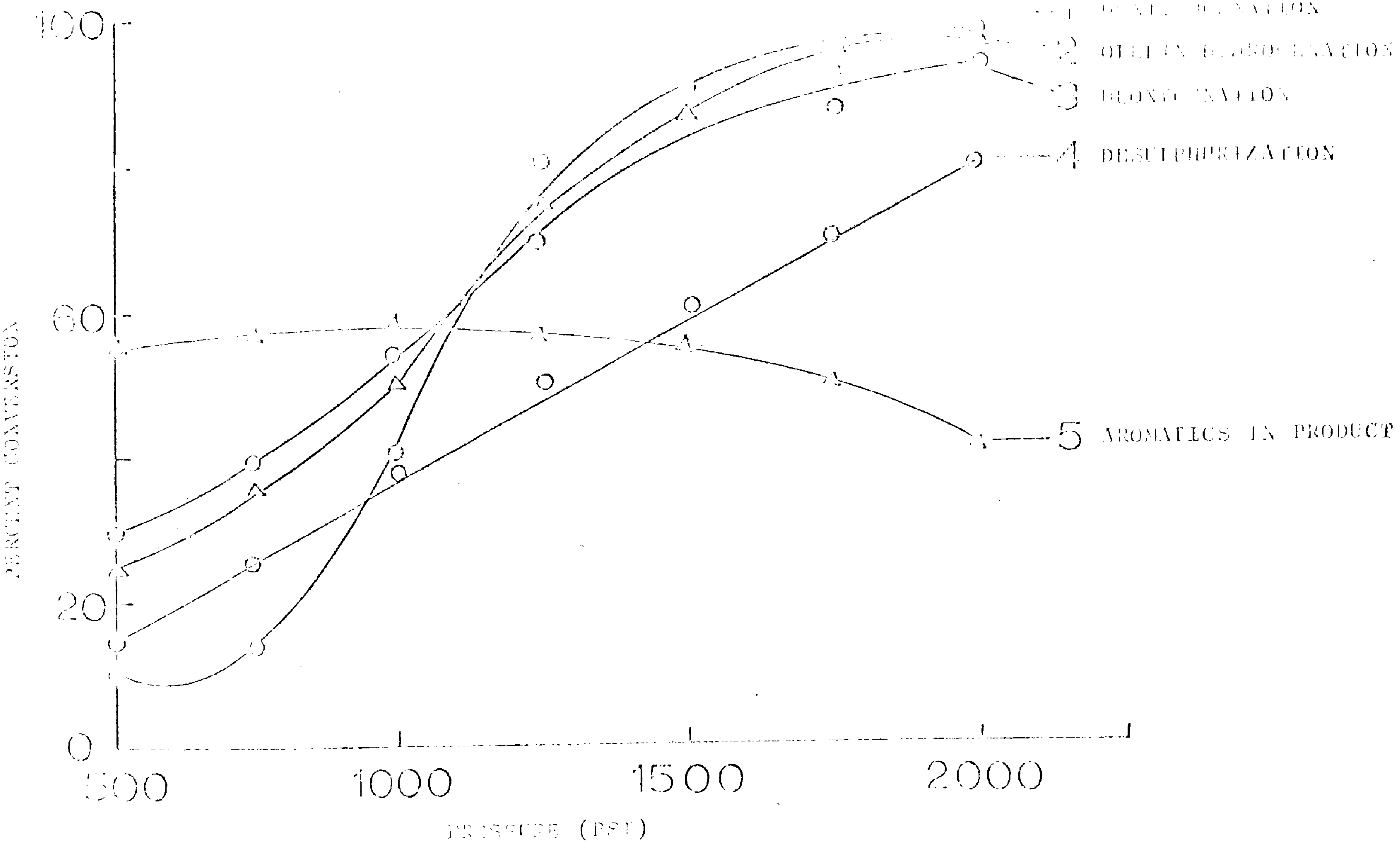


FIG. [illegible] EFFECT OF PRESSURE ON CONVERSION

[illegible]

[illegible]

