



DE82017075

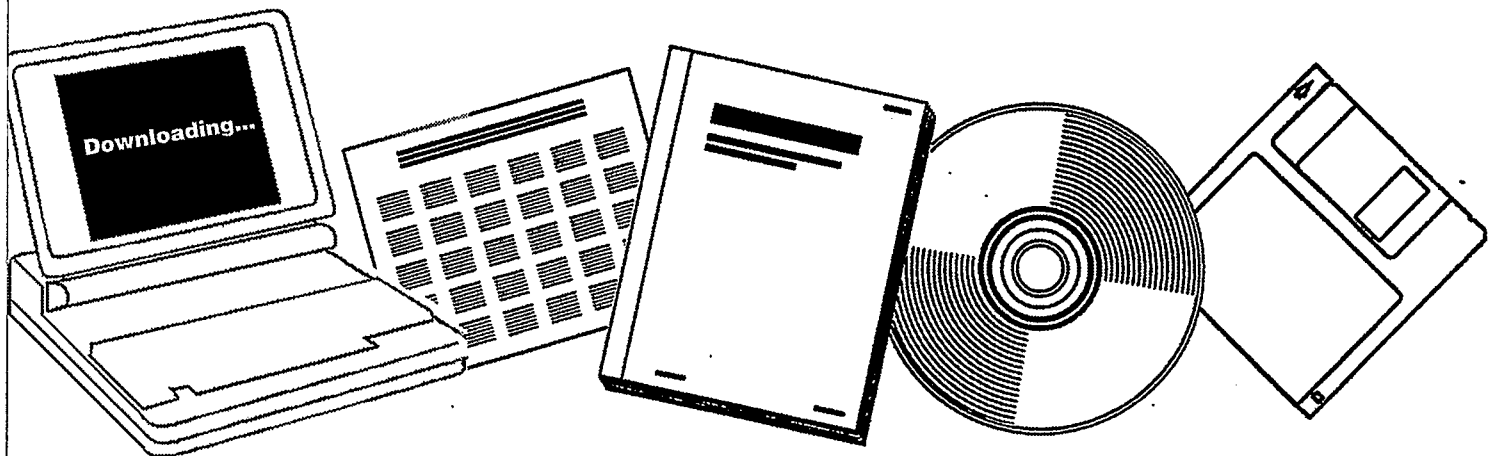
NTIS

One Source. One Search. One Solution.

THEORETICAL STUDY OF PILOT-SCALE PETC COAL-LIQUEFACTION REACTOR. FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING

SEP 1981



U.S. Department of Commerce
National Technical Information Service

DE82017075



MASTER

DOE/PC/30340--T1

DE82 017075

**A THEORETICAL STUDY OF PILOT-SCALE PETC
COAL-LIQUEFACTION REACTOR**

Final Report

September 1981

A. Calimli
J. S. Abichandani
Y. T. Shah

Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, Pennsylvania 15261

Prepared for U.S. Department of Energy
Under Contract Number

DE-FG22-80PC30340

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

1. Introduction	1
2. Mathematical Modeling	2
2.1 Residence Time Calculations	2
2.2 Smoothing of Experimental Data	4
2.3 Kinetic Models	5
2.4 Computer Simulation	8
3. Results and Discussion	9
4. Conclusion	10
Nomenclature	11
References	13
Appendix	14

1. Introduction

The liquefaction of coal leads to the formation of numerous products. It is therefore difficult to describe explicitly each chemical reaction step since the stoichiometric relations are not well understood. It is generally accepted that the performance of a coal liquefaction reactor can be modelled by lumping the products into "kinetically similar" fractions. The products are usually grouped according to their solubility or boiling points. Once the lumped product parameters are identified, the performance prediction of the reactor, requires the knowledge of (a) reaction paths correlating reactants and products and (b) hydrodynamics of the reactor.

In a continuous coal liquefaction reactor, coal slurry (coal + solvent) and gas (hydrogen) flow through a column (either coil or vertical tube). The reaction mixture first passes through a preheater where its temperature is raised to around 425°C. The slurry then passes through the main reactor where the temperature and pressure are kept essentially constant. The extent of conversion depends on the total residence time in the preheater and reactor.

The purpose of this research program was to fit experimental data on coal liquefaction to kinetic networks. The data are obtained by the Department of Energy (DOE) at Pittsburgh Energy Technology Center (PETC) coal liquefaction unit. Figure 1 is a schematic drawing of the liquefaction unit at PETC. Kentucky (Homestead) coal and a coal derived solvent from their 400 lbs/day unit were used in the experiments. Tables I and II give the analysis of the coal and solvent. The products of liquefaction were characterized as Pressphaltenes (P), Asphaltenes (A), Oils (O), Gas (G) and unreacted coal (C), according to their solubilities, as

outlined by Schultz and Mima. (1)

2. Mathematical Modeling

2.1 Residence Time Calculations

The residence of the slurry was calculated after accounting for the slurry holdup in the reactor.

$$t = \frac{L \epsilon_l}{u_l} \quad (1)$$

t = residence time of slurry, sec⁻¹

L = length of reactor, m

ϵ_l = holdup of slurry, dimensionless

u_l = superficial liquid velocity, m/sec

The slurry holdup was calculated by first calculating the gas holdup (ϵ_g) and

$$\epsilon_l = 1 - \epsilon_g \quad (2)$$

Two different expressions were used for the calculations of the gas holdup, and the results were compared. The expressions used were

(A) (Shah et al.) (2)

$$\epsilon_g = 0.07032 \cdot V_g^{0.52} / D^{0.08} \quad (3)$$

where

V_g = gas velocity, cm/sec

D = diameter, cm

and

(B) (Bonnecaze et al.)⁽³⁾

$$\epsilon_g = 1 - \frac{(1-\lambda)}{u_T/u_{NS}} \quad (4)$$

where

u_T = transitional velocity of liquid slug, ft/sec

u_{NS} = no-slip velocity, $\frac{Q_g + Q_l}{A_p}$, ft/sec

Q_g = volumetric flow rate of gas, ft³/sec

Q_l = volumetric flow rate of liquid, ft³/sec

A_p = cross-sectional area, ft²

$$\lambda = Q_l / (Q_l + Q_g) \quad (5)$$

$$u_T = \left[C_1 + \frac{du_{BR}}{u_{NS}} \right] u_{NS} \quad (6)$$

for uphill slug flow, $\delta = 1$

$$C_1 = 1.22$$

$$u_{BR} = 0.325 \left(1 - \frac{\rho_G}{\rho_L} \right) \sqrt{gD} \quad (7)$$

where

g = acceleration due to gravity, ft/sec²

ρ_L = liquid density, lb/ft³

ρ_G = gas density, lb/ft³

D = diameter, ft

u_{BR} = bubble rise velocity, ft/sec

The results obtained for ϵ_g by the two methods were not very different. For example at 450°C

ϵ_g by method (a) : 0.300

by method (b) : 0.243

Method (a) was chosen for all calculations.

2.2 Smoothing of Experimental Data

An attempt was made to fit analytical expressions to the experimental data. However, our results showed that except for unreacted coal, no other data could satisfactorily be represented by any analytical expression. The least square criterion was used to fit the data.

$$\text{Sum of squares of errors (SSE)} : \sum_{i=1}^{N_T} (C_E - C_M)^2 \quad (8)$$

where N_T = number of data points

C_E = experimental data

C_M = model predicted data

To obtain an acceptably small value of SSE, complicated expressions with many constants were needed. Such expressions predicted extremely erroneous results for space times at which experimental data were not available. Hence it was decided to use all the available experimental data.

The experimental data for unreacted coal could very well be represented by an exponential fit of form

$$C_M = \exp(-at) \quad (9)$$

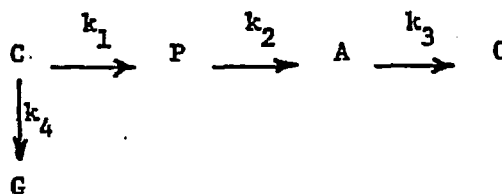
It was confirmed that the optimum rate constants obtained by using all data, agreed with the value obtained for the constant α in all cases ($\alpha = k_1 + k_2 + k_3 + k_4$).

2.3 Kinetic Models

The type of equations which represent the kinetic model depend on the reactor configuration used. The length to diameter ratio of the coal liquefaction reactor at PETC is around 700, hence plug flow conditions are assumed to prevail.

For this study, reactions of dissolution and conversion of intermediates are considered to be first order and irreversible. Three mathematical models based on preassumed kinetic networks involving unreacted coal (C), preasphaltenes (P), asphaltenes (A), oils (O) and gases (G), are investigated and compared with the experimental data. The models are illustrated as follows.

(A) Model 1 (4 constant model)



The differential equations that represent the rate of disappearance and formation of the species, in the above model are as follows

$$\frac{dC}{dt} = - (k_1 + k_4) C \quad (10)$$

6

$$\frac{dP}{dt} = k_1 C' - k_2 P \quad (11)$$

$$\frac{dA}{dt} = k_2 P - k_3 O \quad (12)$$

$$\frac{dO}{dt} = k_3 O \quad (13)$$

and

$$\frac{dG}{dt} = k_4 C' \quad (14)$$

where $C' = C - u \quad (15)$

and $u =$ unreactive fraction of coal.

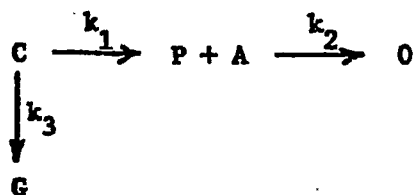
Initial conditions using weight fractions and on moisture and ash free coal basis, are

at $t = 0$

$$\begin{aligned} C &= 1 \\ P = A = O = G &= 0 \end{aligned} \quad (16)$$

It is necessary to incorporate the concept of unreactive fraction of coal because without it the model would predict zero concentration of coal at long residence times, although the data show a finite value for C at long times. For all cases u is assumed to be independent of temperature and equal to 1.25 percent of C .

(B) Model 2 (3 constant model)



This model is essentially the same as model 1 except that pre-asphaltenes and asphaltenes are grouped as one species. The differential equation and initial conditions that describe this model are

$$\frac{dC}{dt} = - (k_1 + k_4) C' \quad (17)$$

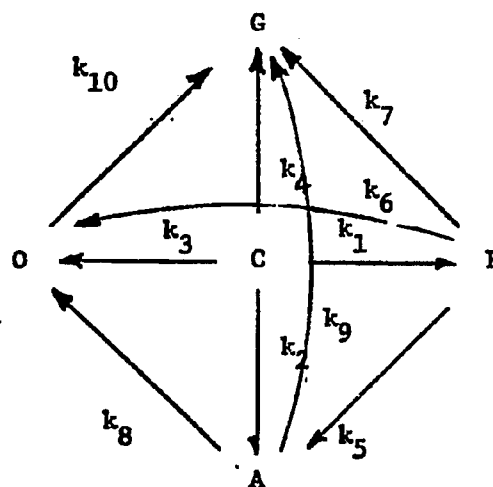
$$\frac{d(P+A)}{dt} = k_1 C' - k_2 (P+A) \quad (18)$$

$$\frac{dO}{dt} = k_2 (P+A) \quad (19)$$

$$\frac{dG}{dt} = k_4 C' \quad (20)$$

and $t = 0$ $C = 1$ $P + A = 0 = G = 0$ (21)

(C) Model 3 (10 constant model)



This mode contains maximum number of constants and was expected to give the best fit to the data. This model was selected so that the goodness of fit for the other two models can be compared to the best fit possible.

Equations:

$$\frac{dC}{dt} = - (k_1 + k_2 + k_3 + k_4) C' \quad (22)$$

$$\frac{dP}{dt} = k_1 C' - (k_5 + k_6 + k_7) P \quad (23)$$

$$\frac{dA}{dt} = k_2 C' + k_5 P - (k_8 + k_9) A \quad (24)$$

$$\frac{dO}{dt} = k_3 C' + k_6 P + k_8 A - k_{10} O \quad (25)$$

$$\frac{dG}{dt} = k_4 C' + k_7 P + k_9 A + k_{10} O \quad (26)$$

The initial conditions are the same as in equation (16).

2.4 Computer Simulation

The integration of the differential equations were carried out with the aid of a International Mathematical and Statistical Library (IMS) package program, DVERK. The rate constants were obtained by using a computer code developed for non-linear continuous optimization problem. The pattern search method developed by Hooke and Jeeves⁽⁴⁾ was used to obtain the best values for the constants. Details of this technique are presented by Krishnamurthy.⁽⁵⁾

The least square criterion was used to optimum values of the rate constants. The objective function was defined as

$$\text{obj. fu} = \frac{\sum_{i=1}^{N_t} \sum_{j=1}^{N_{ch}} (C_m - C_E)^2}{\sum_{i=1}^{N_t} \sum_{j=1}^{N_{ch}} C_E} \quad (27)$$

3. Results and Discussion

The optimum rate constants and the objective functions obtained are presented in Tables III, IV, and V. As expected the objective function for the 10 constant model are the minimum in all cases. However, the rate constants do not follow any particular trend. Hence we conclude that although the 10 constant model mathematically fits the data best, it does not represent the physical nature of the process.

Comparing models 1 and 2, model 1 gives an overall lower value for the objective function, although for 2 isotherms, namely 450 and 400°C, model 2 shows lower sum of squares. It should be noted that although model 1 has 4 degrees of freedom, it models preasphaltenes and asphaltenes as different species, unlike model 2. It is also clear that model 2 provides a poor fit for the isotherm at 425°C.

It is evident that the optimum rate constants obtained for models 1 and 2 exhibit Arrhenius-type temperature behavior, in almost all cases. The rate constants were fitted to the Arrhenius law and the results are included in Tables III and IV. The rate parameters are compared with those obtained by Cronauer et al.⁽⁶⁾ and Shalabi et al.⁽⁷⁾ in Table VI. Most of the kinetic parameters differ substantially from the values calculated here. This is not surprising because the coal and solvents used in all studies are different from each other.

Figures 2 to 37 show the experimental and model predicted data, while the Arrhenius plots for the constants are illustrated in Figures 37 to 44.

4. Conclusion

Three kinetic networks have been fitted to the experimental data on coal liquefaction. The physical nature of the process is well represented by models 1 and 2, while although model 3 gives the best mathematical fit but is conceptually inconsistent. Model 1 gives a better fit to the data compared to model 2. The rate constants have been correlated by the classical Arrhenius law.

The kinetic parameters obtained by other investigators do not compare well with those obtained in this study. This is expected due to the different types of coals and solvents used in different investigations.

Nomenclature

A	asphaltenes, gm/gm _(total)
A _P	cross-sectional area, ft ²
C	coal (total), gm/gm _(total)
C'	reactive part of coal as defined in equation (15), gm/gm _(total)
C _E	experimental data
C _M	model predicted data
D	diameter, cm
E	activation energy, cal/g-mol
g	acceleration due to gravity, ft/sec ²
G	gases, gm/gm _(total)
k	rate constant, min ⁻¹
\bar{k}	frequency factor, min ⁻¹
L	length of reactor, m
N _{Ch}	number of species
N _T	number of data points
O	oils, gm/gm _(total)
P	preasphaltenes, gm/gm _(total)
Q _g , Q _l	volumetric flow rate of gas and liquid, ft ³ /sec
R	gas law constant, cal/g-mol °K
t	space time, min
u	unreactive fraction of coal, gm/gm _(total)
u _{BR}	bubble rise velocity, ft/sec
u _l	superficial liquid velocity, m/sec

u_{NS}	no-slip velocity, ft/sec
u_T	terminal velocity of liquid slug, ft/sec
V_g	gas velocity, cm/sec

Greek Letters

α	constant defined in equation (9)
δ	constant defined in equation (6)
ϵ_g	gas holdup
ϵ_l	liquid holdup
λ	defined in equation (5)
ρ_g	gas density, lb/ft ³
ρ_l	liquid density, lb/ft ³

References

1. Schultz, H. and M.J. Mima, "Comparison of Methods for the Determination of Asphaltenes, Oils, and Insolubles: Part I - A Coal Derived Liquid," PETC/TR-80/3, May (1980).
2. Shah, Y.T., "Gas-Liquid-Solid Reactor Design," McGraw-Hill International Book Company (1978).
3. Bonnexaze, R.H., W. Erskine, Jr., and E.J. Greskovich, "Holdup and Pressure Drop for Two-Phase Slug Flow in Inclined Pipelines," AIChE 17(5), 1109 (1971).
4. Hooke, R. and Jeeves, T.A., "Direct Search Solution of Numerical and Statistical Problems," Journal Association Computing Mach. 8(2), 212 (1961).
5. Krishnamurthy, S., Ph.D. Thesis, University of Pittsburgh (1978).
6. Cronauer, D.C., Y.T. Shah and R.G. Ruberto, "Kinetics of Thermal Liquefaction of Belle Ayr Subbituminous Coal," Ind. Eng. Chem., Proc. Des. Dev., Vol. 17, No. 3, 281 (1978).
7. Shalabi, M.A., R.M. Baldwin, R.L. Bain, J.H. Gray, and J.O. Golden, "Noncatalytic Coal Liquefaction in a Donor Solvent. Rate of Formation of Oil, Asphaltenes, and Preasphaltenes," Ind. Eng. Chem., Process Des. Dev., Vol. 18, No. 3, 474 (1979).

Appendix

In this section a program listing is presented.

REVISED PROGRAM

C*****
C MODEL /*****
C THIS PROGRAM CALCULATES THE RATE CONSTANTS FOR PLUG FLOW
C (DDE PROJECT)
C

1 C SUBROUTINE MODEL (X,Y,KZZZZ)

C
C
C *****
C THIS SUBROUTINE IS CALLED BY EXPLORE TO READ THE
C INITIAL DATA AND TO EVALUATE THE OBJECTIVE FUNCTION
C

C *****
C
C X IS THE VECTOR OF THE RATE CONSTANTS
C
C Y IS THE OBJECTIVE FUNCTION
C WHICH IS DEFINED IN OBJFU
C

C-----
C
C PROGRAM CONTROL :
C KZZZZ = 1 READ THE INITIAL DATA AND RETURN
C
C KZZZZ = 2 DEFINE AND EVALUATE THE CONSTRAINTS
C RETURN
C
C KZZZZ = 3 DEFINE AND EVALUATE THE OBJECTIVE FUNCTION
C AND RETURN
C
C KZZZZ = 4 WRITE OPTIONAL OUTPUT AND RETURN
C

2 C DIMENSION G(25),GB(25),PD(25),SC(25),X(25),XDUMMY(25),XMIN(25),
3 1 XMAX(25)
4 C DIMENSION Q(6),X1(25)
5 C COMMON DELTA,DX,EFAC,EPSLN,G,GRADX,PNLTY,SC,SIGMA0,SIGMA1,TIME,
6 1 XDUMMY,XMIN,XMAX,YDUMMY,ZDUMMY
7 C COMMON IGRAD,IOBJ,IOUT,IT,ITMAX,JEQ,JINEQ,KCLIMB,KMIN,M,N,KIN,KOUT
8 C DOUBLE PRECISION DELTA,DX,EFAC,EPSLN,G,GB,GRADX,PD,PNLTY,PROFIT
9 C DOUBLE PRECISION Q,SC,SIGMA0,SIGMA1,TIME,X,XDUMMY,XMAX,XMIN
10 C DOUBLE PRECISION Y,YDUMMY,ZDUMMY
C COMMON/KK/ X1
C COMMON/AAA/ NK

C
C
C *****
C *****

```

C
C
11          GO TO (10,20,30,50), KZZZZZ
C
C
C*****
C*****
C
C
12 10      CONTINUE
C=====
C
C
C
13          CALL INDAT
C
C
C=====
C
14          RETURN
C
C
C=====
15 20      CONTINUE
16          G(1)=X(1)+X(2)+X(3)+X(4)-0.14986
C          G(2)=X(5)+X(6)+X(7)-0.02068-0.02177-0.1
C          G(3)=X(8)+X(9)- 0.02666055
C=====
C
C
C=====
17          RETURN
C
C
C=====
18 30      CONTINUE
C=====
C
C
19          DO 40 I=1,NK
20             XI(I)=X(I)
21          40 CONTINUE
22             CALL CHECK
23             CALL OBJFU(Y)
C             WRITE(06,845) Y
C
C
C=====
24          RETURN
C
C
C=====

```

```

C
C
25 50 CONTINUE
C=====
C
C
C THE OPTIMUM SET RATE CONSTANTS AND
C THE FINAL OBJECTIVE FUNCTION
C ARE WRITTEN.
C
C
26 WRITE(6,10020)
27 DO 60 IJL=1,NK
28 WRITE(6,10030) IJL,X(IJL)
29 60 CONTINUE
30 WRITE(6,10050) Y
31 WRITE(8,10040) (X(L),L=1,JINEQ)
C
C
C=====
C*****
C=====
C*****
C=====
C
C
32 RETURN
33 10010 FORMAT(' YYYYYYYY',E)
34 10020 FORMAT('1', ' KINETIC PARAMETERS',/' ',20('*'),/' ',20('*'),//)
35 10030 FORMAT(' ', ' K(',12,') = ',E,/)
36 10040 FORMAT((11E13.7))
37 10050 FORMAT(' ', ' FINAL OBJECTIVE FUNCTION= ',E,//////////)
38 END

```

REVISED PROGRAM

1 SUBROUTINE INDAT

C
C
C=====

C THIS SUBROUTINE IS CALLED BY MODEL TO READ THE INITIAL DATA
C
C
C=====

COMPONENT	NUMBER
COAL	1
PREASPHALTENES	2
ASPHALTENES	3
OILS	4
GASES	5

C
C=====

2 COMMON/AA/ NT,NK,NCHESP,TE,C
3 COMMON/AAA/ NNK
4 DIMENSION CINT(5,220),RFRAC(5),II(5,25),IM(5,20)
5 DIMENSION TE(100),C(5,100)
6 DIMENSION I1(10)
7 REAL II
8 REAL IM

C
C=====

C NT : NUMBER OF EXP. DATA
C NK : NUMBER OF RATE CONSTANTS
C NCHESP : NUMBER OF CHEMICAL COMPONENTS
C

9 IF(I3.GT.0) GO TO 10
10 I3=1
11 READ(16,10C10)NT,NK,NCHESP
12 NNK=NK
13 CONTINUE

14 NEXP=NT
15 N=NK

C
C=====

C TE(K) : EXP. RESIDENCE TIME
C C(J,K) EXP. WT. % OF THE CHEMICAL COMPONENT J AT THE RESIDENCE TIME
C

16 IF(I5.GT.0) GO TO 50
17 I5=1
18 DO 40 K=1,NT

```
19      READ(24,*)TE(K),(C(J,K),J=1,NCHESP)
20      SUM=0.0
21      DO 20 J=1,NCHESP
22      SUM=SUM+C(J,K)
23      20 CONTINUE
24      DO 30 J=1,NCHESP
25      C(J,K)=C(J,K)/SUM
26      30 CONTINUE
27      WRITE(6,10030)K,TE(K),(C(J,K),J=1,NCHESP)
28      40 CONTINUE
29      50 CONTINUE
30      RETURN
31      10010 FORMAT(3I)
32      10020 FORMAT(' ',F10.3,5E14.8)
33      10030 FORMAT(' ',I4,F10.3/' ',5E15.4/)
34      END
```



```

C
C      W(J,I) = 1./C(J,I)
C
17      W(J,I)=1.
C
C      W(J,I) =ABS (W(J,I))
C
C
C
18      W(J,I) = W(J,I)**2
      GO TO 30
C
C
19      W(J,I) = 1.0
20      CONTINUE
C
21      TOT = 0.0
C
22      DO 50 J=2,4
C
23          T = 0.0
C
24          DO 40 I=1,NT
C
25              T = T + E(J,I)*W(J,I)
C
C
26          CONTINUE
C
27          TOT = TOT + T
C
28      50 CONTINUE
C
29      Y=TOT
30      WRITE(06,10020) Y
      WRITE(06,865) Y
31      RETURN
C
32 10010 FORMAT(' ERROR ',2I2,E10.4,10E10.4,/)
33 10020 FORMAT('#####E)
34 10030 FORMAT('##### Y',E)
35      END

```


REVISED PROGRAM

```

C
C
1      SUBROUTINE CHECK
C
C
2      DIMENSION Y(5),WORK(205),IWORK(5),CC(24),W(5,9)
3      EXTERNAL F
4      COMMON/AA/ NT,NK,NCHESP,TE,C
5      COMMON/FF/CO,K,NCHES,NK1,IIII(5,20),IL(5,20)
6      REAL K(20),K1(20)
7      DIMENSION CO(5,20),CH(5,100),TE(100),C(5,100)
8      COMMON/KK/ K1
9      COMMON/CC/ CM
C
C=====
10     OPEN (UNIT=56)
11     NCHES=NCHESP
12     NK1=NK
C
C-----
C
13     DO 10 I=1,20
14     K(I)=K1(I)
15     10 CONTINUE
C
C-----
C
16     TMAX = TE(NT)
C
17     DO 20 I=1,NCHESP
18     Y(I)=C(I,1)
19     CM(I,1)=Y(I)
20     20 CONTINUE
21     TOUT=0.0
22     WRITE(56,10040) TOUT,(Y(I),CM(I,1),I=1,5)
C
C-----
C=====
C-----
C
C
C
C      THE CONFIGURATION MATRIX IS READ
C-----
C
23     NCHESP = 5
24     NEQN = NCHESP
C
25     IF(I2.GT.0) GO TO 40
26     I2=1
27     DO 30 I=1,NCHESP
28     DO 30 L=1,NK
29     READ(10,10020) CO(I,L),LL,ID
30     IIII(I,L) = LL
31     IL(I,L) = ID
C
C
C      WRITE(6,105) CO(I,L),I,L,IIII(I,L),IL(I,L)
C

```

```

32 30 CONTINUE
33 40 CONTINUE
C
C
C
C
C
C=====
C
C
C=====
C
C      INTEGRATION
C-----
34      T=0.0
35      TOL=0.0001
36      IDN=1
37      LL=1
38      TOUT=0.0
39 50 CONTINUE
40      LL=LL+1
41      IF(LL.GT.NT) GO TO 70
42      TOUT=TE(LL)
43      CALL DVERK(NCHESP,F,T,Y,TOLT,TOL,IDN,CC,NCHESP,W,IER)
44      DO 60 LI=1,5
45      CM(LI,LL)=Y(LI)
46 60 CONTINUE
47      WRITE(56,10040) TOUT,(Y(I),C(I,LL),I=1,5)
C
48      GO TO 50
49 70 CONTINUE
50      CLOSE (UNIT=56)
C
C-----
C
51      RETURN
52 10010 FORMAT(10E)
53 10020 FORMAT(" ",F3.0,2I1)
54 10030 FORMAT(" THE VALUE OF IFLAG = ",I)
55 10040 FORMAT(" ",12E)
56 10050 FORMAT(" ",F3.0,2X,4(2X,I5)//)
57 10060 FORMAT(10E)
58      END

```


TABLE II
 FB-60 FEED VEHICLE ANALYSIS SUMMARY

Source: Vehicle oil from operations on 400 lb/d unit
 Homestead Ky coal
 2000 psig
 no catalyst, empty reactor

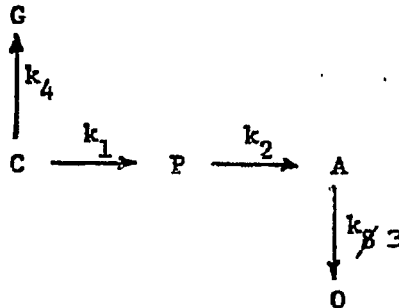
<u>Ultimate Analyses</u>	<u>Operation FB-60¹</u>	<u>Operation FB-57³</u>
C	85.49 wt%	85.83 wt%
H	7.87	7.27
N	1.4	1.43
S	0.60	.63
Fe ²	.46	.34
 <u>Solvent Analysis Summary</u>		
Oils	68.83 wt%	57.5 wt%
Asphaltene	26.45	34.5
Benzene Insolubles	4.72	5.7
Ash on \emptyset Insols	41.6	39.47

¹ Average of nine analyses.

