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1. Introduction.

A new solution of the one-dimensional time-independent hydrodynamic equations for an ozone flame which avoids some approximations made in earlier calculations yields some qualitatively different results.

The mathematical model is summarized in Section 2, the physical model and numerical parameters in Section 3, the numerical methods and the character of the eigenvalue problem in Section 4. The solution curves are analyzed in Section 5 in terms of the physical and chemical processes within the flame as a part of a study of how these processes depend upon fuel properties. The main conclusions are summarized in Section 6.

2. Mathematical Model.

This study uses the one-dimensional time-independent hydrodynamic equations in the forms suggested by Hirschfelder and Curtiss¹

$$\text{Continuity of species } i: dG_i / dZ = m_i R_i / M \quad (1a)$$

$$\text{Diffusion of species } i: dx_i / dZ = (K / n) \sum_{j \neq i} D_{ij}^{-1} \left\{ (x_i G_j) / m_j - (x_j G_i) / m_i \right\} \quad (1b)$$

$$\text{Energy balance: } dT / dZ =$$

$$(M / \lambda) \sum_j \left\{ (H_j G_j) / m_j - \lim_{Z \rightarrow \infty} (H_j G_j) / m_j \right\} \quad (1c)$$

$$P = n R T \quad (1d)$$

where

$$G_i = \text{the fractional mass-flow rate of species } i = m_i n_i v_i / M \quad (1e)$$

m_j : the mass of species j in g./gmol.

n_j : the concentration of species j in molecules/cc.

v_j : the average velocity of particles of type j with respect to a fixed axis system.

M : the total mass-flow rate with respect to a fixed axis system = $\sum_j n_j m_j v_j$.

D_{ij} : the binary diffusion coefficient for the pair i, j in $\text{cm}^2 \cdot \text{sec}^{-1}$.

$x_j = n_j / n$, the mol-fraction of species j

n : the total concentration in molecules/cc. = $\sum_j n_j$

H_j : the enthalpy of species j in cal./gmol

λ : the thermal conductivity of the gas mixture in $\text{cal} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1} \cdot \text{deg}^{-1}$

P : the pressure in atm.

R : the ideal gas constant in $\text{cc} \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{gmol}^{-1}$

T : the absolute temperature.

The approximations required to derive these equations have been discussed elsewhere². However, for the ozone flame, special justification is required for the omission of terms in kinetic-energy of gas flow in the equation of energy balance (cf. Section 4).

The Hirschfelder-Curtiss model assumes that the hot boundary is defined by an asymptotic approach to chemical, thermal, and diffusion equilibrium

$$\lim_{Z \rightarrow \infty} dT / dZ = \lim_{Z \rightarrow \infty} dx_i / dZ = \lim_{Z \rightarrow \infty} dG_i / dZ. \quad (2)$$

The cold boundary is defined by a non-zero value of the temperature gradient, $(dT / dZ)_{Z \text{ cold}} > 0$ (3)

$Z \text{ cold}$: cold boundary, and the continuity of the fractional mass-flow rates.

The mol-fractions may be subject to a discontinuity and are mathematically unspecified. For one class of idealized systems, it has been shown that: (a) the discontinuity exists; (b) its magnitude depends upon $(dT / dZ)_{Z \text{ cold}}$. The latter quantity can be varied over a range of values which will leave the discontinuity experimentally insignificant and which will not affect the flame solution as much as 0.01%.³

It has been shown that M can be viewed as an eigenvalue to be adjusted in fitting the cold-boundary conditions on the fractional mass-flow rates for one of the major constituents of the fuel.⁴

3. Physical Model and Numerical Parameters.

A critical review of experimental studies of oxygen and ozone-oxygen reaction kinetics⁵ supported Hirschfelder and Curtiss' choice of the three following reactions to describe the ozone flame:



Let: f_i^f (f_i^r): specific rate with respect to mol-fractions for the i -th forward (reverse) reaction at a total pressure of 1 atm. (5)

The specific rates have been assigned a functional form recommended for use in flame studies⁷

$$f_i^p(T) = a_i^p T^{b_i} \exp(-\epsilon_i^p / T), \quad p = f, r \quad (6)$$

a_i^p , b_i^p , ϵ_i^p : constants.

If the reactions occur at a rate which allows approximate equilibration among the states of the reacting species, then the forward and reverse rates must approximately satisfy the thermodynamic equation

$$K_i^x = f_i^f / f_i^r \quad (7)$$

K_i^x : the equilibrium constant with respect to mol-fractions for the i -th reaction.

The equations given in the review for the equilibrium constants were changed for mol-fractions.^{5a} The parameters are recorded in Table 1.

Table 1

Parameters In Mol-Fraction Equilibrium Constants At $P = 1$ atm.

Reaction	a_i^x	b_i^x	ϵ_i^x
1	(+6) + 1.2799 <u>33367</u>	(-1) + 2.5	(+4) + 1.2920 <u>85</u>
2	(+2) + 6.0937 <u>32368</u>	(-1) - 7.5	(+4) - 4.6783 <u>15</u>
4	(-4) + 4.7609 <u>76251</u>	(+0) - 1.0	(+4) - 5.9704 <u>00</u>

Legend: The parameters are for the equation

$$K_i^x = a_i^x T^{b_i^x} \exp(-\epsilon_i^x / T).$$

The reaction numbers refer to Eq. (4).

$$(\pm Z) y.yy \text{ is } (y.yy) \times 10^{\pm Z}.$$

The equations for reactions (1, $M = O_3$) and (2) were taken from the review ^{5b} and changed for mol-fractions. The thermodynamically consistent reverse rates were obtained from the data of Table 1. The results are shown in Table 2.

Table 2

Parameters In Eq. (6) For Mol-Fraction Specific Rates When $P = 1$ atm.

i	p	a_i^p	b_i^p	ϵ_i^p
1, $M=O_3$	f	(+12) 1.98	- 2.0	(+4) + 1.243
	r	(+6) 1.546 <u>9555</u>	- 2.25	(+2) - 4.908 <u>5</u>
2*	f	(+8) 8.08	- 2.0	(+3) + 2.133
	r	(+6) 1.325 <u>9520</u>	- 1.25	(+4) + 4.891 <u>615</u>
4, $M=O_2$	f	(+12) 4.6	- 4.0	0
	r	(+15) 9.661 <u>8839</u>	- 3.0	(+4) + 5.970 <u>400</u>

Legend: An entry ($\pm Z$) y.yy denotes the number $(y.yy) \times 10^{\pm Z}$. A line beneath digits of a_i^p or ϵ_i^p for $i = 1, 2$ indicates that according to the review, the digits are uncertain. They are retained to maintain thermodynamic consistency to eight significant figures.

* Within the accuracy of existing data, $a_{1,M} \equiv f_{1,M}^p / f_{1,O_3}^p$ is constant.

$a_{1,O_2} = 0.33$ ^{5c}. a_0 was arbitrarily assigned the value $a_0^3 = 1.5$.

+ The specific rates for reaction 2 are for the consumption of O_3 (i.e., one-half of the rates for the production of O_2).

** The specific rates for reaction 4 are for the production of O_2 , i.e., one half of the values for the consumption of O . $a_{4,i} \equiv f_{4,i}^p / f_{4,O_2}^p$ was assumed to be constant. The following values were arbitrarily assumed:

$a_{4,O_3} = 2$, $a_{4,O} = 1.33$

Several investigators have published data on reaction (4) since the preparation of the review. Unfortunately, there is only order of magnitude agreement for specific rates as shown in Table 3.

Table 3

M	10 ⁻¹⁴ k _{4,M} ^f cc. ² -mol ⁻² -sec. ⁻¹ at 3500°		
	[8]	Reference [9]	[10]
A	—	0.52	0.45
X _e	1.3	—	—
O ₂	4.6	1.6	4.8
O	14.	13.	9.9

Legend: The data are taken from reference [8]. They are for

$$d [O_2] / dt = k_{4,M}^f [M] [O]^2.$$

The most reliable determinations of recombination rates have been made by inserting dissociation rates measured in a shock tube into the thermodynamic equation between forward and reverse rates. The applicability of the equilibrium relation has been checked in shock tube studies of the coupling between dissociation and recombination ¹¹. Under the conditions of the experiment, the vibrational relaxation in dissociating O₂ - A mixtures was sufficiently rapid that the coupling was completely negligible up to 5000°.

