CHAPTER 5.0

DISCUSSION

We will first show how we estimated the coverage from experimental data utilizing the surface CSTR model. Then we will discuss how well the surface CSTR model features the experimental transient curve.

5.1 ESTIMATION OF THE COVERAGE

The surface CSTR tells us, see Section 2.4, that,

$$\tau_k = k_N/k_R \qquad \text{(c.f. Eq.2-32)}$$

Since

$$k_R = k_{R'} + k_{R''} \qquad \text{(c.f. Eq.2-1)}$$

and

$$k_R = k{-}1_{R''} \qquad \text{(c.f. Eq.2-3)}$$

substituting these into Eq.2-32 yields,

$$k{-}1_{R''} = k_{R'} + k_{R''} \qquad (5\text{-}1)$$

We can write the following equations for k=2, 3, 4,...., n.

$$^{1}R'' = {}^{2}R' + {}^{2}R'' \tag{5-2}$$

$$^{2}R'' = {}^{3}R' + {}^{3}R'' \tag{5-3}$$

$$^{3}R'' = {}^{4}R' + {}^{4}R'' \tag{5-4}$$

......

$$^{n-1}R'' = {}^{n}R' + {}^{n}R'' \tag{5-5}$$

Addition of these equations yields:

$$^{1}R'' = {}^{2}R' + {}^{3}R' + \ldots + {}^{n}R' + {}^{n}R'' \tag{5-6}$$

Assuming a Flory-Schultz distribution yields:

$$^{2}R' = \alpha \cdot {}^{1}R' \tag{5-7}$$

$$^{3}R' = \alpha^{2} \cdot {}^{1}R' \tag{5-8}$$

$$^{4}R' = \alpha^{3} \cdot {}^{1}R' \tag{5-9}$$

......

$$^{n}R' = \alpha^{n-1} \cdot {}^{1}R' \tag{5-10}$$

Therefore, Eq.5-6, after having been substituted by the above equations, yields;

$$^{1}R'' = (\alpha + \alpha^{2} + \alpha^{3} + \ldots + \alpha^{n-1}) \cdot {}^{1}R' + {}^{n}R'' \tag{5-11}$$

Therefore,

$$^1R = {}^1R' + {}^1R'' \qquad \text{(c.f. Eq.2-1)}$$

$$= (1 + \alpha + \alpha^2 + \alpha^3 + \ldots + \alpha^{n-1}) \cdot {}^1R' + {}^nR'' \qquad (5\text{-}12)$$

as $n \to \infty$, ${}^nR'' \to 0$. The above equation becomes,

$$^1R = {}^1R' / (1 - \alpha) \qquad (5\text{-}13)$$

Therefore,

$$\tau_1 = {}^1N / {}^1R = {}^1N(1 - \alpha) / {}^1R'$$

$$= (1 - \alpha){}^1N / {}^1R' / N_s$$

$$= (1-\alpha)\theta_1 / TOF_1 \qquad (5\text{-}14)$$

or

$$\theta_1 = \tau_1 \cdot TOF_1 / (1 - \alpha) \qquad (5\text{-}15)$$

The same procedure can be carried out for pool C_k. The result is,

$$\theta_k = \tau_k \cdot TOF_k / (1 - \alpha) \qquad (5\text{-}16)$$

Our present method of data analysis is based on Eq.5-16. We treat our data as if they were generated by pools described in Chapter 2. τ_k can be determined from the transient data according to the model developed in Chapter 2. Gas Chromotography can give us TOF_k and α, c.f. Table 4-2. Accordingly, θ_k can be calculated from Eq.5-16.

Fig.4-10 shows θ_k at various D_2/CO ratios. It is seen that only a certain fractional coverage belongs to chain growth.

5.2 COMPARISON BETWEEN EXPERIMENTAL DATA AND THE MODEL

From our present findings it emerges that the surface CSTR model can approximately interprete the transient data. The reasons for arriving at this conclusion are discussed below.

When considering the distribution of species i in C_k products, one may intuitively think of statistical distribution. By statistical distribution we mean, for example, in all the C_2 compounds, $^{2}F^{13}C_{2} = (^{1}F^{13}C)^{2}$, $^{2}F^{12}C_{2} = (^{1}F^{12}C)^{2}$, and $^{2}F^{12}C_{1}{}^{13}C_{1} = 2\cdot(^{1}F^{13}C)(^{1}F^{12}C)$, which, according to the definition on page 10, leads to $F^{13}C\ in\ C_2 = {}^{1}F^{13}C$. in general, for statistical distribution in C_k products,

$$^{k}F_{i} = k!/i!/(k-i)!\cdot(^{1}F^{12}C)^{i}(^{1}F^{13}C)^{k-i} \qquad (5\text{-}17)$$

and

$$F^{13}C\ in\ C_{k} = {}^{1}F^{13}C \qquad (5\text{-}18)$$

Fig.5-1 demonstrates the experimental data when $^{1}F^{13}C$ = 0.5 and 0.6. It is readily seen that the product distributed non-statistically.

From the surface CSTR model, we know that the statistical distribution is just a special case of the CSTR model where $\tau_b = \tau_1$ and $\tau_2 = \tau_3 = 0$. Therefore, a choice of the parameters other than $\tau_b = \tau_1$, $\tau_2 = 0$ and $\tau_3 = 0$ will not lead to Eq.5-17 and Eq.5-18. In other words, the non-statistical distribution can be interpreted as $\tau_b \ngtrless \tau_1$, $\tau_2 \ngtrless 0$, and $\tau_3 \ngtrless 0$, as shown in Fig.5-1.

Another feature of the experimental data is that the transient responses of the intermediates ($^{12}C_1{}^{13}C_1$ and $^{12}C_1{}^{13}C_2$) rise simultaneously with $^{13}C_1$. What underlies is that the lifetime for either C_1-building surface intermediates or C_2 and C_3 surface intermediates must be very short. By adjusting parameters τb, τ_2 and τ_3 in the CSTR model, we can obtain a good simulation for this simultaneously-rising feature (Fig.2-4 and 2-5).

When we compare the experimental data with the predicted values, we find that:

(1) For C_1 and C_2 products, when $^{1}F_{^{13}C} < 0.8$, the model can give quite good estimation (Fig.4-3 and 4-5) for the transient responses of C_1 and C_2 species at a give time. Only when $^{1}F_{^{13}C}$ is greater than 0.8, a large discrepancy between the predicted and the experimental data for both C_1 and C_2 is observed. Therefore, we conclude that the surface CSTR model approximately describe the transient behavior of C_1 and C_2 species.

(2) For C_3 products, except $^{13}C_3$, C_3 products can be predicted up to $^{1}F_{^{13}C}$ = 0.3 (Fig.4-[illegible]. For ^{13}[illegible], the model

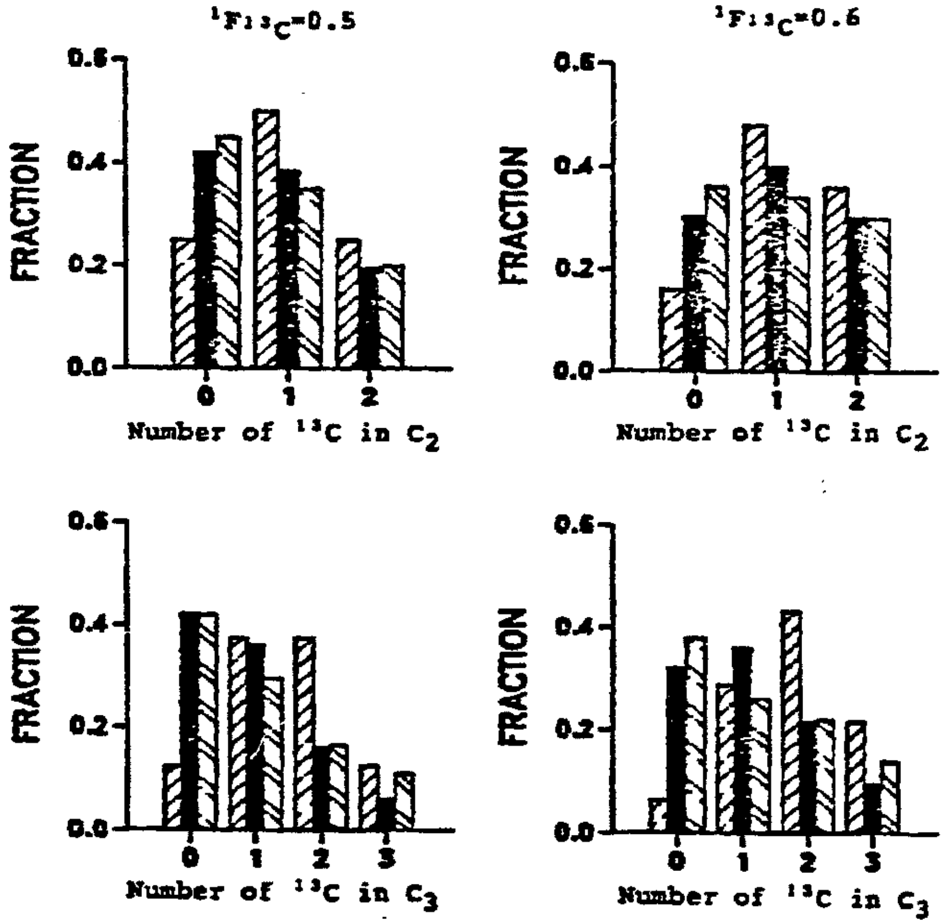


Figure 5-1: Non-Statistic Distribution of the Products

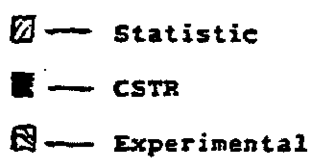


Table 5-1: Comparison of Estimated and Experimental $F^{13}C_{in}C_2$

$^1F^{13}C$	Exp.	CSTR*
0.0	0.0	0.0
0.1	0.065	0.04
0.2	0.142	0.10
0.3	0.22	0.185
0.4	0.315	0.290
0.5	0.375	0.40
0.6	0.48	0.50
0.7	0.62	0.62
0.8	0.72	0.72
0.9	0.86	0.86
1.0	1.0	1.0

*): with $\tau_b/\tau_1 = 0.1$, $\tau_2/\tau_1 = 0.7$.

**): for statistic distribution, $F^{13}C_{in}C_2 = {}^1F^{13}C$.

***): residual mean square error is 0.02683.

Table 5-2: Comparison of Estimated and Experimental $F^{13}C$inC$_3$

$^1F^{13}C$	Exp.	CSTR*
0.0	0.0	0.0
0.1	0.065	0.015
0.2	0.115	0.065
0.3	0.15	0.125
0.4	0.232	0.210
0.5	0.32	0.30
0.6	0.38	0.375
0.7	0.54	0.50
0.8	0.65	0.63
0.9	0.79	0.78
1.0	1.0	1.0

*): with $\tau_b/\tau_1 = 0.1$, $\tau_2/\tau_1 = \tau_3/\tau_1 = 0.7$.

**): for statistical distribution, $F^{13}C$inC$_3$=$^1F^{13}C$.

***): residual mean square error is 0.03512.

is essentially a very rough interpretation for the real situation. However, when we plot $F_{^{13}C\,in\,C_3}$ (Fig.4-5), we find that the transient response of ^{13}C in C_3 can be described well with the surface CSTR model up to $F_{^{13}C}$ in C_3 = 0.65, due to the compromise between the underestimation in $^{13}C_3$ and the overestimation in other responses.

(3) The estimated and the experimental data of ^{13}C in C_2 and ^{13}C in C_3 for a given $^1F_{^{13}C}$ are shown in Table 5-1 and 5-2. It can be seen that within the experimental error, the model is essentially suitable for $0.0 < {^1F_{^{13}C}} < 1.0$. This implies that factors which result in the deviation between the experimental and the predicted values for $^1F_{^{13}C}$ at a given time when $^1F_{^{13}C} > 0.8$, as stated before, may be the same as that for $F_{^{13}C\,in\,C_2}$ and $F_{^{13}C\,in\,C_3}$. Although it is not clear what these factors are, the effect on transient responses by these factors can be sure to be very small, i.e., the effect is apparent only after $^1F_{^{13}C} > 0.8$, a fact that allows us to utilize the surface CSTR model to have an order of magnitude for the lifetime of the surface intermediates and their coverage on the catalyst surface.

From the above discussion we can draw the following conclusions:

(1) The surface CSTR model can feature the experimental data better than the statistical distribution consideration.

(2) The surface CSTR model can approximately [illegible]

the transient behavior of C_1 and C_2 products. Although it gives a poor estimation for individual species of C_3 products, it can essentially predict the transient behavior of ^{13}C in C_3.

CHAPTER 6.0

SUMMARY

The isotope transient technique has been utilized in the study of the Fischer-Tropsch synthesis over cobalt catalyst. With a switch from a $^{12}CO/D_2$ to $^{13}CO/D_2$ feed, the transient response behavior can be approximately described by a surface CSTR model presented in this thesis. At T = 210°C and D_2/CO = 1 to 6.545, the estimated lifetimes for C_1, C_2 and C_3 surface intermediates are around 20, 14 and 14 sec, respectively, whereas the lifetime for C_1 surface intermediate which participates in the chain growth is around 2 sec. Only a certain surface carbons participate in the chain growth.

APPENDIX A

(IN) FORMS IN EQ.2-22

APPENDIX A.

(IN) FORMS IN EQ.2-22

Table A-1: (in) Forms in Eq.2-22

pool	τ_k	${}^{k}\dot{F}_i$	(in) $(= {}^{k}F_i^{o})$
CO	τ_0	${}^{0}F\,{}^{12}CO$	0
CO	τ_0	${}^{0}F\,{}^{13}CO$	1
C_1	τ_1	${}^{1}F\,{}^{12}C_1$	${}^{0}F\,{}^{12}C_1$
C_1	τ_1	${}^{1}F\,{}^{13}C_1$	${}^{0}F\,{}^{13}C_1$
C_b	τ_b	${}^{b}F\,{}^{12}C_1$	${}^{0}F\,{}^{12}C_1$
C_b	τ_b	${}^{b}F\,{}^{12}C_1$	${}^{0}F\,{}^{12}C_1$
C_2	τ_2	${}^{2}F\,{}^{12}C_2$	${}^{1}F\,{}^{12}C_1\,{}^{b}F\,{}^{12}C_1$
C_2	τ_2	${}^{2}F\,{}^{13}C_2$	${}^{1}F\,{}^{13}C_1\,{}^{b}F\,{}^{13}C_1$
C_2	τ_2	${}^{2}F\,{}^{12}C_1{}^{13}C_1$	${}^{1}F\,{}^{12}C_1\,{}^{b}F\,{}^{13}C_1 + {}^{1}F\,{}^{13}C_1\,{}^{b}F\,{}^{12}C_1$
C_3	τ_3	${}^{3}F\,{}^{12}C_3$	${}^{2}F\,{}^{12}C_1\,{}^{b}F\,{}^{12}C_1$
C_3	τ_3	${}^{3}F\,{}^{13}C_3$	${}^{2}F\,{}^{13}C_1\,{}^{b}F\,{}^{13}C_1$
C_3	τ_3	${}^{3}F\,{}^{12}C_2{}^{13}C_1$	${}^{2}F\,{}^{12}C_2\,{}^{b}F\,{}^{13}C_1 + {}^{2}F\,{}^{13}C_1{}^{12}C_1\,{}^{b}F\,{}^{12}C_1$
C_3	τ_3	${}^{3}F\,{}^{12}C_1{}^{13}C_2$	${}^{2}F\,{}^{13}C_2\,{}^{b}F\,{}^{12}C_1 + {}^{2}F\,{}^{13}C_1{}^{12}C_1\,{}^{b}F\,{}^{13}C_1$

APPENDIX B

THE TRANSIENT RESPONSE FROM THE CSTR MODEL

APPENDIX B.