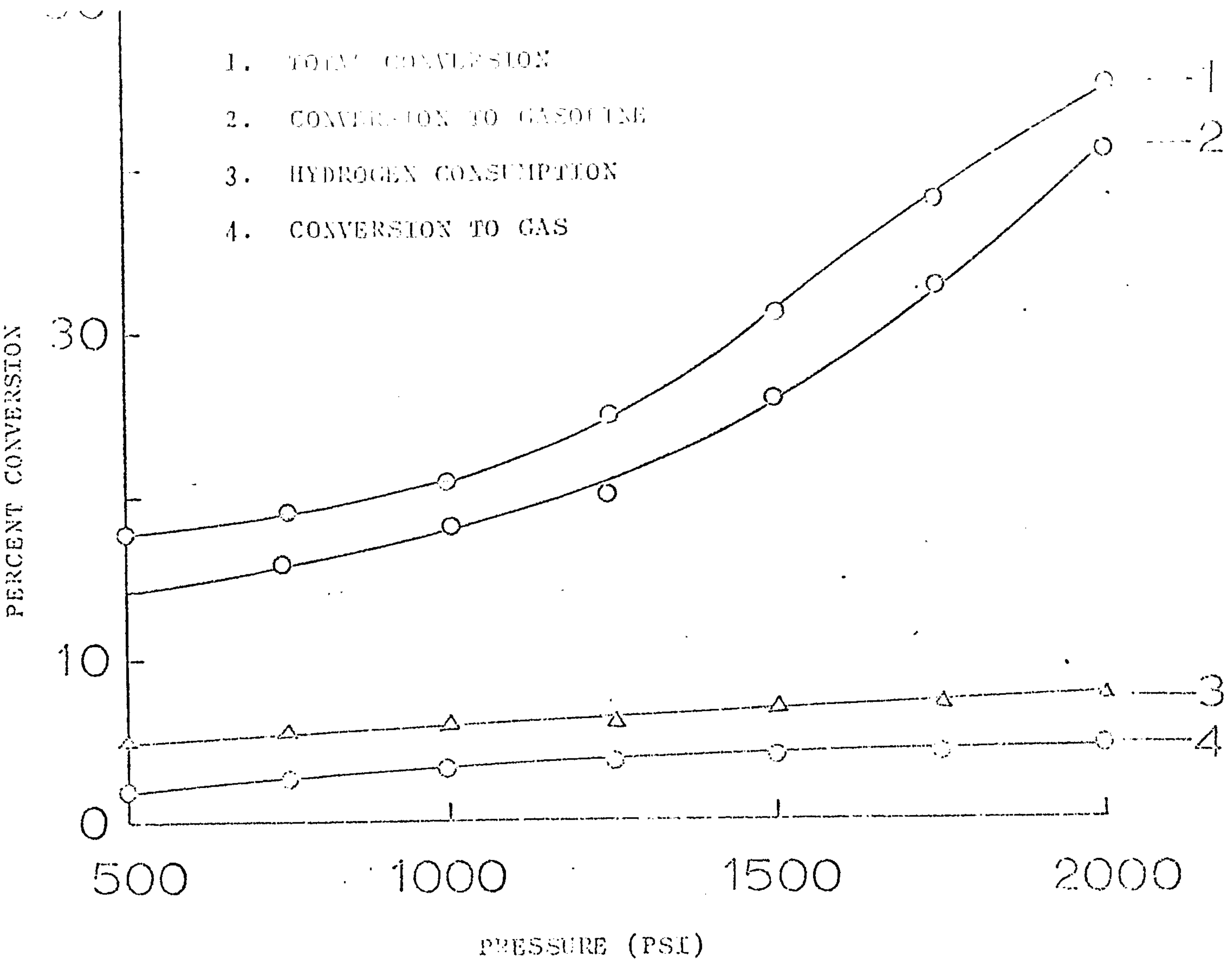
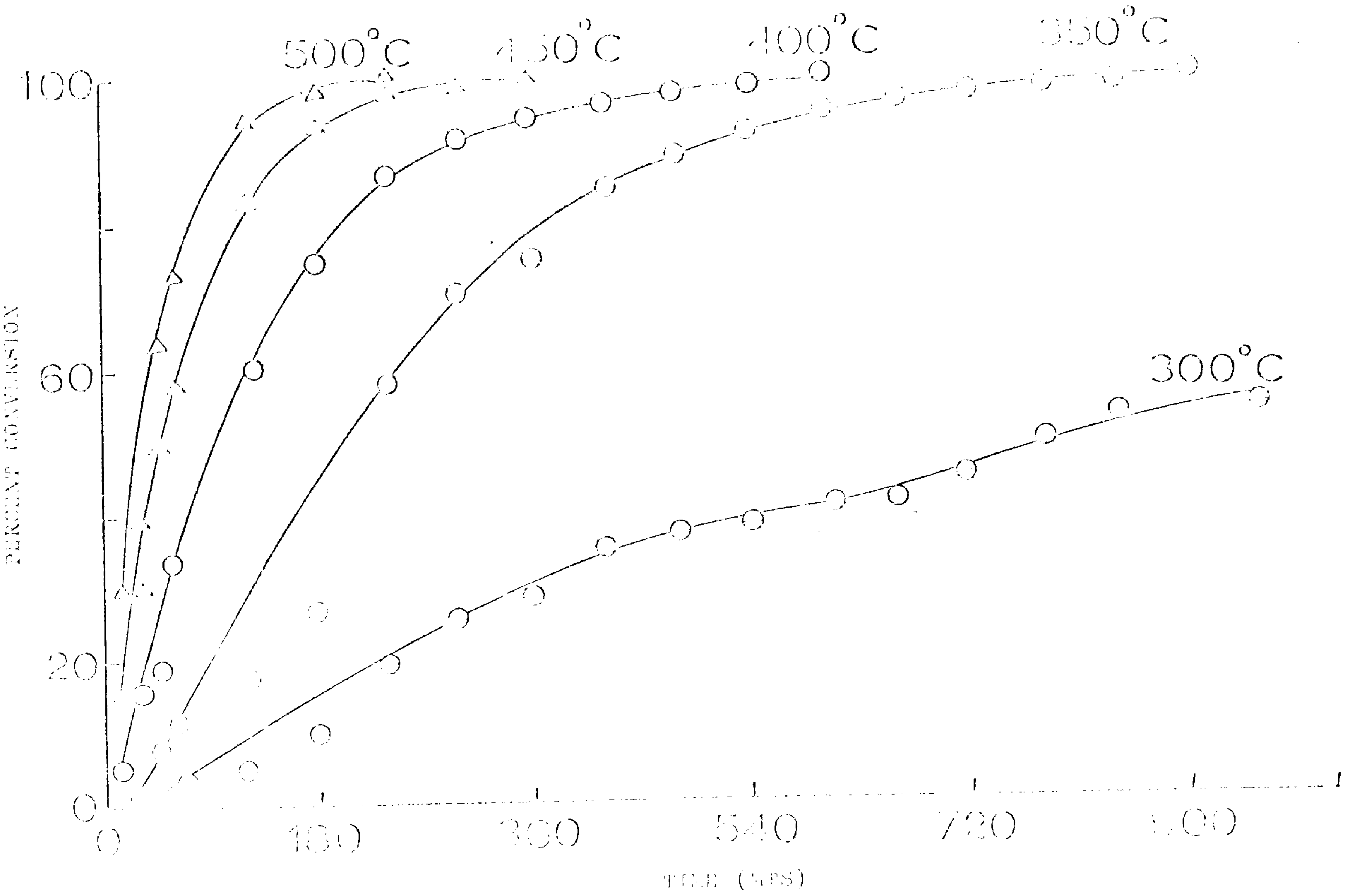


FIG. 8. EFFECT OF TEMPERATURE ON CONVERSION

TEMPERATURE (°C) : 400

REACTION TIME : 2 [illegible]


500°C
450°C
400°C
350°C
300°C
PERCENT CONVERSION
100
60
20
0
0
180
360
540
720
900
TIME (MINS)

[illegible]