² Fe determined separately.

³ Average of four analyses.

TABLE III
RATE CONSTANTS FOR MODEL 1



Model 1 (4 constant model)

Temperature °C	450	425	400	375
k_1 (min ⁻¹)	0.1548	0.1478	0.0992	0.0806
k_2	0.1226	0.1293	0.0573	0.0280
k_3	0.0636	0.0224	0.0175	0.0426
k_4	0.0157	0.0065	0.0026	0.0022
Obj. fn	0.0469	0.0958	0.1262	0.0298

Arrhenius fit: T in °K, R = 1.98 cal/g-mol °K.

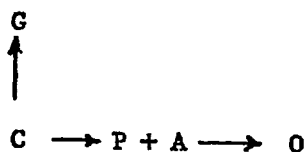
$$k_1 = 76.26 \exp \{-8.819 * 10^3/RT\}$$

$$k_2 = 1.39 * 10^5 \exp \{-1.97 * 10^4/RT\}$$

$$k_3 = 1.71 * 10^6 \exp \{-2.479 * 10^4/RT\}$$

$$k_4 = 6.75 * 10^5 \exp \{-2.549 * 10^4/RT\}$$

TABLE IV
RATE CONSTANTS FOR MODEL 2



Model 2 (3 constant model)

Temperature °C	450	425	400	375
k_1 (min ⁻¹)	0.1548	0.1478	0.0992	0.0806
k_2	0.03944	0.01247	0.00787	0.01009
k_3	0.0157	0.0065	0.0026	0.0022
obj. fn.	0.04072	0.2439	0.1123	0.0698

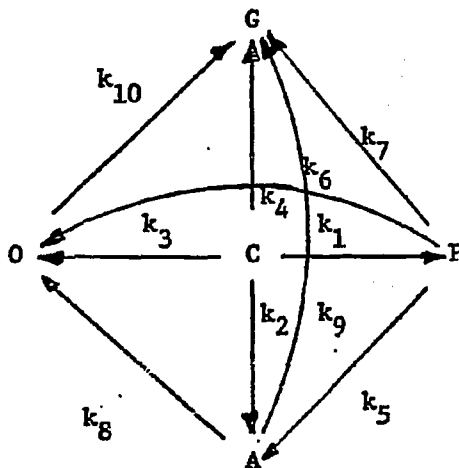
Arrhenius fit: T in °K, R = 1.987 cal/g-mol°K

$$k_1 = 76.26 \exp \{-8.819 * 10^3 / RT\}$$

$$k_2 = 8.13 * 10^7 \exp \{-3.1 * 10^4 / RT\}$$

$$k_3 = 6.75 * 10^5 \exp \{-2.549 * 10^4 / RT\}$$

TABLE V
RATE CONSTANTS FOR MODEL 3



Model 3 (10 constant model)

Temperature °C	450	425	400	375
k_1 (min^{-1})	0.1792	0.0321	0.0352	0.0636
k_2	0.0	0.079	0.0431	0.0
k_3	0.0024	0.043	0.0208	0.0204
k_4	0.0	0.0093	0.003	0.0
k_5	0.0011	0.0	0.0085	0.0169
k_6	0.0307	0.011	0.0	0.0
k_7	0.0058	0.0	0.0	0.0
k_8	0.0	0.0006	0.0028	0.0
k_9	0.0	0.0	0.0002	0.0
k_{10}	0.00226	0.0	0.0	0.0073
obj. fn.	0.026	0.032	0.0191	0.016

TABLE VI
COMPARISON OF KINETIC PARAMETERS

Reactor	CSFR (a)		Batch (b)		Plug Flow (c)	
Technique	Isothermal (400-470°C)		Isothermal (350-400°C)		Isothermal (375-450°C)	
Coal	Belle Ayr (Subbituminous)		Kentucky No. 9 (Bituminous)		Homestead, Kentucky Coal	
Solvent	Hydrogenated Anthracene Oil	Hydrogenated Phenanthrene	Tetralin		Coal Derived Solvent	
Reaction (d)	E	\bar{k}	E	\bar{k}	E	\bar{k}
C → P	13800	$2.81 \cdot 10^3$	4300	4.94	29000	$2.25 \cdot 10^6$
P → A	12800	$9.66 \cdot 10^2$	33900	$2.48 \cdot 10^9$	19700	$1.39 \cdot 10^5$
A → O	16000	$1.42 \cdot 10^3$	25600	$1.53 \cdot 10^7$	24790	$1.71 \cdot 10^6$
C → G	21500	$8.72 \cdot 10^5$	10500	$3.85 \cdot 10^2$	25490	$6.75 \cdot 10^5$

(a) Cronauer et al. (1978), Ref. No.

(b) Shalabi et al. (1979), Ref. No.

(c) This work.

(d) E: Activation Energy, cal/g-mol, \bar{k} = frequency factor min⁻¹.

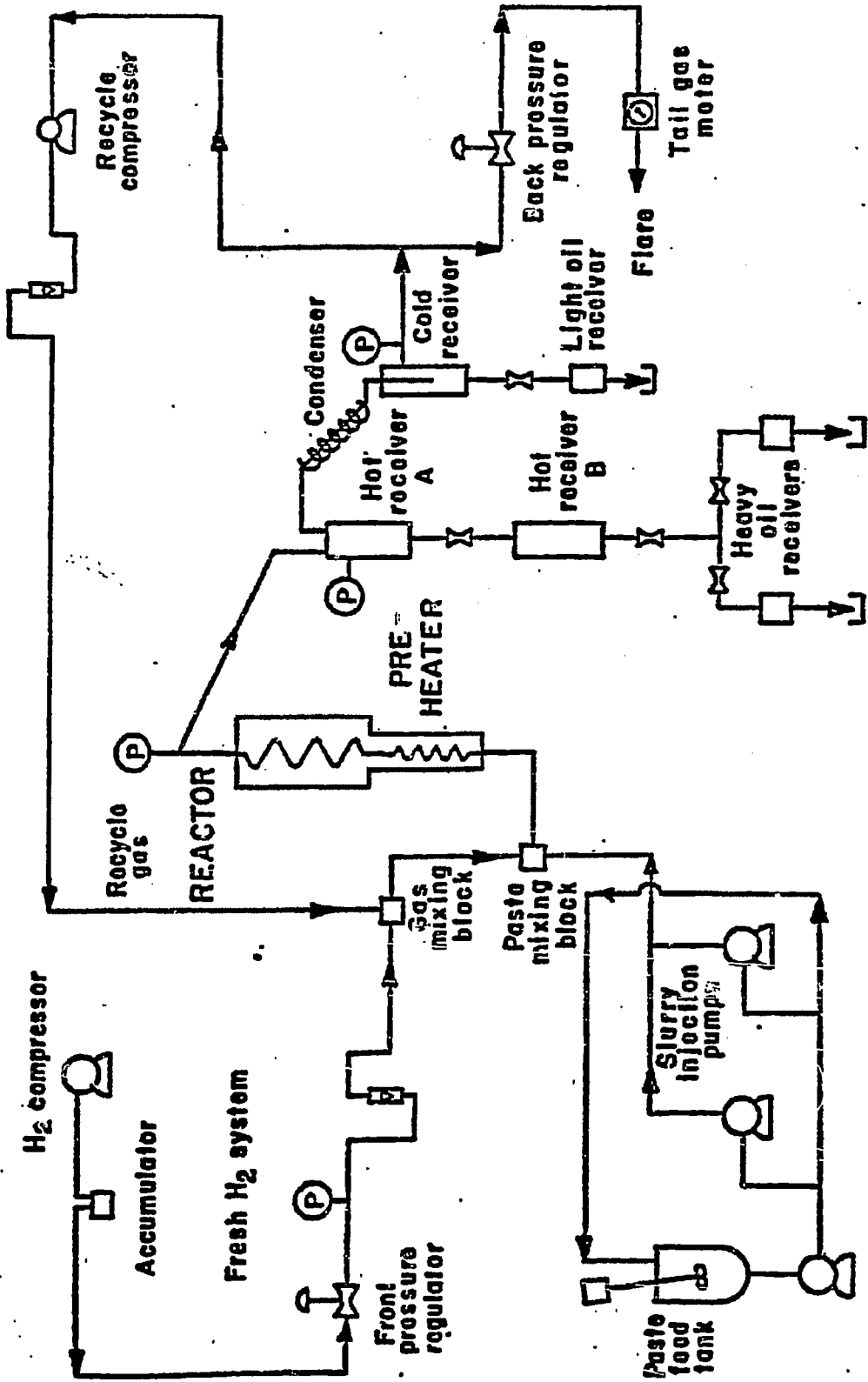


FIGURE 1: continuous liquefaction unit.

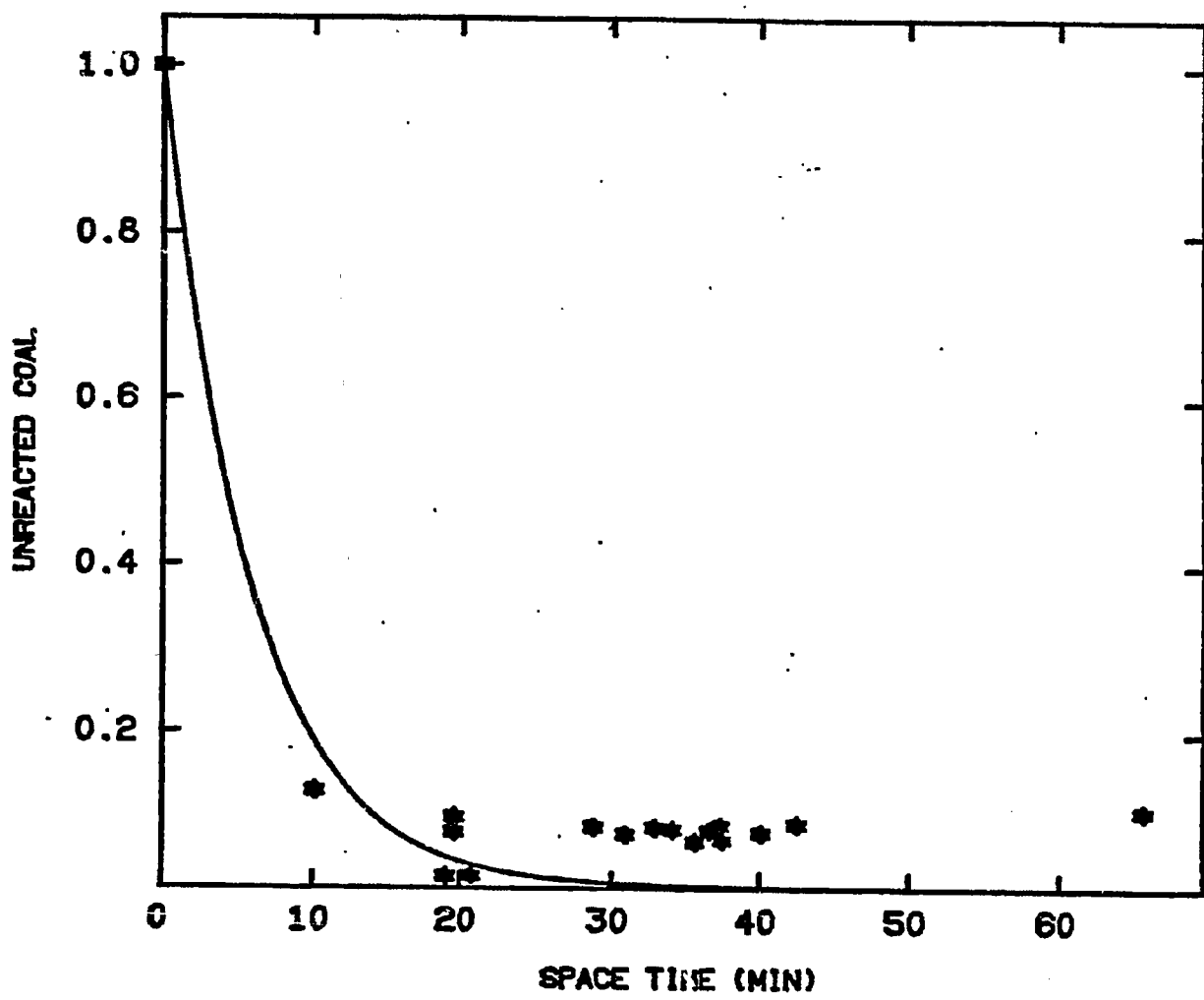


FIGURE 2: Model 1: Unreacted Coal (Temperature 450°C)

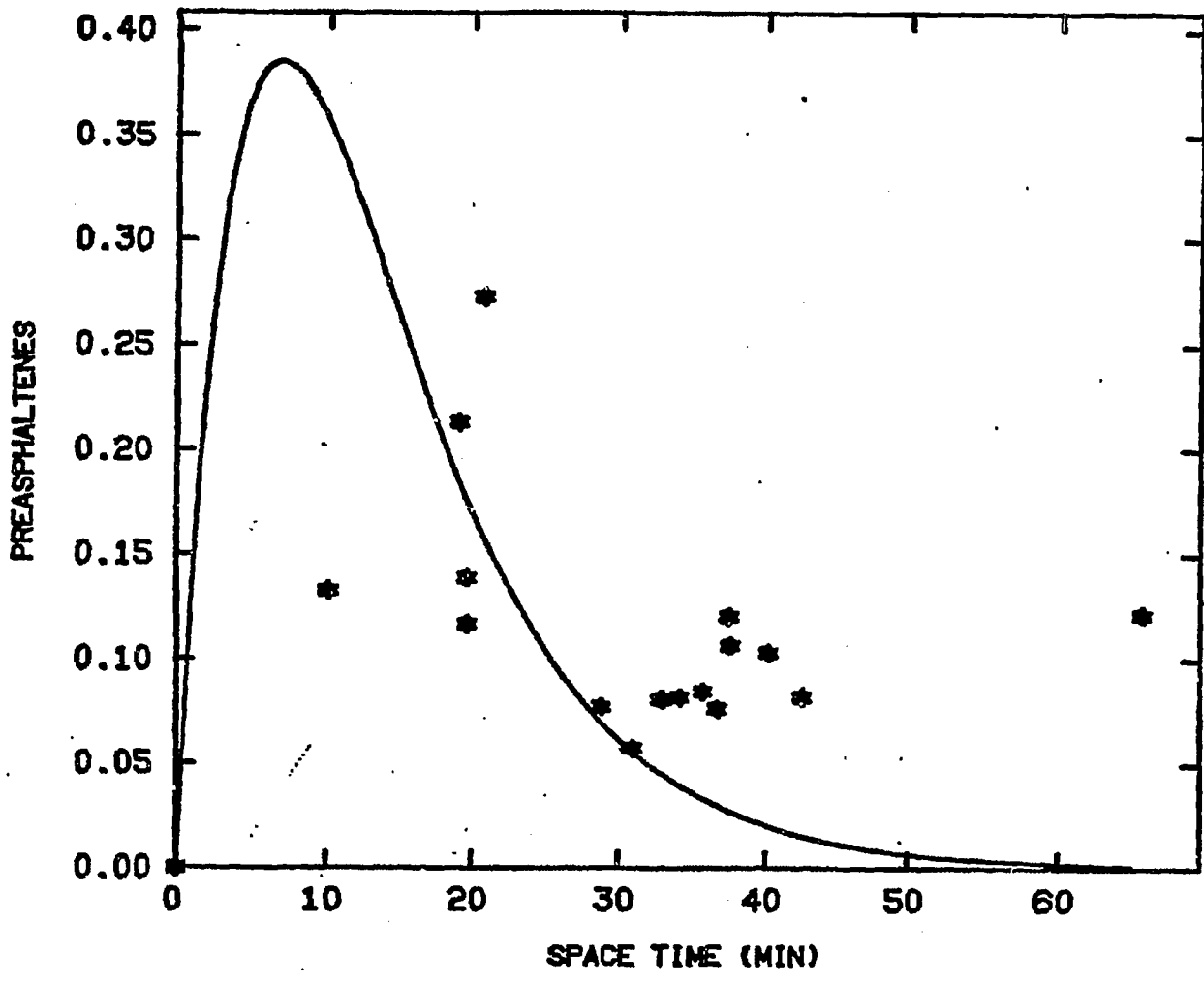


FIGURE 3: Model 1: Preasphaltenes (Temperature 450°C)

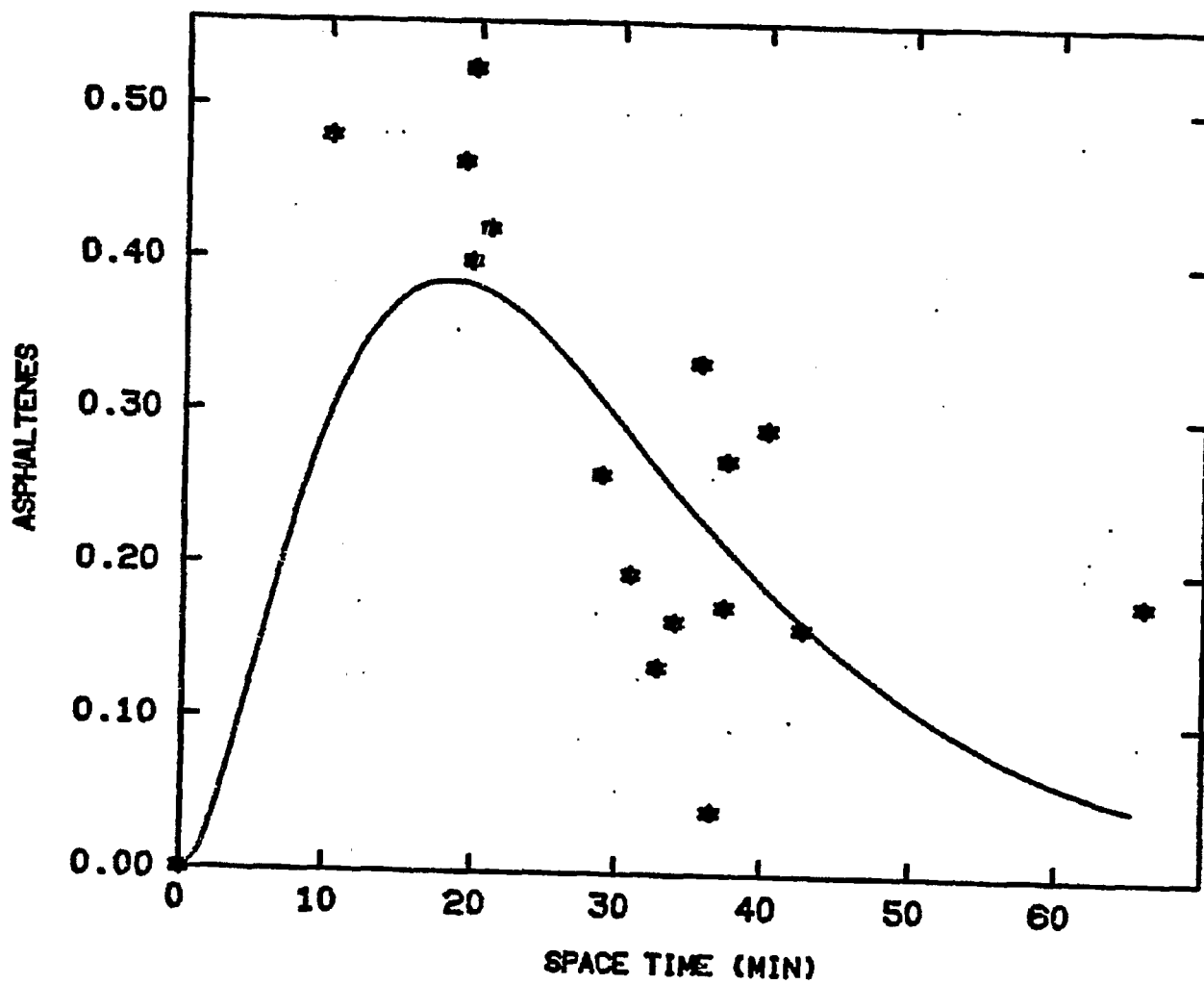


FIGURE 4: Model 1: Asphaltenes (Temperature 450°C)

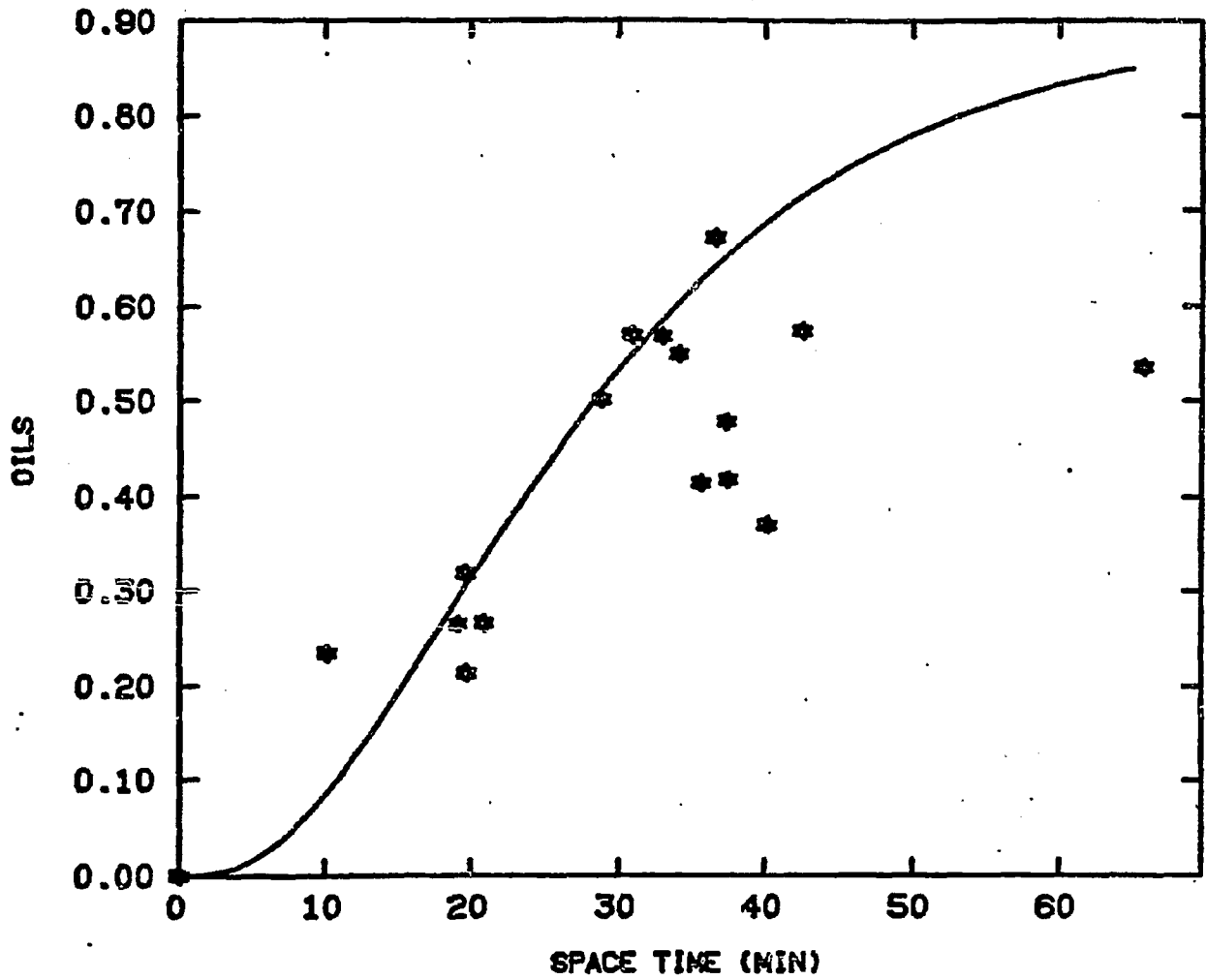


FIGURE 5: Model 1: Oils (Temperature 450°C)