THE TRANSIENT RESPONSE FROM THE CSTR MODEL

The transient response of species i from pool C_k is as follows:

Let:

$$y0 = \exp(-t/\tau_0) \quad \text{(B-1)}$$

$$yb = \exp(-t/\tau_b) \quad \text{(B-2)}$$

$$y1 = \exp(-t/\tau_1) \quad \text{(B-3)}$$

$$y2 = \exp(-t/\tau_2) \quad \text{(B-4)}$$

$$y3 = \exp(-t/\tau_3) \quad \text{(B-5)}$$

Then

For pool CO,

$$^{0}F^{12}_{CO} = y0 \quad \text{(B-6)}$$

$$^{0}F^{13}_{CO} = 1 - y0 \quad \text{(B-7)}$$

For pool C_1,

$$^{1}F^{12}_{C} = A \times y0 - B \times y1 \quad \text{(B-8)}$$

$$^{1}F^{13}_{C} = 1 - A \times y0 + B \times y1 \quad \text{(B-9)}$$

where,

$$A = \tau_0 \ / \ (\tau_0 - \tau_1) \qquad \text{(B-10)}$$

$$B = \tau_1 \ / \ (\tau_0 - \tau_1) \qquad \text{(B-11)}$$

For pool C_b,

$$^{b}F^{12}_{C} = C \times y0 - D \times yb \qquad \text{(B-12)}$$

$$^{b}F^{13}_{C} = 1 - C \times y0 - D \times yb \qquad \text{(B-13)}$$

where,

$$C = \tau_0 \ / \ (\tau_0 - \tau_b) \qquad \text{(B-14)}$$

$$D = \tau_B \ / \ (\tau_0 - \tau_b) \qquad \text{(B-15)}$$

For pool C_2,

$$^{2}F^{12}_{C_2} = (1 - CS1)*y2 + R1*y0^2 - R2*y0*y1 - R3*y0*yb + R4*y1*yb \qquad \text{(B-16)}$$

$$^{2}F^{13}_{C_2} = 1 - T1*y0 + T2*y1 - T3*y0 + T4*yb + R1*y0^2 - R2*y0*y1 - R3*y0*yb + R4*y1*yb - CS2*y2 \qquad \text{(B-17)}$$

$$^{2}F^{12}_{C_1}{}^{13}_{C_1} = 1 - {}^{2}F^{12}_{C_2} - {}^{2}F^{13}_{C_2} \qquad \text{(B-18)}$$

where

$$R1 = A*C*\tau_0 \ / \ (\tau_0 - 2*\tau_2) \qquad \text{(B-19)}$$

$$R2 = B*C*\tau_0*\tau_1 \ / \ (\tau_0*\tau_1 - \tau_2*(\tau_0 - \tau_1)) \qquad \text{(B-20)}$$

$$R3 = A*D*\tau_0 8\tau_b / (\tau_0*\tau_b - \tau_2*(\tau_0+\tau_b) \quad (B-21)$$

$$R4 = B*D*\tau_1 8\tau_b / (\tau_1*\tau_b - \tau_2*(\tau_1+\tau_b) \quad (B-22)$$

$$CS1 = R1 - R2 - R3 + R4 \quad (B-23)$$

$$T1 = A*\tau_0/(\tau_0-\tau_2) \quad (B-24)$$

$$T2 = B*\tau_1/(\tau_1-\tau_2) \quad (B-25)$$

$$CQ1 = T1 - T2 \quad (B-26)$$

$$T3 = C*\tau_0/(\tau_0-\tau_2) \quad (B-27)$$

$$T1 = D*\tau_b/(\tau_b-\tau_2) \quad (B-28)$$

$$CQ2 = T3 - T4 \quad (B-29)$$

$$CS2 = 1 - CQ1 - CQ2 + CS1 \quad (B-30)$$

For pool C_3,

$$^3F^{12}{}_{C_3} = V1*y3 + C*U1*y0^3 - C*U2*y0^2*y1$$
$$- C*U3*yo^2*yb + C*U4*y0*y1*yb$$
$$+ C*(1-CS1)*CP2*y0*y2 - D*U5*y0^2*yb$$
$$+ D*U6*Y0*y1*yb + D*U7*y0*yb^2$$
$$- D*U8*y1*yb^2 - D*(1 - CS1)*CP4*y2*yb \quad (B-31)$$

$$^{3}F_{1\,^{3}C_3} = V2*y3 + 1\text{-}U23*y0 + U24*y1 - U25*y0 + U26*yb$$
$$+ U19*y0^2 - U20*y0*y1 - U21*y0*yb + U22*y1*yb$$
$$- CS2*CP13*y2 - C*CP5*y0 + C*U9*y0^2 - C*U10*y0*y1$$
$$+ C*U11*y0^2 - C*U12*y0*yb - C*U1*y0^3$$
$$+ C*U2*y0^2*y1 + C*U3*y0^2*yb - C*U4*y0*y1*yb$$
$$+ CS2*C*CP2*y0*y2 + D*CP8*yb - D*U13*y0*yb$$
$$+ D*U14*y1*yb - D*U15*y0*yb + D*U1v*yb$$
$$+ D*CS2*CP4*y2*yb - D*U5*y0^2*yb + D*U6*y0*y1*yb$$
$$+ D*U7*y0*yb^2 - D*U8*y1*yb^2 \qquad \text{(B-32)}$$

$$^{13}F_{1\,^{2}C_2\,^{13}C_1} = V3*y3 + U17*y0 - U18*yb$$
$$+ U19*y0^2 - U20*y0*y1 - U21*y0*yb$$
$$+ U22*y1*yb + (1-CS1)*CP13*y2$$
$$- {}^{3}F_{1\,^{3}C_3} + U2*y3$$
$$- 2*{}^{3}F_{1\,^{2}C_3} + 2*U1*y3 \qquad \text{(B-33)}$$

$$^{3}F_{1\,^{2}C_1\,^{13}C_2} = 1 - {}^{3}F_{1\,^{2}C_3}$$
$$- {}^{3}F_{1\,^{3}C_3} - {}^{3}F_{1\,^{2}C_2\,^{13}C_1} \qquad \text{(B-34)}$$

Where

$$U1 = P1*\tau_0/(\tau_0 - 3*\tau_3) \qquad \text{(B-35)}$$

$$U2 = R2*\tau_0*\tau_1/(\tau_0*\tau_1 - \tau_3*(\tau_0+2*\tau_1)) \qquad (B\text{-}36)$$

$$U3 = R3*\tau_0*\tau_b/(\tau_0*\tau_b - \tau_3*(\tau_0+2*\tau_b)) \qquad (B\text{-}38)$$

$$U4 = R4*\tau_0*\tau_1/(\tau_0*\tau_1*\tau_b - \tau_3*(\tau_0*\tau_1 + \tau_0*\tau_b + \tau_1*\tau_b)) \qquad (B\text{-}39)$$

$$CP1 = U1 - U2 - U3 + U4 \qquad (B\text{-}40)$$

$$CP2 = \tau_0\tau_2/(\tau_0\tau_2 - \tau_3*(\tau_0+\tau_2)) \qquad (B\text{-}41)$$

$$U5 = R1*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_0+2*\tau_b)) \qquad (B\text{-}42)$$

$$U6 = R2*\tau_0*\tau_1/(\tau_0*\tau_1*\tau_b - \tau_3*(\tau_0*\tau_1 + \tau_0*\tau_b + \tau_1*\tau_b)) \qquad (B\text{-}43)$$

$$U7 = R3*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_b+2*\tau_0)) \qquad (B\text{-}44)$$

$$U8 = R4*\tau_1\tau_b/(\tau_1\tau_b - \tau_3*(\tau_b+2*\tau_1)) \qquad (B\text{-}45)$$

$$CP3 = U5 - U6 - U7 + U8 \qquad (B\text{-}46)$$

$$CP4 = \tau_b\tau_2/(\tau_b\tau_2 - \tau_3*(\tau_b+\tau_2)) \qquad (B\text{-}47)$$

$$CP5 = \tau_0/(\tau_0 - \tau_3) \qquad (B\text{-}48)$$

$$U9 = T1*\tau_0/(\tau_0 - 2*\tau_3) \qquad (B\text{-}49)$$

$$U10 = T2*\tau_0\tau_1/(\tau_0\tau_1 - \tau_3*(\tau_0+\tau_1)) \qquad (B\text{-}50)$$

$$CP6 = U9 - U10 \tag{B-51}$$

$$U11 = T3*\tau_0/(\tau_0 - 2*\tau_3) \tag{B-52}$$

$$U12 = T4*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_0+\tau_b)) \tag{B-53}$$

$$CP7 = U11 - U12 \tag{B-54}$$

$$CP8 = \tau_b/(\tau_b - \tau_3) \tag{B-55}$$

$$U13 = T1*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_0+\tau_b)) \tag{B-56}$$

$$U14 = T2*\tau_1\tau_b/(\tau_1\tau_b - \tau_3*(\tau_1+\tau_b)) \tag{B-57}$$

$$CP9 = U13 - U14 \tag{B-58}$$

$$U15 = T4*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_0+\tau_b)) \tag{B-59}$$

$$U16 = T4*\tau_b/(\tau_b-2*\tau_3) \tag{B-60}$$

$$CP10 = U15 - U16 \tag{B-61}$$

$$U17 = C*\tau_0/(\tau_0 - \tau_3) \tag{B-62}$$

$$U18 = D*\tau_b/(\tau_b - \tau_3) \tag{B-63}$$

$$CP11 = U17 - U18 \tag{B-64}$$

$$U19 = R1*\tau_0/(\tau_0 - 2*\tau_3) \tag{B-65}$$

$$U20 = R2*\tau_0\tau_1/(\tau_0\tau_1 - \tau_3*(\tau_0+\tau_1)) \quad \text{(B-66)}$$

$$U21 = R3*\tau_0\tau_b/(\tau_0\tau_b - \tau_3*(\tau_0+\tau_b)) \quad \text{(B-67)}$$

$$U22 = R4*\tau_1\tau_b/(\tau_1\tau_b - \tau_3*(\tau_1+\tau_b)) \quad \text{(B-68)}$$

$$CP12 = U19 - U20 - U21 + U22 \quad \text{(B-69)}$$

$$CP13 = \tau_2/(\tau_2-\tau_3) \quad \text{(B-70)}$$

$$CP14 = CP12 + (1-Cs1)*CP13 \quad \text{(B-71)}$$

$$U23 = T1*\tau_0/(\tau_0 - \tau_3) \quad \text{(B-72)}$$

$$U24 = T2*\tau_1/(\tau_1 - \tau_3) \quad \text{(B-73)}$$

$$U25 = T3*\tau_0/(\tau_0 - \tau_3) \quad \text{(B-74)}$$

$$U26 = T4*\tau_b/(\tau_b - \tau_3) \quad \text{(B-75)}$$

$$CP15 = 1 - U23 + U24 - U25 + U26 + CP12 - CS2*CP13 \quad \text{(B-76)}$$

V1, V2, V3 can be solved from the [illegible] conditions (Eq. 2-28 and 2-2[illegible]).