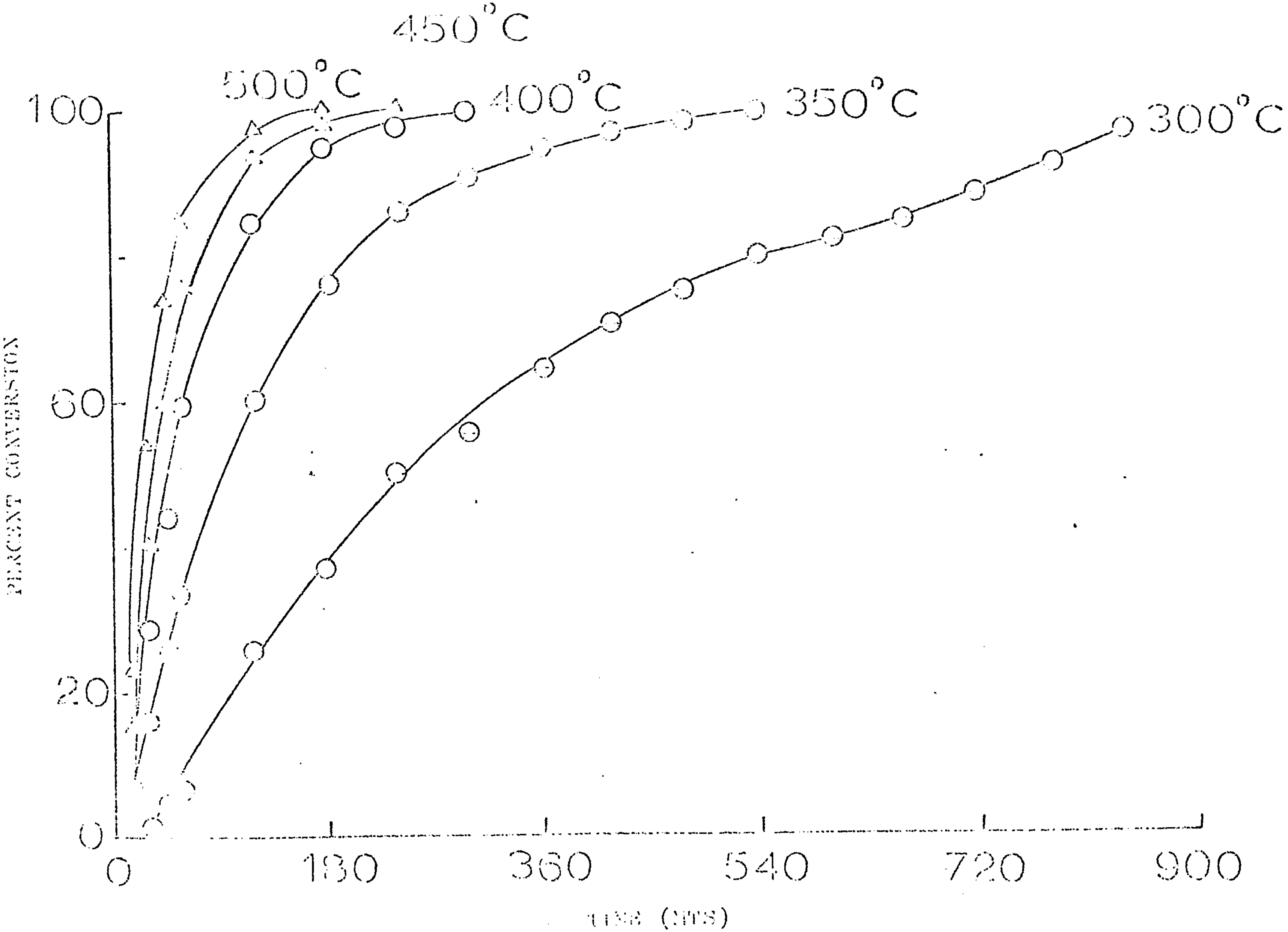
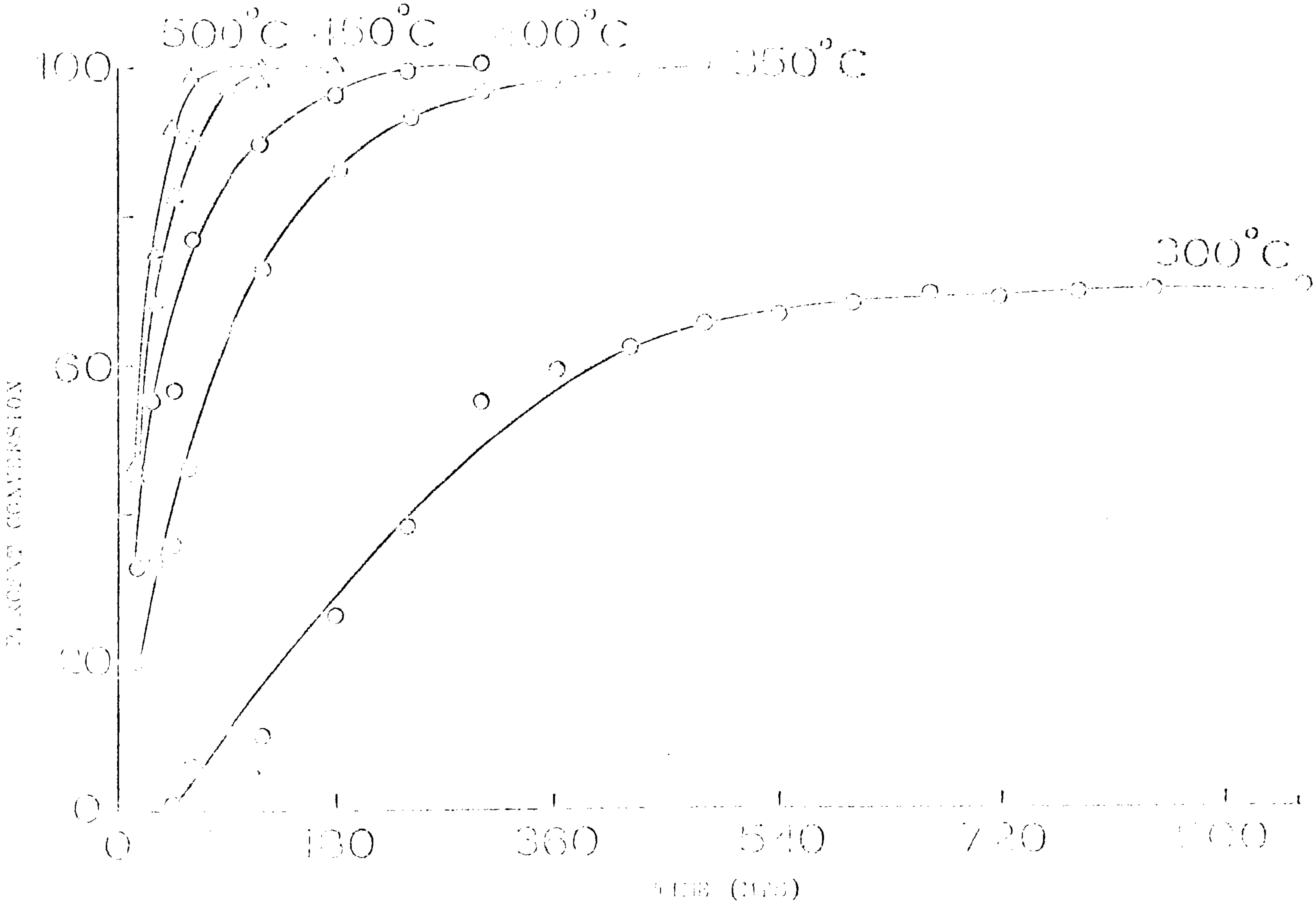