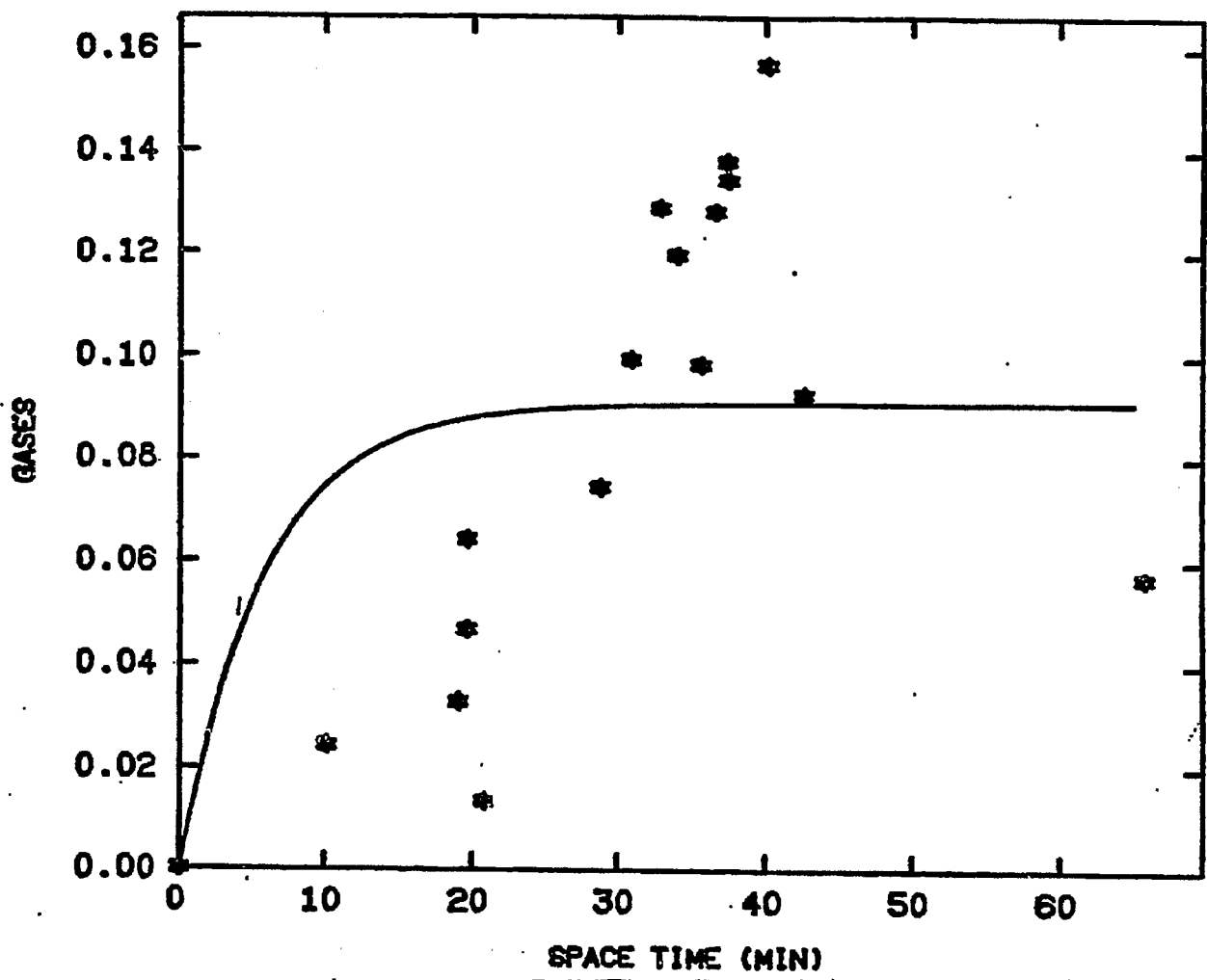


FIGURE 6: Model 1: Gases (Temperature 450°C)

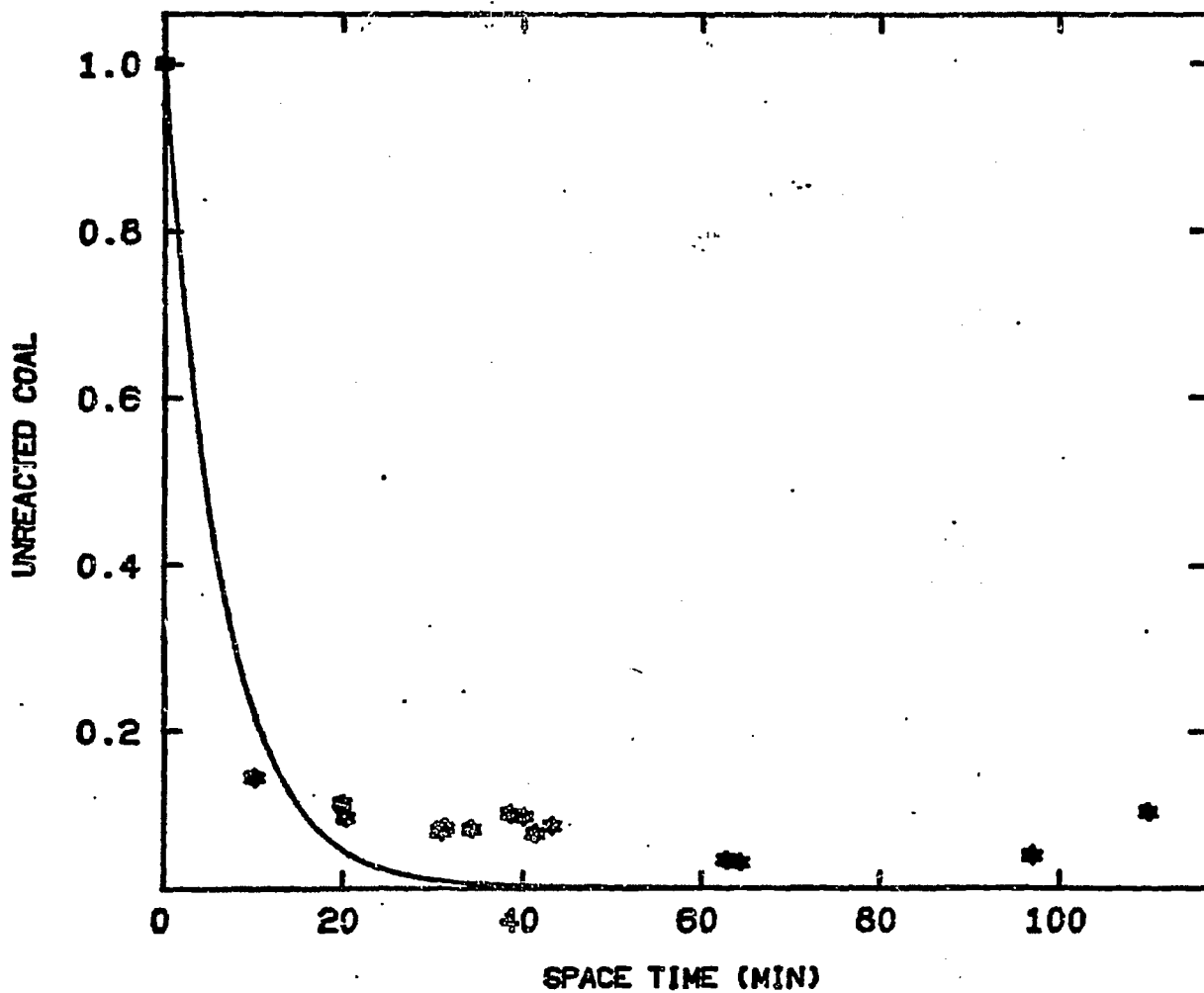


FIGURE 7: Model 1: Unreacted Coal (Temperature 425°C)

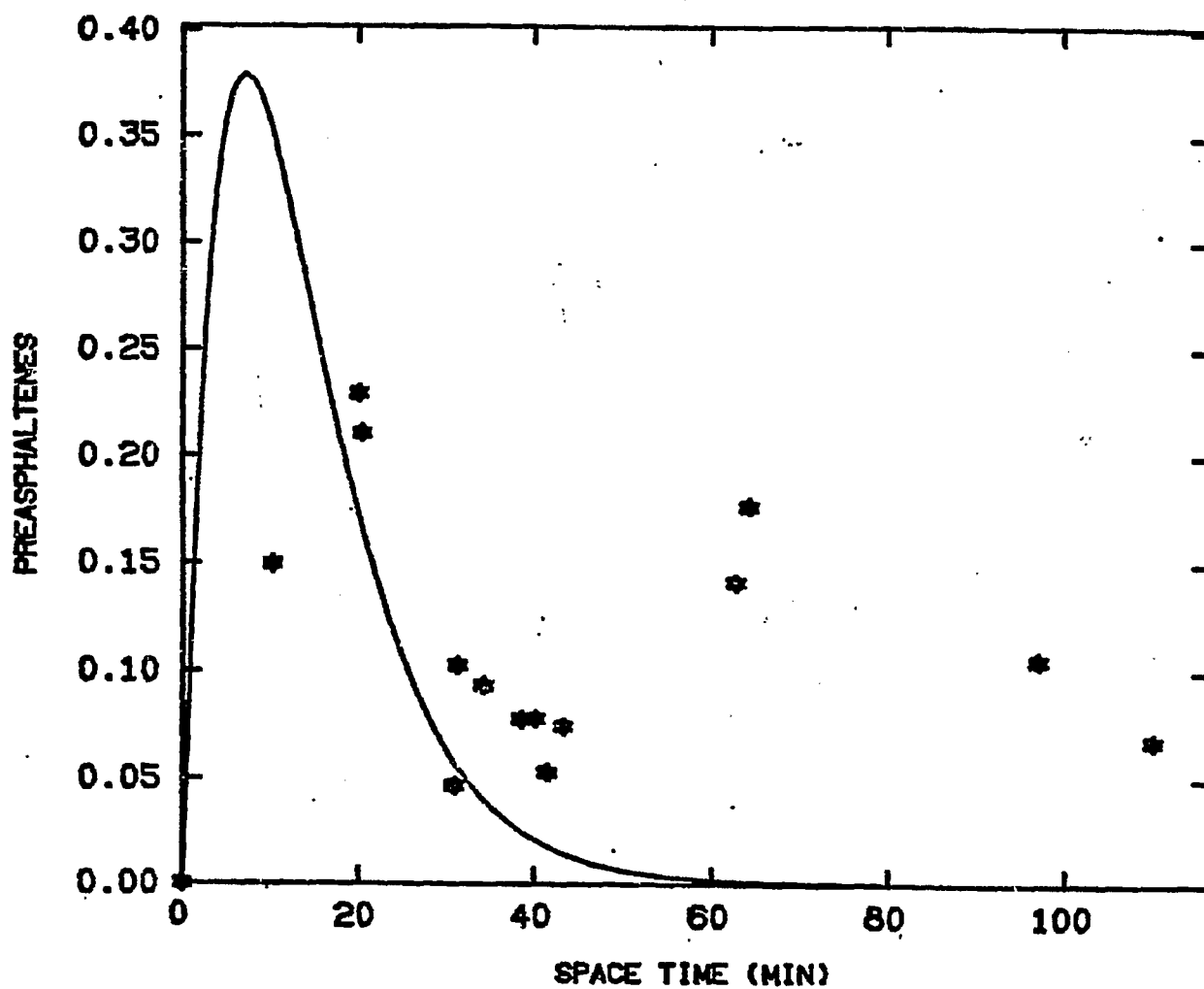


FIGURE 8: Model 1: Preasphaltenes (Temperature 425°C)

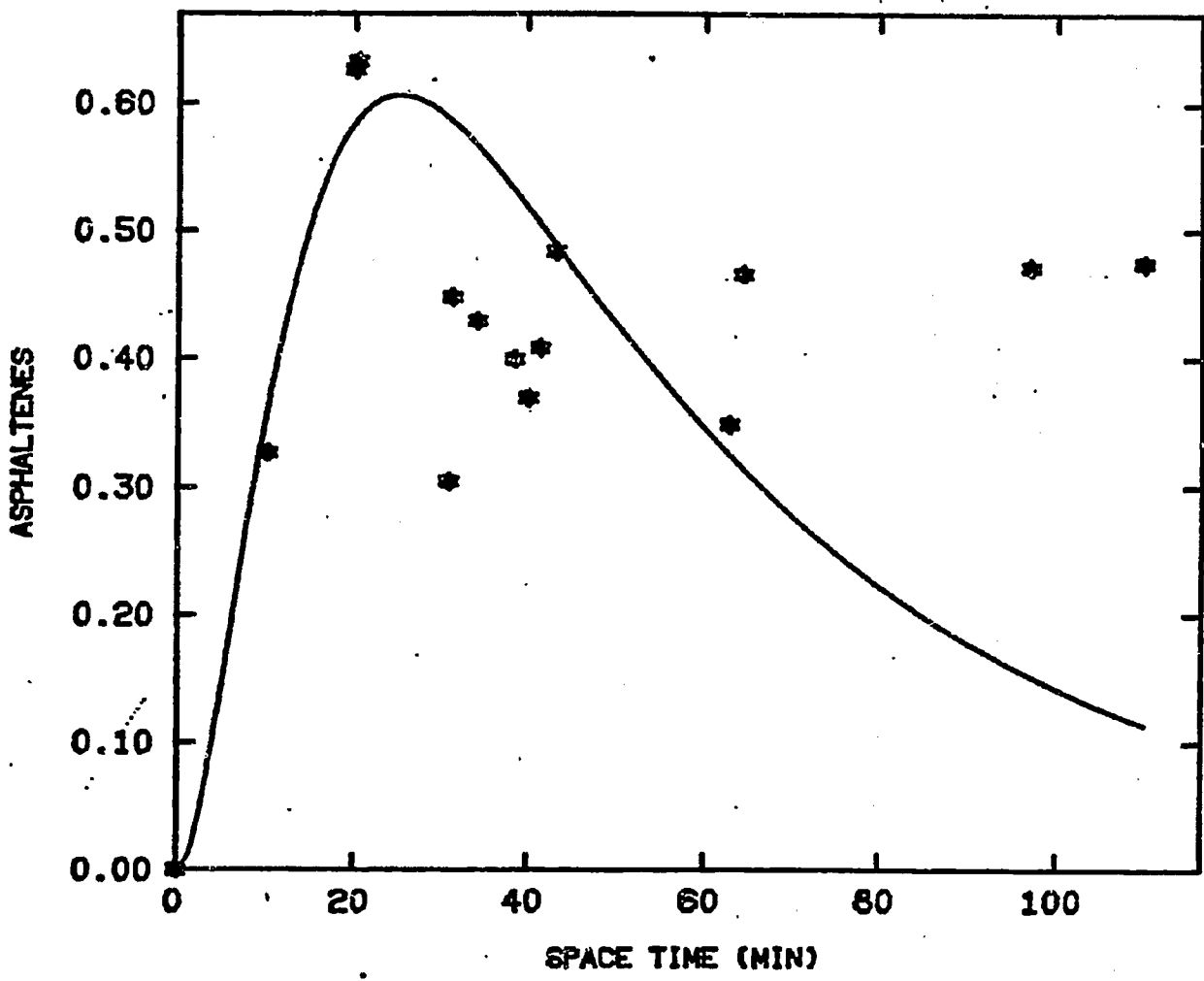


FIGURE 9: Model 1: Asphaltenes (Temperature 425°C)

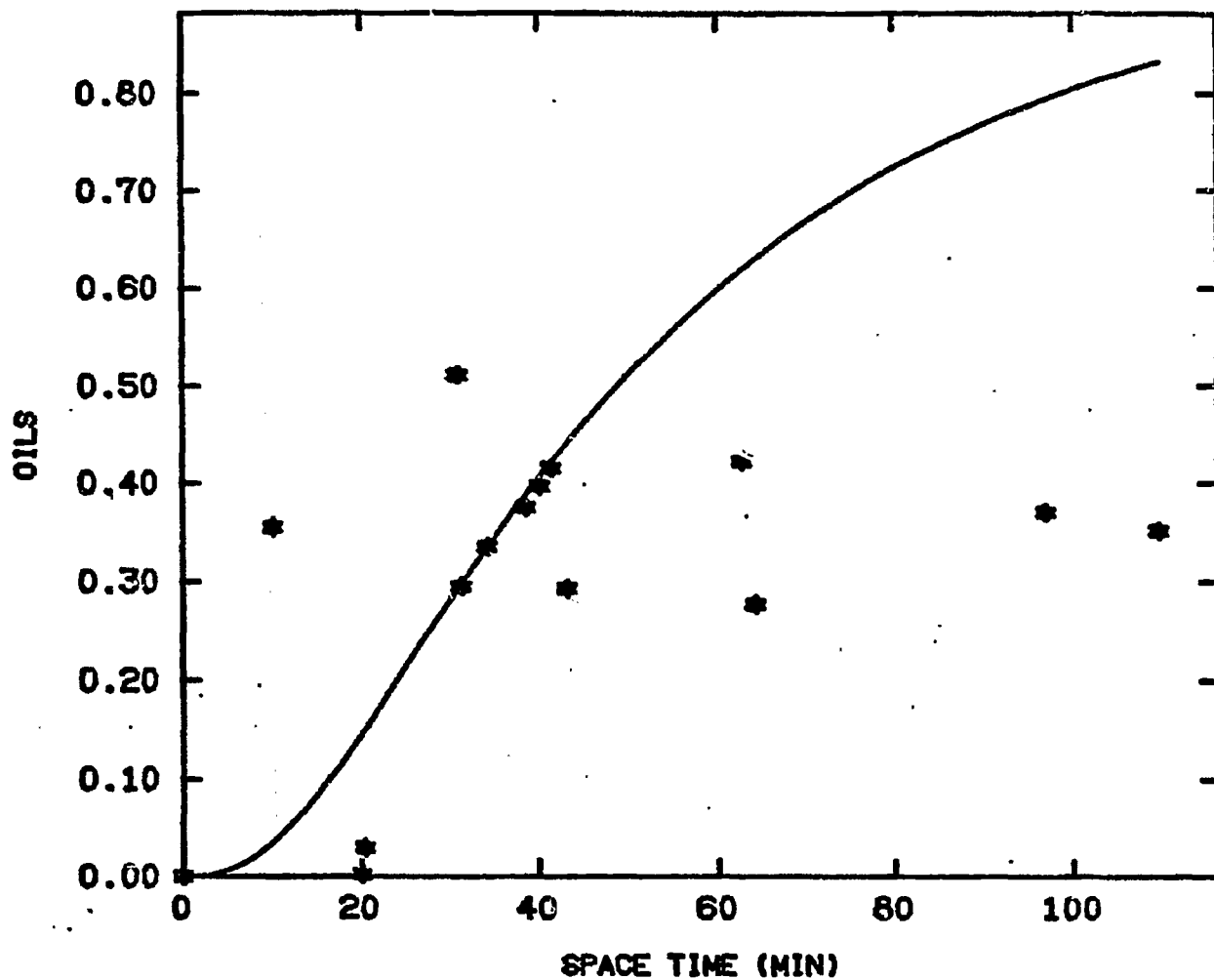


FIGURE 10: Model 1: Oils (Temperature 425°C)

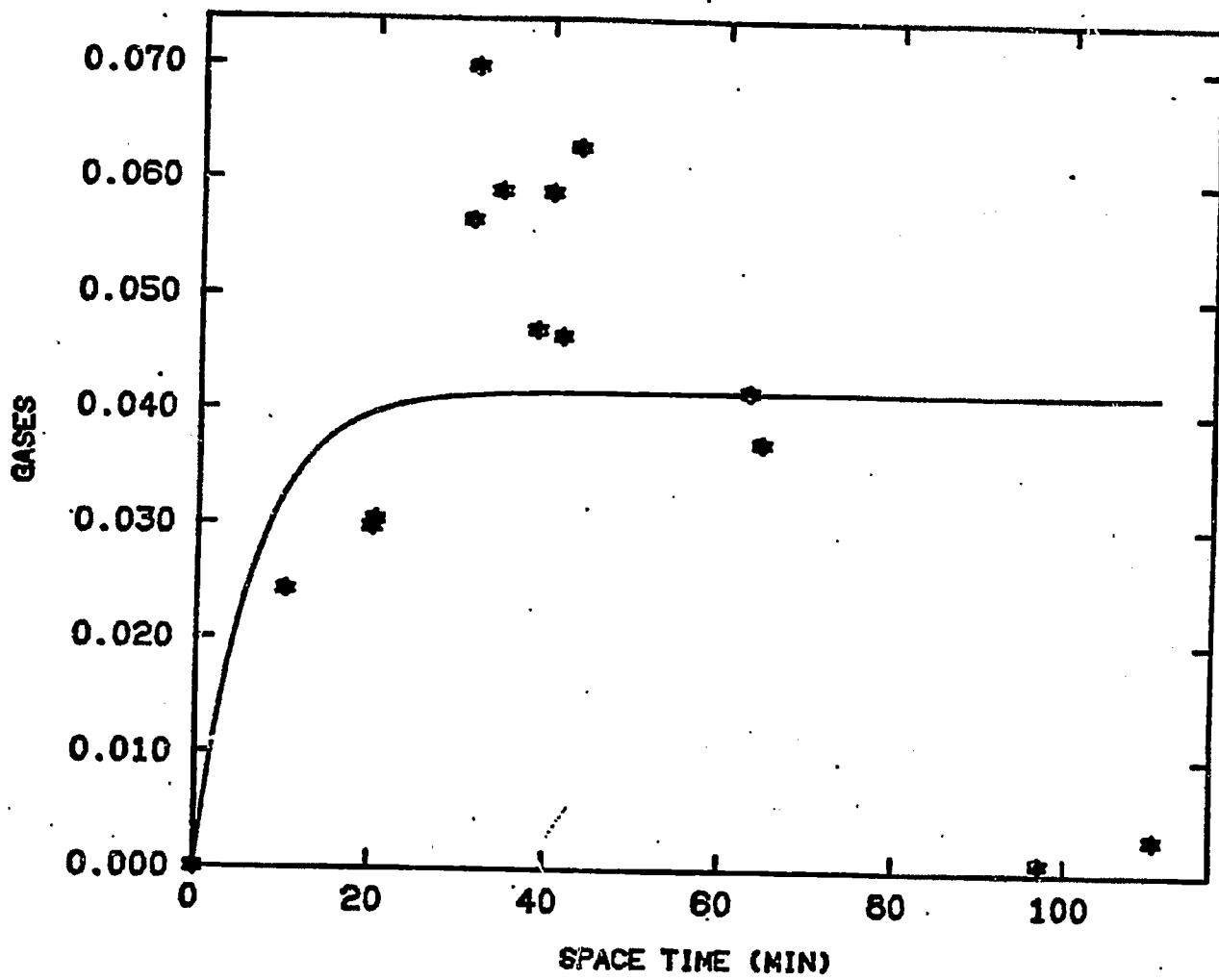


FIGURE 11: Model 1: Gases (Temperature 425°C)