APPENDIX C

COMPUTER SIMULATION PROGRAM

```
      DIMENSION FFC2(123),FFC3(123),FFIN(123) ,X(123)
      DIMENSION F1(123),F2(123),F3(123),F4(123)
      DIMENSION FC1(123),FC2(123),CO1(123),CO2(123)
      COMMON UTB(4)
      COMMON    UT2(4,4),UT3(4,4,4),AR1(4,4,4),AR2(4,4,4,4)
      INTEGER A0,B0(2),C0(4) , A1(2),A2(2),A3(2)
      INTEGER D1(2)
      DATA A0/'TIME'/
      DATA B0/'RESPO','NSE'/
      DATA C0/' COMP','UTER ','SIMUL','ATION'     /

      DATA E0/'STAND'/
      DATA  A1/'+T(B/','+T1)'/

      DATA  A2/'+T(2/','+T1)'/
      DATA  A3/'+T(3/','+T1)'/
      DATA  B1/'L/CGR'/,E1/'L/CST'/,
     *      FU/'+'/ ,       G1/'('/,G2/')'/
      T1=20.54
      T0=T1*0.05
      X(1)=0
      NCY=121
      NO=9
      A=T0/(T0-T1)
      B=T1/(T0-T1)
      X(1)=0.
      DO 15 I=1,NCY
      E=EXP(-X(I)/T0)
      F=EXP(-X(I)/T1)
      CO2(I)=1-E
      FC1(I)=A*E-B*F
      FC2(I)=1-FC1(I)
      AREA=AREA+FC1(I)
C     WRITE(8,5) CO2(I),FC2(I),CO1(I)
      X(I+1)=X(I)+2.896
15    CONTINUE
      AREA=AREA*2.896
      TB=0.013*T1
C*****************************
      DO 90 J=1,1
      UTB(J)=TB/T1
      C=T0/(T0-TB)
      D=TB/(T0-TB)
      T2=1.00001 *T1
      DO 80 I=1,1
      UT2(J,I)=T2/T1
      RA1=A*C*T0/(T0-2*T2)
      RA2=B*C*T0*T1/(T0*T1-T2*(T0+T1))
      RA3=A*D*T0*TB/(T0*TB-T2*(T0+TB))
      RA4=B*D*T1*TB/(T1*TB-T2*(T1+TB))
      C1=RA1-RA2-RA3+RA4
      RA5=A*T0/(T0-T2)
      RA6=B*T1/(T1-T2)
      C2=RA5-RA6-C1
      RA7=C*T0/(T0-T2)
      RA8=D*TB/(TB-T2)
      C3=RA7-RA8-C1
      C4=1.-C1-C2-C3
C     PRINT*,RA1,RA2,RA3,RARA5,RA6,RA7,RA8
C     PRINT*,C1,C2,C3,C4
```

```
C         GOTO 89
          DO 12 I1=1,5
          AR1(J,I,I1)=0.
12        CONTINUE
          X(1)=0.
          DO 20 K=1,NCY
          E=EXP(-X(K)/T0)
          F=EXP(-X(K)/T1)
          G=EXP(-X(K)/T8)
          U=EXP(-X(K)/T2)
          R1=RA1*E*E-RA2*E*F-RA3*E*G+RA4*F*G
          R2=RA5*E-RA6*F-R1
          R3=RA7*E-RA8*G-R1
          R4=1.-R1-R2-R3
          FFC2(     K)=R1+(1-C1)*U
          FFC3(     K)=R4-C4*U
          FFIN(     K)=R2+R3-(C2+C3)*U
          AR1(J,I,1)=AR1(J,I,1)+FFC2(     K)
          AR1(J,I,2)=AR1(J,I,2)+FFIN(     K)
          AR1(J,I,3)=AR1(J,I,3)+1.-FFC3(     K)
          X(K+1)=X(K)+2.896
C         WRITE(9 ,5)FFC2(J,I,K),FFC3(J,I,K),FFIN(J,I,K)
20        CONTINUE
C5        FORMAT(1X    ,3(5X    ,F10.8))
C6        FORMAT(4(5X,F10.8))
C         GOTO 89
          Z='ALBUT'
          CALL CALCMP
          CALL SHDCHR(90.,1,0.01,1)
          CALL PAGE(11.,8.5)
          CALL SWISSB
          CALL UCCHAR
          CALL MX1ALF(E0,G2)
          CALL MX2ALF(E1,G1)
          CALL MX3ALF(B1,FU)
          CALL AREA2D(8.,5.)
          CALL XNAME(A0,4)
          CALL YNAME(B0,8)
          CALL HEADIN(C0,20,2.,1)
          CALL GRAF(.0,50.,360.,.0,.2,1.2)
          CALL RLMESS(A1,10,50.,1.2)
          X1=UT8(J)
          CALL RLREAL(X1,4,Z,1.2)
          CALL RLMESS(A2,10,200.,1.2)
          X2=UT2(J,I)
          CALL RLREAL(X2,4,Z,1.2)
          CALL CURVE(X,FC2,NCY,0)
          CALL CURVE(X,FFC2 ,NCY,0)
          CALL CURVE(X,FFC3, NCY,0)
          CALL CURVE(X,FFIN ,NCY,0)
          CALL ENDPL(1)
          DO 19 I0=1,3
19        AR1(J,I,I0)=AR1(J,I,I0)*2.896/T1
89        T3=0.451   *T1
C*********************************************
          DO 30 L=1,2
          UT3(J,I,L)=T3/T1
          UC1=C*RA1*T0/(T0-3.*T3)
          UC2=D*RA1*T0*T8/(T0*T8-T3*(T0+2.*T8))
          UC3=C*RA2*T0*T1/(T0*T1-T3*(T0+2.*T1))
```

```
      UC4=D*RA2*T0*T1*TB/(T0*T1*TB-T3*(T0*T1+T1*TB+TB*T0))
      UC5=C*RA3*T0*TB/(T0*TB-T3*(T0+2.*TB))
      UC6=D*RA3*T0*TB/(T0*TB-T3*(TB+2*T0))
      UC7=C*RA4*UC4/D/RA2
      UC8=D*RA4*T1*TB/(T1*TB-T3*(TB+2.*T1))
      AC1=UC1-UC2
      AC2=UC3-UC4
      AC3=UC5-UC6
      AC4=UC7-UC8
      CU1=AC1-AC2-AC3+AC4
      TC1=C*T0/(T0-2*T3)
      TC2=D*T0*TB/(T0*TB-T3*(T0+TB))
      CT1=TC1-TC2
      TC3=C*T0*T1/(T0*T1-T3*(T0+T1))
      TC4=D*T1*TB/(T1*TB-T3*(T1+TB))
      CT2=TC3-TC4
      CU2=RA5*CT1-RA6*CT2-CU1
      TT1=C*T0*TB/(T0*TB-T3*(T0+TB))
      TT2=D*TB/(TB-2*T3)
      CT3=TT1-TT2
      CU3=RA7*CT1-RA8*CT3-CU1
      Q1=C*T0/(T0-T3)
      Q2=D*TB/(TB-T3)
      BF=Q1-Q2
      CU4=BF-CU1-CU2 -CU3
      RQ1=RA1*T0/(T0-2*T3)
      RQ2=RA2*T0*T1/(T0*T1-T3*(T0+T1))
      RQ3=RA3*T0*TB/(T0*TB-T3*(T0+TB))
      RQ4=RA4*T1*TB/(T1*TB-T3*(T1+TB))
      CR1=RQ1-RQ2-RQ3+RQ4
      Q3=RA5*T0/(T0-T3)
      Q4=RA6*T1/(T1-T3)
      CR2=Q3-Q4-CR1
      Q5=RA7*T0/(T0-T3)
      Q6=RA8*TB/(TB-T3)
      CR3=Q5-Q6-CR1
      CR4=1-CR1-CR2-CR3
      CR5=T2/(T2-T3)
      Q7=C*T0*T2/(T0*T2-T3*(T0+T2))
      Q8=D*TB*T2/(TB*T2-T3*(T2+TB))
      CR6=Q7-Q8
      CU41=CR4-CU4
      CUIN=CR2+CR3-(C2+C3)*CR5
      CUT2=CR5-CR6
      CS1=CU1+(1-C1)*CR6
      CS2=CU41-C4*CUT2
      CS3=CU2+CU3-(C2+C3)*CR6
      CS4=CR1+(1-C1)*CR5-CS1
      CS5=CUIN-CS3
      CS6=CU4-C4*CR6
      DO 13 I2=1,4
      AR2(J,I,L,I2)=0.
   13 CONTINUE
      X(1)=0.
      DO 25 KK=1,NCY
      E=EXP(-X(KK)/T0)
      F=EXP(-X(KK)/T1)
      G=EXP(-X(KK)/TB)
      U=EXP(-X(KK)/T2)
      V=EXP(-X(KK)/T3)
```

```
      AU1=UC1*E*E*F-UC2*F*E*G
      AU2=UC3*E*E*F-UC4*E*F*G
      AU3=UC5*E*E*G-UC6*E*G*G
      AU4=UC7*F*F*G-UC8*F*G*G
      U1=AU1-AU2-AU3+AU4
      TU1=TC1*E*E-TC2*G*E
      TU2=TC3*F*E-TC4*G*F
      U2=RA5*TU1-RA6*TU2-U1
      TU3=TT1*E*G-TT2*G*G
      U3=RA7*TU1-RA8*TU3-U1
      FB=Q1*E-Q2*G
      U4=FB-U1-U2-U3
      RU1=RQ1*E*E-RQ2*E*F-RQ3*E*G+RQ4*F*G
      RU2=Q3*E-Q4*F-RU1
      RU3=Q5*E-Q6*G-RU1
      RU4=1.-RU1-RU2-RU3
      UB=CR5*U
      RU6=Q7*U*E-Q8*U*G
      U41=RU4-U4
      RUIN=RU2+RU3-(C2+C3)*UB
      RUT2=UB -RU6
      S1=U1+(1-C1)*RU6
      S2=U41-C4*RUT2
      S3=U2+U3-(C2+C3)*RU6
      S4=RU1+(1-C1)*UB-S1
      S5=RUIN-S3
      S6=U4-C4*RU6
      PRINT*,S1,CS1,S2,CS2,S3,CS3,S4,CS4,S5,CS5,S6,CS6
      PRINT*,U41,CU41,RUT2,CUT2

      F1(KK)=S1+(1-CS1)*V
      F2(KK)=S2-CS2*V
      F3(KK)=S3+S4-(CS3+CS4)*V
      F4(KK)=S5+S6-(CS5+CS6)*V
      AR2(J,I,L,1)=AR2(J,I,L,1)+F1(       KK)
      AR2(J,I,L,2)=AR2(J,I,L,2)+1.-F2(        KK)
      AR2(J,I,L,3)=AR2(J,I,L,3)+F3(       KK)
      AR2(J,I,L,4)=AR2(J,I,L,4)+F4(       KK)
      X(KK+1)=X(KK)+2.896
C     WRITE(10,16) F1( KK),F2(KK),F3(KK),F4(KK)
25    CONTINUE
C16   FORMAT(1X,4(5X,F10.8))
C6    FORMAT(4(5X,F10.8))
C     GOTO 99
      CALL CALCMP
      CALL SHDCHR(90.,1,0.01,1)
      CALL PAGE(11.,8.5)
      CALL SWISSB
      CALL MX1ALF(E0,G2)
      CALL MX2ALF(E1,G1)
      CALL MX3ALF(B1,FU)
      CALL AREA2D(8.,5.)
      CALL XNAME(A0,4)
      CALL YNAME(B0,8)
      CALL HEADIN(C0,20,2.,1)
      CALL GRAF(.0,50.,360.,.0,.2,1.2)
      CALL RLMESS(A1,10,30.,1.2)
      X1=UTB(J)
      CALL RLREAL(X1,4,Z,1.2)
```

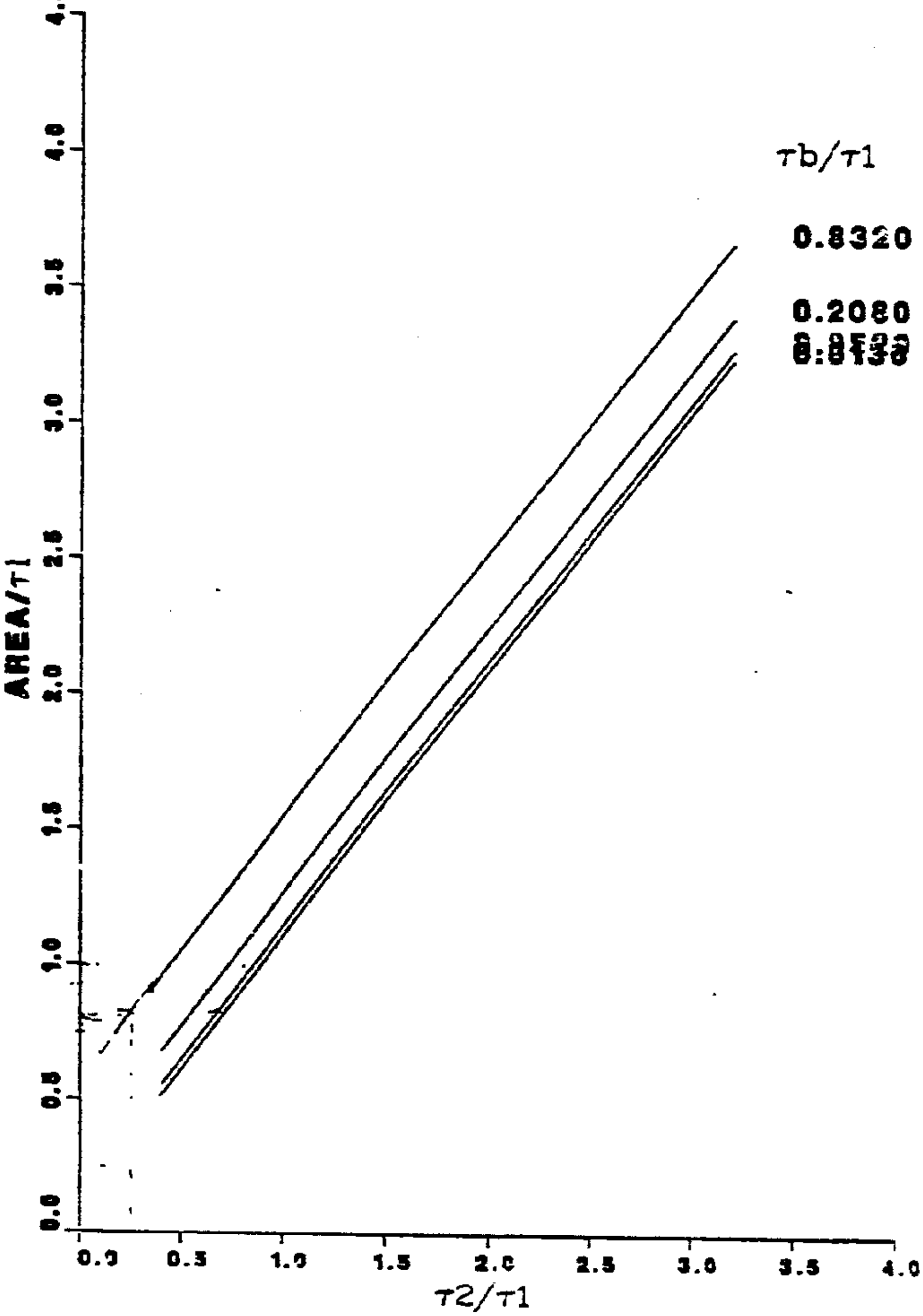
```
      CALL RLMESS(A2,10,150.,1.2)
      X2=UT2(J,I)
      CALL RLREAL(X2,4,Z,1.2)
      CALL RLMESS(A3,10,270.,1.2)
      X3=UT3(J,I,L)
      CALL RLREAL(X3,4,Z,1.2)
      CALL CURVE(X,FC2,NCY,0)
      CALL CURVE(X,F1,NCY,0)
      CALL CURVE(X,F2,NCY,0)
      CALL CURVE(X,F3,NCY,0)
      CALL CURVE(X,F4,NCY,0)
      CALL ENDPL(1)
99    DO 14 I3=1,4
      AR2(J,I,L,I3)=AR2(J,I,L,I3)*2.896/T1
14    CONTINUE
C     GOTO 100
      T3=T3*2.
30    CONTINUE
      T2=T2*2.
80    CONTINUE
      TB=TB*4.
90    CONTINUE
C     CALL APLO
      WRITE(13,1)T1,AREA
      DO 9 I=1,4
      WRITE(13,2)UTB(I)
      DO 8 J=1,4
      WRITE(13,3) UT2(I,J),(AR1(I,J,IJ),IJ=1,3)
      DO 7 K=1,4
      WRITE(13,4) UT3(I,J,K),(AR2(I,J,K,IJ),IJ=1,4)
 7    CONTINUE
 8    CONTINUE
 9    CONTINUE
 1    FORMAT(1X,F7.4,5X,F12.7)
 2    FORMAT(1X,F7.4)
 3    FORMAT(1X,F7.4,3(5X,F12.7))
 4    FORMAT(1X,F7.4,4(5X,F12.7))
 100  STOP
      END
```