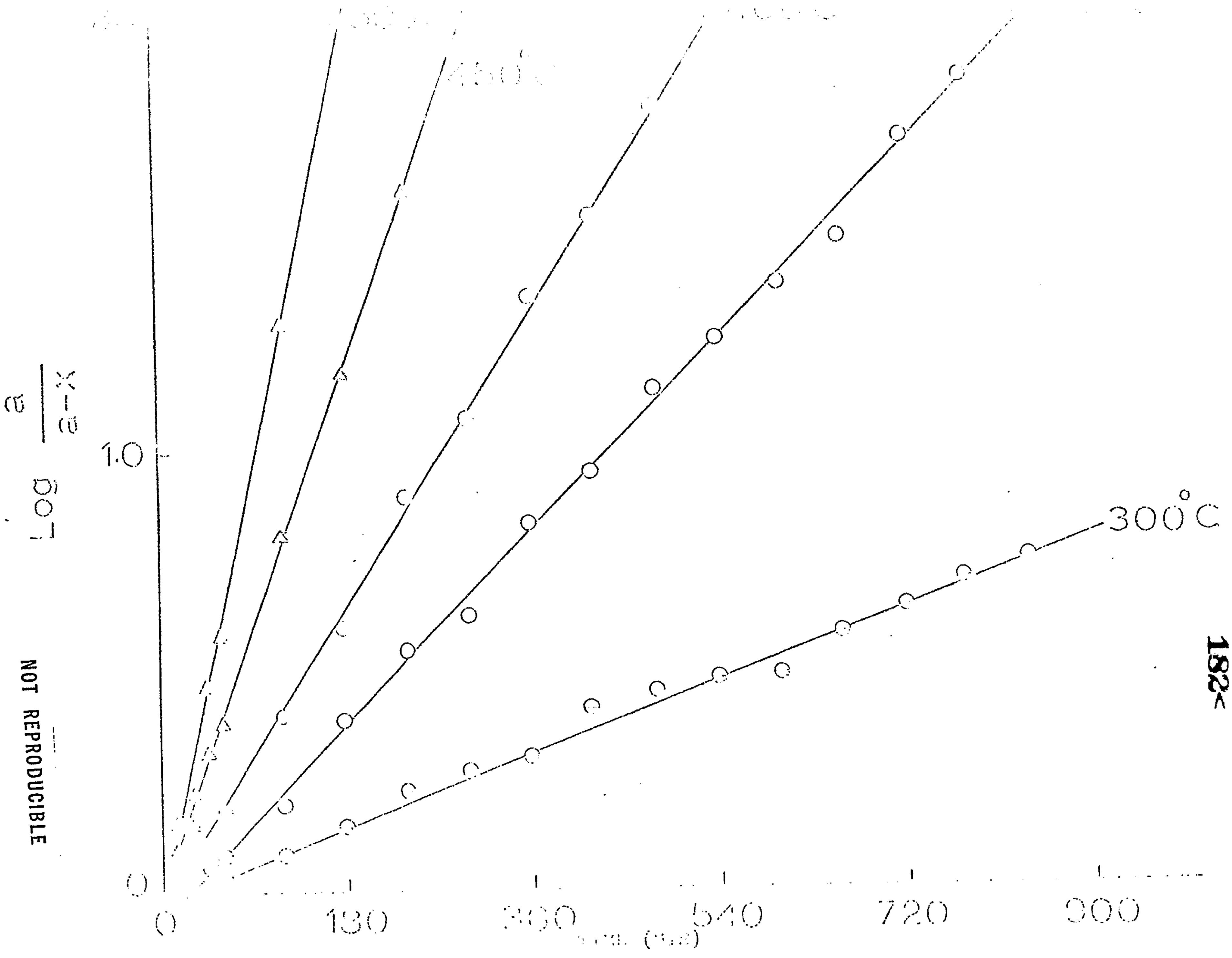
FIG. 10. EFFECT OF REACTION TIME ON DEOXYGENATION

PRESSURE (PSI) = 1500
TEMPERATURE (°C) 300-500



[illegible]

PRESSURE [illegible]
TEMPERATURE [illegible]