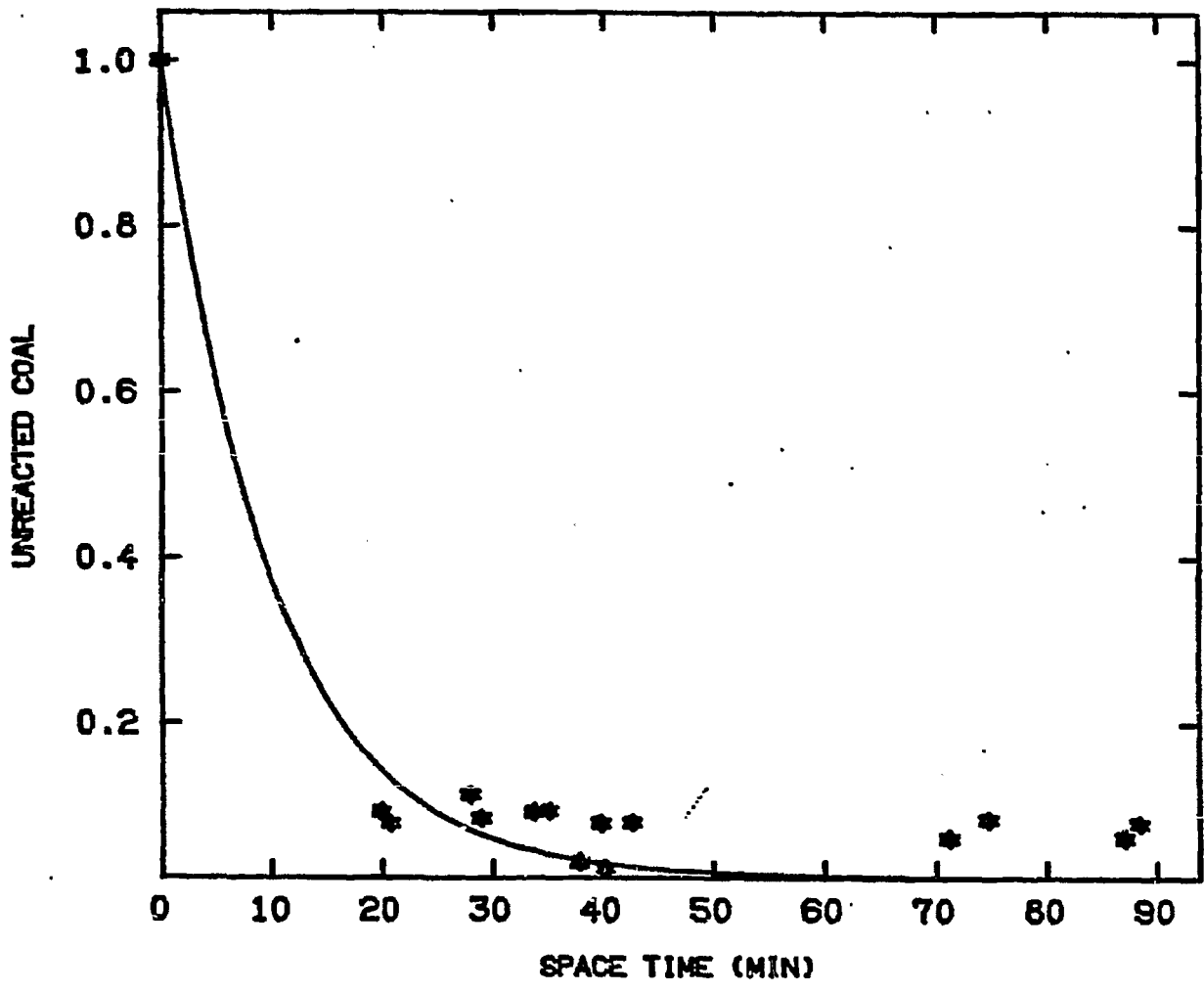


FIGURE 12: Model 1: Unreacted Coal (Temperature 400°C)

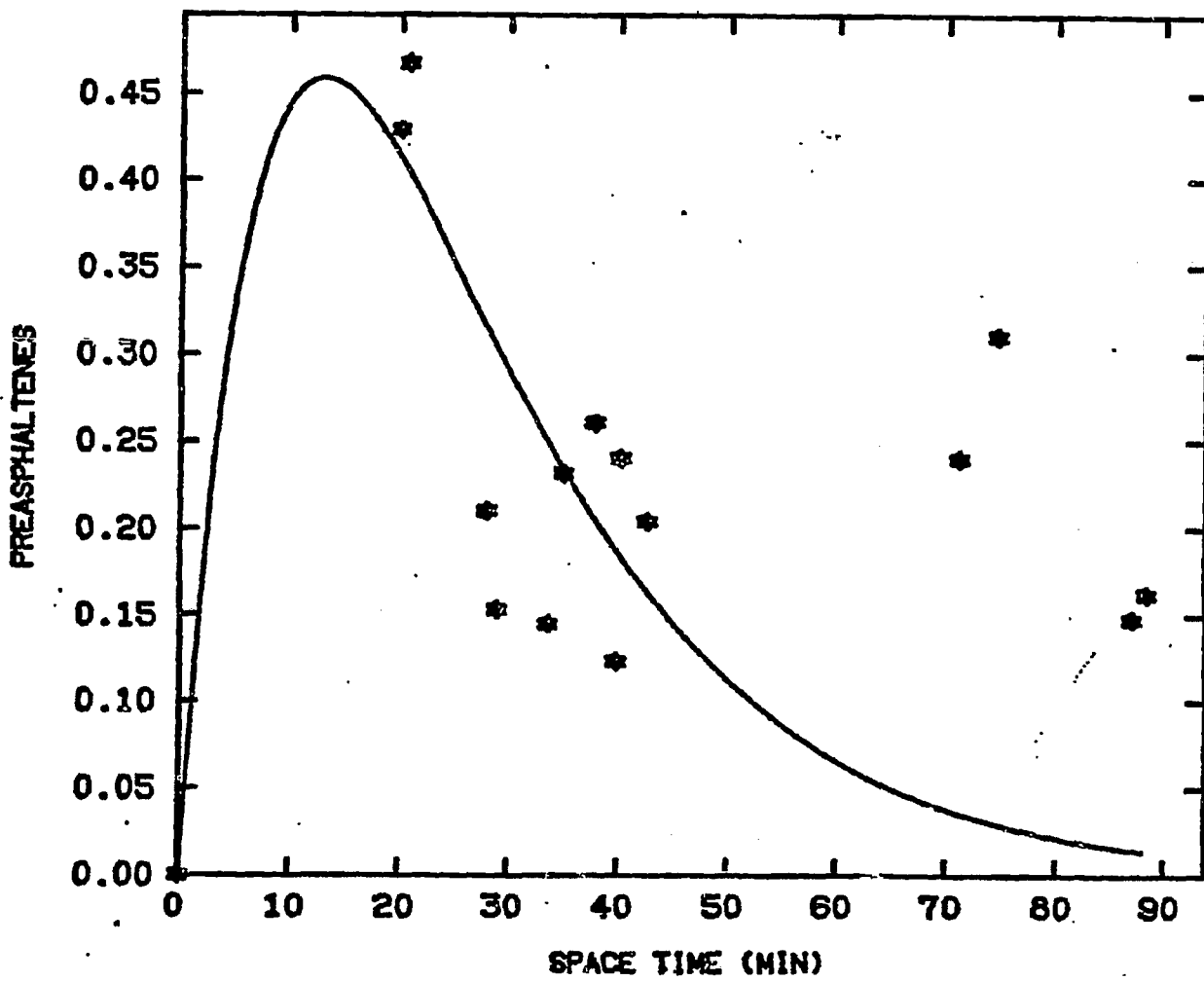


FIGURE 13: Model 1: Preasphaltenes (Temperature 400°C)

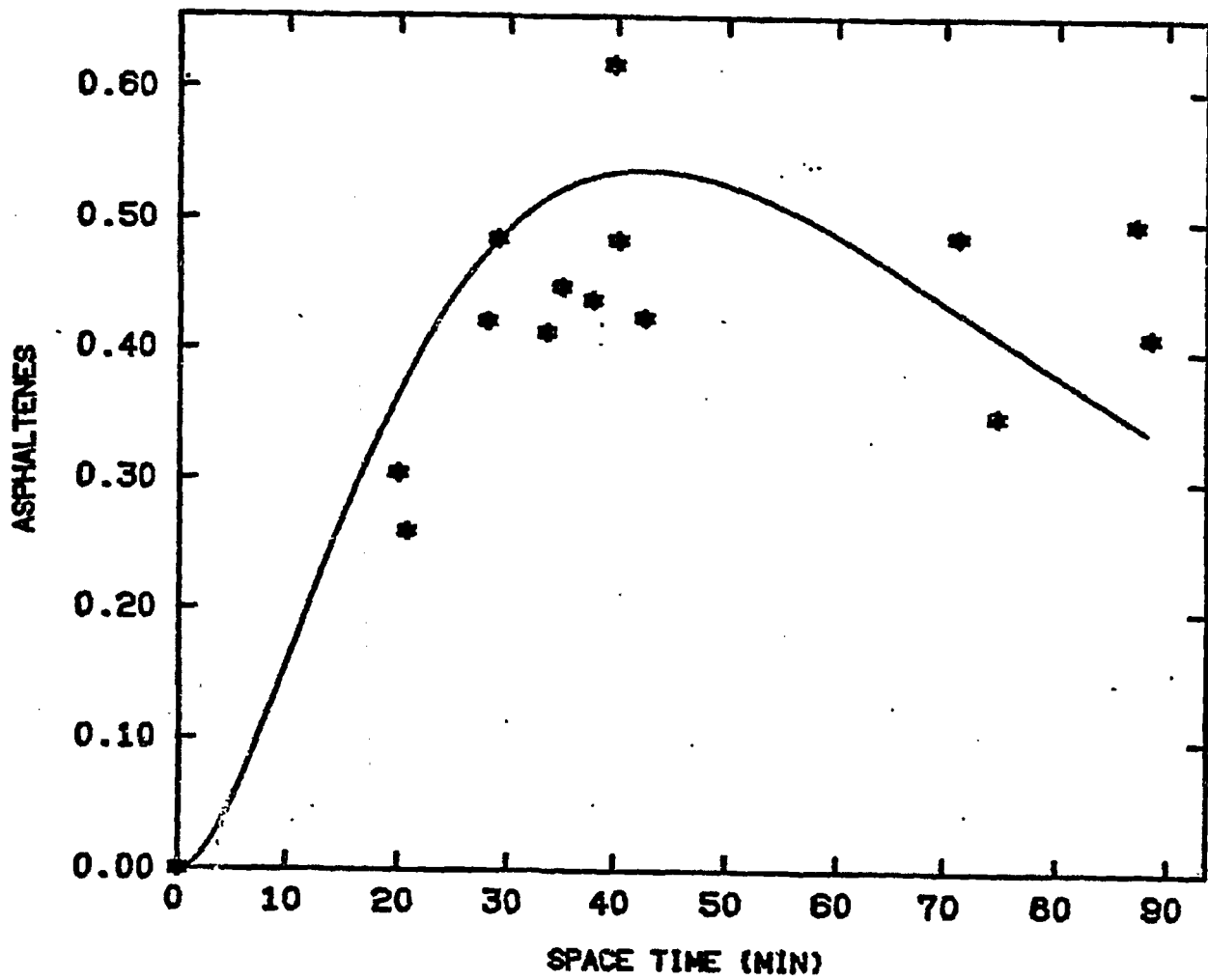


FIGURE 14:--Model 1: Asphaltenes (Temperature 400°C)

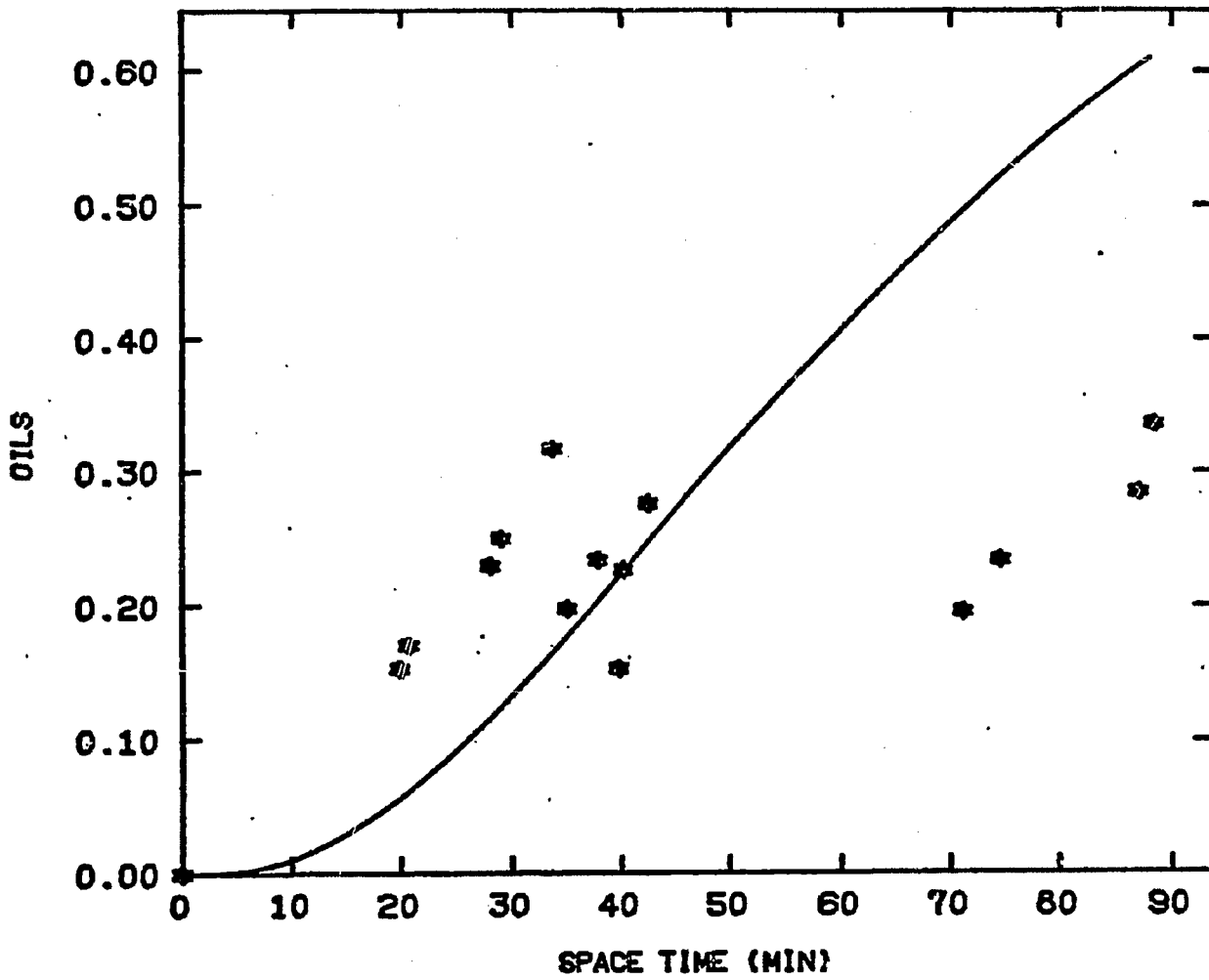


FIGURE 15: Model 1: Oils (Temperature 400°C)

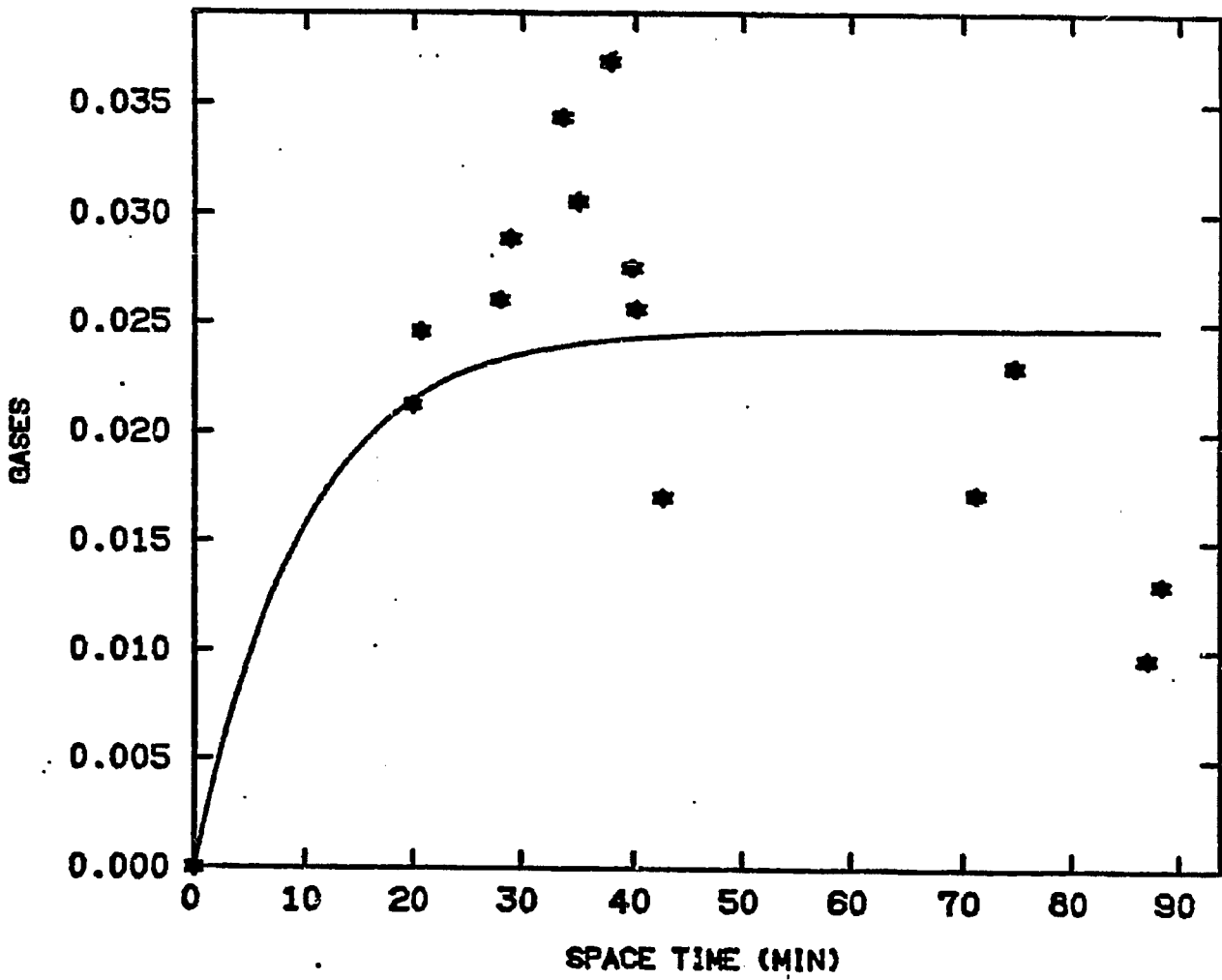


FIGURE 16: Model 1: Gases (Temperature 400°C)

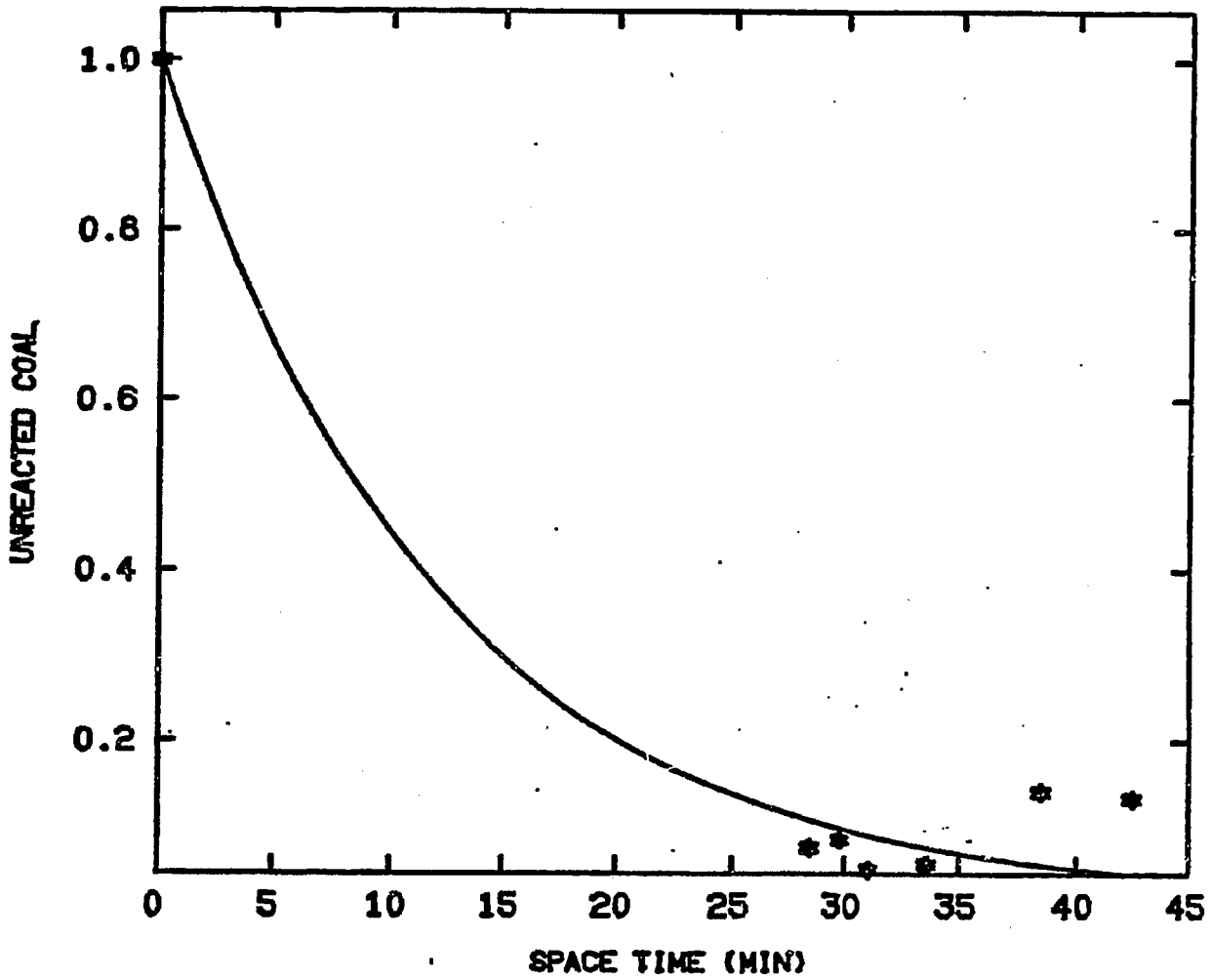


FIGURE 17: Model 1: Unreacted Coal (Temperature 375°C)

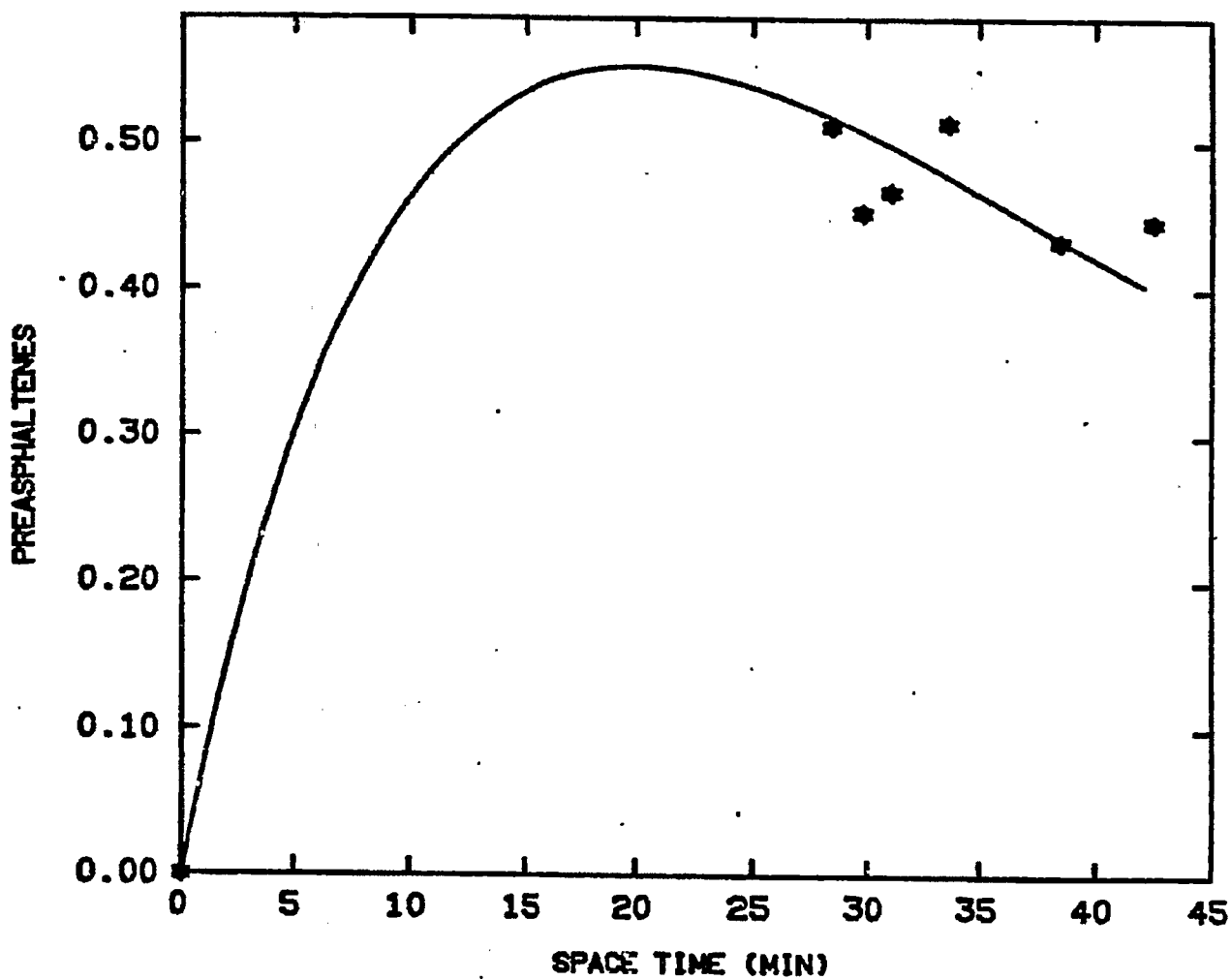


FIGURE 18: Model 1: Preasphaltenes (Temperature 375°C)