Since it seemed difficult to select one significantly more reliable value, the equation suggested by reference [8] was arbitrarily adopted. It should be recognized that the temperature dependence for recombination was selected arbitrarily by the authors on the basis of other people's results. Their equation for recombination was changed for use with mol-fractions and the thermodynamically consistent dissociation rate was obtained using the parameters of Table 1. The results are recorded in Table 2.

While reactions (2) and (4) are important for determination of the asymptotic equilibrium values as Z → ∞, because of the large activation energies, they would not be expected to affect the first few digits in calculations at any other point in the flame. Comparisons with rates used in previous theoretical studies are made in Sections (5.1, 5.6).

The transport coefficients suggested in the review ⁵ have been adopted. They will be tabulated for reference.

Table 4

Parameters For Binary Diffusion Coefficients At P = 1 atm.

β γ	$d_{\beta\gamma} \times 10^5 \text{ cm.}^2 \text{ - sec.}^{-1} \text{ - deg.}^{-3/2}$	$d_{\beta\gamma}^0 \times 10^{-2} \text{ deg.}$
O ₂ O ₃	<u>4.59</u>	<u>1.808</u>
O ₂ O	<u>7.36</u>	<u>1.471</u>
O O ₃	<u>5.81</u>	<u>1.808</u>

Legend: The parameters are taken from the review [5d] for use in the empirical equation

$$D_{\beta\gamma}(T) = d_{\beta\gamma} T^{3/2} / (1 + d_{\beta\gamma}^0 T^{-1}).$$

A line beneath a digit indicates that in the review that digit was considered to be uncertain.

Table 5

Parameters For The Thermal Conductivity of The Pure Gases

	a(cal.-cm. ⁻¹ -sec. ⁻¹ -deg. ⁻¹)deg. ^{-1/2}	b°K	c°K
O ₂	6.726x10 ⁻⁶	265.9	10
O ₃	<u>5.83</u> x10 ⁻⁶	<u>467</u>	<u>10</u>
O*	3x10 ⁻⁶	400	0

Legend: The parameters are taken from the review ^{5e} for use in the empirical equation

$$\lambda = a T^{1/2} / \{1 + bT^{-1} \exp[-cT^{-1} \ln 10]\}$$

A line underneath a digit indicates that in the review that digit was considered to be uncertain.

* As a result of an error, parameters for O atom were used which predict a lower thermal conductivity for O than for O₂. At 1097°, where x₀ has its maximum, the thermal conductivity for O is about a factor of 3 smaller than recent theoretical estimates. However, the maximum in x₀ is less than three per cent and the estimated error in λ_{mix} is only 2.6%.

The thermal conductivity of the gaseous mixture was estimated from the thermal conductivity of the pure components by the simple linear combination rule ^{5f}:

$$\lambda_{mix} = \sum_i \lambda_i x_i \quad (8)$$

The enthalpies were assumed to be linear functions of temperature given by the review ^{5g}. The values used for the heat capacities were averages taken over the range [300°K, 1300°K], rounded to the nearest one-quarter in C_α/R. The parameters are summarized for reference in Table 6.

Table 6

Parameters For The Enthalpy Equations

α	H _α (1300°) cal./gmol	C _α /R
O	(+4) 6.563 <u>6</u>	2.5
O ₂	(+4) 1.004 <u>5</u> <u>2</u>	4.0
O ₃	(+4) 4.93 <u>59</u>	6.25

Legend: The parameters are for H_α(T) = H_α(1300°) + C_α(T-1300°).

(±Z) y.yy denotes the number (y.yy)x10^{±Z}. The review ^{5g} considered the underlined digits to be uncertain.

The total mass-flow rate, M, is an eigenvalue. The value required for solution of the flame equations can be compared with one calculated from the experimental burning velocity v(Z_c),

$$M = \rho(Z_c) v(Z_c) \quad (9)$$

ρ(Z_c): gas density at the burner in g./cm³.

v(Z_c): mass average velocity at the burner in cm./sec.

Z_c: the (arbitrary) distance coordinate for the burner.

Streng and Grosse measured the burning velocity of a set of ozone-oxygen mixtures ¹². The data in this paper are for their mixture with the parameters

$$\begin{aligned}
 P &= 1 \text{ atm.} \\
 T(Z_c) &= 300^{\circ}\text{K} \\
 x_{O_3}(Z_c) &= 0.23 \\
 x_{O_2}(Z_c) &= 0.72 \\
 v(Z_c) &= 52.2 \text{ cm./sec.}
 \end{aligned} \tag{10}$$

The Hirschfelder-Curtiss model for the flame holder has been shown for one idealized flame to require an experimentally negligible discontinuity in the mol-fractions at Z_c (vide Section 2). Thus, for the mathematical model the mol-fractions of Eq. (10) represent $\lim_{Z \rightarrow Z_c^-} X_\alpha(Z) \neq \lim_{Z \rightarrow Z_c^+} X_\alpha(Z)$. The remaining boundary values were calculated using the boundary conditions for the Hirschfelder-Curtiss model (cf. Section 2). The entire set of values is summarized for reference * :

$$M = 0.07736 \text{ g.-cm.}^{-2}\text{-sec.}^{-1}$$

	$Z = Z_c$	$\lim_{Z \rightarrow +\infty}$
G_0	0.0	(-7) 1.904 4986
G_{O_2}	(-1) 6.315 7895	(-1) 9.999 9981
G_{O_3}	(-1) 3.684 2105	(-9) 1.101 6955
X_0	—	(-7) 3.808 9965
X_{O_2}	—	(-1) 9.999 9962
X_{O_3}	—	(-10) 7.344 6352
T^+	(+2) 3.00	(+3) 1.344 2328

4. Methods of Numerical Integration; Character of the Eigenvalue Problem.

Previously published techniques¹³ were used to construct a Taylor Series of the thirtieth order about the hot boundary temperature, T_{\max} (which is a singular point of the differential equation system), as a local solution over an interval

$$\begin{aligned}
 & [T_1, T_{\max}] \\
 T_{\max} &= \lim_{Z \rightarrow \infty} T(Z) \quad **
 \end{aligned} \tag{12}$$

- * ($\pm Z$) y.yy denotes the number (y.yy) $\times 10^{\pm Z}$.
- + This value corresponds to $(dT/dZ)_{Z_c} = 0$. The actual value of $T(Z_c)$ must be such that $(dT/dZ)_{Z_c}$ has a positive value. The exact value is of no importance³.
- ** In order to scale the magnitudes of successive power series coefficients, it is essential to use a reduced temperature. $t = (T - T_{\max})/T_{\max}$ has been found to be a suitable choice⁴.

The power series coefficients were checked by a test which has been used repeatedly to detect any errors of inconsistency ^{13a}.

Mathematical instability of the equation system ⁴ prevents continuation of the solution from T_1 by a straightforward application of conventional methods of numerical integration. Alteration of the last of eight digits in single precision computer calculations was sufficient to cause the solution to diverge either positively or negatively along a priori ridiculous curves (e.g., dG_{O_3}/dT goes to zero in the high temperature region).

Furthermore, the first stage of a previously published method of successive approximation could be constructed over only a part of the remaining temperature range of interest ⁴. Therefore, the results discussed in this paper were obtained by further development of previous work ¹⁴. A computer program was developed in which the machine made the necessary logical choices to correct its integration and to follow the desired solution ¹⁵. The validity of the procedure was tested with: (a) the check discussed at the end of this Section; (b) comparison of the solution with that obtained by the first stage of the successive approximation technique. Over a temperature range common to both, the difference between the function values for the two solutions was at most a few per cent *.

All previous calculations on ozone which took diffusion into account were based either on the kinetic steady-state ^{18,19} or on improved algebraic approximation related to the kinetic steady-state ²⁰ which gave solutions approximately following the kinetic steady-state. It has been shown that ⁴: (a) the kinetic steady-state incurs a solution with a satisfactory approximation to the boundary condition $G_0 = 0$; (b) with this approximation any three component system requires only a single eigenvalue, M .

Since the present calculation neither assumes nor predicts any reasonable approximation to the kinetic steady-state, it is surprising that the solution for this mixture could be constructed with M as the sole eigenvalue. The basis for the last statement consists of the following facts: (1) Starting values at T_1 off the hot boundary which give negative or positive divergence agreed with the sum of the series constructed at T_{max} to within one unit in the eighth digit; (2) Solutions which approximately satisfy the cold boundary conditions $G_0 = 0$, $x_0 \approx 0$ were obtained (in the sense that (a) x_0 and $|G_0|$ decreased to less than 0.01 of their maximum values; (b) Inspection of the bounding curves showed that the ratios would have been lowered if the bounds were brought closer); (3) M could be adjusted to fit $G_{O_3}(Z_c)$.