NOT REPRODUCIBLE

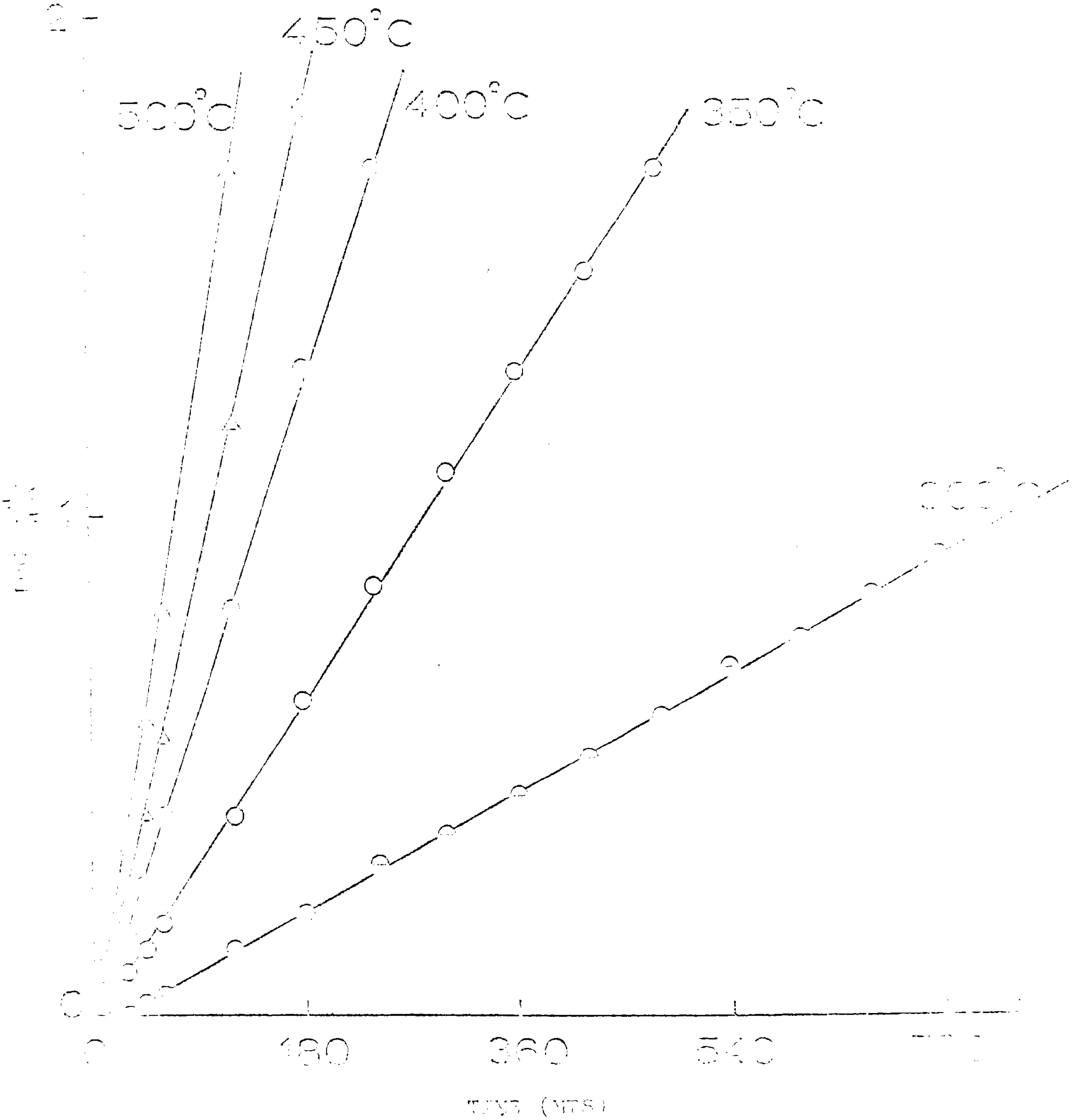


FIG. 13. PLOT OF FIRST ORDER EQUATION FOR DEOXYGENATION