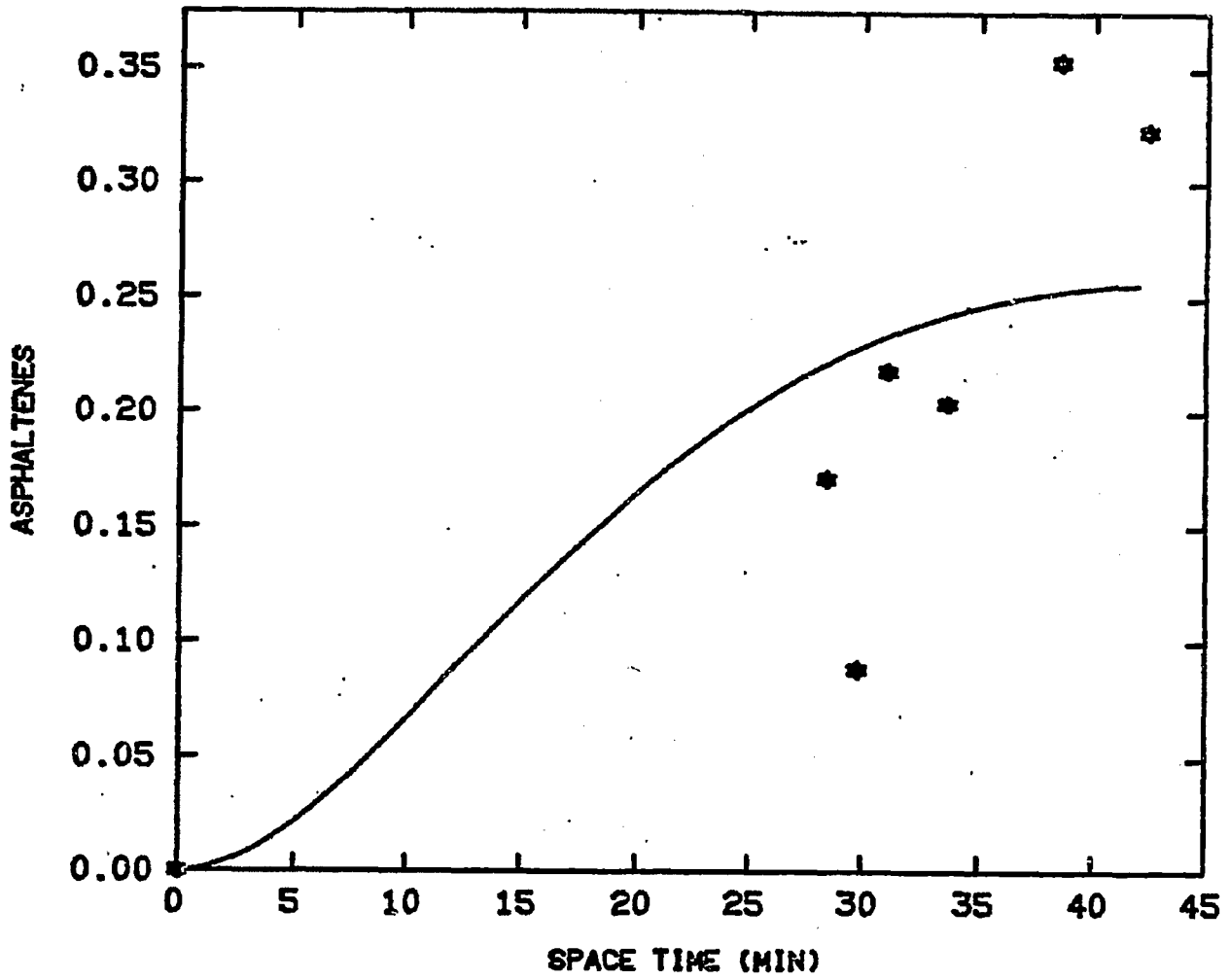


FIGURE 19: Model 1: Asphaltenes (Temperature 375°C)

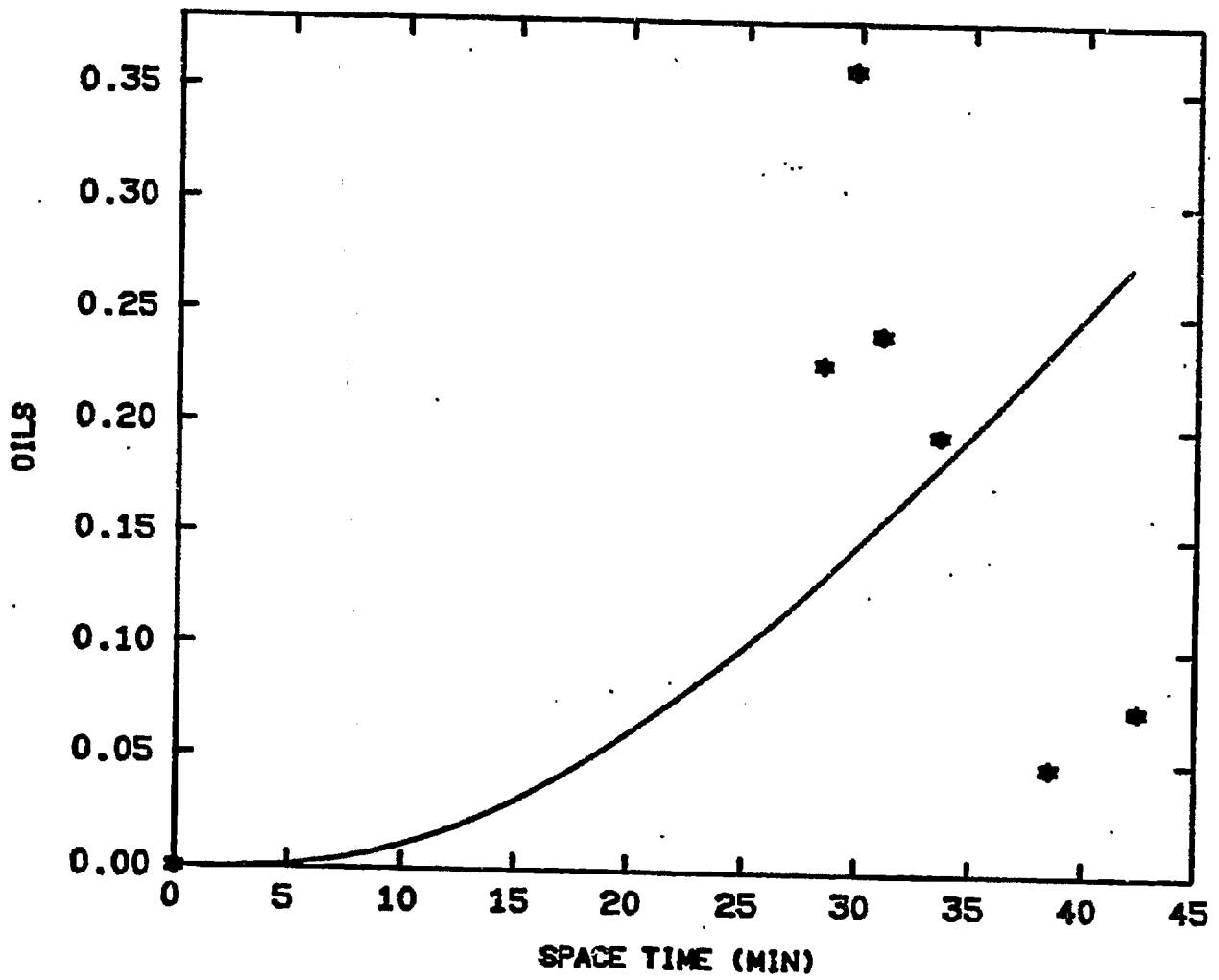


FIGURE 20: Model 1: Oils (Temperature 375°C)

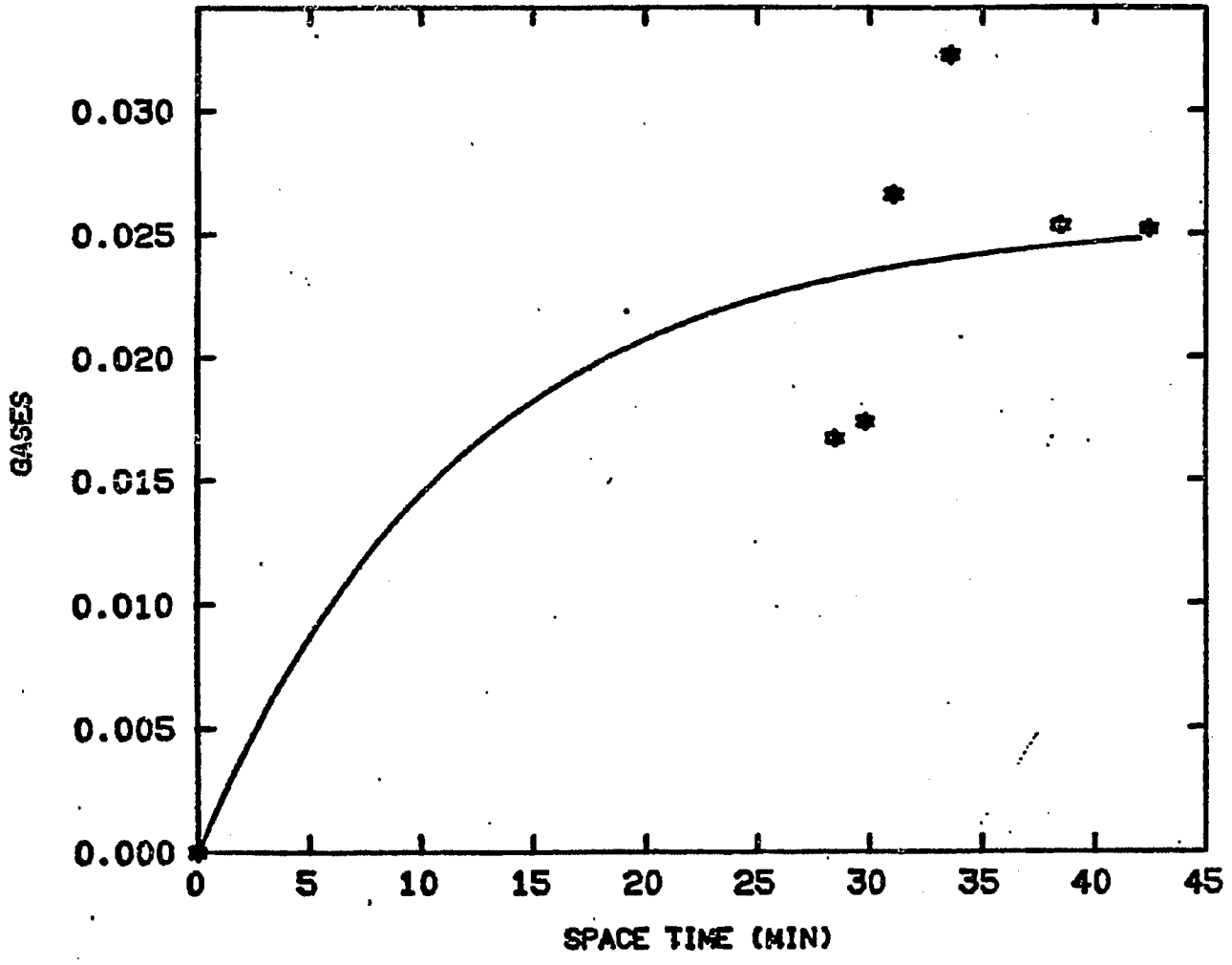


FIGURE 21: Model 1: Gases (Temperature 375°C)

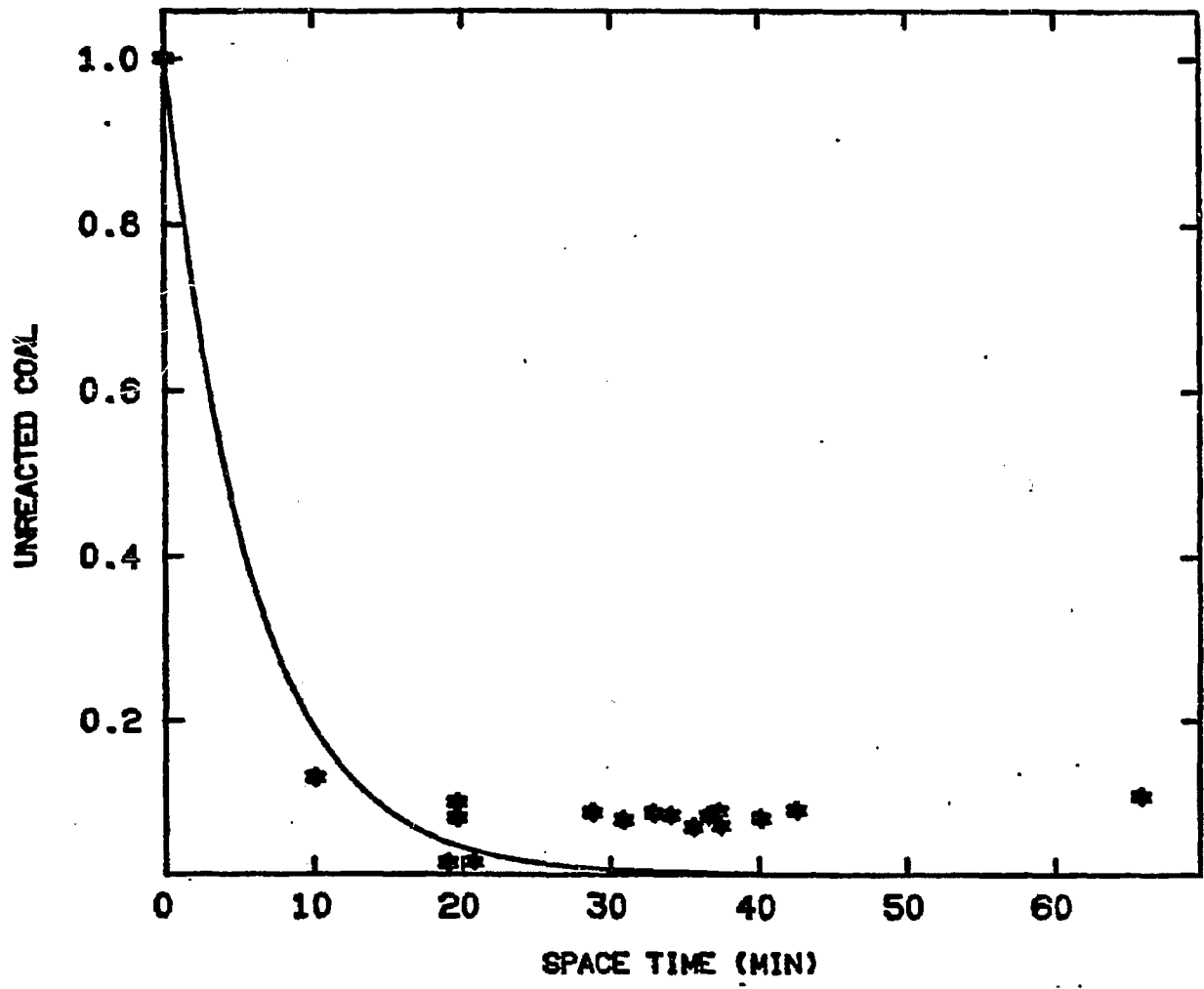


FIGURE 22: Model 2: Unreacted Coal (Temperature 450°C)

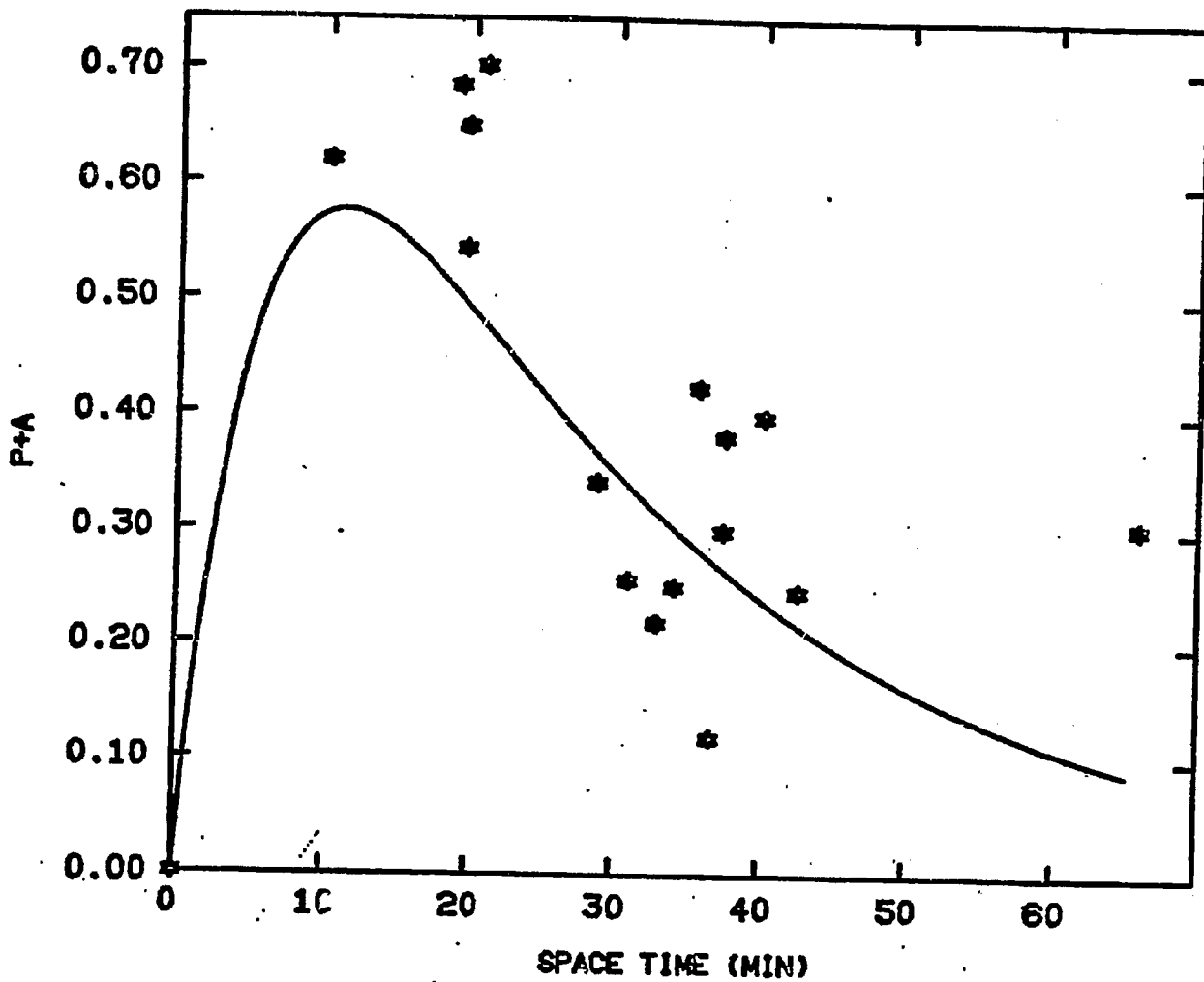


FIGURE 23: Model 2: Preasphaltenes + Asphaltenes (Temperature 450°C)

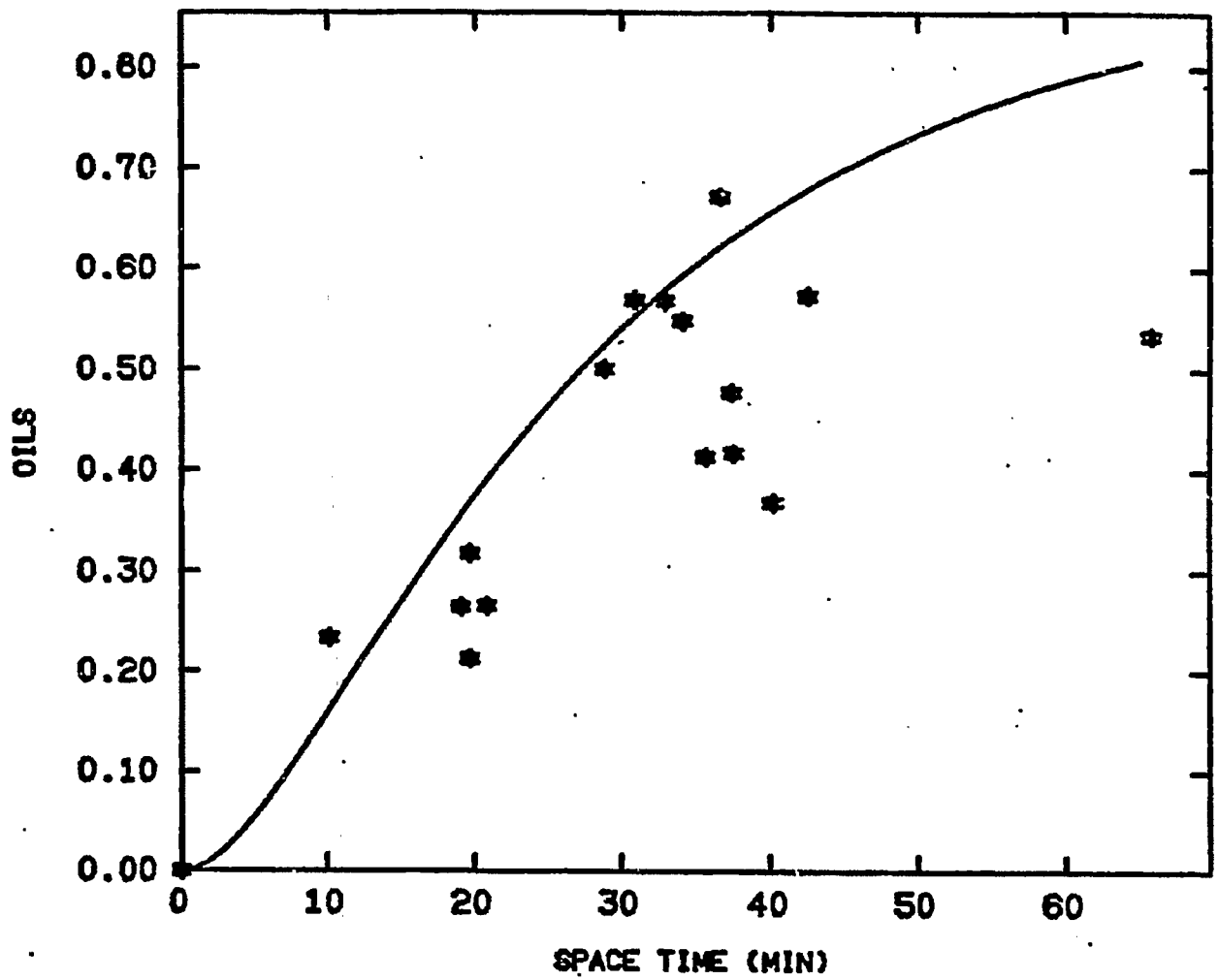


FIGURE 24: Model 2: Oils (Temperature 450°C)