Conversely, for richer ozone flames (i.e., higher T_{max}) calculations already performed show that: (1) the series solution including EE terms in some cases predicts starting values which differ by a factor; (2) it seems impossible to fit the cold boundary value on $G_{O_3}(Z_c)$ and G_0 using only a single eigenvalue and the equations present a two eigenvalue problem.

- In previous studies, similar numerical techniques were applied to a hypothetical flame (with the difference that all decisions were made manually). A similar comparison supported the validity of the solution for the idealized system ^{14b, 17}.

Contrary to previous belief 18, 19, 20, 21, it seems that a single eigenvalue approximation is adequate only for (a) sufficiently lean flames, or, (b) an incorrect approximation omitting the kinetic energy term in the equation of energy balance for richer flames.

5. Discussion of Results.

5.1. Free Radical Curves; Applicability of the Kinetic Steady-State Approximation; Comparison With Other Calculations.

Consider an intermediate, α , whose net rate is given as a sum of rates for forward and reverse reactions

$$R_{\alpha} = \sum_i (R_{\alpha,i}^f - R_{\alpha,i}^r) . \quad (13)$$

Since the kinetic steady-state approximation

$$R_{\alpha} = 0 \quad (14)$$

has been frequently used to determine x_{α} , a convenient measure of the adequacy of the approximation is given by a relative deviation, r_{α} , defined as 3a

$$r_{\alpha} = R / R_{\alpha,i}^f \quad (15)$$

Graph (1) shows that r_0 is of the order of unity for most of the flame so that the kinetic steady-state is not a useful approximation for calculations which are at all sensitive to the profile $x_0(T)$. von Karman and Penner ¹⁸

conjectured that the approximation would be useful in calculating burning velocities. Since there is evidence that flame speeds are comparatively insensitive, their suggestion seems to be useful for rough approximations. Thus, previous calculations on an idealized system showed that M varied by only a factor of about 0.75 with changes in kinetic and diffusion parameters which removed any approximation to the kinetic steady-state (cf. Section 5.6). The assumption that a similar result holds for the ozone flame suggests that, for a fixed set of parameters, the use of the steady-state approximation might give a result of the right order of magnitude even if it grossly distorts profiles.

The existence of a single internal maximum in an intermediate mol-fraction has been attributed to the kinetic steady-state approximation *+. Since

*When von Kármán and Penner ¹⁸ interpreted the existence of a maximum in terms of the kinetic steady-state approximation, they contrasted their suggestion with Hirschfelder and Curtiss' ²² interpretation. However, the contrast was based on an incomplete paraphrase which omitted the words in italics: "The reason for this is that the free radicals, in this case oxygen atoms, are essentially in equilibrium with fuel molecules in the region of the hot boundary. This is the significance of setting $K_1=0$." In Hirschfelder and Curtiss' notation, K_1 is the net rate of O atom production, so that $K_1=0$ is just the kinetic steady-state approximation.

+See Westenberg and Fristrom ¹⁶, p. 598 for comments on experimental studies which have shown maxima in radical concentrations and for references to the literature.

Graph (2) for $x_0(\gamma)$ shows such a maximum in the absence of the kinetic steady-state, this interpretation must be abandoned. However, another one which predicts a single internal maximum for a wide class of intermediates ³ does apply. Furthermore, if

$$t = (T - T_{\max}) / T_{\max} \quad (16)$$

$$\mathcal{J} = [M C_{O_3} / \lambda(T_{\max})] Z, \text{ where } \mathcal{J}=0 \text{ is}$$

an arbitrary origin,

then Graphs (2) of $x_0(\gamma)$, (3) of $x_0(\mathcal{J})$, and (4) of dt/dZ show that the previous conjecture ³ for such intermediates applies to the O atom in the ozone flame: despite the steeper τ gradient on the hot side of the maximum, the larger \mathcal{J} gradient lies on the cold side (due to the rapid increase in dt/dZ in the region of rapid chemical reaction).

These results on the significance of the deviations from the kinetic steady-state differ qualitatively from the assumptions of earlier studies ^{23,19} and the conclusions of a third ²⁰. The extremely large deviations reported here would have been somewhat lower in the region about the hot boundary if the older specific rate for O atom recombination had been used. In the earlier study the recombination rate was determined from Eq.(7) using the dissociation rate calculated with the pre-exponential factor for the simple bimolecular collision theory. Subsequent experiments have shown that dissociation reactions have abnormally large pre-exponential factors *. Thus the specific recombination rate used was too low by a factor of the order of 100 at 1250° and of the order of 1000 at 400°. To obtain a lower bound on the effect of this difference, $R'_0 = R_0 + 2 R_4^f$ can be computed using the data of this study.

At a temperature 120° off the hot boundary, use of R'_0 rather than R_0 would give a relative deviation of -0.15 instead of -0.80.

However, this decrease does not alter the qualitative difference which can not be due to the difference between the specific rates and transport coefficients adopted in this study and those assumed in previous investigations. This conclusion was deduced from

$$\text{PS}_1 : \text{a local solution at the hot boundary} \\ \text{in the form of a twentieth order power} \\ \text{series constructed with the earlier set} \quad (17) \\ \text{of parameters.}$$

PS_1 predicted the same qualitative result found in this study. It is not x_0 , but x_{O_3} which approximately obeys the steady-state over a wide temperature interval about the hot boundary:

$$\begin{aligned} T \geq 1217 (\tau \geq 0.88) : r_{O_3} &\leq 0.01 \\ T \geq 1167 (\tau \geq 0.83) : r_{O_3} &\leq 0.033. \end{aligned} \quad (18)$$

* Br_2 can be taken as a typical example ²⁴.

+ The sign of the temperature coefficient was also wrong since the estimate was made before experiments established the negative temperature coefficient for recombination rates.

Although the net production rates of O and of O₃ are related by the equation

$$R_{O_3} = R_{O_2} - 2(R_1 + R_4) \quad (19)$$

and $R_{O_2} \gg 100R_{O_3}$ through a temperature range of over 100°, two of these studies equated R_{O_2} to zero and left R_{O_3} be non-zero. von Karman and Penner made this approximation when they were attempting to simplify the ozone equations in their study of flame speeds. They argued that R_1 would be negligible compared with other reactions except in a temperature range about the hot boundary which they felt would be unimportant for the calculation of flame speeds. Sandri made the same approximation in his calculations [19]. According to the results of this study, omission of R_1 alters R_{O_3} by orders of magnitude over this region. While it is true that previous studies of an idealized system would support the contention that any change which left R_{O_2} comparatively small could be expected to be without significant effect, it does not necessarily follow that this could be expected for a drastic alteration in R_{O_3} unless the temperature range itself were a negligible fraction of the whole. Unfortunately, this approximation also gives an erroneous estimate of the size of the temperature region. In any case, it should not be made in any study of flame structure and processes.

In the third study, a Taylor series approximation using second derivatives was used to predict values at $T = T_{max} - 2^\circ$. Tangent integration with 2 degree intervals starting from these values gave solution curves which oscillated violently. After a change to much larger values for G_{O_3} and x_{O_3} gave solution curves which were smooth and more reasonable. The oscillations in the earlier solution were attributed to the "much too small" values of G_{O_3} and x_{O_3} given by the Taylor series. This explanation does not appear to be correct since: (a) Inspection of PB₁ showed that use of second derivatives gave starting values certain to about one decimal, which were not off in magnitude; (b) This study has shown that the ozone differential equations in the neighborhood of the solution determined by the hot boundary conditions are so mathematically unstable that the curves are sensitive to the last of eight digits carried in usual computers. Therefore, they require special methods of solution (see Section 4). The introduction of the larger values of G_{O_3} and x_{O_3} avoided the unstable region in which G_{O_2} and x_{O_2} are increasing and x_{O_3} approximately follows a kinetic steady-state. Thus these larger values were responsible for the report that x_{O_3} has a maximum within two degrees of the hot boundary. For the remainder of the flame, x_{O_3} was calculated not from the kinetic steady-state approximation but from the equation

$$d [x_{O_3}/x_{O_3}^{ss}]/dT = 0 \rightarrow d x_{O_3}/dT = [x_{O_3}/x_{O_3}^{ss}] d x_{O_3}^{ss}/dT \quad (20)$$

$x_{O_3}^{ss}$: the value of x_{O_3} given by the kinetic steady-state approximation.