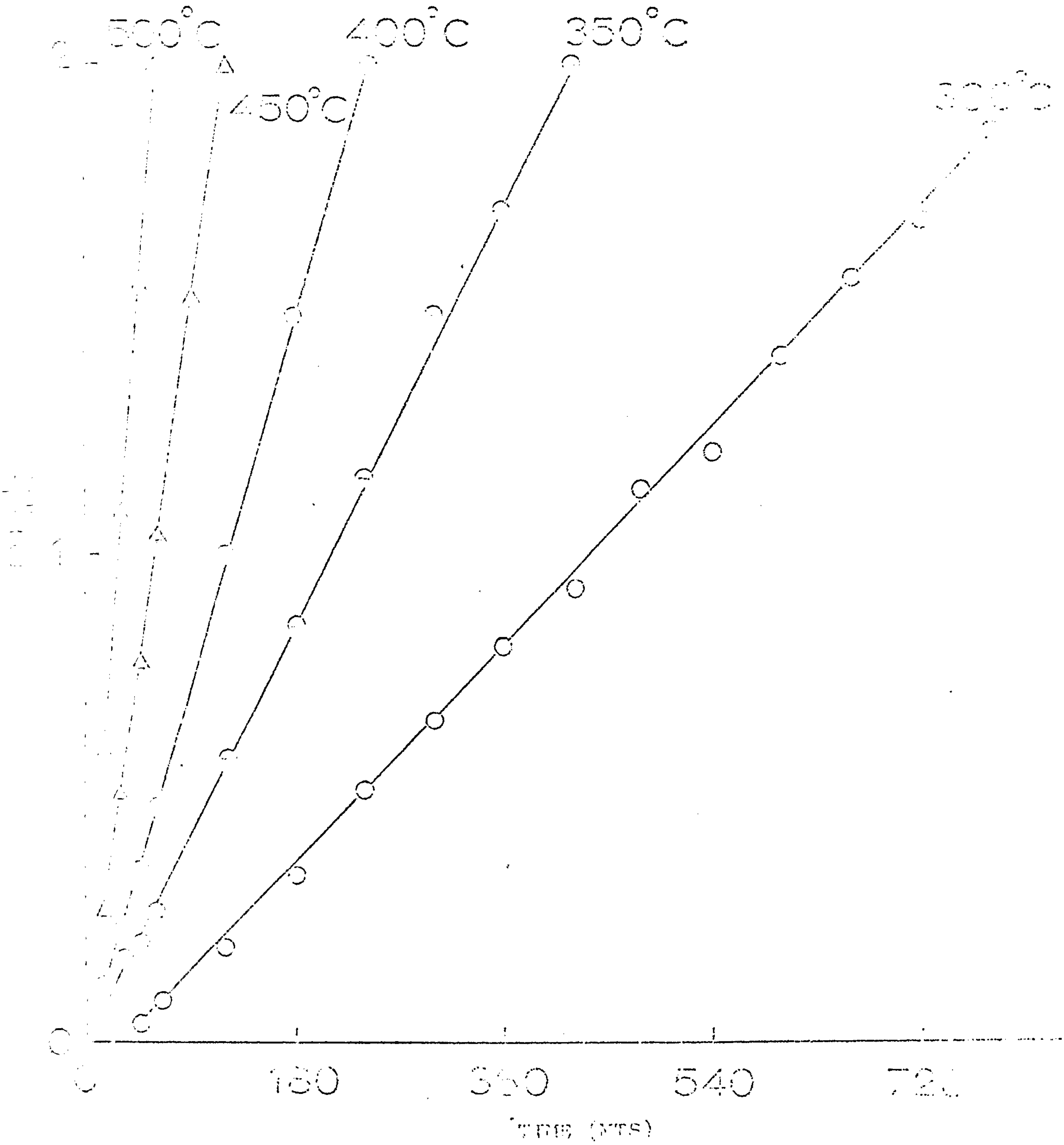


FIG. 14. PLOT OF FIRST ORDER EQUATION FOR DENITROGENATION

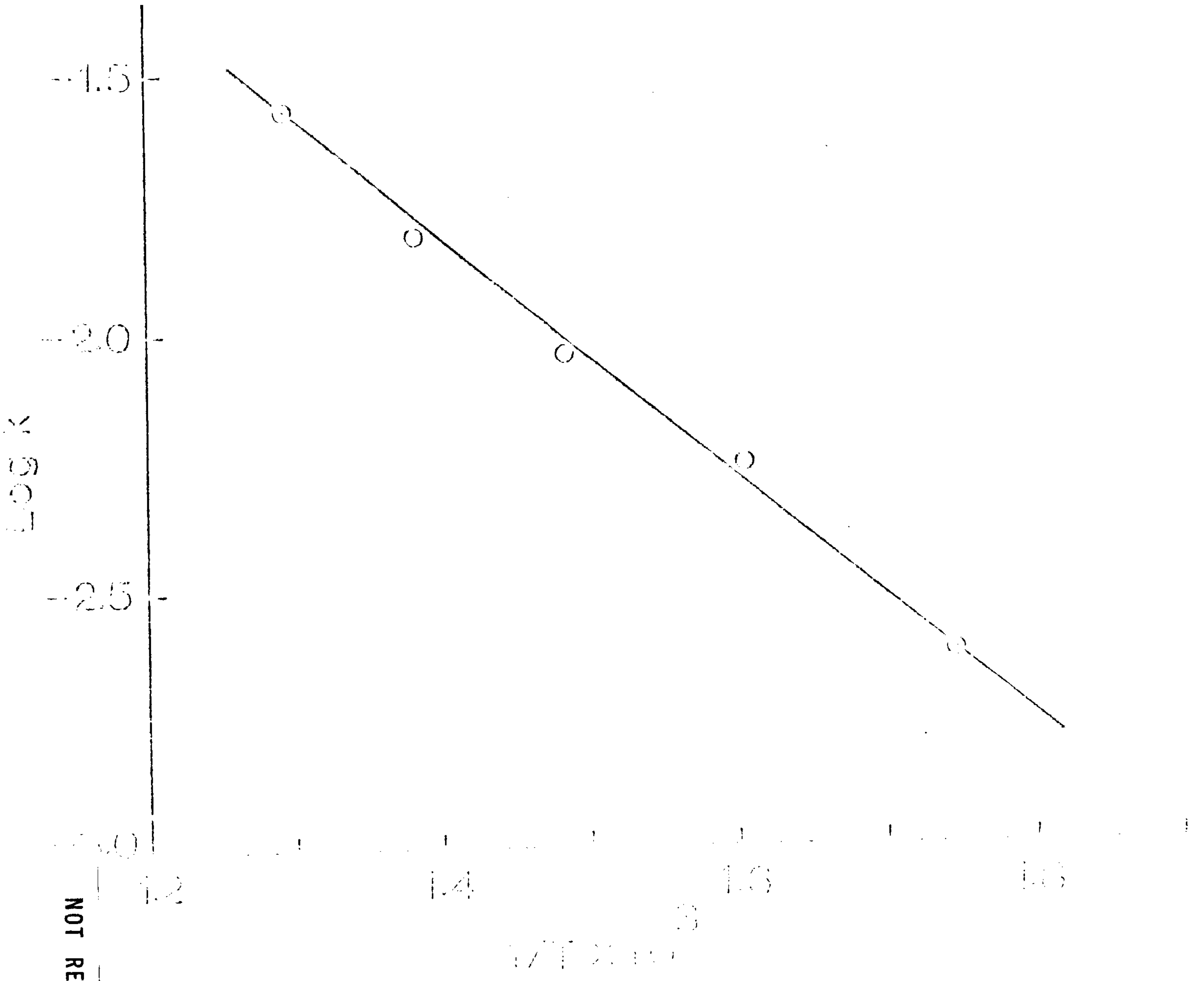