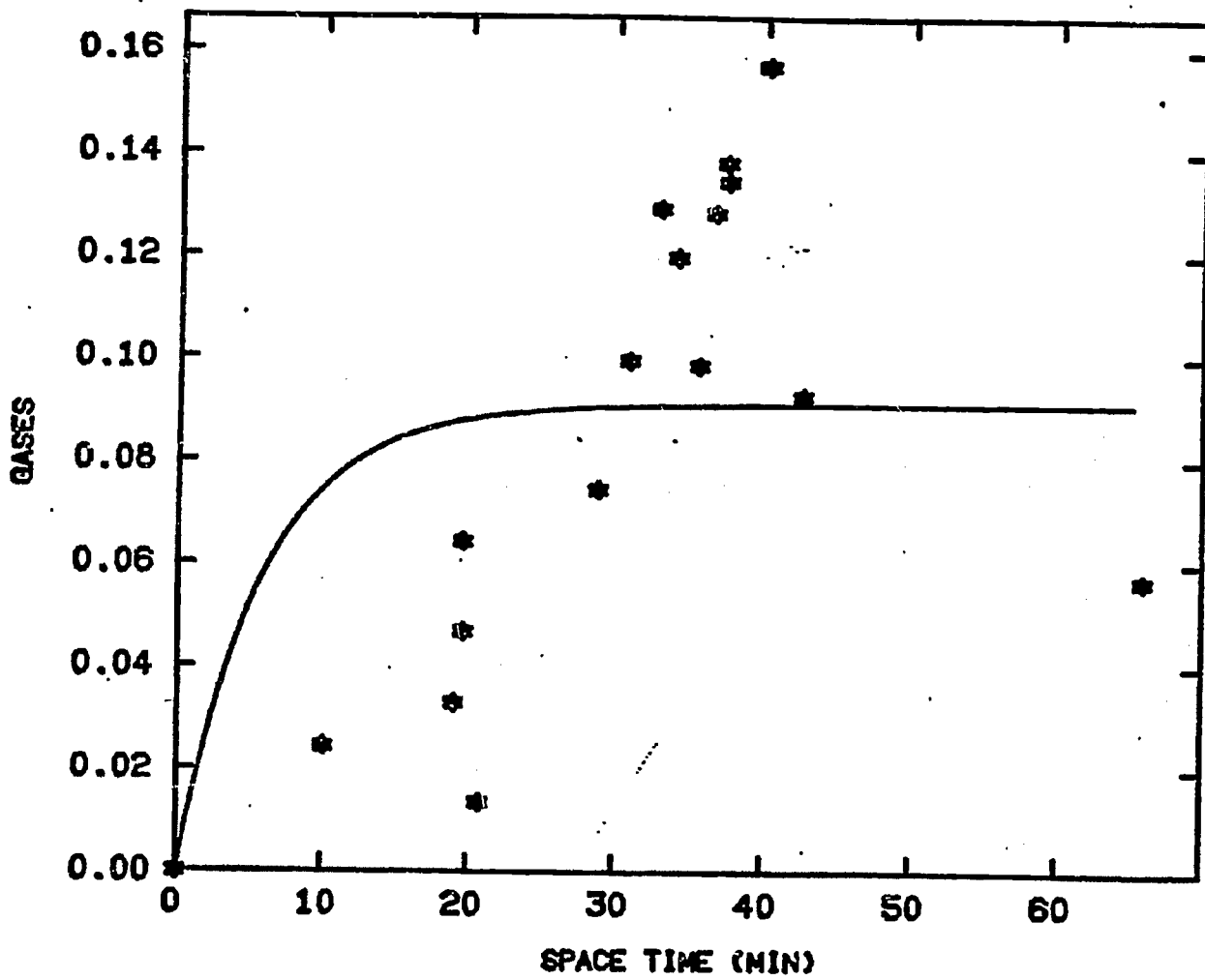


FIGURE 25: Model 2: Gases (Temperature 450°C)

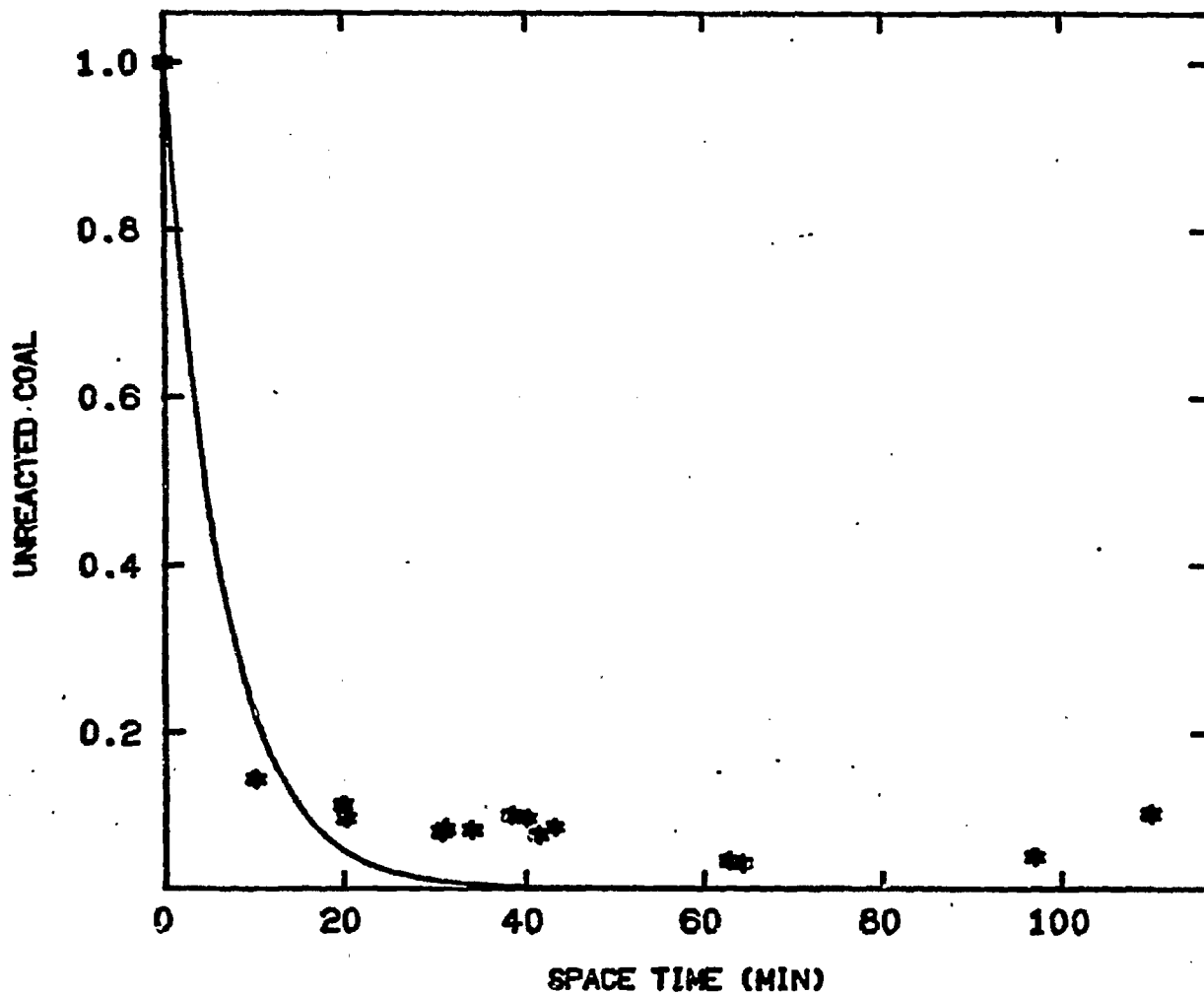


FIGURE 26: Model-2: Unreacted Coal (Temperature 425°C)

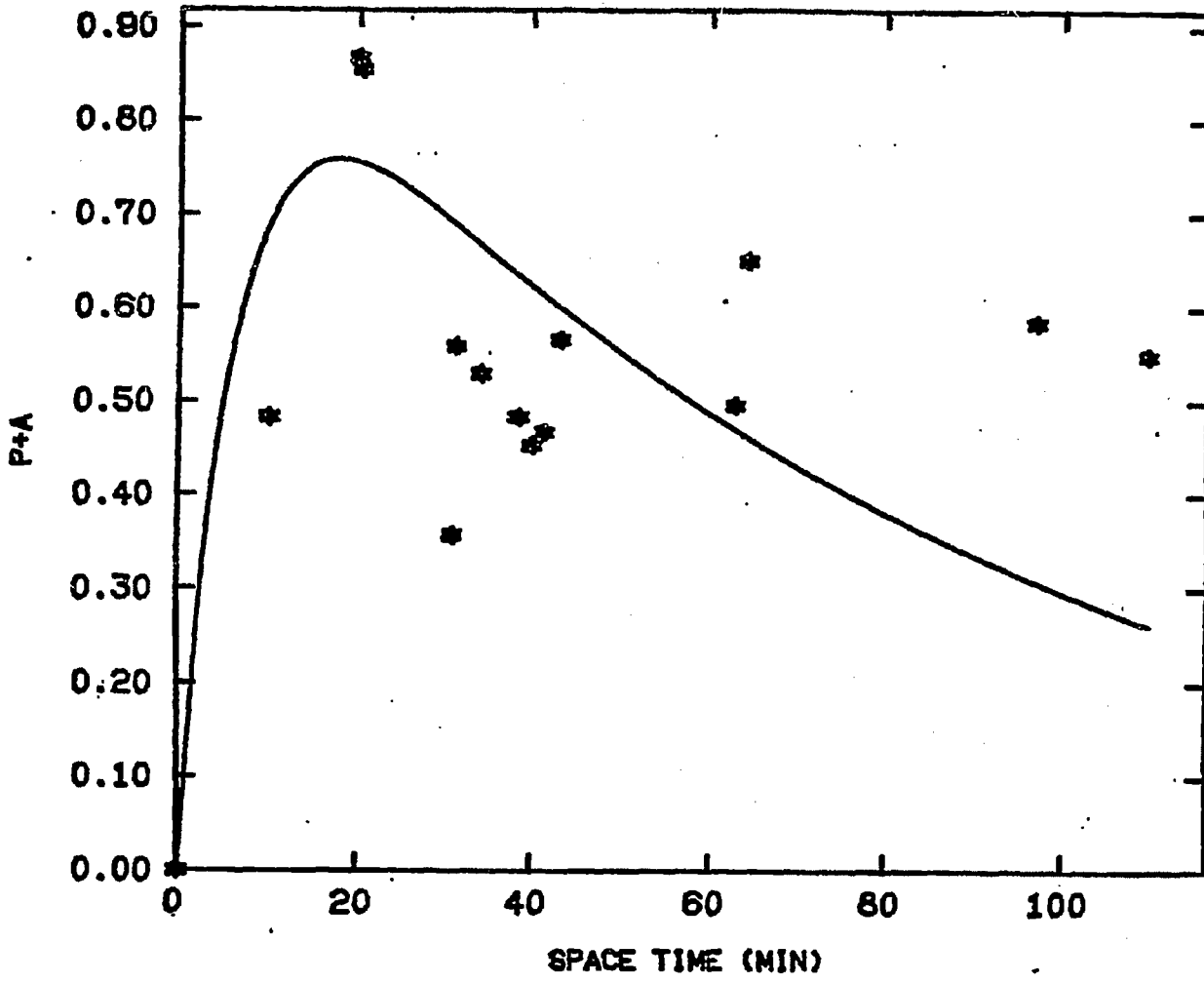


FIGURE 27: Model 2: Preasphaltenes + Asphaltenes (Temperature 425°C)

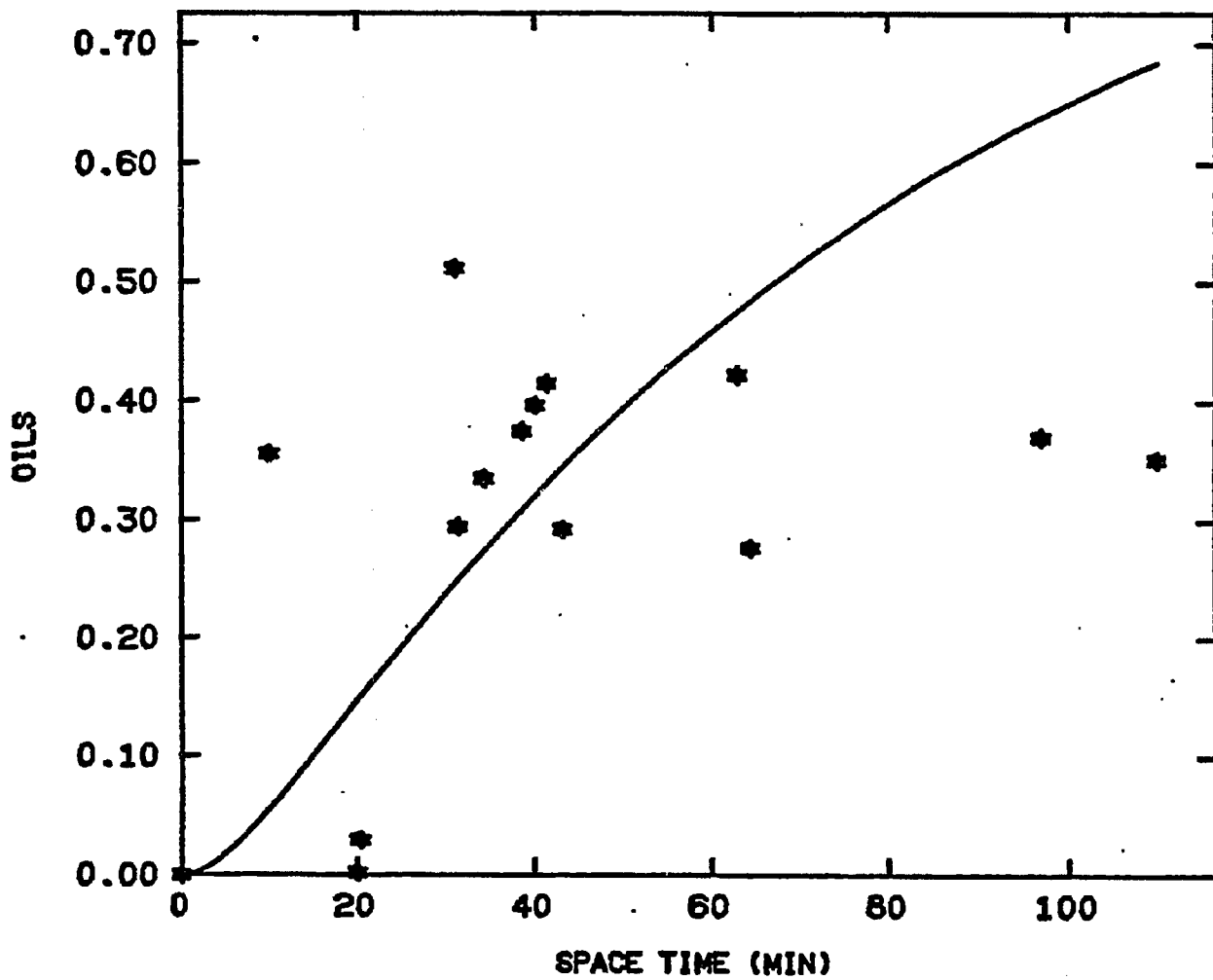


FIGURE 28: Model 2: Oils (Temperature 425°C)

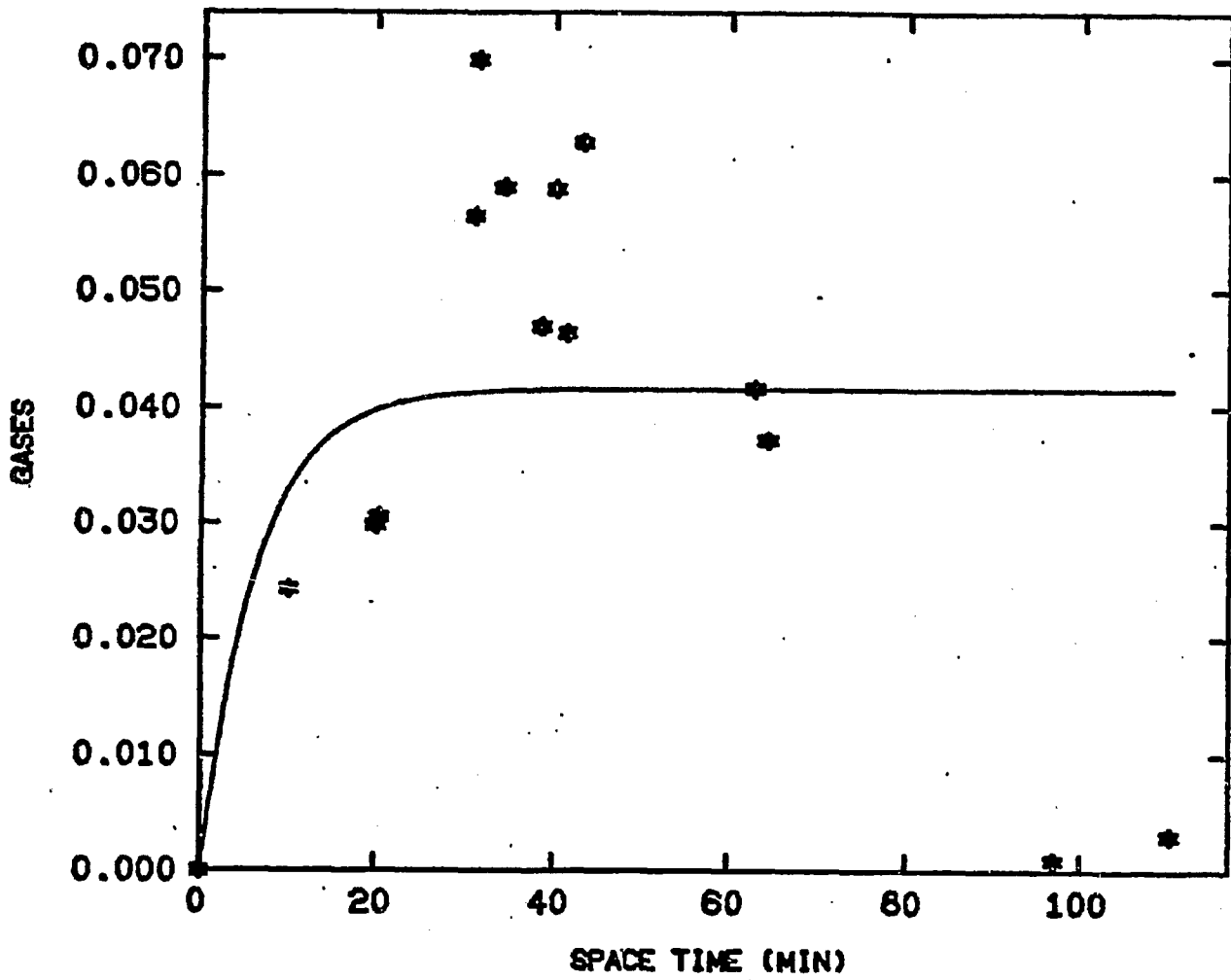


FIGURE 29: Model 2: Gases (Temperature 425°C)

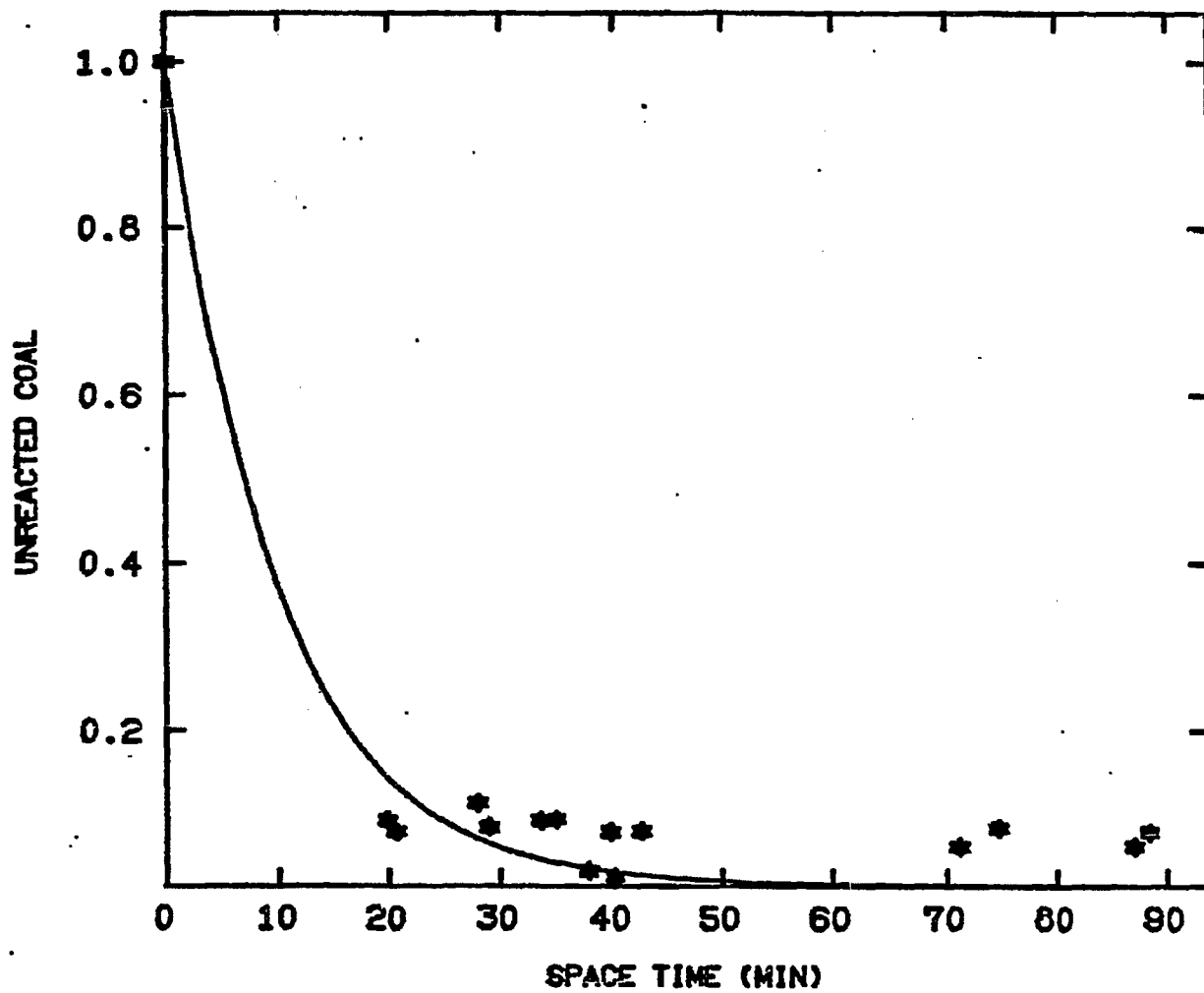


FIGURE 30: Model 2: Unreacted Coal (Temperature 400°C)

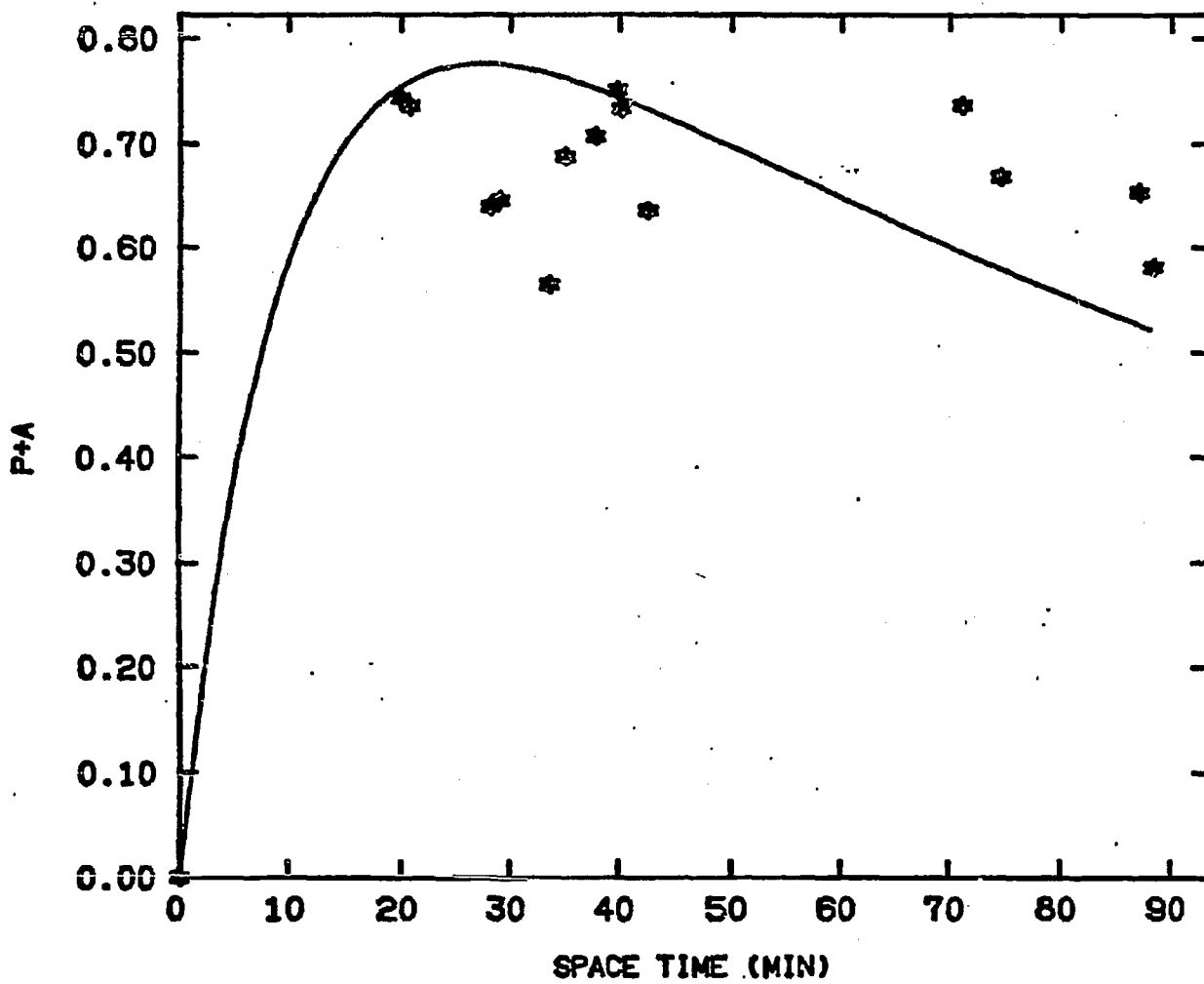


FIGURE 31: Model 2: Preasphaltenes + Asphaltenes (Temperature 400°C)