The present study shows that this would not be useful approximation for a solution determined by the hot boundary conditions. In the neighborhood of the hot boundary, a kinetic steady-state is a better approximation by two orders of magnitude for x_{O_3} than for x_{O_2} . Thus for such a solution, Eq. (20) replaces the larger

$d [x_0/x_0^{ss}] / dT$ by zero rather than the smaller $d [x_{O_3}/x_{O_3}^{ss}] / dT$.

The previous studies agree within about 13% on predicted flame speeds (cf. Section 5.6). Although it may be that the assumptions and approximations as discussed above did not greatly affect the calculated flame speed, this could only be proven by repeating the present calculations for the older parameters (cf. Section 5.6).

The following considerations suggested that it would be worth-while to determine how a change in the specific rate for free-radical recombination would affect the calculated M . Table 7 shows that radical recombination provides one of the most important terms in R_0 , the net rate of O atom production, until R_0 becomes positive. As this occurs, R_0 , and therefore G_{O_3} , begin a much more rapid rise to provide the major change in G_{O_3} . Therefore, it seemed possible that a change in recombination rate might significantly affect the temperature at which R_0 becomes positive. The resulting shift in the temperature at which G_{O_3} begins its rapid rise would change M . This suggested that if there is any flame in which recombination rates have a marked effect upon burning velocities, ozone might be one.

The tests were performed using somewhat different free-radical diffusion coefficients (cf. Section 5.5). Two different calculations were made with the specific rates of Section 3:

M	$G_{O_3}(Z_c)$	$P \equiv M G_{O_3}(Z_c)$	
0.07736	0.7097	0.05490	(21)
0.149	0.3977	0.05918	

According to Section 5.6 the product P can be approximated roughly as a linear function of $G_{O_3}(Z_c)$. A straight line through the data of Eq. (21) gave

$$P = 0.05958 \quad M = 0.1617. \quad (22)$$

A third calculation with doubled rates for atom recombination and dissociation and the same value of M gave:

$$M = 0.149 \quad G_{O_3}(Z_c) = 0.3986 \quad P = 0.05939. \quad (23)$$

The assumption that $dP/dG_{O_3}(Z_c)$ would be about the same for the data of Eqs. (21,23) gave

$$P = 0.05981 \quad M = 0.1623. \quad (24)$$

Thus a two fold increase in the recombination rate gave only a 0.4% increase in M . Therefore, the sensitivity to free-radical recombination and

Table 7

Rates of Reactions

T	τ	R_1^f	R_1^i	R_2^f	$2R_4^f$	R_0	R_{O_3}
(+3)+1.231	0.8214	(-3)+1.207	(-3)+1.287	(-5)+8.929	(-4)+8.644	(-3)-1.034	(-6)-8.592
(+3)+1.205	0.8567	(-3)+1.534	(-3)+1.678	(-4)+1.643	(-3)+1.409	(-3)-1.718	(-5)-1.979
(+3)+1.168	0.8508	(-3)+2.040	(-3)+2.329	(-4)+3.569	(-3)+2.550	(-3)-3.196	(-5)-6.799
(+3)+1.159	0.8222	(-3)+2.196	(-3)+2.502	(-4)+4.304	(-3)+2.899	(-3)-3.636	(-4)-1.247
(+3)+1.151	0.8148	(-3)+2.407	(-3)+2.655	(-4)+5.195	(-3)+3.224	(-3)-3.992	(-4)-2.714
(+3)+1.135	0.7999	(-3)+3.702	(-3)+2.975	(-4)+9.647	(-3)+3.941	(-3)-4.173	(-3)-1.692
(+3)+1.126	0.9251	(-3)+5.550	(-3)+3.136	(-3)+1.587	(-3)+4.324	(-3)-3.488	(-3)-4.011
(+3)+1.120	0.7651	(-3)+9.208	(-3)+3.293	(-3)+2.871	(-3)+4.705	(-3)-3.1661	(-3)-8.765
(+3)+1.104	0.7703	(-2)+2.611	(-3)+3.555	(-3)+2.871	(-3)+4.705	(-3)-1.661	(-3)-3.208
(+3)+1.089	0.7554	(-2)+5.843	(-3)+3.590	(-3)+9.519	(-3)+5.350	(-3)+7.688	(-2)-3.208
(+3)+1.066	0.7332	(-1)+1.159	(-3)+3.674	(-2)+2.400	(-3)+5.637	(-2)+2.511	(-2)-7.874
(+3)+1.035	0.7335	(-1)+1.533	(-3)+3.674	(-2)+5.383	(-3)+5.428	(-2)+5.300	(-1)-1.661
(+3)+1.001	0.5144	(-1)+1.653	(-3)+3.571	(-3)+6.624	(-3)+4.676	(-2)+7.156	(-1)-2.535
(+2)+9.596	0.6319	(-1)+1.679	(-3)+3.190	(-1)+1.204	(-3)+3.793	(-2)+6.701	(-1)-2.933
(+2)+9.030	0.5775	(-1)+1.164	(-3)+2.841	(-1)+1.118	(-3)+2.639	(-2)+4.176	(-1)-2.855
(+2)+8.927	0.5976	(-1)+1.035	(-3)+2.306	(-1)+1.966	(-3)+1.843	(-4)+3.423	(-1)-2.253
(+2)+8.411	0.5182	(-2)+6.236	(-3)+2.509	(-3)+6.956	(-3)+1.698	(-3)-6.187	(-1)-2.128
(+2)+7.668	0.4490	(-2)+2.301	(-3)+1.953	(-2)+6.115	(-3)+1.112	(-2)-3.020	(-1)-1.500
(+2)+7.069	0.3937	(-3)+7.617	(-3)+1.536	(-2)+4.044	(-4)+5.964	(-2)-4.027	(-2)-8.263
(+2)+6.449	0.3303	(-3)+1.905	(-3)+1.246	(-2)+4.044	(-4)+3.412	(-2)-3.441	(-2)-4.680
(+2)+5.417	0.2315	(-5)+8.085	(-3)+1.016	(-2)+2.472	(-4)+1.910	(-2)-2.403	(-2)-2.561
			(-4)+7.204	(-3)+8.763	(-5)+6.696	(-3)-9.470	(-3)-8.124

Legend: The reactions are defined by Eq. (4). R_0 and R_{O_3} are the net rates of production of O and of O_3 respectively. $R_0 = R_1 - R_2 - 2R_4$, $R_{O_3} = -R_1 - R_2$. The number (\pm) \pm Y.YY denotes (\pm Y.YY) $\times 10^{12}$.

dissociation rates appears to be of the same order for the ozone system and for a previously studied free-radical system^{26a}. In the latter flame a 300 fold decrease in the free-radical specific rates increased M by a factor of about 1.3. Inspection of the calculations suggests that the difference in the direction of the shift can be attributed to the fact that an increase in free-radical rates* in ozone disturbs the kinetic steady-state approximation for O_3 in the region about the hot boundary.

5.2 Energy Transfer; Constant Specific Enthalpy Approximation.

For consideration of the relative contribution which various physical processes make to energy transfer, the terms in the energy balance equation (1c) will be regrouped. Since the equation assumes an asymptotic approach to thermal and diffusion equilibrium as $Z \rightarrow +\infty$, the energy conservation can be conveniently expressed in the form

$$M \sum_i H_i G_i / m_i - \lambda dT/dZ = M \lim_{Z \rightarrow \infty} \sum_i H_i G_i / m_i$$

$$= M \lim_{Z \rightarrow \infty} (H/m) \quad (25)$$

$$H = \sum_i H_i x_i = \text{enthalpy/mol}$$

$$m = \sum_i m_i x_i = \text{mean molecular weight.}$$

The first term in Eq. (25) can be written as the sum of a term due to diffusion and a convection term due to the mass average gas velocity:

$$M (H/m) + n \sum_i H_i x_i V_i - \lambda dT/dZ$$

$$= M \lim_{Z \rightarrow \infty} (H/m) \quad (26)$$

V_i : the diffusion velocity of species i .

In order to show the relative importance of the three processes in dimensionless units, the following ratios have been graphed:

$$R_{DIFF} = \frac{\text{Diffusion Term}}{\text{Conduction Term}} = \frac{n \sum_i H_i x_i V_i}{\lambda dT/dZ} \quad (27)$$

$$R_{CONV} = \frac{\text{Convection Term}}{\text{Conduction Term}} = \frac{M [H/m]}{\lambda dT/dZ}$$

* In this system, Reaction (1) is the idealized analogue of a free-radical dissociation-recombination reaction.