FIG. 15. PLOT OF LOG K VS $\frac{1}{T}$ FOR

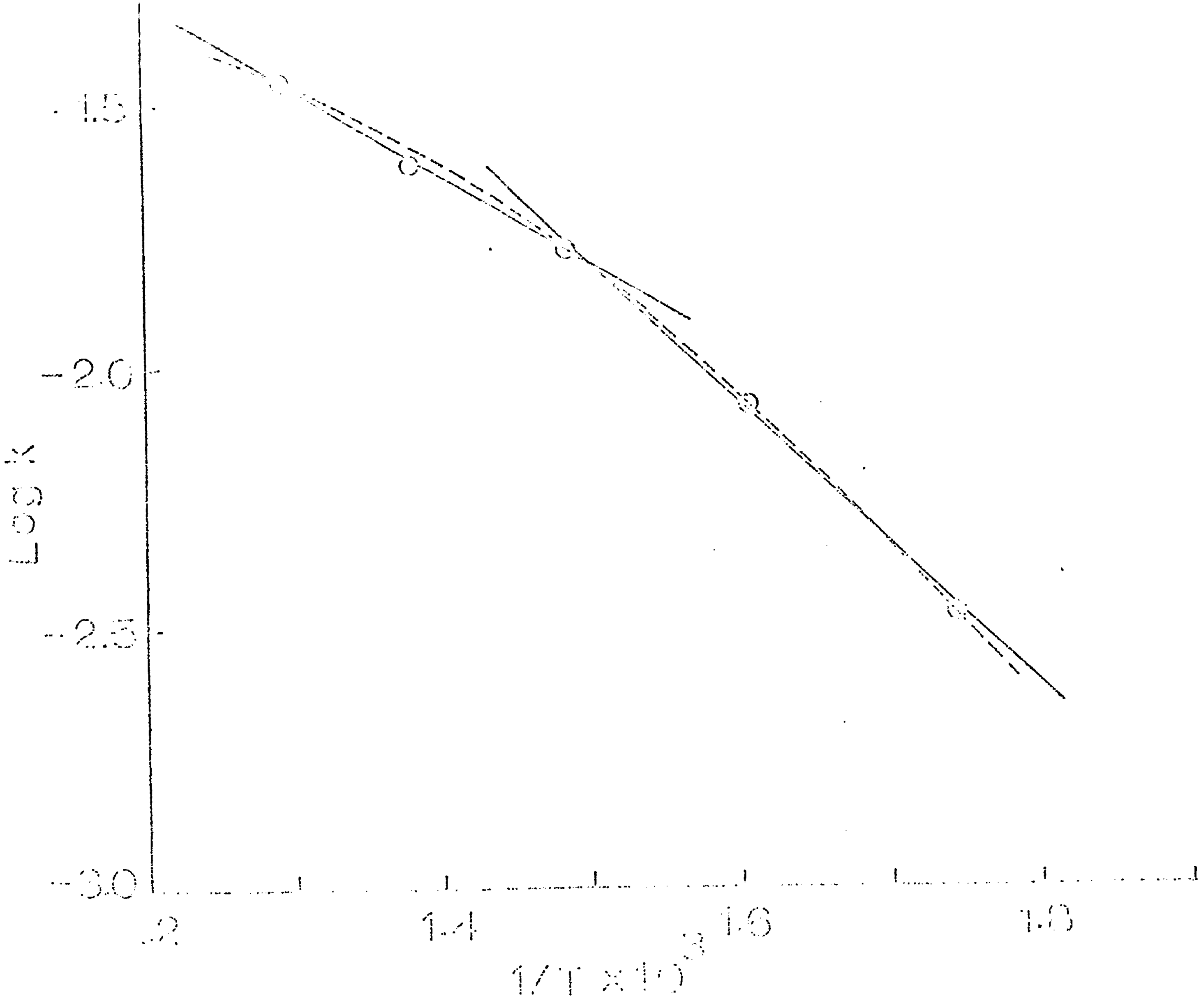
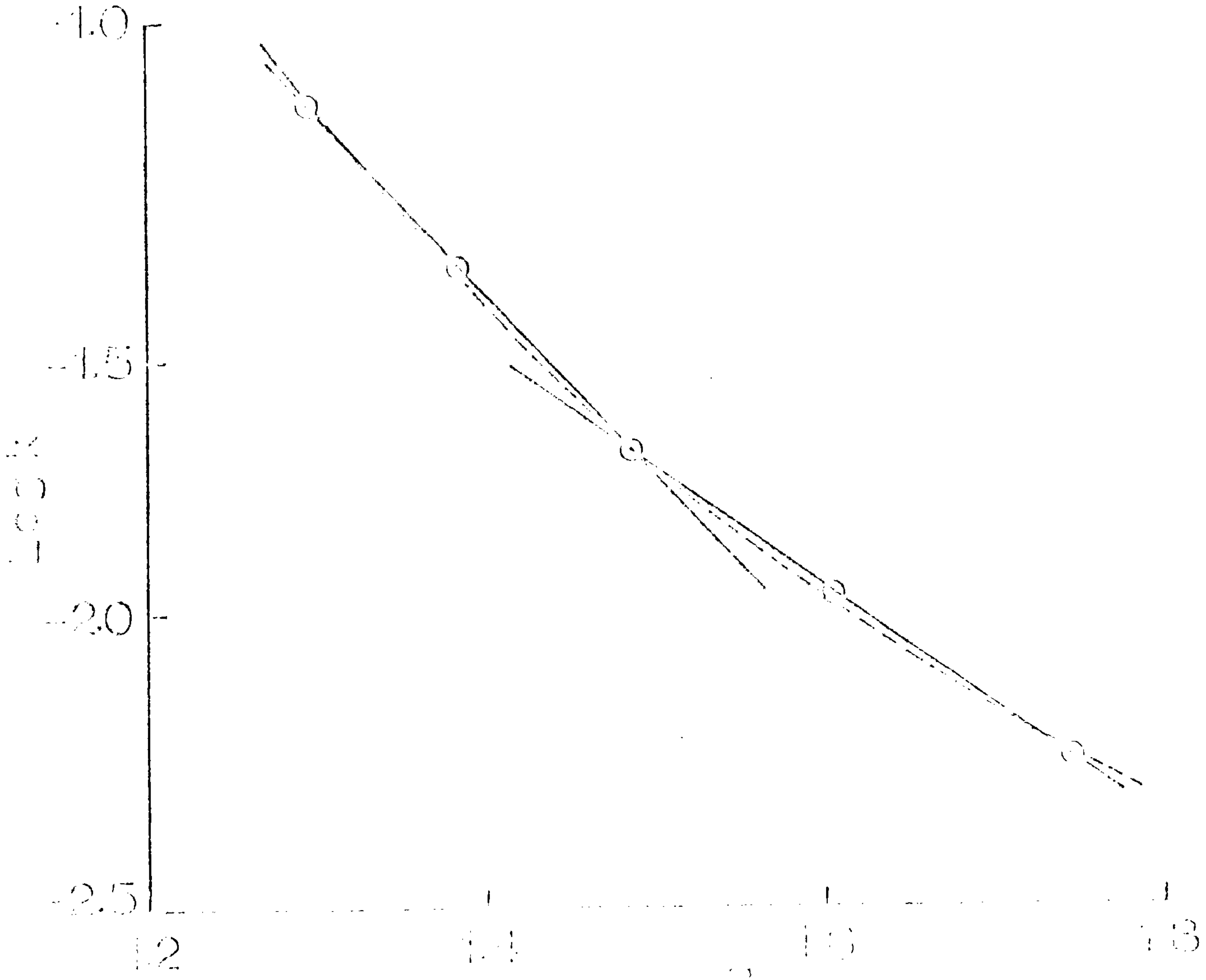