END.......USER: XUEZHI [114125,374231].........JOB: A..........SEQ: 11048 FINISH
****

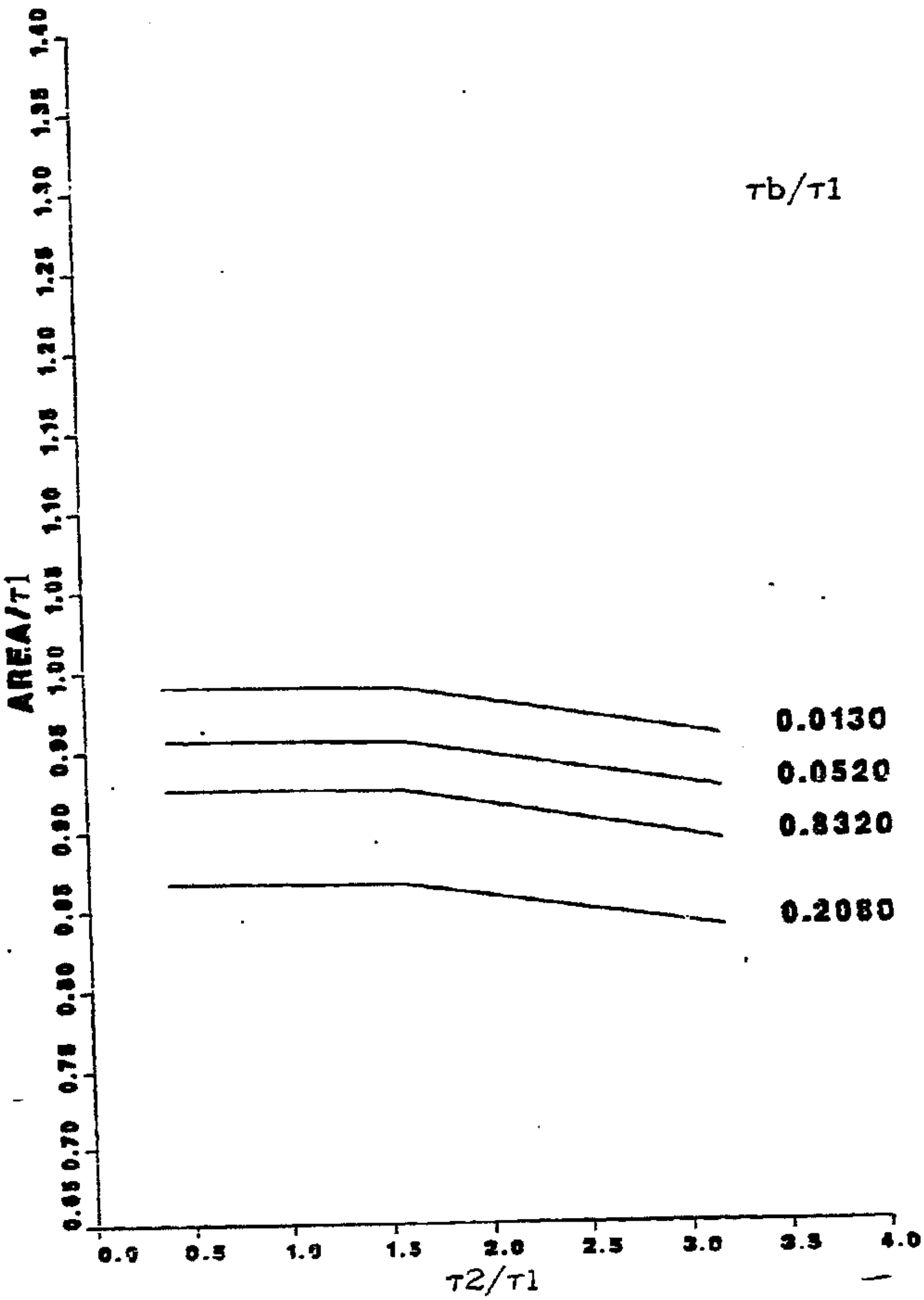
****

APPENDIX D

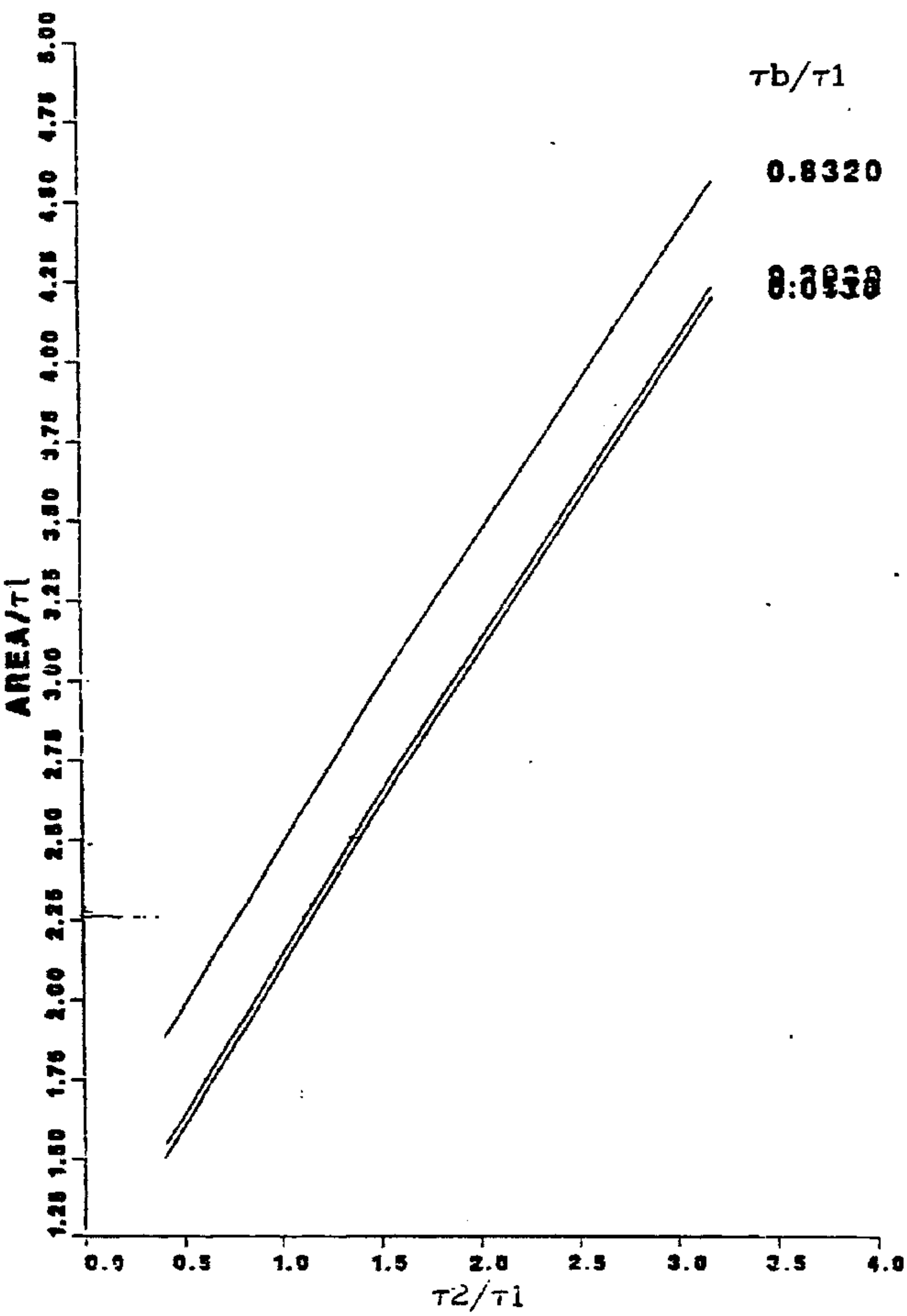
AREA VS LIFETIME PLOTS


τb/τ1
0.8320
0.2080
AREA/τ1
τ2/τ1
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5

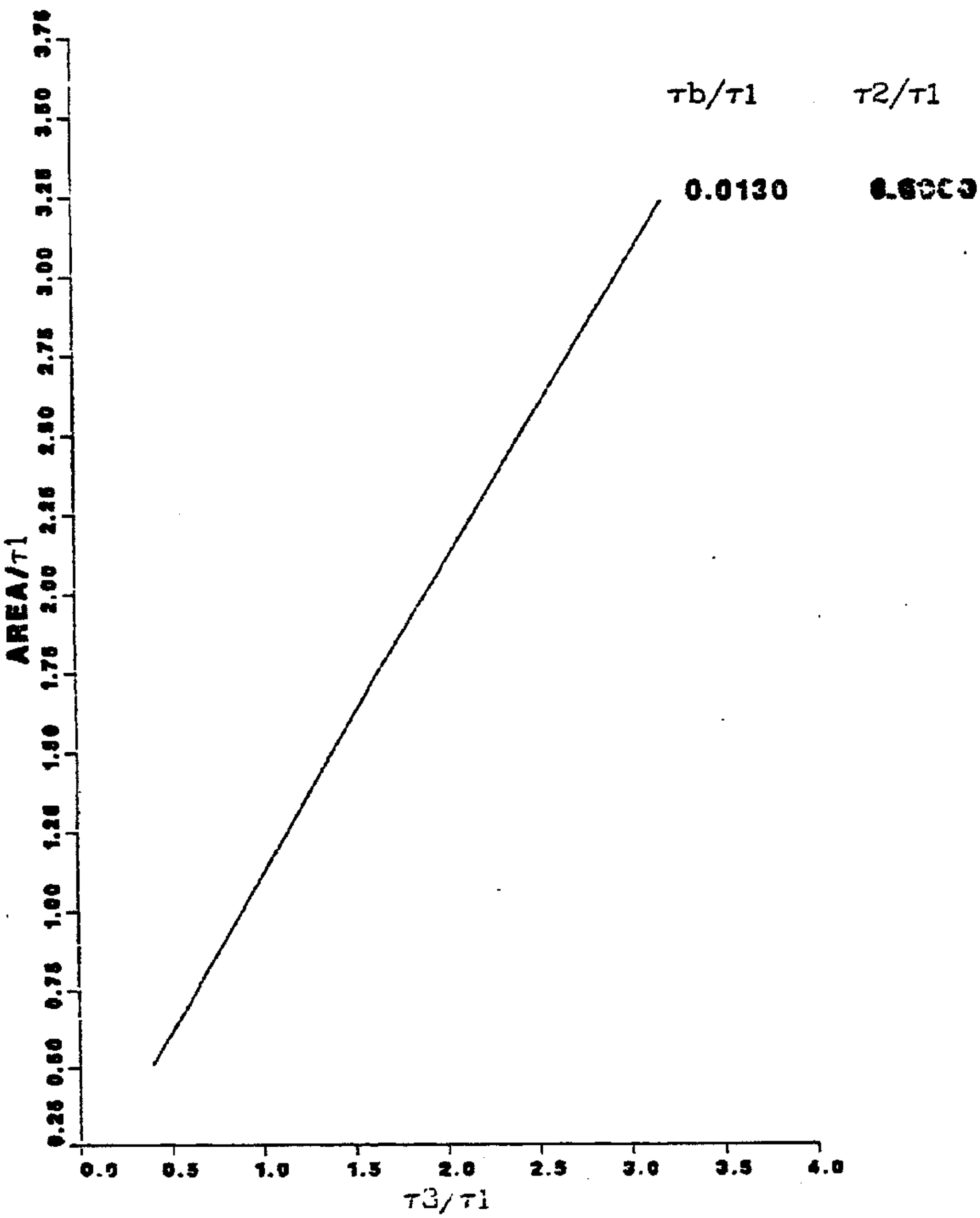
$^{12}C_1{}^{13}C_1$


τb/τ1
AREA/τ1
τ2/τ1
0.0130
0.0520
0.8320
0.2080
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
1.25
1.30
1.35
1.40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