Since dT/dZ approaches zero as $Z \rightarrow Z_{\text{cold}}$ and has a limiting value of zero as $Z \rightarrow \infty$, it is apparent that $RGMV$ must increase as $Z \rightarrow Z_{\text{cold}}$ and must approach infinity as $Z \rightarrow +\infty$. In contrast with the idealized flame previously studied, for which convection was the least important process, Graph 5 shows that convection is the most important process throughout the entire flame and is over a factor of 10 more important throughout the hottest region until G_0 has attained between 0.4 and 0.5 of its limiting cold boundary value. Hirschfelder²⁵ has shown that when the approximations of Eqs. (1b, 1c) are used, the enthalpy per gram is constant \leftrightarrow all Lewis numbers are unity. Thus the processes of diffusion and thermal conduction are of equal importance $\leftrightarrow RDIFF = 1 \leftrightarrow$ the specific enthalpy is constant \leftrightarrow all Lewis numbers are unity. Thermal conduction will be the more important process $\leftrightarrow RDIFF < 1 \leftrightarrow H \lim_{Z \rightarrow \infty} H$.

Graph 6 of $RDIFF$ shows the quantitative effect of non-unit Lewis numbers upon the relative importance of the two processes. The ratio has the same qualitative variation found in an idealized system for "light" free-radicals (those whose binary diffusion coefficients are larger than the coefficients for major component pairs)³: diffusion is the more important process in the hotter region ($\tau > 0.75$) and thermal conduction is the more important for ($\tau < 0.75$).

The suggestion has been made that the constant specific enthalpy approximation might be used to determine one of the mol-fractions. This approximation has been applied specifically to the ozone flame by von Kármán and Penner²⁶. Let

α' : be the species such that $H_{\alpha'} x_{\alpha'}$ is the largest term in

$$H/m = m^{-1} \sum H_{\alpha} x_{\alpha} . \quad (28)$$

Then, at this point the ratio

$$RH = \frac{(H/m) - \lim_{Z \rightarrow \infty} (H/m)}{\lim_{Z \rightarrow \infty} (H/m)} \quad (29)$$

Shows the relative error in $x_{\alpha'}$, that would be made if this approximation were used. For this ozone flame, Graph 7 shows the variation in the error which is never greater than eight per cent. However, if this approximation were used in any theoretical calculation, the effect on the integral curves might be greater than the effect at one arbitrary point.

5.3 Heat Release by Radical Recombination.

To test the suggestion²⁷ that, since radicals are highly energetic species they might serve as an important means of energy transport by diffusing toward the cold boundary and recombining, the relative contribution free-radical recombination makes to the total volume rate of heat release due to chemical reaction

$$HREL = \frac{R_4 (H_0 - 2H_0)}{R_1 (H_0 - H_0 - H_0) + R_2 (H_0 + H_0 - 2H_0) + 2R_4 (H_0 - 2H_0)} , \quad (30)$$

is given by Graph 8.

Contrary to this suggestion, the contribution of the main combustion reaction in the colder region is more important by an order of magnitude. This contrasts strikingly with the fact that the fraction contributed by radical recombination $\geq 1/2$ for sufficiently hot T ($\tau \geq 0.77$).

For the ozone flame, HREL is qualitatively different than a previously studied idealized flame³. In the latter flame Reaction (1) is the analogue of the recombination-dissociation reaction. It contributes much less than a few percent of the total volume rate of heat release. Whereas in the ozone system, dissociation is completely negligible and the contribution is always positive, in the idealized system the contribution is both positive and negative. This is qualitatively the same as the contribution of the $\text{Br} - \text{Br}_2$ reaction in the $\text{H}_2 - \text{Br}_2$ system.

5.4. Spatial Separation of Processes.

There are both experimental and theoretical reasons for examining the spatial separation of processes in the ozone flame. Theoretically, study of the relative importance of processes in the neighborhood of the hot boundary might suggest useful alternative models. Experimentally, studies of the methane-oxygen system have shown that the adiabatic model (which is used in theoretical studies) is rather good for that system: the calculated and corrected experimental flame temperatures differ by only 10° ²⁸.

What is of particular interest here is that the methane-oxygen flame has a rather marked separation into three spatial regions^{28a}: (1) a low temperature region, commonly expected in flames, in which there is comparatively little chemical reaction but a marked temperature rise due to energy transport; (2) an intermediate temperature region dominated by one sequence of reactions; (3) a higher temperature region extending to the maximum flame temperature dominated by a different sequence of reactions. The Table 7 of reaction rates and the Graph 9 of τ (3) [cf. Eq. 16] shows the separation of the ozone flame into the first two regions. The separation into two different kinetic regions will now be demonstrated. When the temperature is still 200° ($T = 1143^\circ$) below its limiting hot boundary value, the fuel mol-fraction has decreased to 10^{-3} of its maximum value which occurs at the cold boundary. Conversely, x_{O} is still 0.67 of its maximum value. Both are, of course, orders of magnitude greater than those for complete thermodynamic equilibrium.

Inspection of the graphs (10,11,2) for the mol-fractions and fractional mass-flow rates shows the greater importance of changes for O atom in this region.

In terms of reaction kinetics, $-R_{\text{O}} > -R_{\text{O}_3} > 0$ and $R_{\text{O}}/R_{\text{O}_3}$ increases rapidly with increasing T until it reaches a value of over 100 [cf. Table 7]. Thus, in this region the net rate of free-radical production is more important. Table 7 of reaction rates shows the importance of recombination to the net production. For example, at $T = 1143^\circ$, recombination contributes 0.84 of the total (negative) net rate of production. This recalls Fristrom's²⁹ observation that recombination reactions must be important in the high temperature region of the methane-oxygen flame. The Section 5.3 on heat release has already shown that O recombination is the dominant source of heat release by chemical reactions in this region.

Just as R_{O} dominates R_{O_3} in kinetics, G_{O} dominates G_{O_3} by two orders of magnitude so that free-radical mass-flow makes a more important contribution to energy conservation than fuel mass-flow does.

As Section 5.5 shows, there is an approach to diffusion equilibrium prior to thermal equilibrium. Conversely, there is no approach to chemical equilibrium prior to thermal equilibrium. Both x_0 and x_{O_3} increase rapidly with respect to thermal equilibrium values, although not so rapidly as in a previous study²⁰. Thus at a temperature one degree below the hot boundary temperature, x_0 and x_{O_3} are 77 and 79 times greater, respectively, than their equilibrium values.

5.5 The Role of Diffusion.

To provide a basis for estimating the significance of diffusion throughout the flame, two different sets of graphs are given: (1) the ratios (v_i/v) of the average speed for a particle of type i to the mass average speed (Graph 12); (2) the ratios of V_i/M of the actual diffusion velocity to the total mass flow rate, M (Graph 13). Although Section 5.4 shows that there is no approach to chemical equilibrium before thermal equilibrium, there is a prior approach to diffusion equilibrium ($v_i/v \approx 1$). Conversely, at certain lower temperatures, diffusion contributes more than the average mass flow to the motion of both O_3 and of O . Thus v_1/v attains values of 2.75 and -2.5 for O_3 and O respectively.

von Karman and Penner's approximate equation for the burning velocity predicts that it will vary as the inverse square root of the ozone-oxygen molecule binary diffusion coefficient^{18b}. By accident, there has also been a test of the significance of the oxygen atom binary diffusion coefficients. A key-punch error in one run, and a duplication error in a second altered their temperature dependence so that they were decreased twenty-five percent and more in the x_0 diffusion equation in the region of most rapid chemical reaction. This gave an estimated M of 0.1617 [cf. Eq. (22)] compared with $M = 0.1812$ [cf. Eq. (34)] for the diffusion coefficients of Section 3.

5.6 Comparison with Experiment and Other Calculations.

The sole experimental data on the ozone flame are burning velocities determined for several mixtures. Strain and Crocco¹² report a burning velocity of 52.2 cm./sec. for the ozone-oxygen mixture considered here. This corresponds to an experimental value for the total mass-flow rate of

$$M_{\text{exp}} = 0.07730. \quad (31)$$

The M assumed in the calculations reported here

$$M_{\text{use}} = 0.177 \text{ g.-cm.}^2/\text{sec.} \quad (32)$$

gave

$$C_{O_3}(Z_{\text{cold}}) = 0.3759.$$

* His α_1 , defined by his Eq. (41) is inversely proportional to D_{O_2, O_3} .