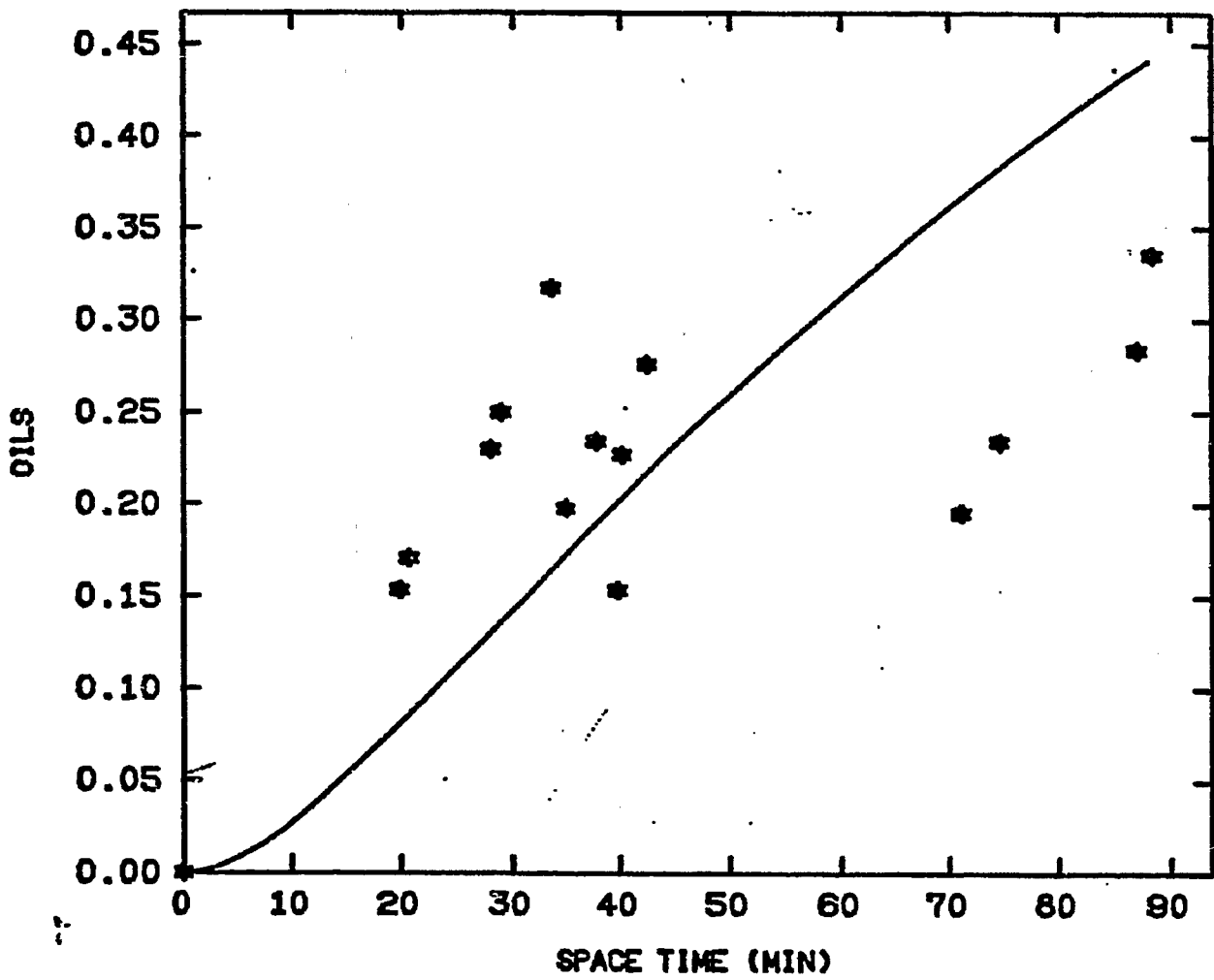


FIGURE 32: Model 2: Oils (Temperature 400°C)

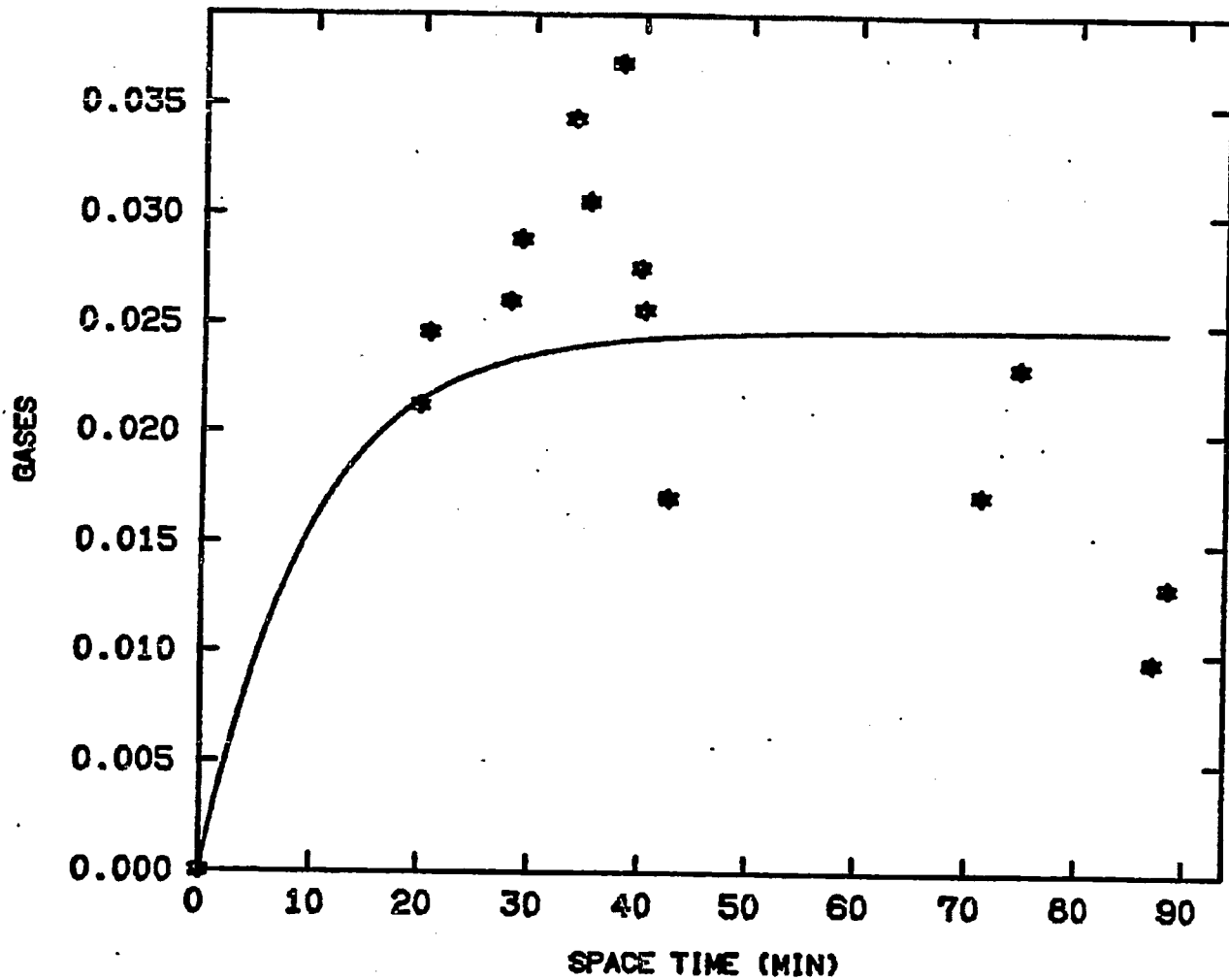


FIGURE 33: Model 2: Gases (Temperature 400°C)

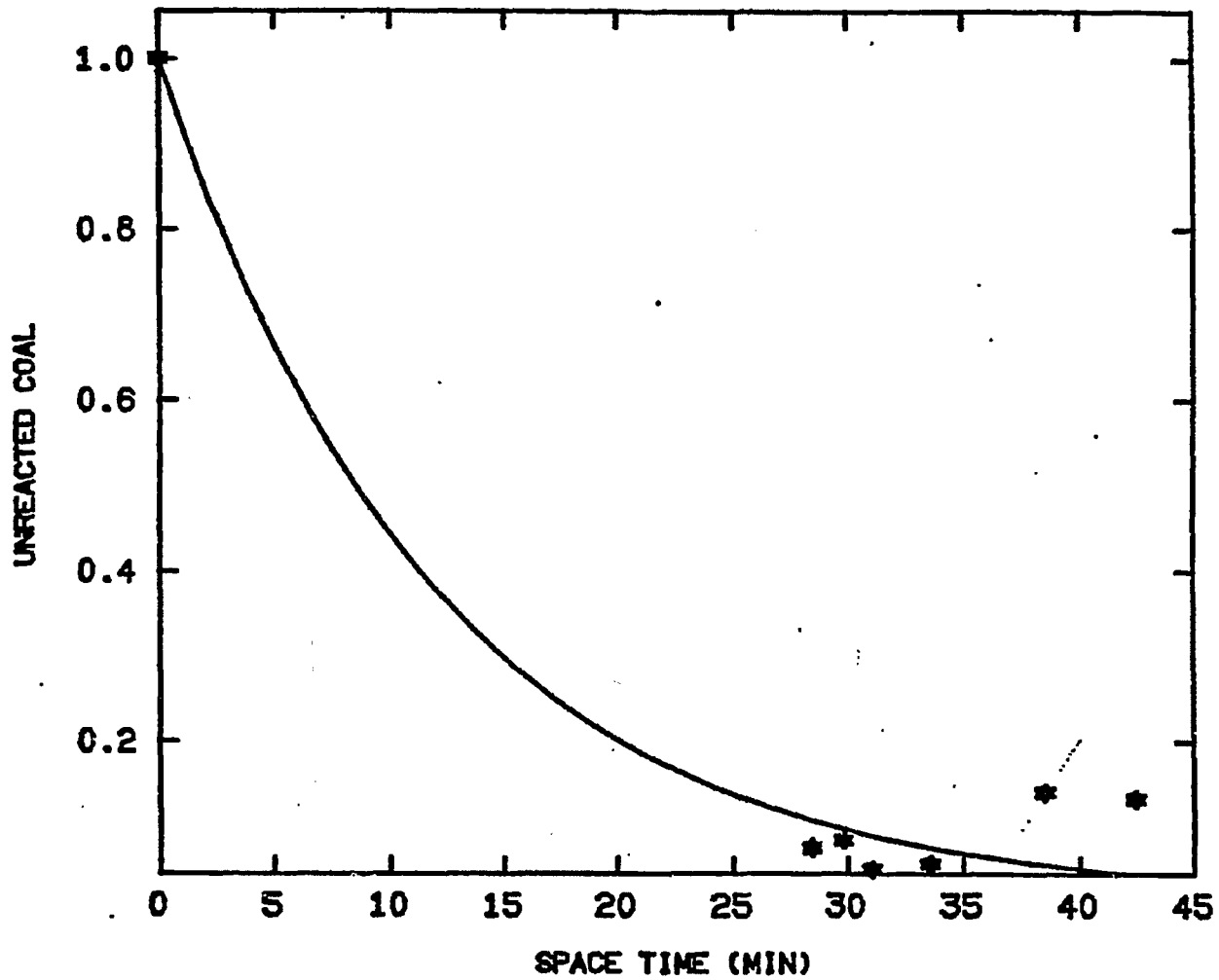


FIGURE 34: Model 2: Unreacted Coal (Temperature 375°C)

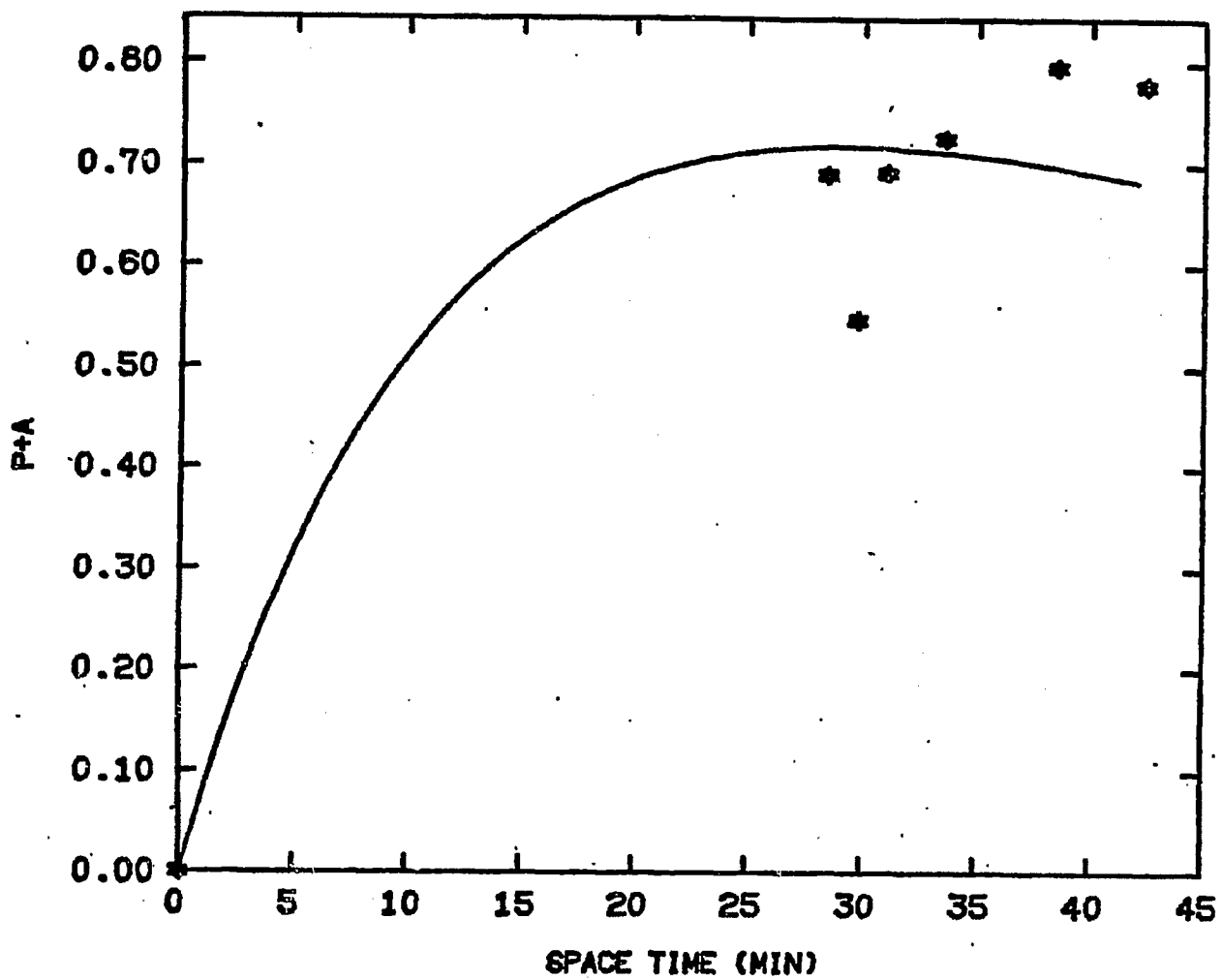


FIGURE 35: Model 2: Preasphaltenes + Asphaltenes (Temperature 375°C)

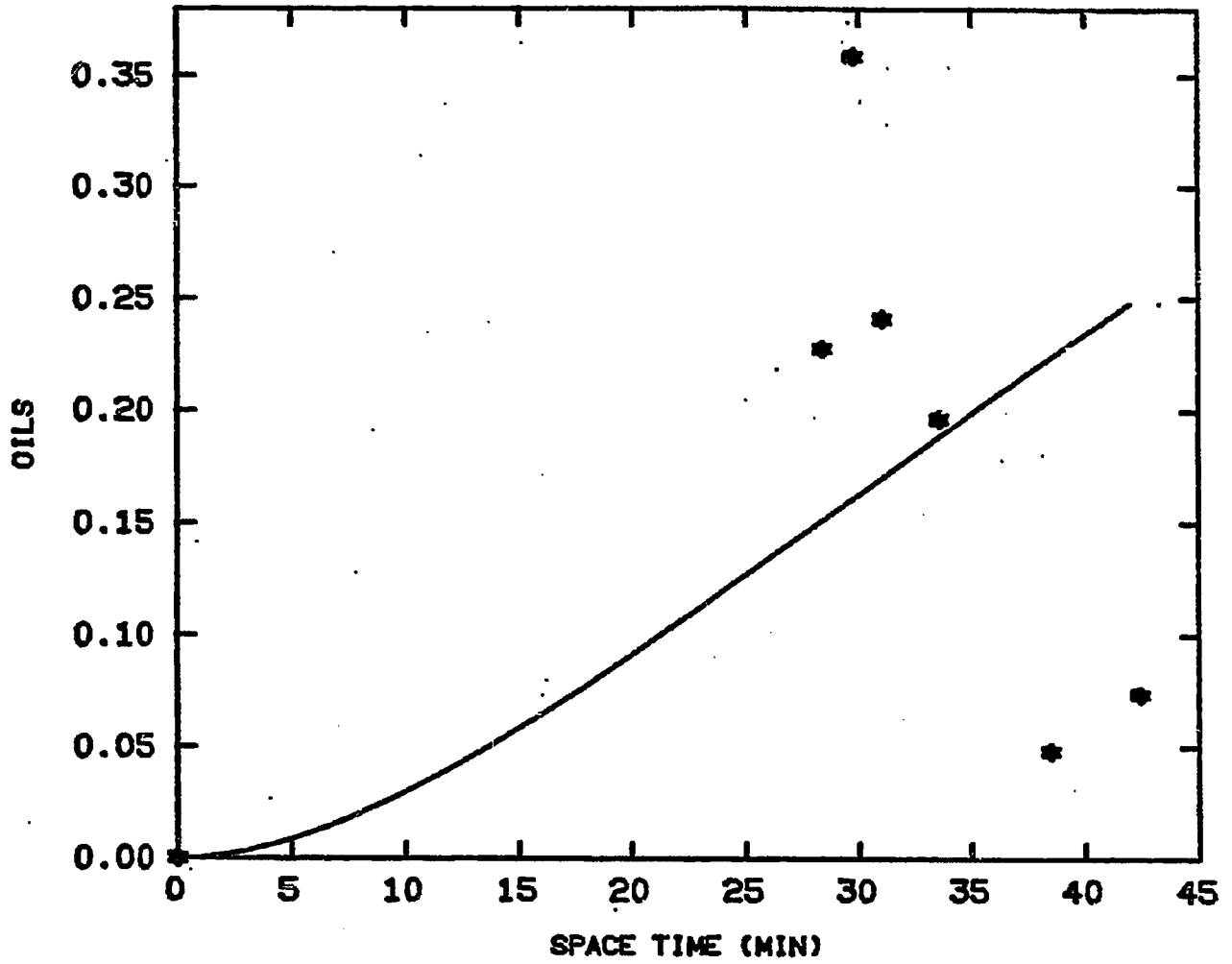


FIGURE 36: Model 2: Oils (Temperature (375°C))

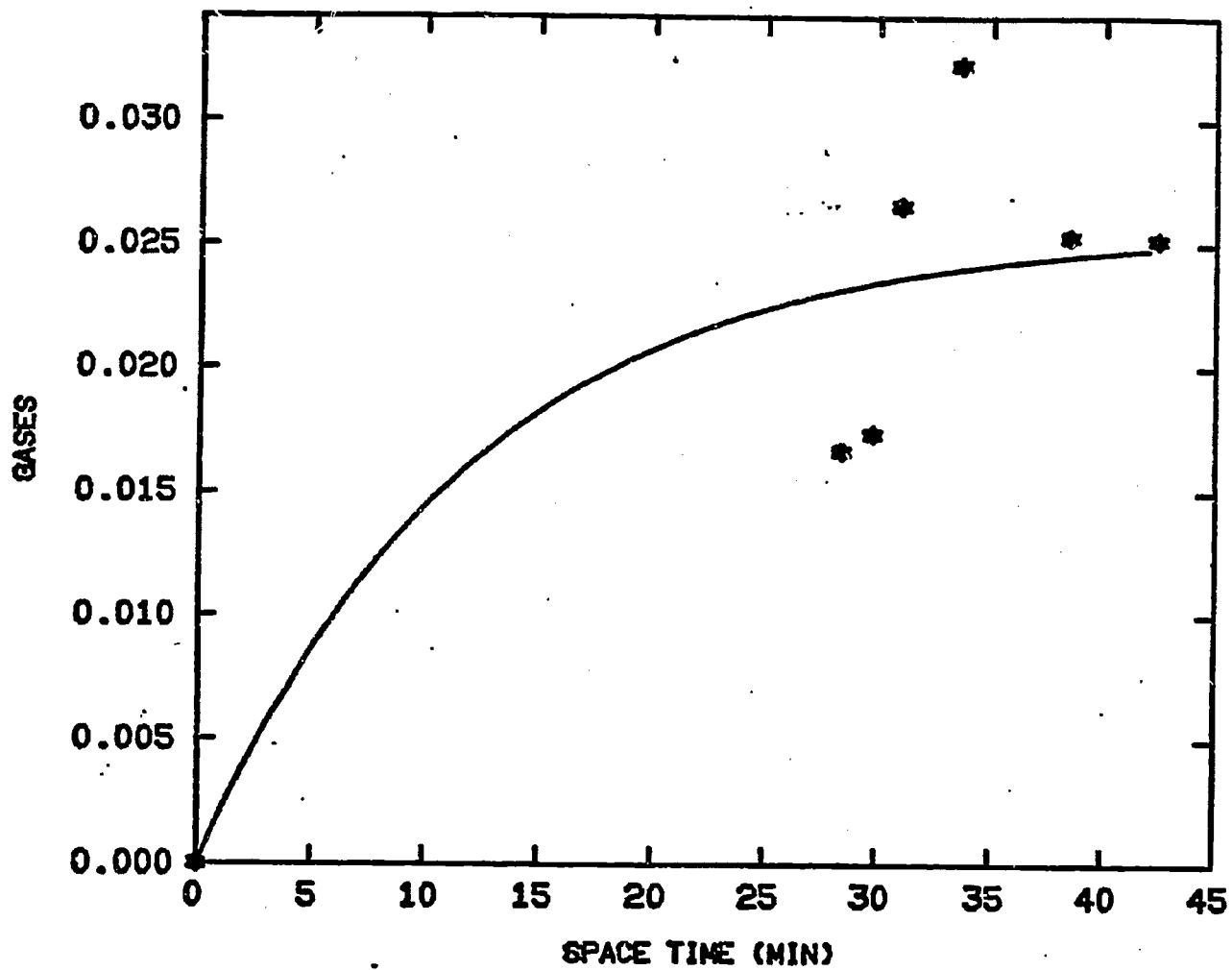


FIGURE 37: Model 2: Gases (Temperature 375°C)