$^{13}C_2$

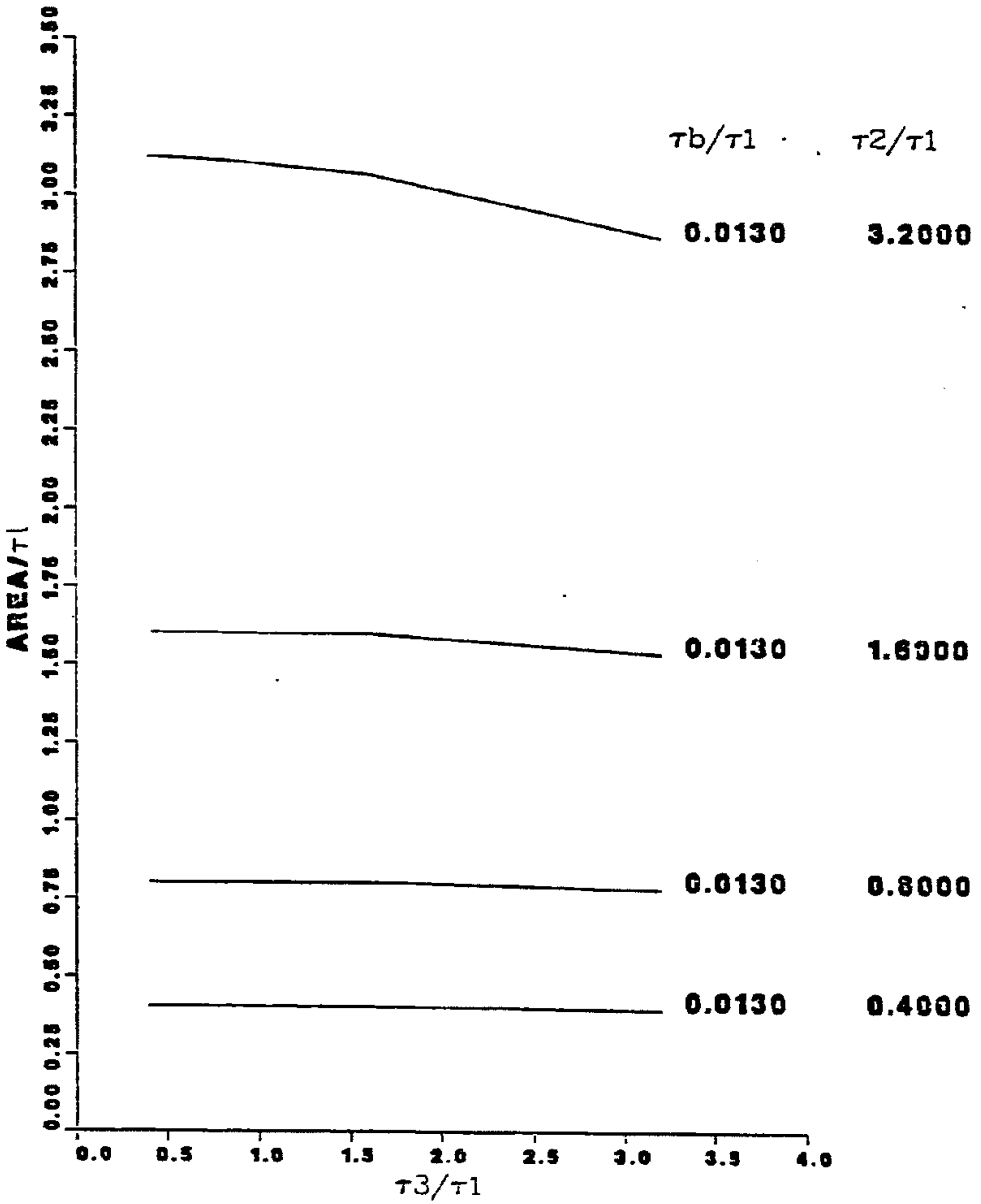


$^{12}C_3$

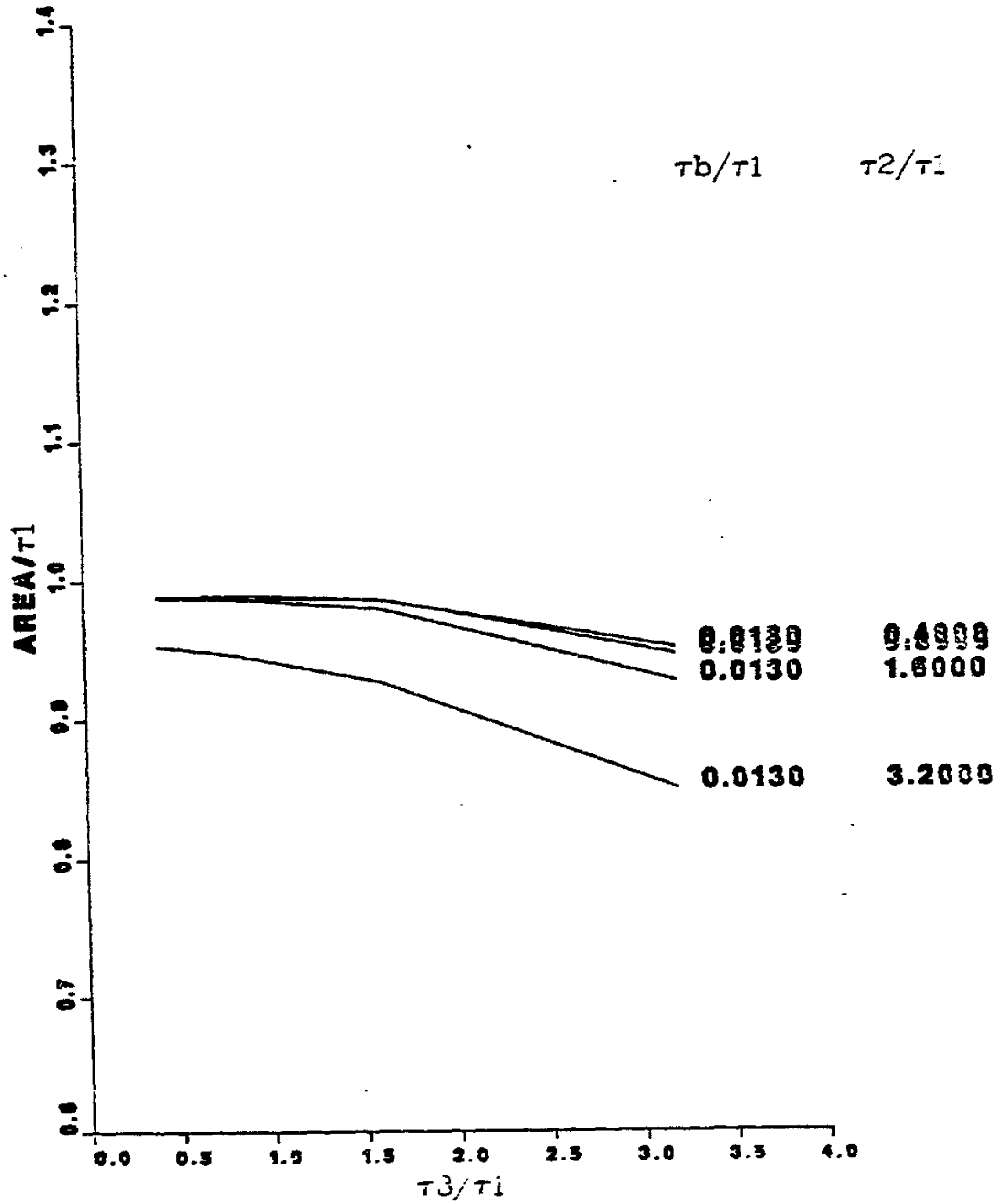

τb/τ1
τ2/τ1
0.0130
0.6000
AREA/τ1
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
3.25
3.50
3.75
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1

[redacted]

C_2 C_1

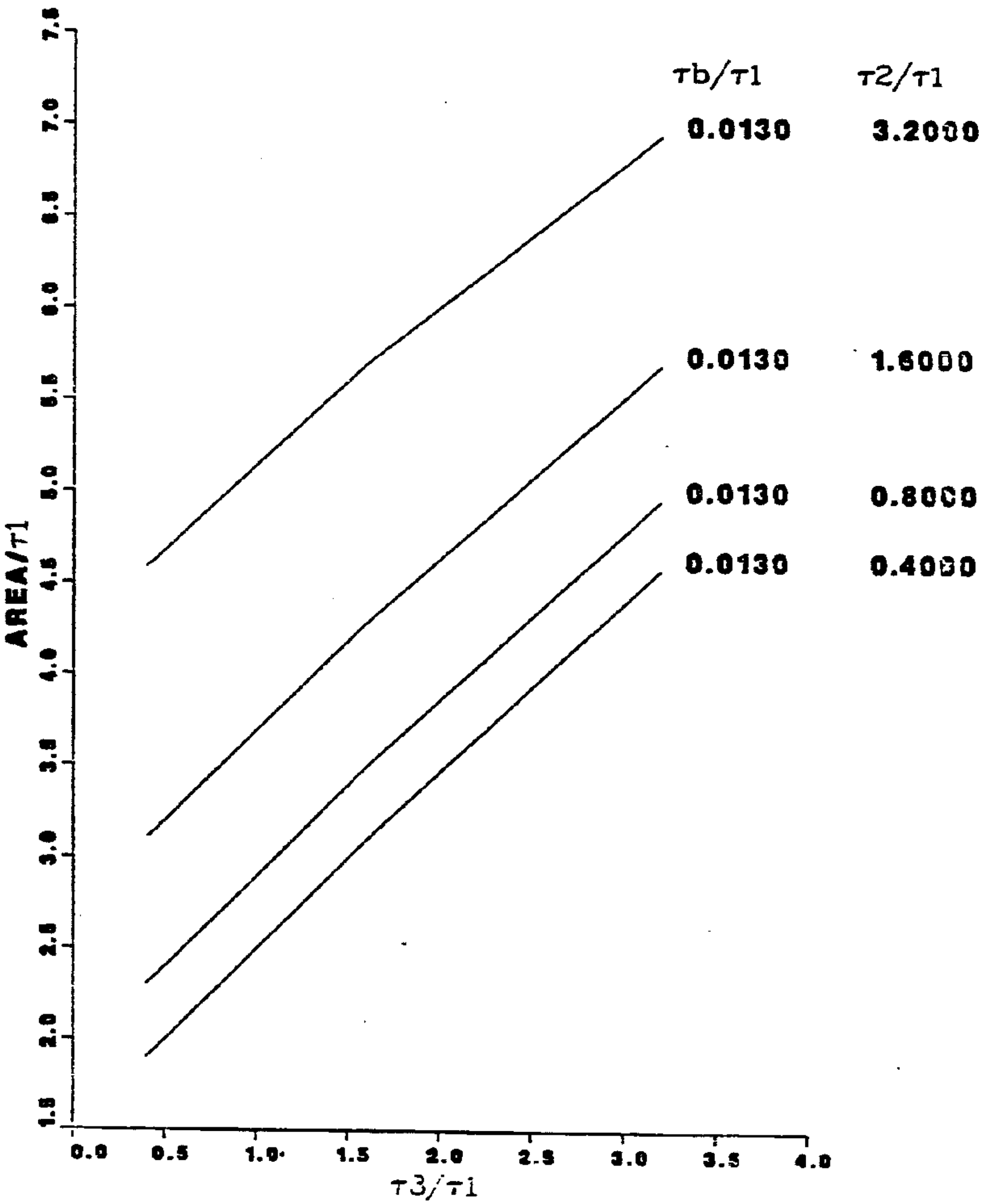


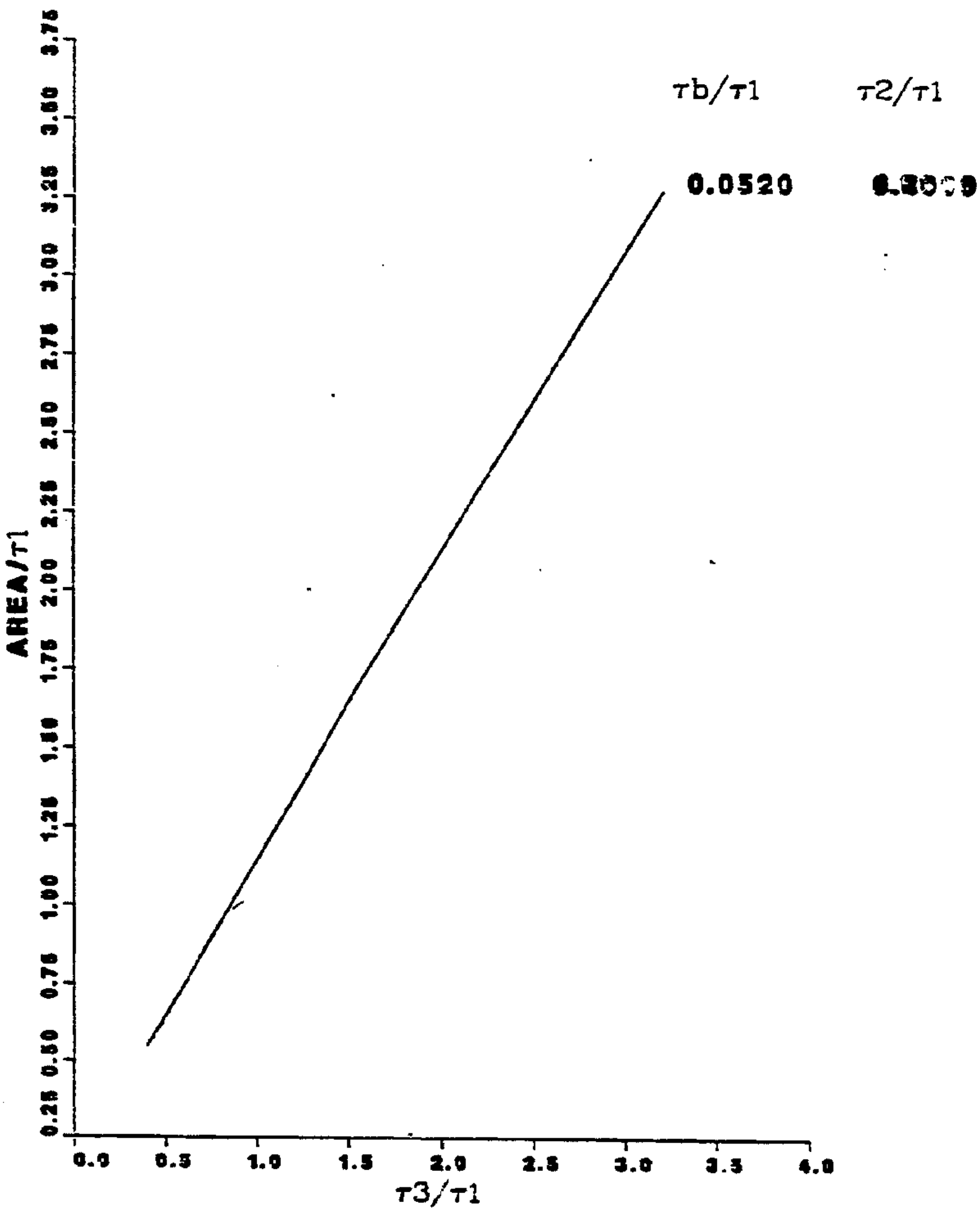
$^{12}C_1{}^{13}C_2$


τb/τ1
τ2/τ1
AREA/τ1
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.0
0.5
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1
0.0130
1.6000
0.0130
3.2000

[redacted]