Previous studies by the author have shown that for a three component flame, the product of $M G_{\text{fuel}}(Z_c)$ varies slowly with $G_{\text{fuel}}(Z_c)$ and can be roughly approximated as a linear function. Therefore, a theoretical value corresponding to the experimental G_{O_3} at the cold boundary was estimated by passing a straight line through two different calculated values:

$$M G_{O_3}(Z_c) = 0.06653 - 0.03086 (G_{O_3} - 0.3789). \quad (33)$$

This gave

$$M_{\text{the}} = 0.1812. \quad (34)$$

Since Professor Grosse feels that this discrepancy greatly exceeds the likely experimental error ³⁰, it is necessary to consider possible sources of the disagreement. Results of previous calculations on an idealization of a free-radical flame can be used to suggest probable sources of error ^{26,3}. For an appropriate choice of dimensionless variables, it was found that M could be combined with other parameters to form a dimensionless constant, μ^* , which varied rather slowly with certain parameters:

$$\mu^* = \frac{(m^*)^2 \lambda (T_{\text{max}})}{M^2 C^*} \quad (35)$$

m^*, C^* : The molecular weight and constant pressure heat capacity for a species, β , where M is adjusted to make $G_{\beta}(Z)$ satisfy its cold boundary condition.

k^* : any multiplicative factor in the specific rate for one of the most important reactions in the net rate of production of β .

Thus for 13 and 15-fold variations in the two binary diffusion coefficients involving free-radicals and a 300 fold variation in the ratio of the specific rates for the main combustion reaction to those for the free-radical reaction, μ^* varied only by a factor of 1.8. This suggests that the large ratio $M_{\text{the}}/M_{\text{exp}}$ should be attributed to either too high a value for one or more of the following quantities: (a) $\lambda(T_{\text{max}})$, and, therefore, $\lambda(T)$; (b) the specific rates of reactions which contribute most to dG_{O_3}/dT in the region of most rapid chemical reaction. For the ozone flame, the two most important reactions in the temperature domain responsible for most of the rise in G_{O_3} are: (1) R_1^1 at the higher temperatures within this region; (2) R_2^1 at the

lower. (Note that because of the failure of the kinetic steady-state, R_1^1 and R_2^1 are not directly related). Although further experimental work would be required to choose between the alternatives, it seems less likely that the thermal conductivity is off by over a factor of two. It is worth noting that the activation energy for both R_1^1 and R_2^1 are subject to considerable uncertainty. For example, the ratio of the (1) specific rate assumed here to the one proposed by Benson and Asworthy ³¹ is

$$2.9 \exp[-350/T]. \quad (36)$$

At $T = 1000^\circ$, a temperature in the range where R_1^1 makes a large contribution, this ratio is approximately two. Correction of Benson and Asworthy's parameters for (2)

to take account of their use of an older equilibrium constant gave a higher activation energy than the one used in this report ^{5f}. Apparently this was due to their use of graphical instead of least squares data analysis ^{5g}. Conversely, flow system studies gave a lower value which would predict a somewhat lower specific rate at flame temperatures.

Previous theoretical studies predicted burning velocities for a mixture of similar composition

$$x_{O_3} (Z_{cold}) = 0.25 \quad (37)$$

for which Lewis and von Elbe reported a burning velocity of 55 cm.-sec.⁻¹ ³². The results, depending upon the value assumed for the reduced diffusion coefficient range from 47 or 51 ²⁰ to 42 or 46 ¹⁸. There is much better agreement between their calculations and experiment than between the results presented here and experiment.

As shown in Section 5.1, it is not certain that the calculated speeds are correct for the parameters assumed. If they are correct, inspection of Eq. (35) shows that the discrepancy between them and the present results is not related in a simple fashion to the difference in parameters since: (1) The values for the thermal conductivity of the gas mixture used in the two studies are within several percent of each other; (2) According to preceding discussion in this section, the two reactions which are responsible for most of the change in G_{O_3} (which determines M) are R_1^f and R_2^f . Whereas a decrease in either would decrease the theoretical M, the ratios of specific rates in the present study to those used in the earlier work are:

Reaction	\bar{f}	\bar{f}	
T = 1230°	9.9	0.045	(38)
872°	13.1	0.07	
397°	15.8	0.36	

5.7 Test of the Significance of the Kinetic Energy Term in the Equation of Energy Balance.

Previously, heuristic argument has been given to support the contention that kinetic energy of over all gas flow can be an important term in the energy balance equation even when viscosity makes no significant contribution. The argument suggested that the former term would be most important where there was the greatest cancellation in the usual terms of the equation of energy balance, i.e., in the neighborhood of the hot boundary ⁴. Therefore, as a check upon the importance of kinetic energy, a thirtieth order power series was constructed including those terms. The series sums are:

$$(T - T_{max}) = -0.1125 T_{max}$$

	without K.E.	with K.E.	% Error	
G_{O_3}	1.9409×10^{-4}	1.9959×10^{-4}	2.8	(39)
x_{O_3}	1.1540×10^{-4}	1.1835×10^{-4}	2.5	
G_0	1.0607×10^{-2}	1.0936×10^{-2}	3.0	
x_0	1.9129×10^{-2}	1.9990×10^{-2}	2.8	

Although these values suggest that the kinetic energy term does not make an important contribution to this flame, calculations on richer ozone flames with higher maximum temperatures (to be included in a later paper) show that it changes the eigenvalue character of the problem.

5.6 Significance of Theoretical Flame Calculations.

As Sandri³³ observed, it is simpler to measure burning velocities than to make theoretical calculations. He argued that the calculations should be used as a means of studying chemical kinetics by comparing theoretical and experimental velocities for appropriate models. The discussion of Sections 5.1, 5.6 illustrates the facts that flame speeds are not particularly sensitive to many parts of a kinetic scheme and that such a comparison could be useful only if the transport coefficients and all but one specific rate which contributed markedly to the rate of consumption of a major fuel component were reasonably well known. However, theoretical calculations could be very useful when the greater detail given by experimental studies of temperature and composition profiles are known. For major components, these have been determined for the methane-oxygen system³⁴. Work on determining free-radical profiles is in progress³⁵. Theoretical calculations would obviate the use of approximations in the diffusion equations made in analyzing current experimental studies and the uncertainty from double differentiation of experimental data³⁶.

Alternatively, they can be used to develop a general understanding of the relation between fuel properties and the comparative importance of various processes. For the particular case of ozone, it seems unlikely that uncertainties in the parameters will qualitatively alter any of the results presented here. This conclusion is founded on a comparison of: (a) the various calculations discussed here; (b) unreported calculations using different specific rates for reactions (1) and (2) which were 6 fold larger for (1) and 45 fold larger for (2) at the hot boundary; (c) unreported calculations for various assumed values of K ; (d) unreported calculations on richer ozone mixtures.

6. Summary of Major Conclusions.

The major conclusions will be summarized according to sections for convenient reference.

Section 4. A single eigen value approximation appears to be adequate for the 20 mole percent ozone flame. Two eigenvalues must be used for sufficiently rich ozone mixtures burning at higher temperatures.

Section 5.1.

(a) It seems that the kinetic rate k_1 may give burning velocities accurate within a factor of about 2 and generally better. Since x_0 does not follow a semblance of the approximation in this (and a fortiori in higher temperature ozone flames), the approximation should be used in calculating any property at all sensitive to x_0 (1).

(b) It is not x_0 but x_0 ^{not} which approximately satisfies a kinetic steady-state condition in a temperature interval of over 175° about the hot boundary.

(c) The existence of a single internal maximum should not be interpreted in

terms of the kinetic steady-state approximation. An alternative approximation applies.

(d) Radical recombination in this ozone flame plays an important role but only for temperatures within about 300° of the hot boundary.

(e) von Karman and Penner underestimated the temperature range over which $R_1^r : M+O_2+O \rightarrow M+O_3$ would be important. It exceeds $R_1^r : M+O_3 \rightarrow O_2+O+M$ over a temperature range of about 200° . The effect of this upon the flame velocity is uncertain.

Sections 5.1 and 5.6. The qualitative differences between the results reported here and those of earlier studies is due to the removing of certain earlier approximations.

Section 5.2.

(a) Convection is the dominant process at all temperatures. Diffusion is more important than conduction at higher temperatures, less at lower.

(b) The specific enthalpy varies over a range of $\pm 8\%$.