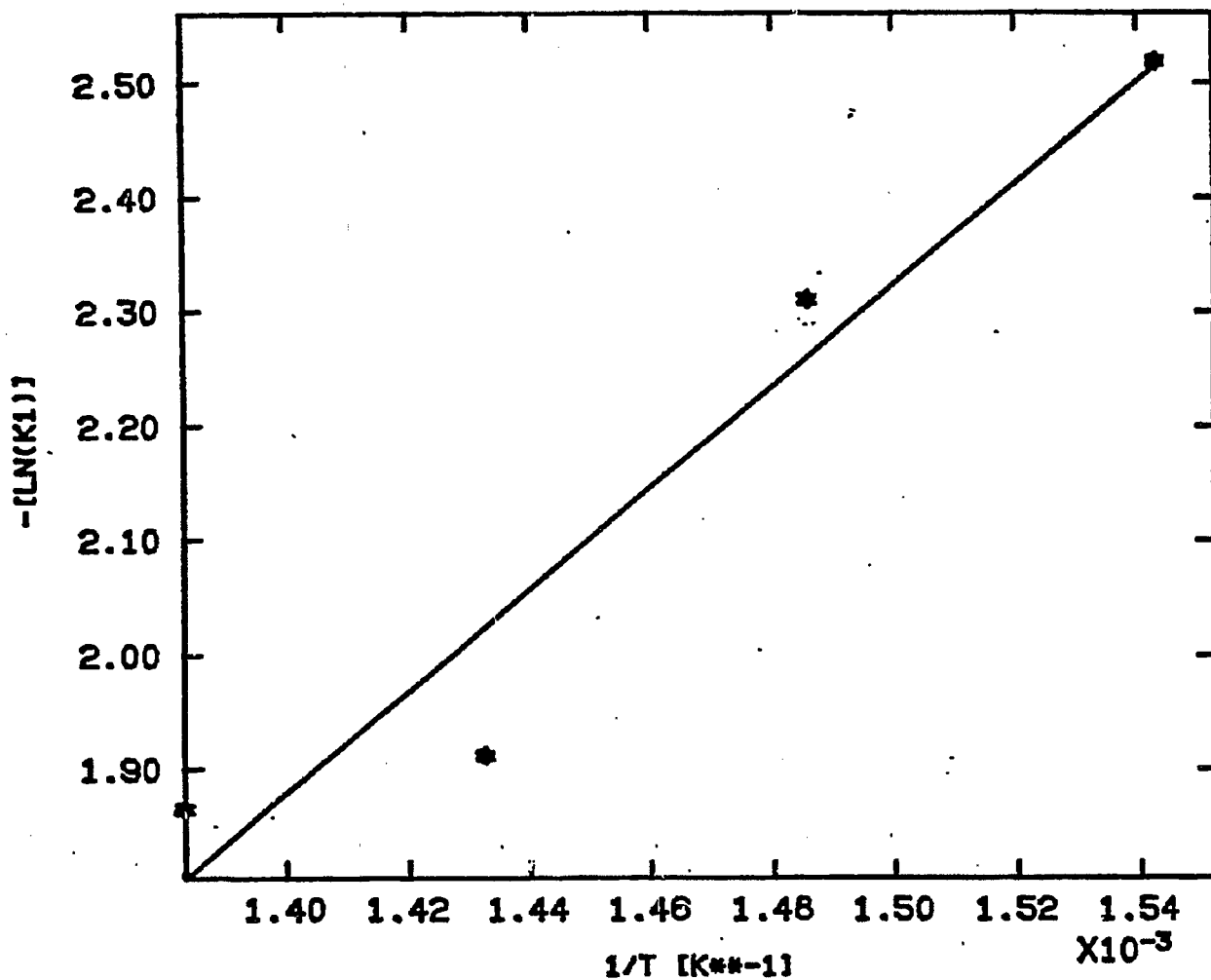


FIGURE 38: Arrhenius Plot: Model 1: Rate Constant k_1

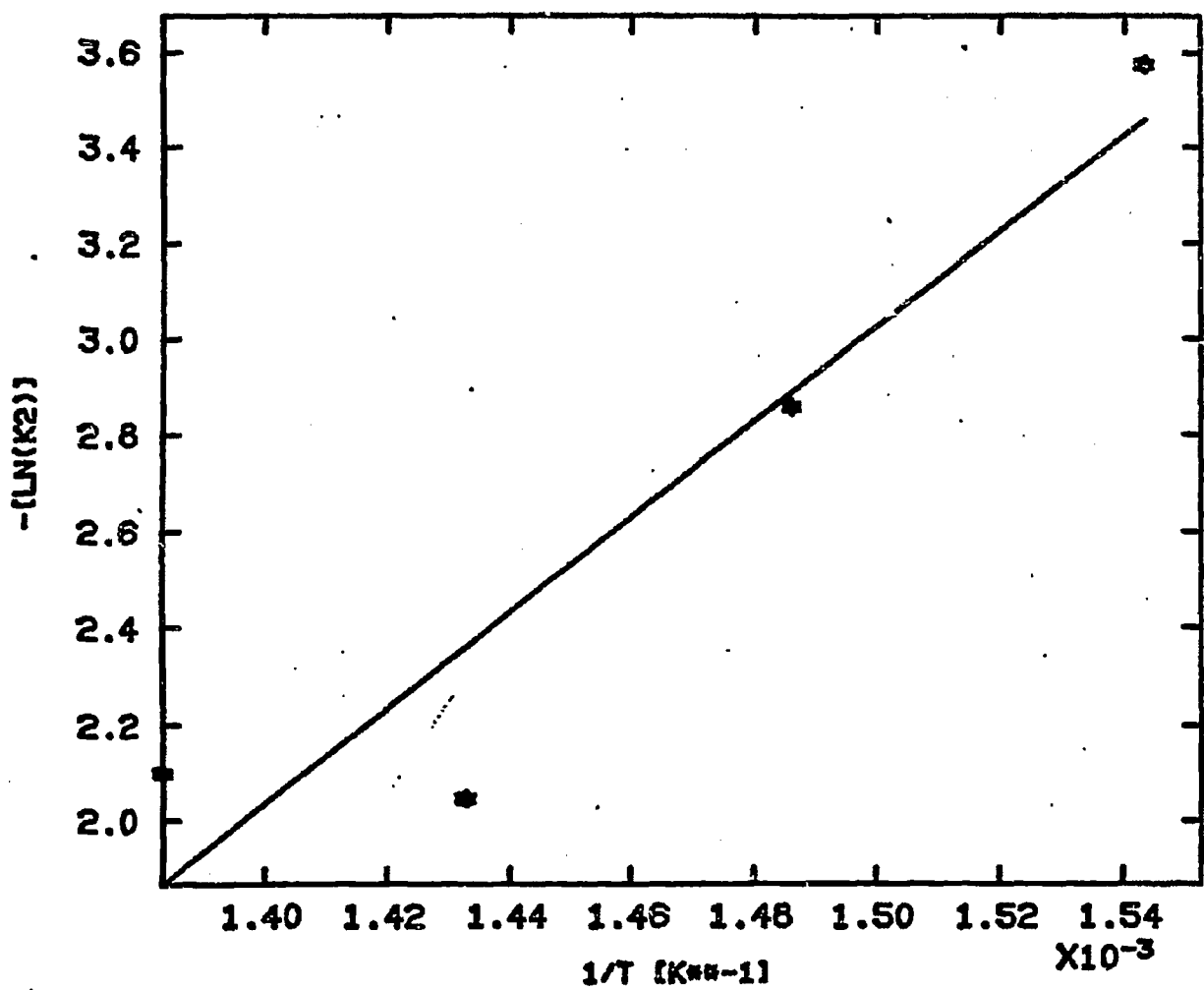


FIGURE 39: Arrhenius Plot: Model 1: Rate Constant k_2

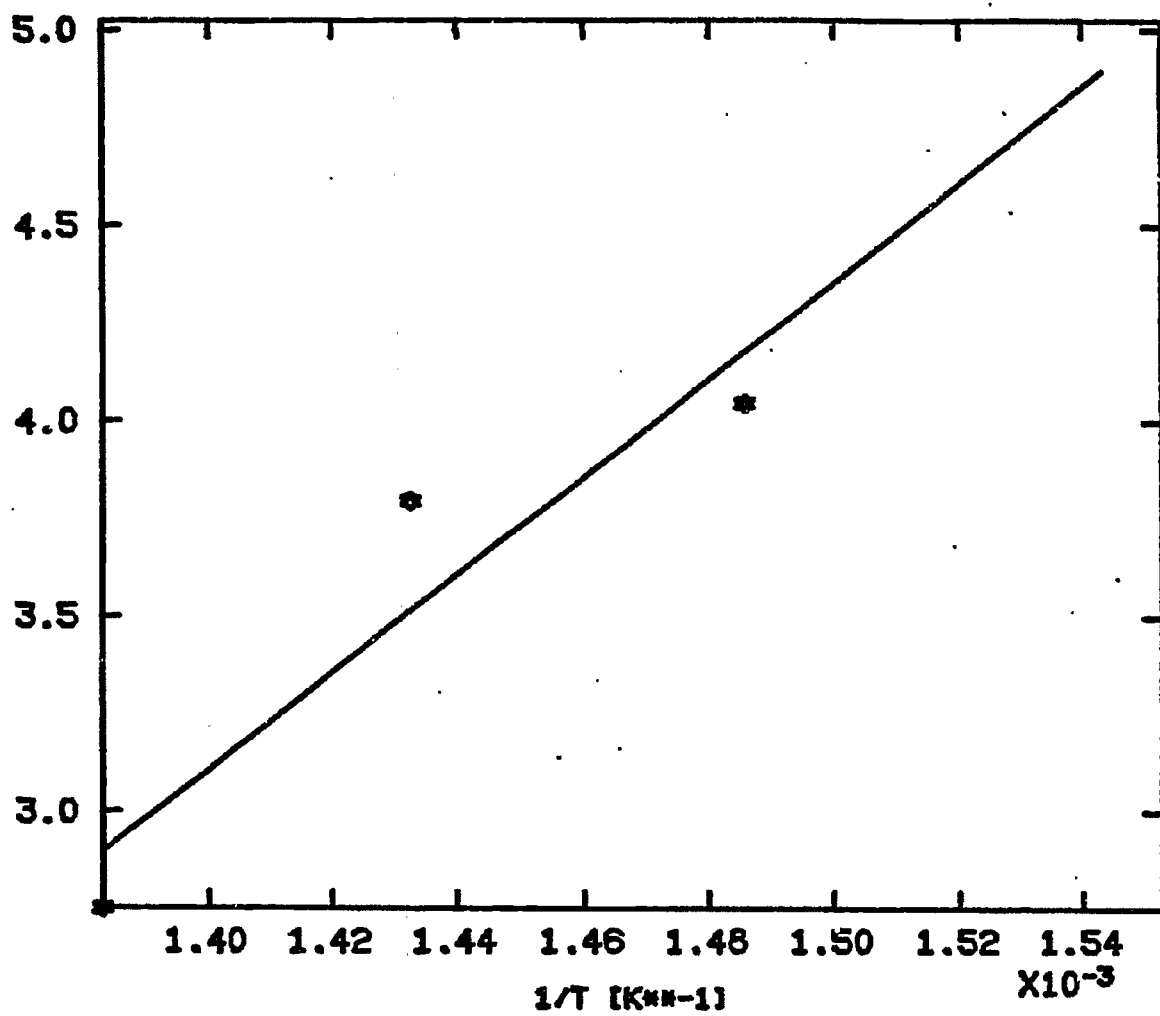


FIGURE 40: Arrhenius Plot: Model 1: Rate Constant k_3

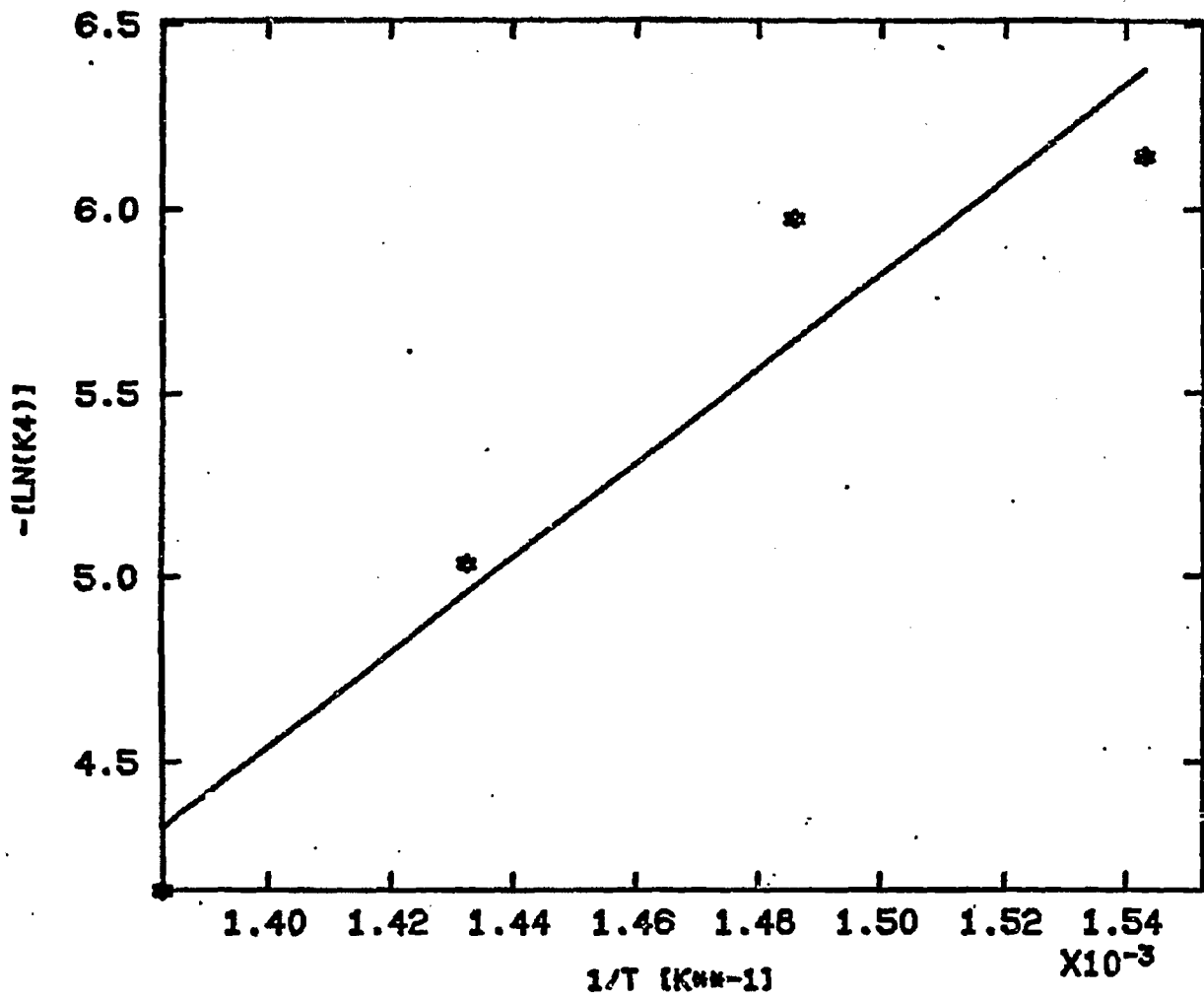


FIGURE 41: Arrhenius Plot: Model 1: Rate Constant k_4

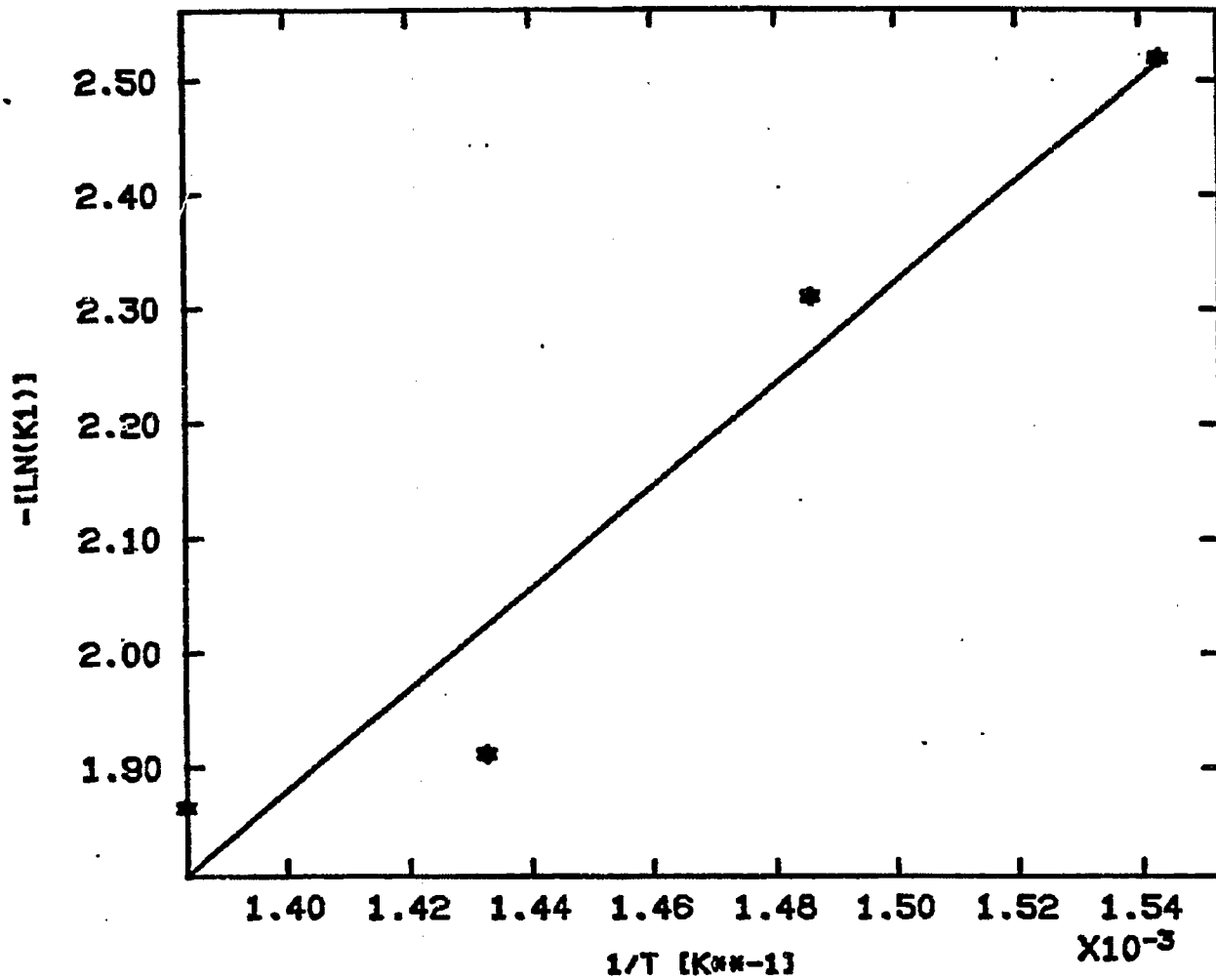


FIGURE 42: Arrhenius Plot: Model 2: Rate Constant k_1

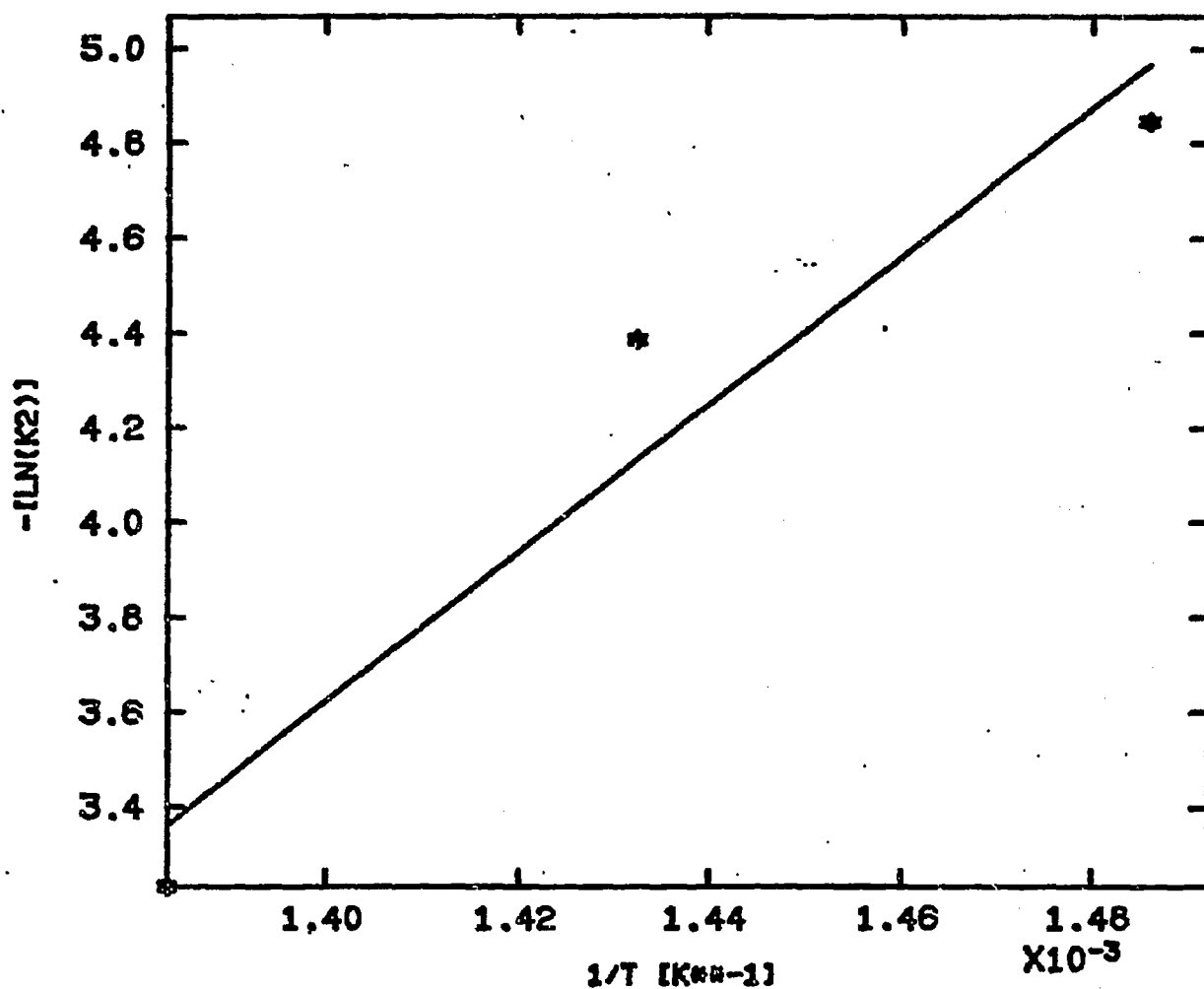


FIGURE 43: Arrhenius Plot: Model 2: Rate Constant k_2

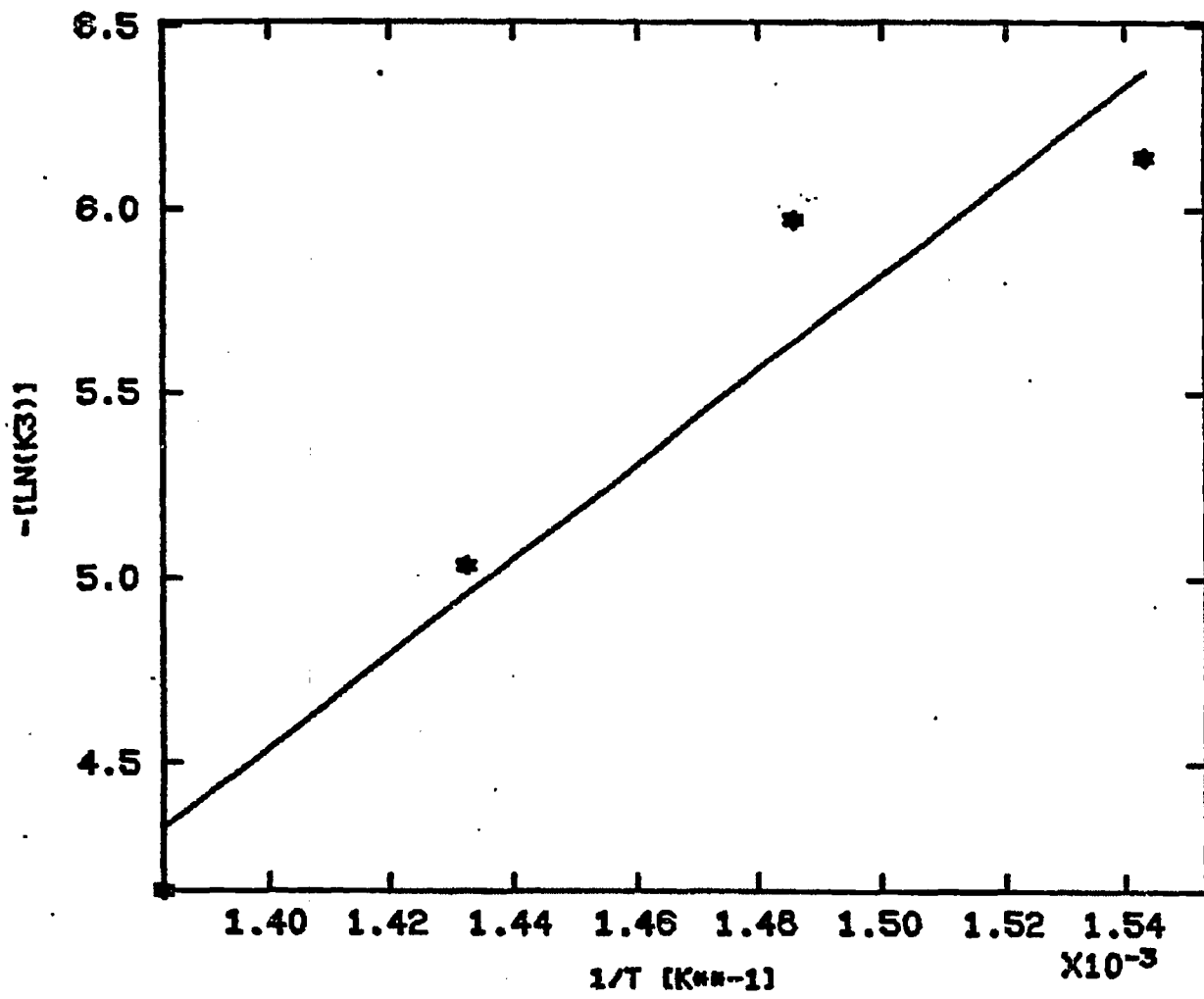


FIGURE 44: Arrhenius Plot: Model 2: Rate Constant k_3