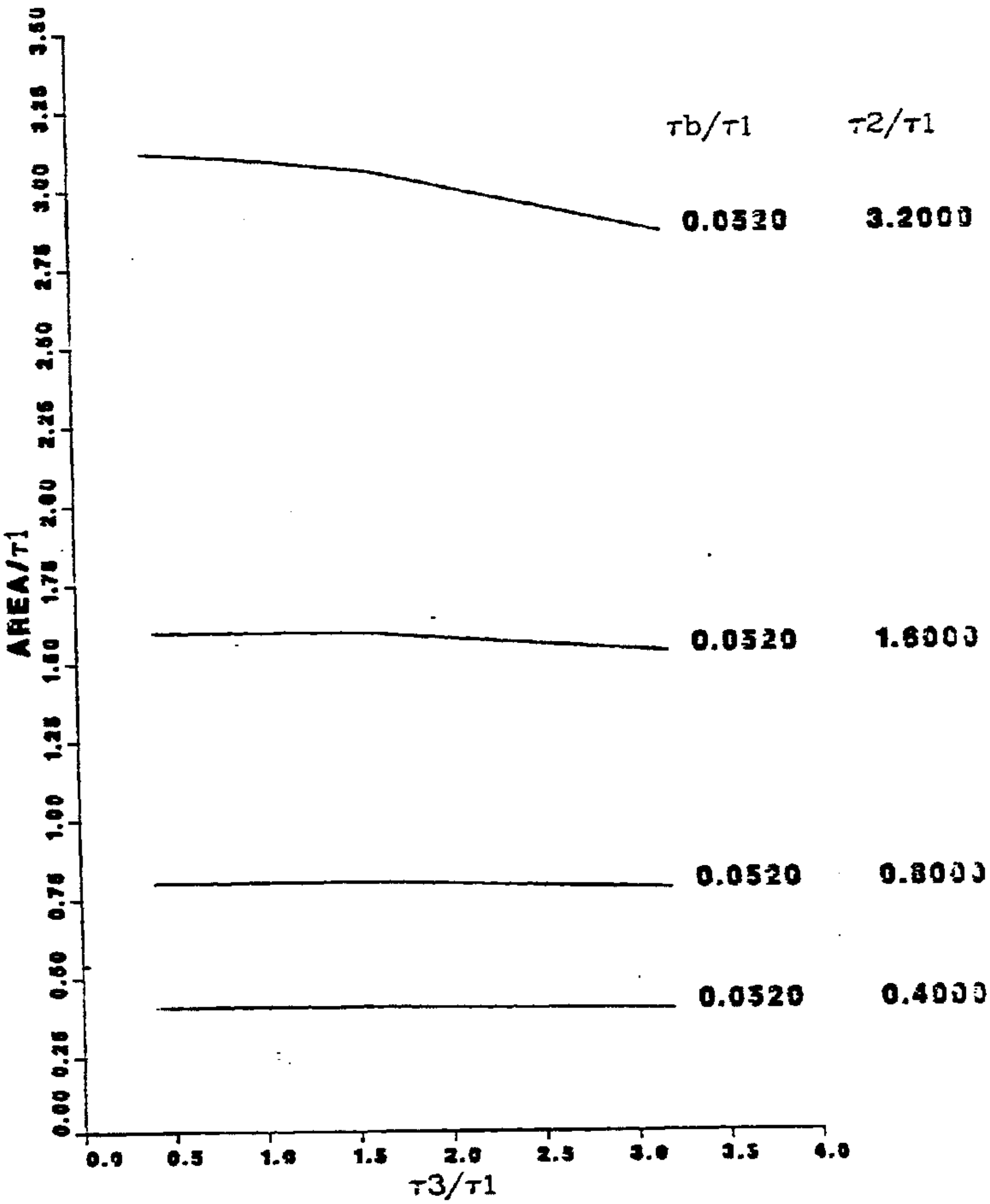
$^{13}C_3$



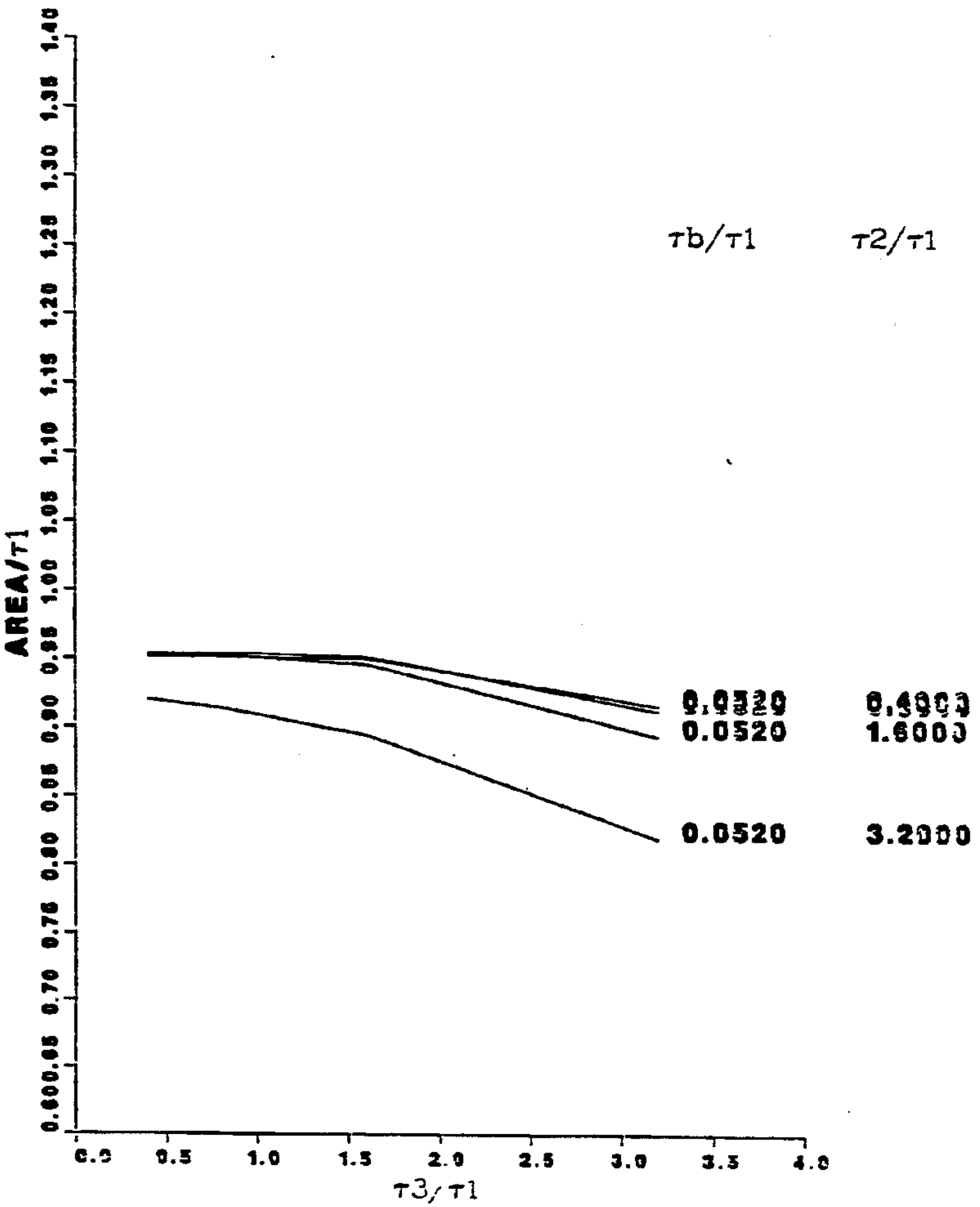

τb/τ1
τ2/τ1
0.0520
AREA/τ1
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
3.25
3.50
3.75
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1

[redacted]