Section 5.3. The rate of heat release per unit volume due to radical recombination is over half the total rate for a temperature interval of over 200° about the hot boundary. Contrary to a previous suggestion, it becomes negligible in the cooler part of the flame. Radicals which diffuse there from the hotter regions are effective primarily in $R_2^r : O+O_3 \rightarrow 2 O_2$.

Section 5.4. The spatial separation of kinetic processes is reminiscent of the separation found experimentally in the methane-oxygen flame. There is no approach to chemical before thermal equilibrium.

Section 5.5. There is an approach to diffusion equilibrium before thermal (and chemical) equilibrium. The magnitude of the diffusion velocity exceeds the mass average speed for $T < \text{ca. } 1020^\circ$ for O and from about $T = 910^\circ$ to $T = 1130^\circ$ for O_3 .

Section 5.6. The theoretical M is too large by over a factor of 2. The most likely major sources of the error are too high values at flame temperatures of the rate of $R_1^r : O_3+M \rightarrow O_2+O+M$, or of $R_2^r : O_3+O \rightarrow 2 O_2$, or both.

Section 5.7. The kinetic energy of overall gas flow does not appear to be very important for this ozone flame. Conversely, it can not be ignored for sufficiently rich ozone flames where it changes the character of the eigenvalue problem.

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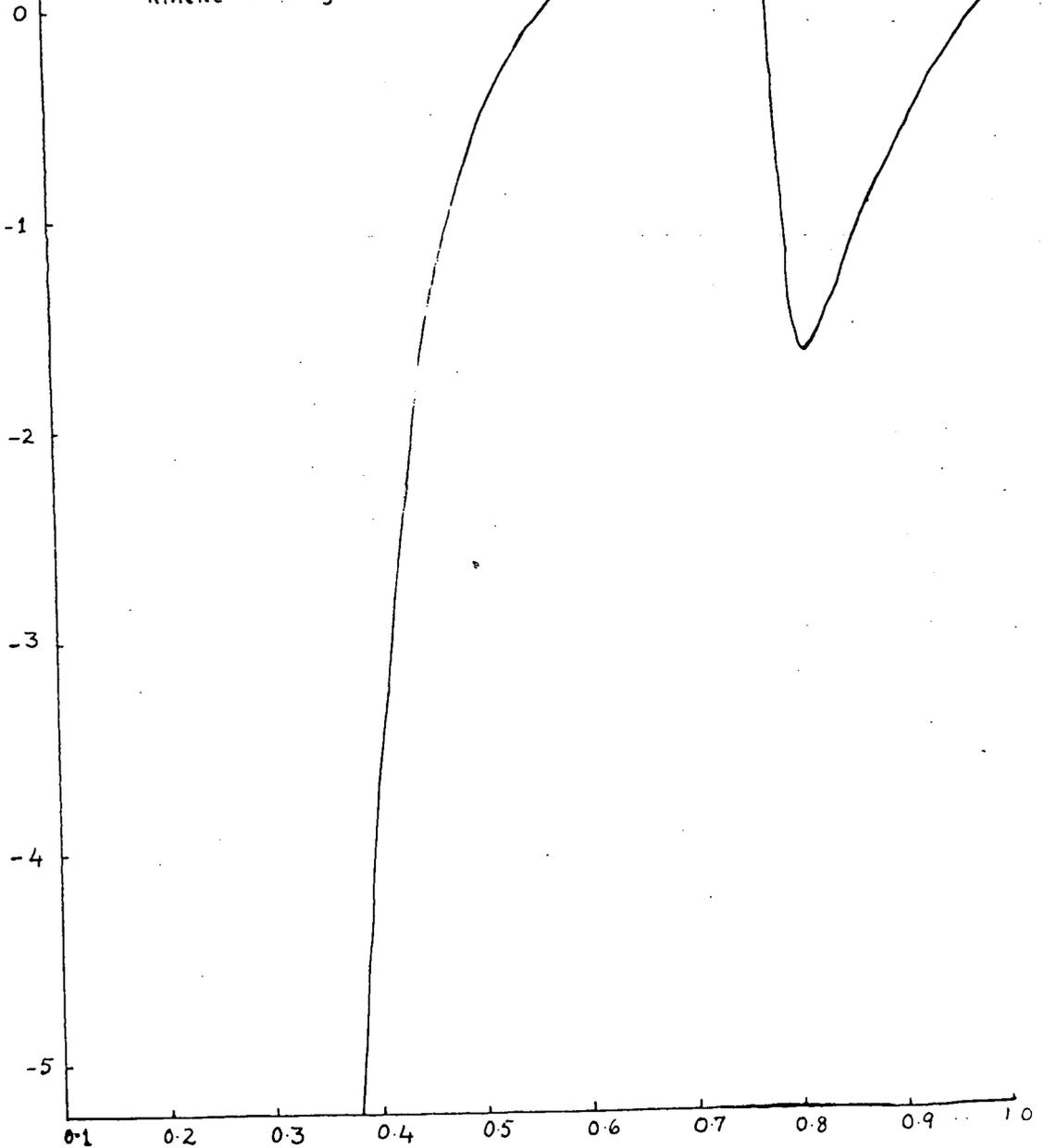
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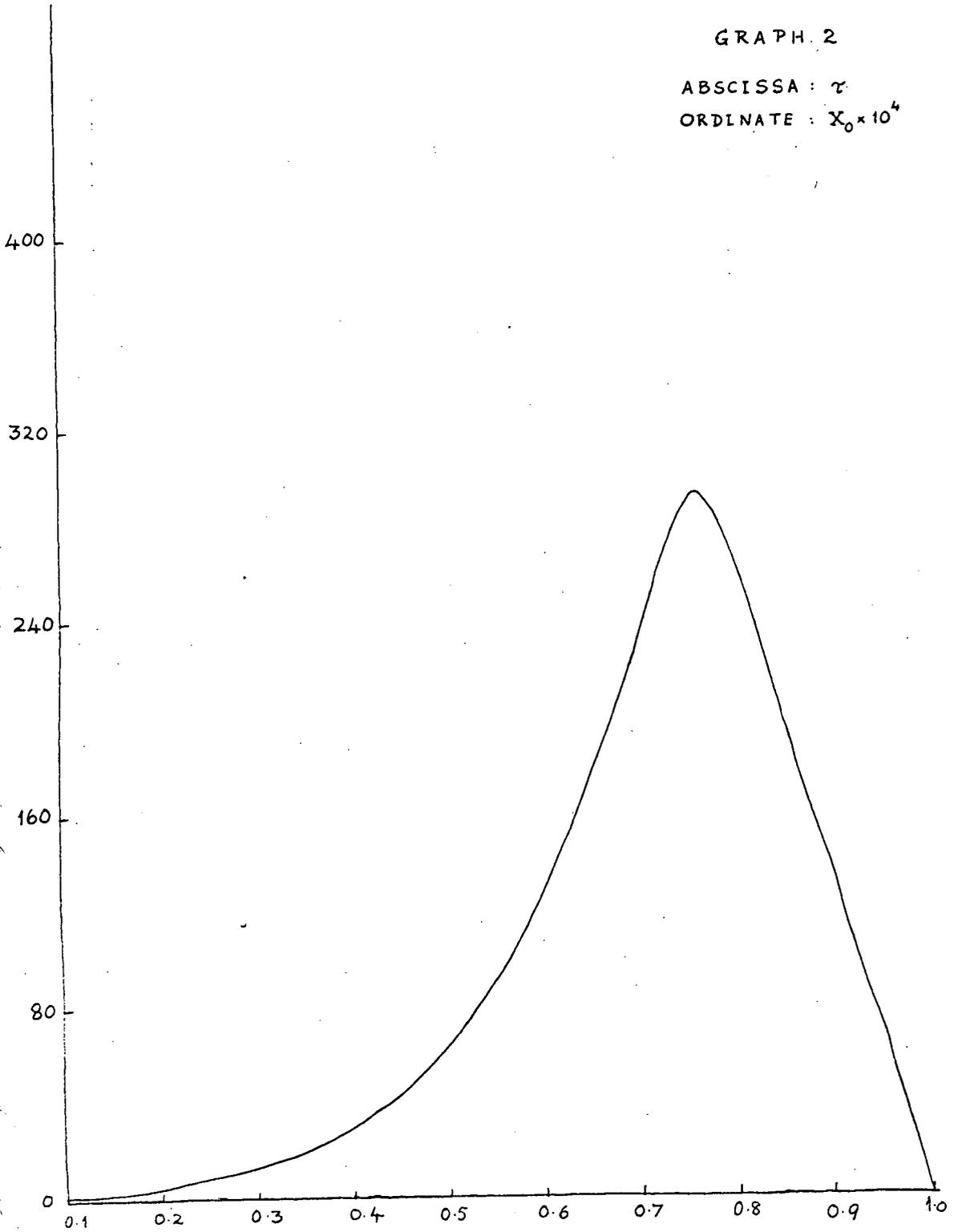
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GRAPH 1

ABSCISSA: τ
ORDINATE: f_0 = Relative
Deviation from the
Kinetic Steady-State.