FIG. 16. PLOT OF LOG K VS $\frac{1}{T}$ FOR DEOXYGENATION


-1.0
-1.5
-2.0
-2.5
Log k
1.2
1.4
1.6
1.8
1/T x 10^3

[illegible]

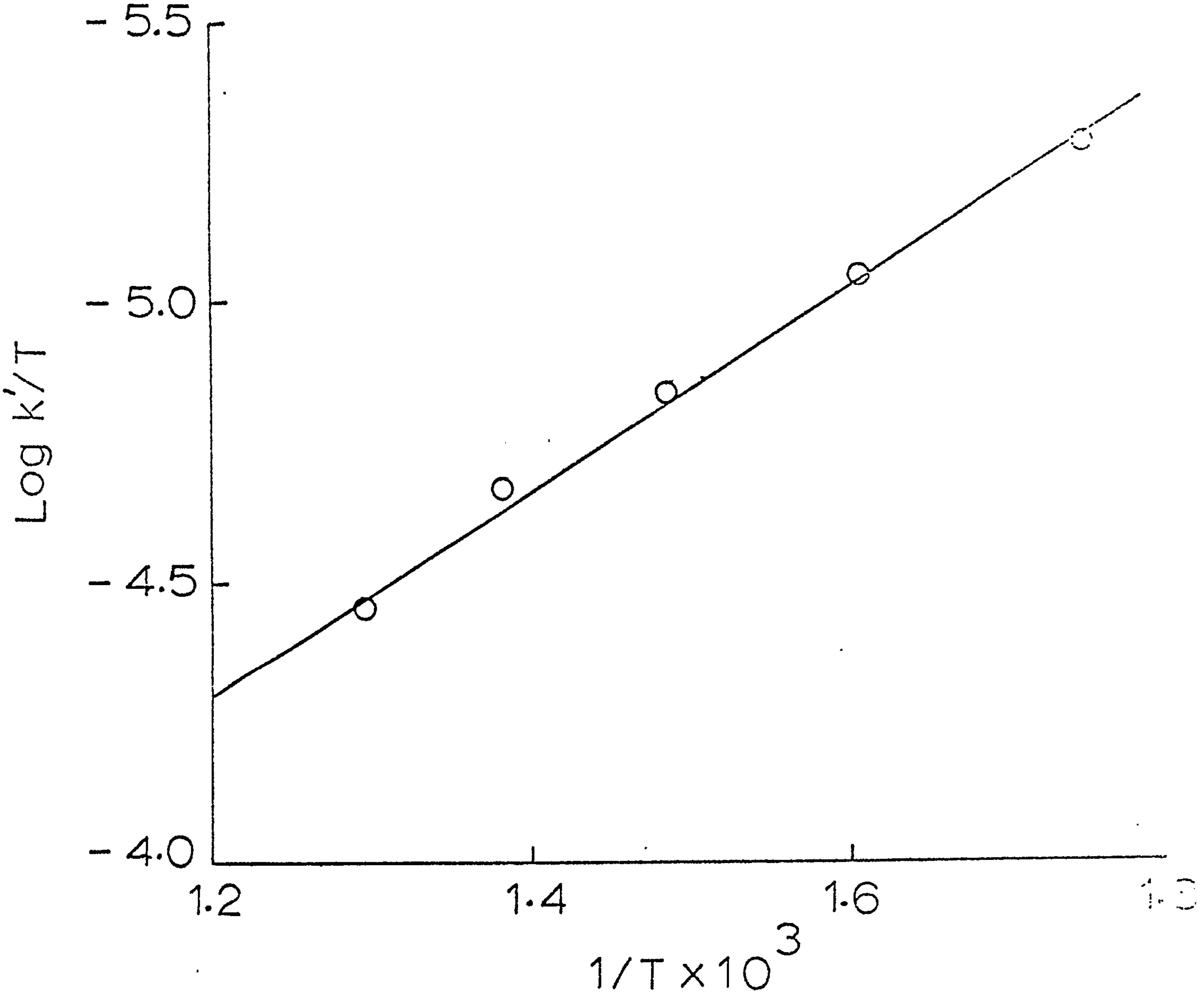


FIG. 18. ABSOLUTE REACTION RATE PLOT FOR DESULPHURIZATION

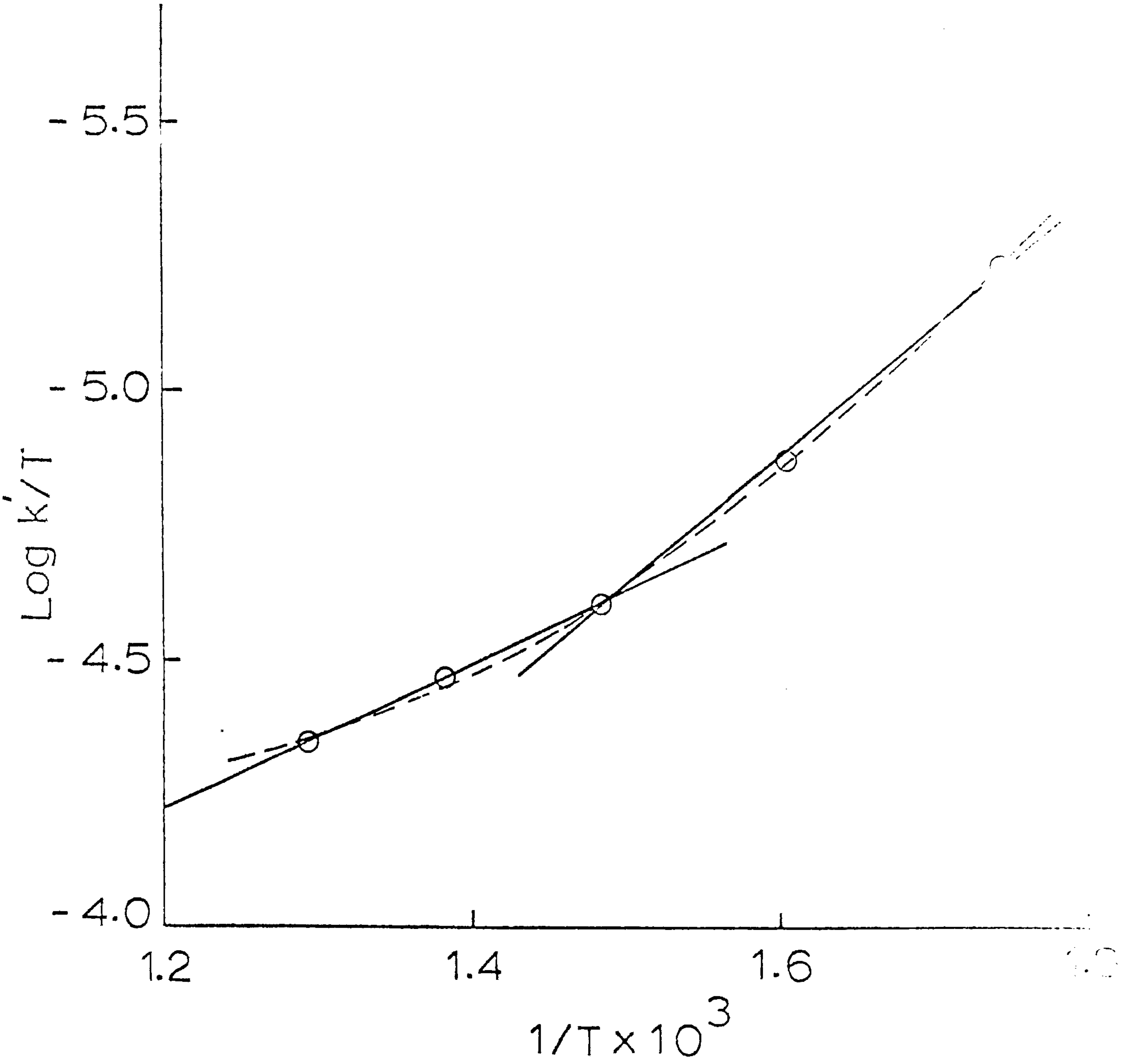


FIG. 19. ABSOLUTE RATE REACTION PLOT FOR DEOXYGENATION

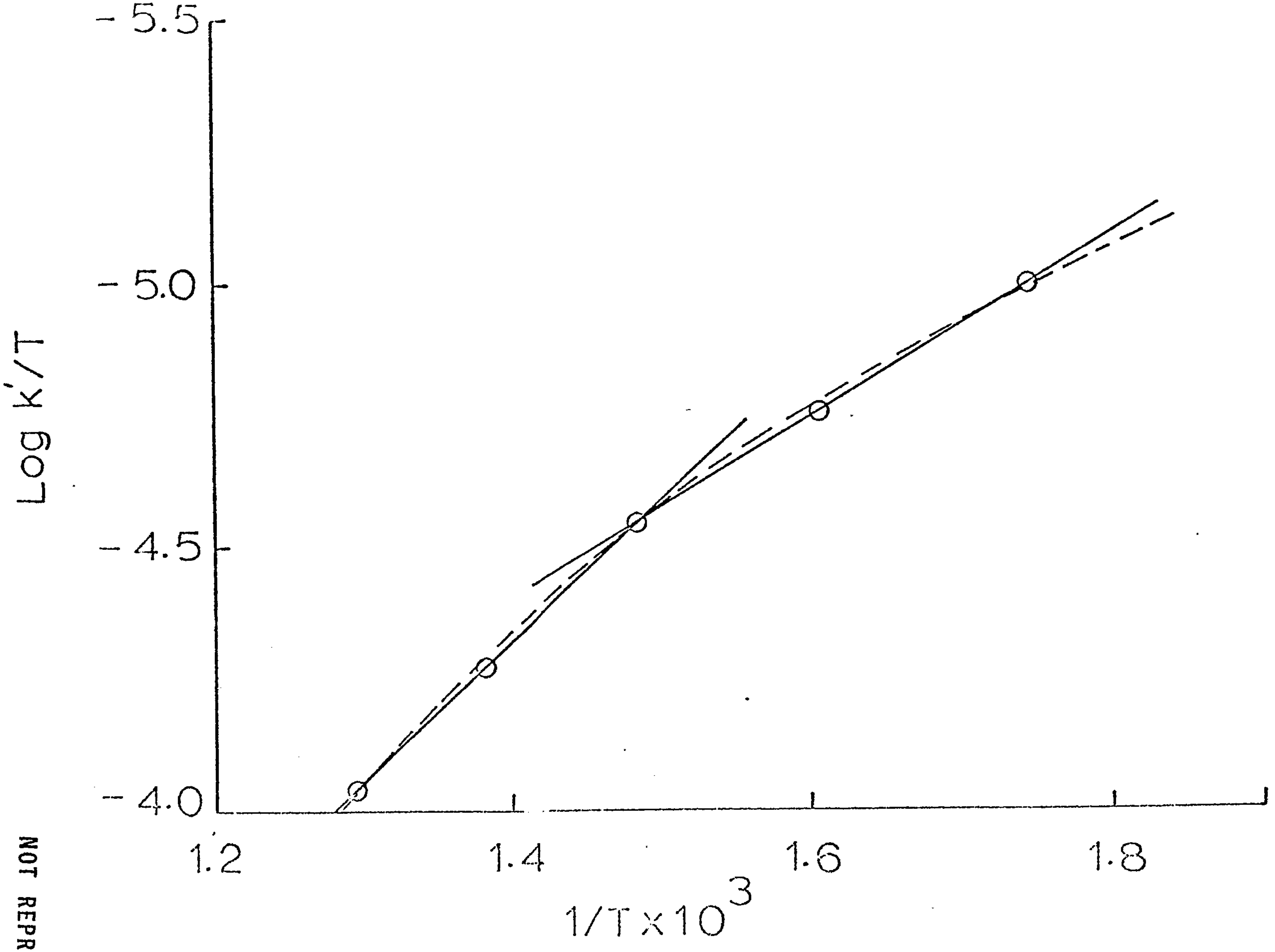


FIG. 20. ABSOLUTE REACTION RATE PLOT FOR DENITROGENATION

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