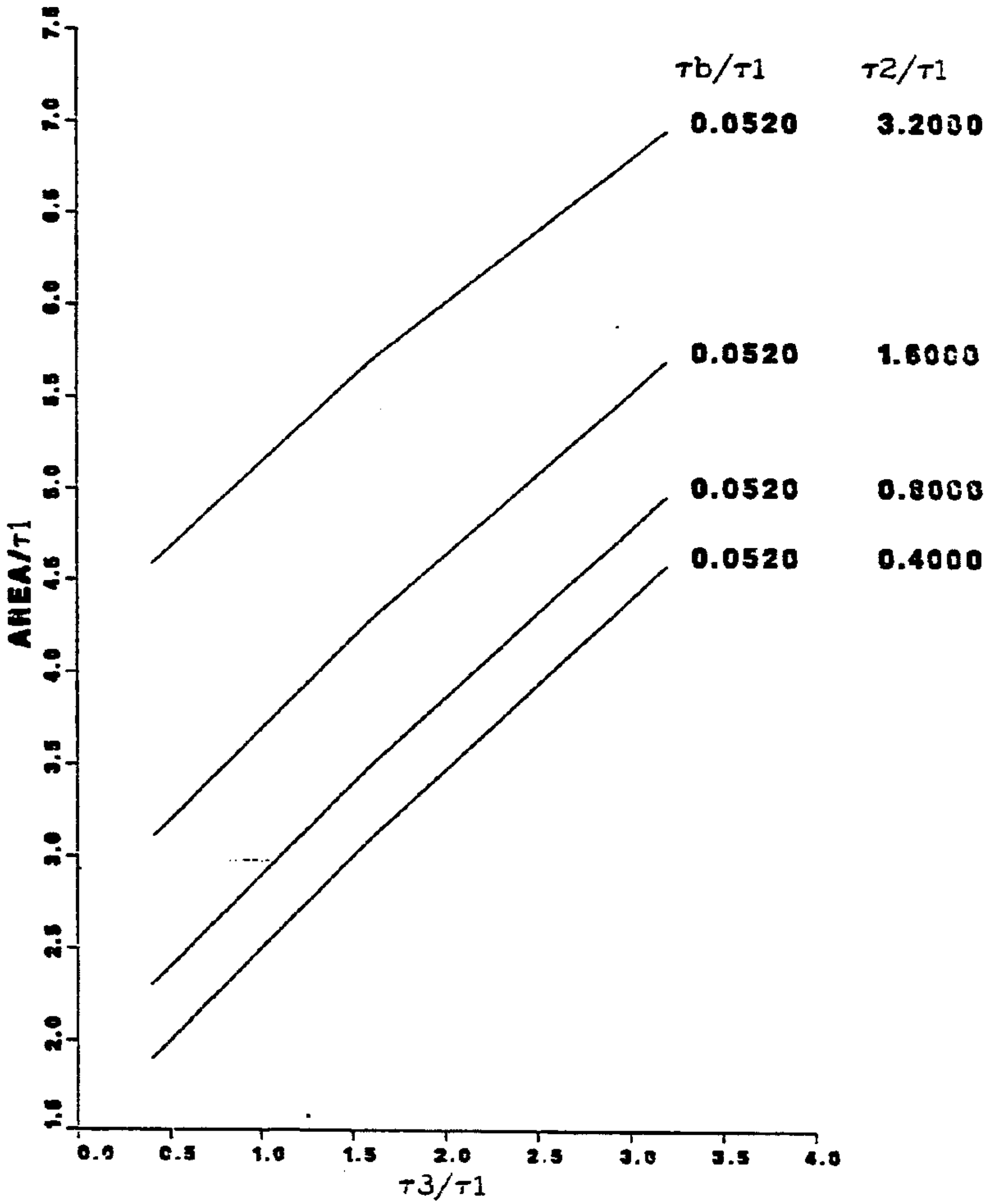
$^{12}C_2\,^{13}C_1$



$^{12}C_1{}^{13}C_2$

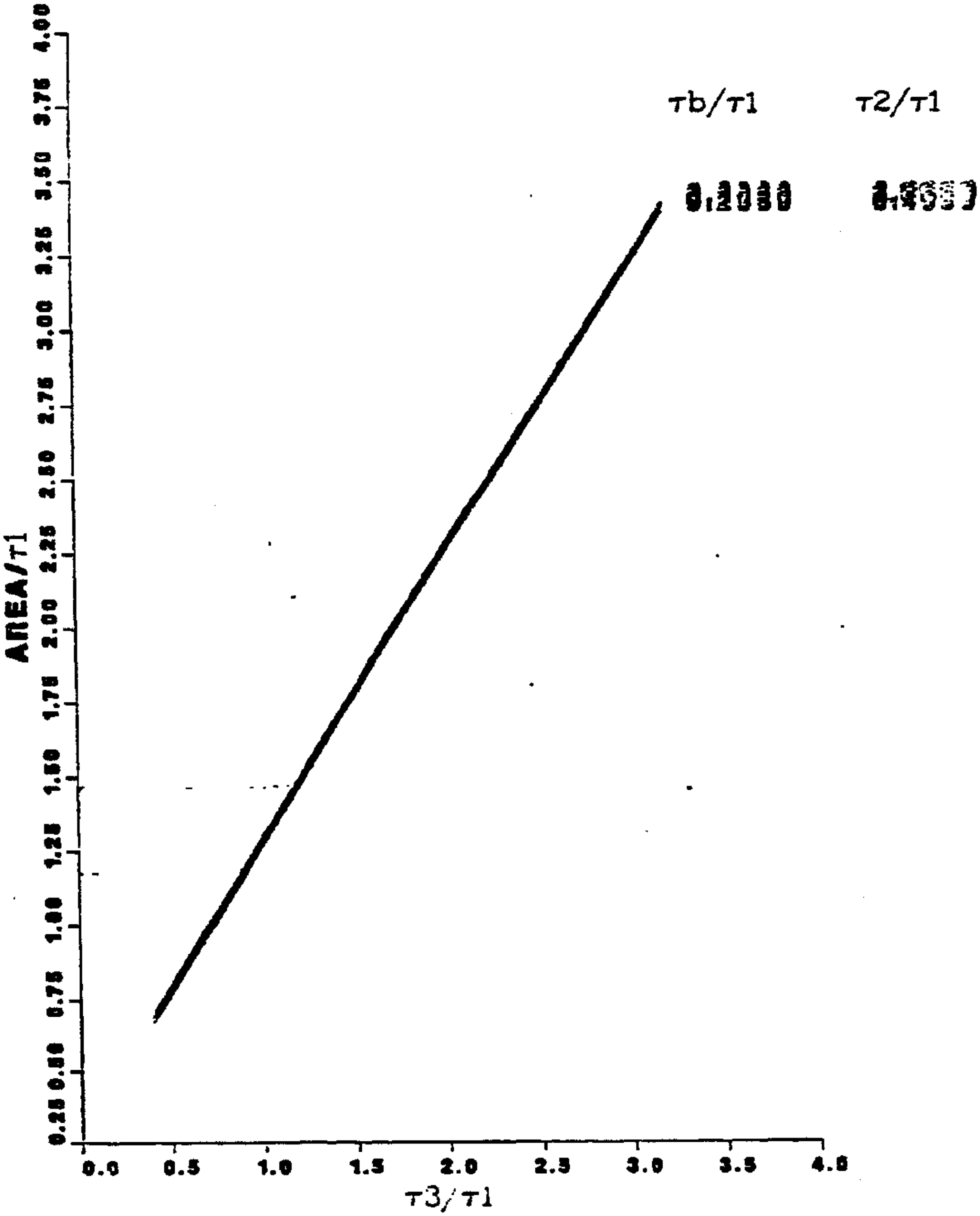


$^{13}C_3$

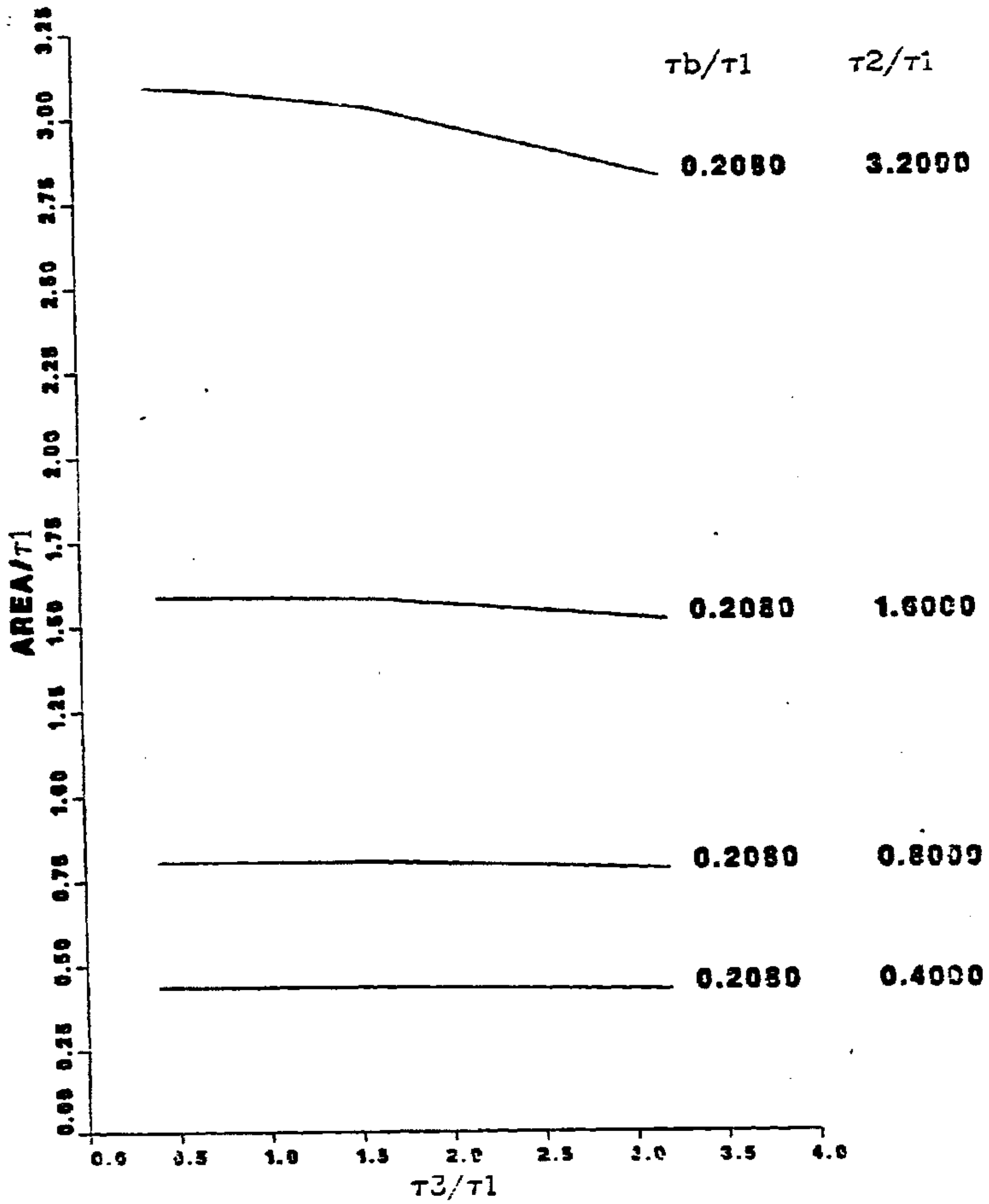


τb/τ1
τ2/τ1
0.0520 3.2000
0.0520 1.6000
0.0520 0.8000
0.0520 0.4000
AREA/τ1
τ3/τ1
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

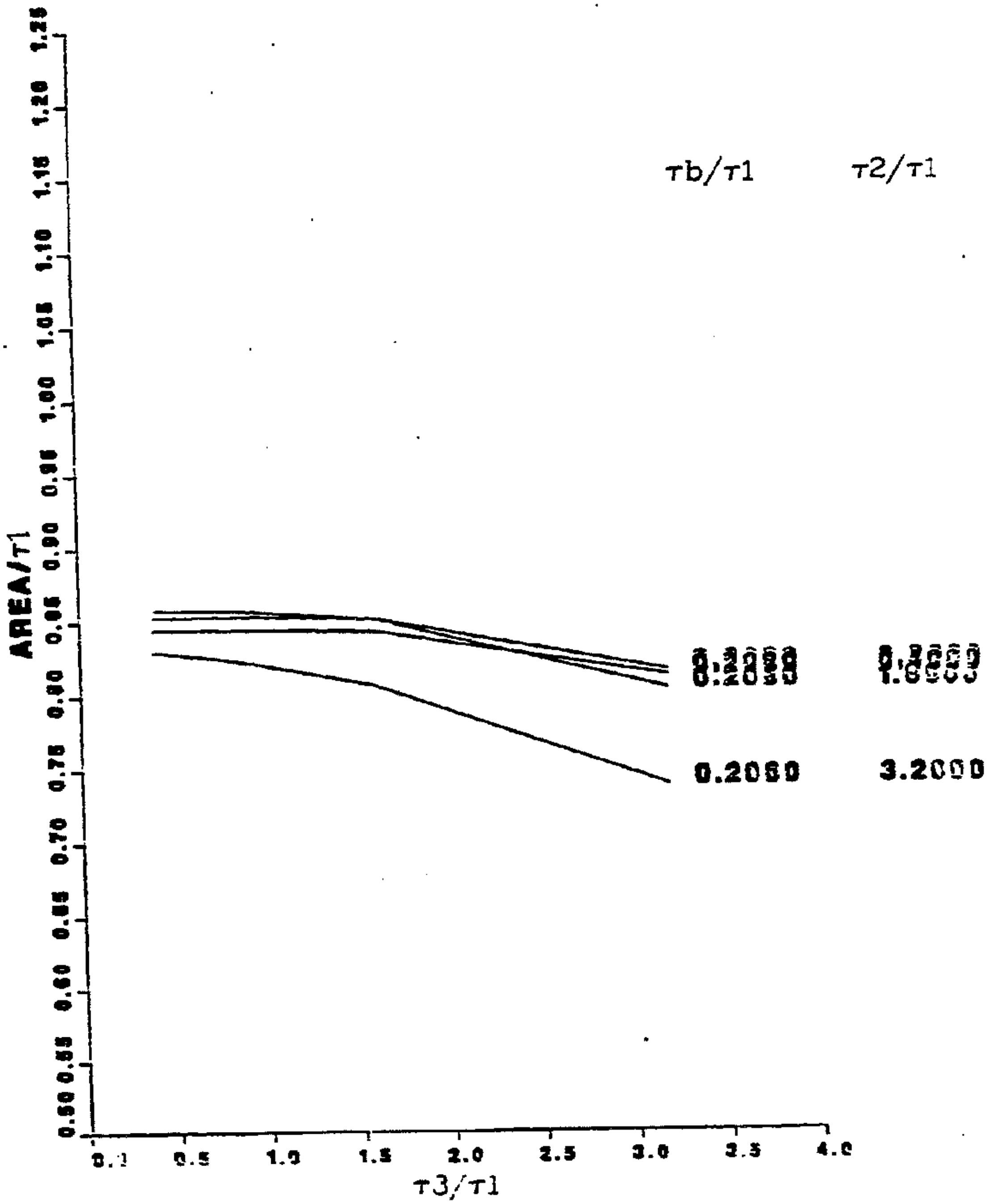
$^{12}C_3$


τb/τ1
τ2/τ1
AREA/τ1
4.00
3.75
3.50
3.25
3.00
2.75
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1

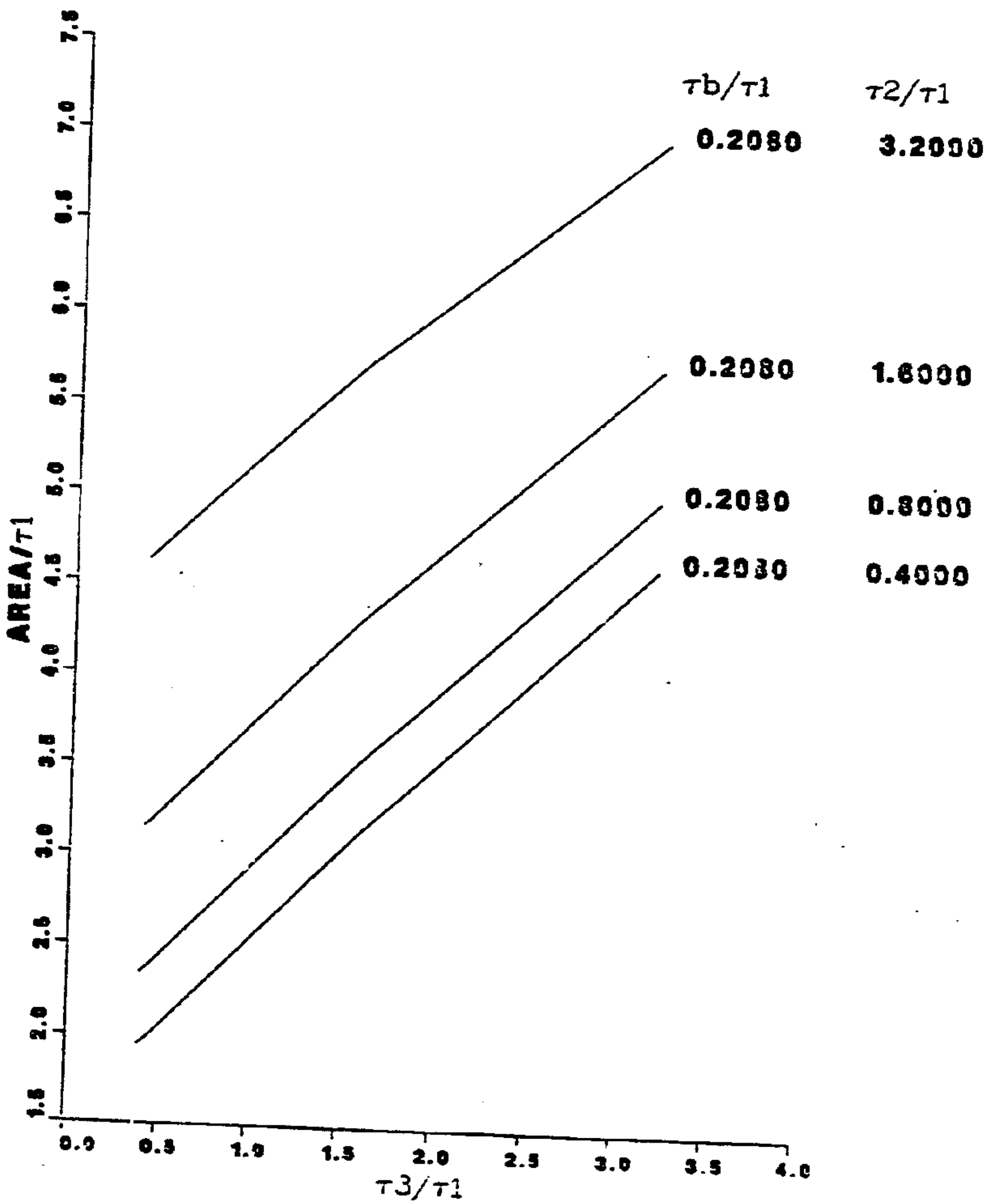
$^{12}C_2{}^{13}C_1$


τb/τ1
τ2/τ1
0.2080
3.2000
0.2080
1.6000
0.2080
0.8000
0.2080
0.4000
AREA/τ1
τ3/τ1

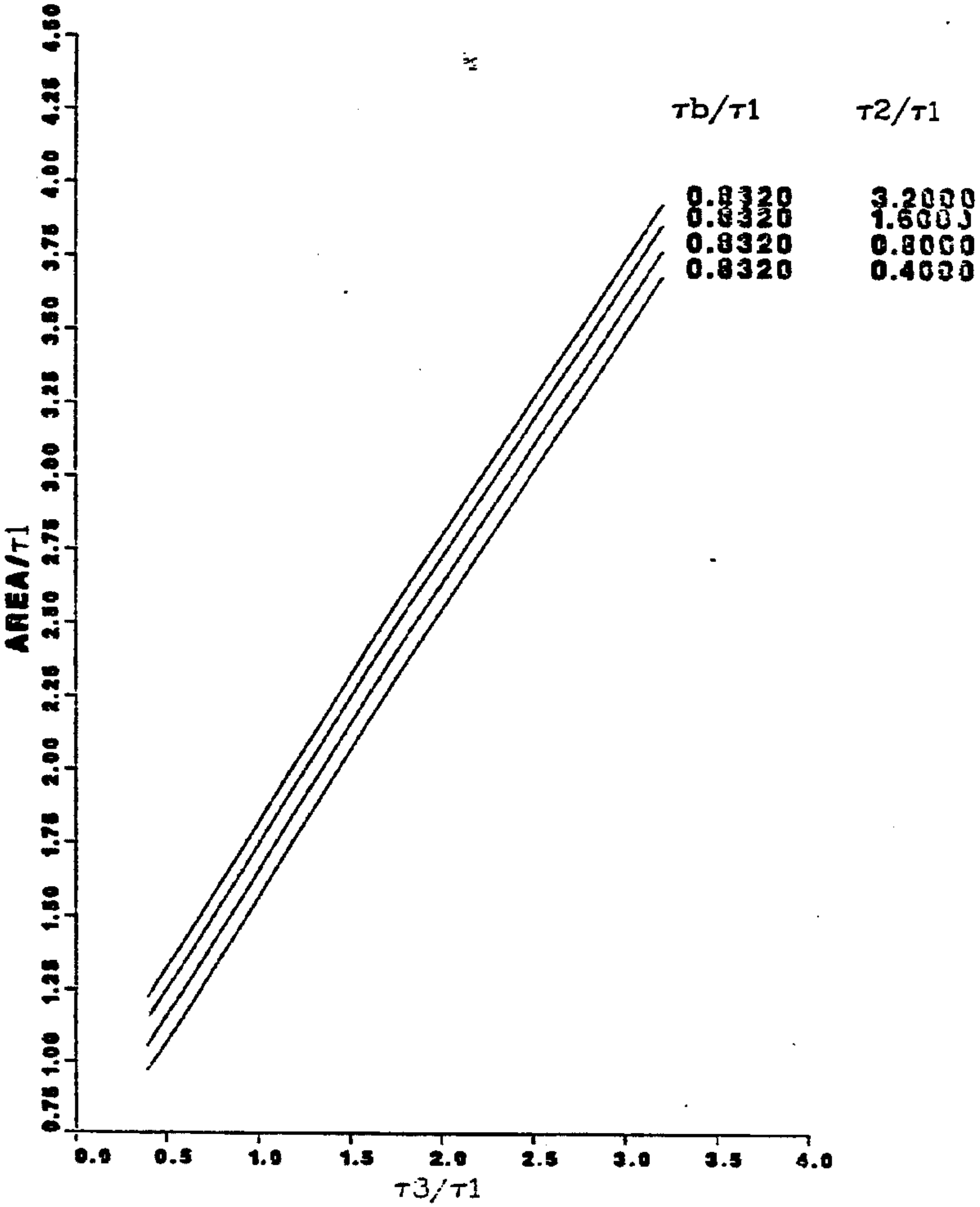
[redacted]


τb/τ1
τ2/τ1
0.2080
3.2000
AREA/τ1
τ3/τ1
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
1.25
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

$^{13}C_3$

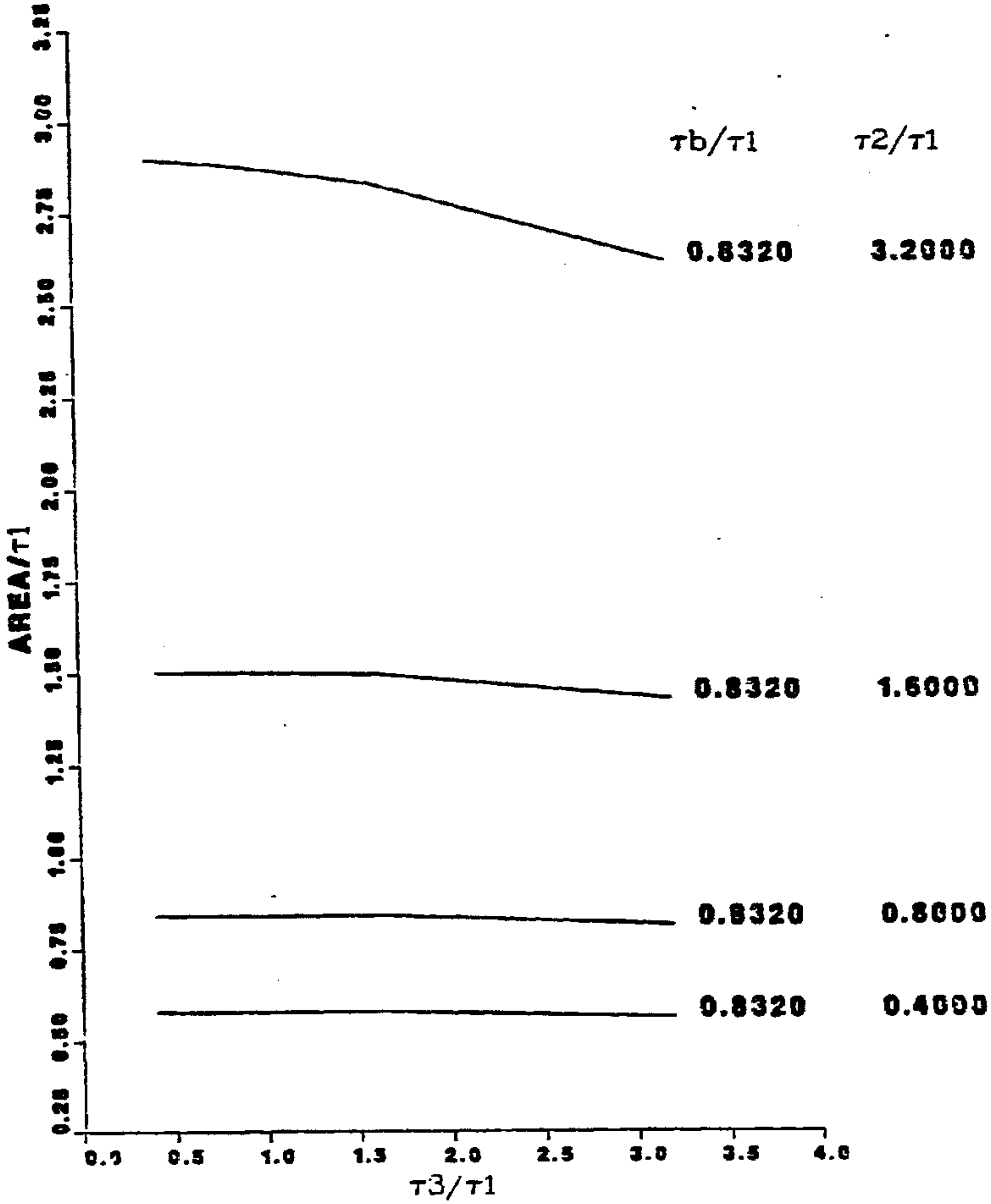

τb/τ1
τ2/τ1
0.2080
3.2000
0.2080
1.6000
0.2080
0.8000
0.2030
0.4000
AREA/τ1
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1

$^{12}C_3$



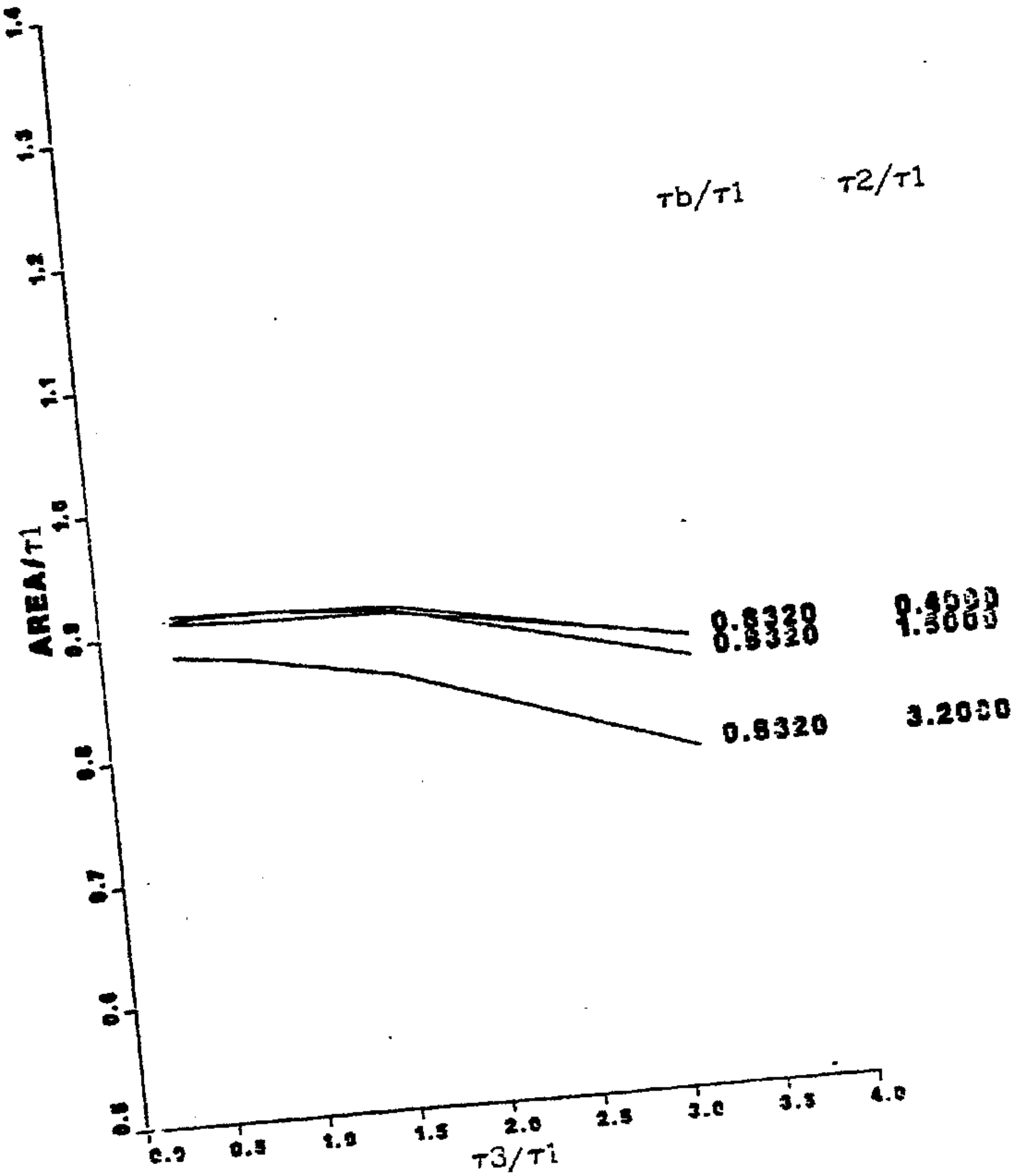
AREA/τ1
0.75 1.00 1.25 1.50 1.75 2.00 2.25 2.50 2.75 3.00 3.25 3.50 3.75 4.00 4.25 4.50
τb/τ1
τ2/τ1
0.8320 3.2000
0.8320 1.6000
0.8320 0.8000
0.8320 0.4000
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0
τ3/τ1

$^{12}C_2{}^{13}C_1$

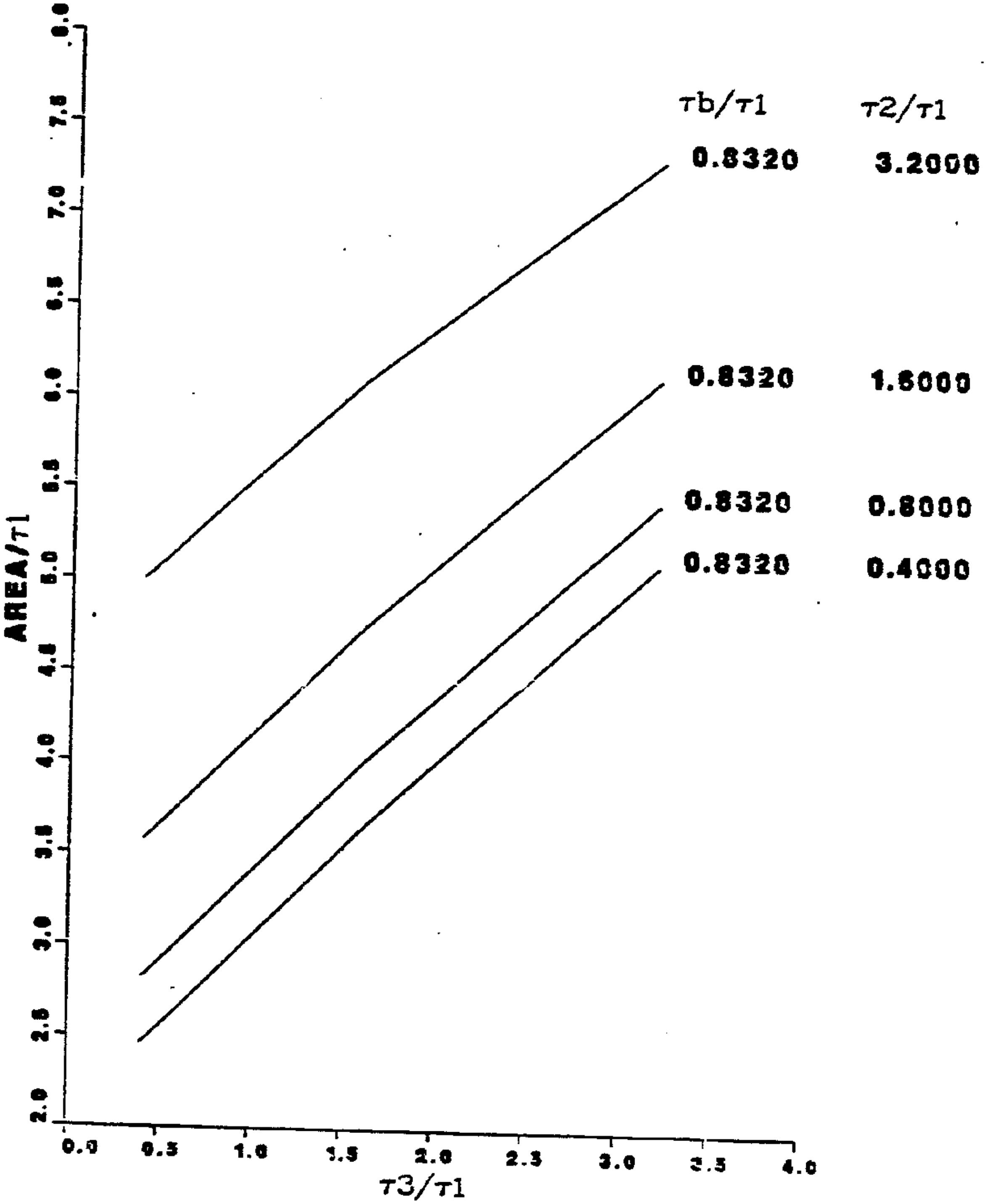


AREA/τ1
3.25
3.00
2.75
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
τb/τ1
τ2/τ1
0.8320 3.2000
0.8320 1.6000
0.8320 0.8000
0.8320 0.4000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
τ3/τ1

$^{12}C_1{}^{13}C_2$


τb/τ1
τ2/τ1
AREA/τ1
τ3/τ1
0.8320 0.4000
0.8320 1.5000
0.8320 3.2000
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

$^{13}C_3$


τb/τ1
τ2/τ1
0.8320 3.2000
0.8320 1.6000
0.8320 0.8000
0.8320 0.4000
AREA/τ1
τ3/τ1
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

REFERENCES

References

1. Bell,A.T., and Baker,J.A., "Hydrogenation of Carbon Monoxide over Ruthenium," *J.Catal.*, Vol. 78, 1982, pp. 165-181.

2. Bennett,C.O., Binanchi,D., Tau,L.M., and Borcar,S., "Nature of Surface Species on Supported Iron during CO/H_2 Reaction," *J.Catal.*, Vol. 84, 1983, pp. 358-374.

3. Bennett,C.O. and Tau,L.M., "Reaction Intermediates on Fe/TiO_2 during CO/H_2 Reaction," *J.Catal.*, Vol. 89, 1984, pp. 327-333.

4. Biloen, P., Helle, J.N. and Sachtler, W.M.H., "Incorporation of Surface Carbon into Hydrocarbons during Fischer-Tropsch Synthesis," *J.Catal.*, Vol. 58, 1979, pp. 95.

5. Biloen, P. and Sachtler, W.M.H., "Mechanism of Hydrocarbon Synthesis over Fischer-Tropsch Catalysts," *Adv.Catal.*, Vol. 30, 1981, pp. 165-216.

6. Biloen, P., Helle, J.N., F.G.A. VAN Den BERG,and Sachtler, W.M.H., "On the Activity of Fischer-Tropsch and Methanation Catalysts," *J.Catal.*, Vol. 81, 1983, pp. 450-480.

7. Happel,J., Suzuki,I., Kokayeff,P., and Fthenakis,V., "Multiple Isotope Tracing of Methanation over Nickel Catalyst," *J.Catal.*, Vol. 65, 1980, pp. 59-77.

8. Happel,J, Suzuki,I., Kokayeff,P., and Fthenakis,V., "Mutiple Isotope Tracing of Methanaiton over Nickel Catalyst," *J.Catal.*, Vol. 75, 1982, pp. 314-328.

9. Rao, V.U.S., Gormly, R.J., Schehl, R.R., Rhe, K.H., Chi, R.D.H., and Pantages, G., "ACS Symposium on Conversion of Synthesis Gas and Alcohols to Chemicals," White Haven, PA, April 6-8, 1983,.

10. Rautavuoma, A.O.I., *The Hydrogenation of Carbon Monoxide on Cobalt Catalysts*, PhD dissertation, Technological University, Eindhoven, The Netherlands, 1979.