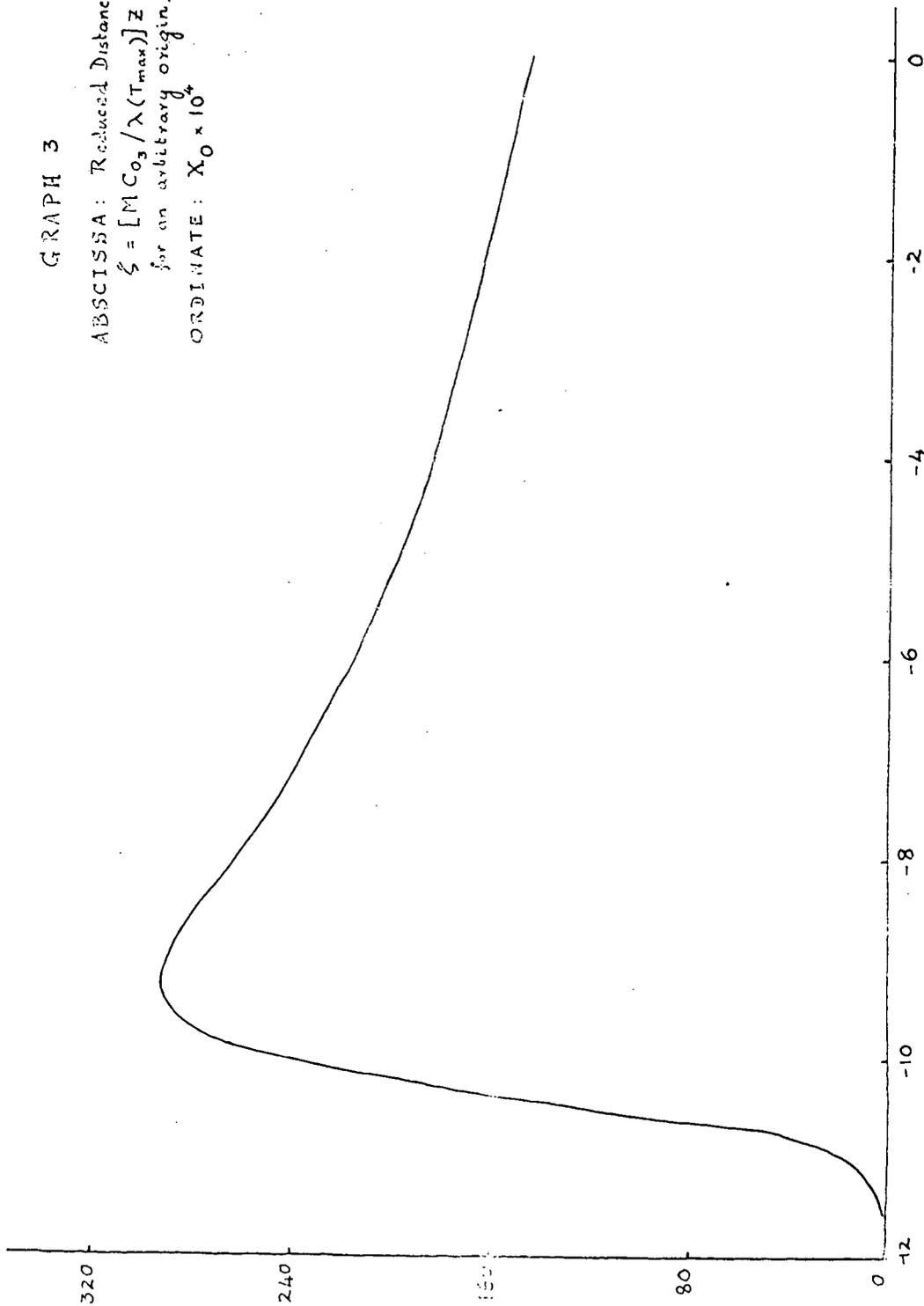
GRAPH 2

ABSCISSA : τ ORDINATE : $X_0 \times 10^4$ 

GRAPH 3

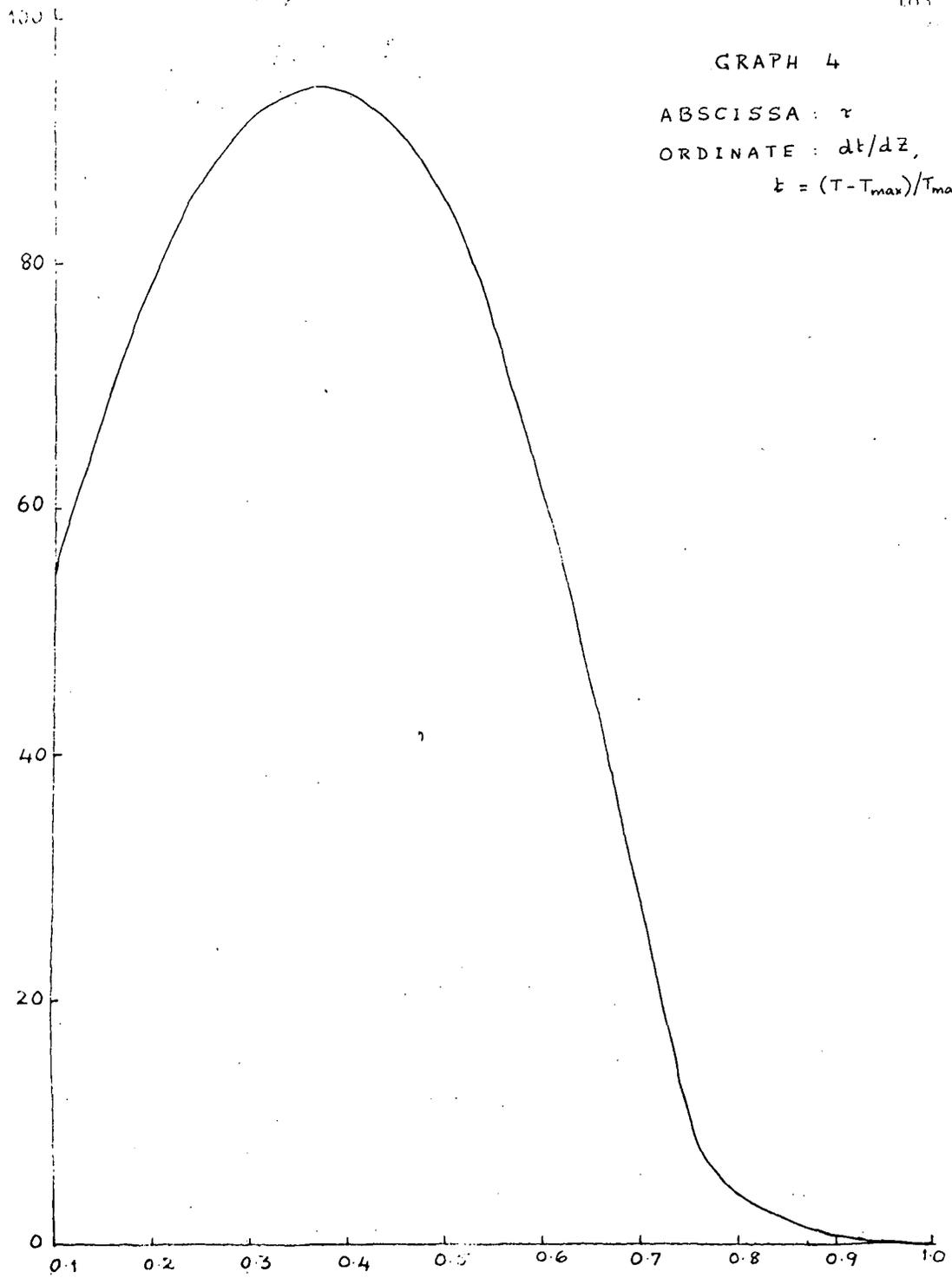
ABSCISSA: Reduced Distance,
 $\xi = [M C_0 / \lambda (T_{max})] z$
for an arbitrary origin.

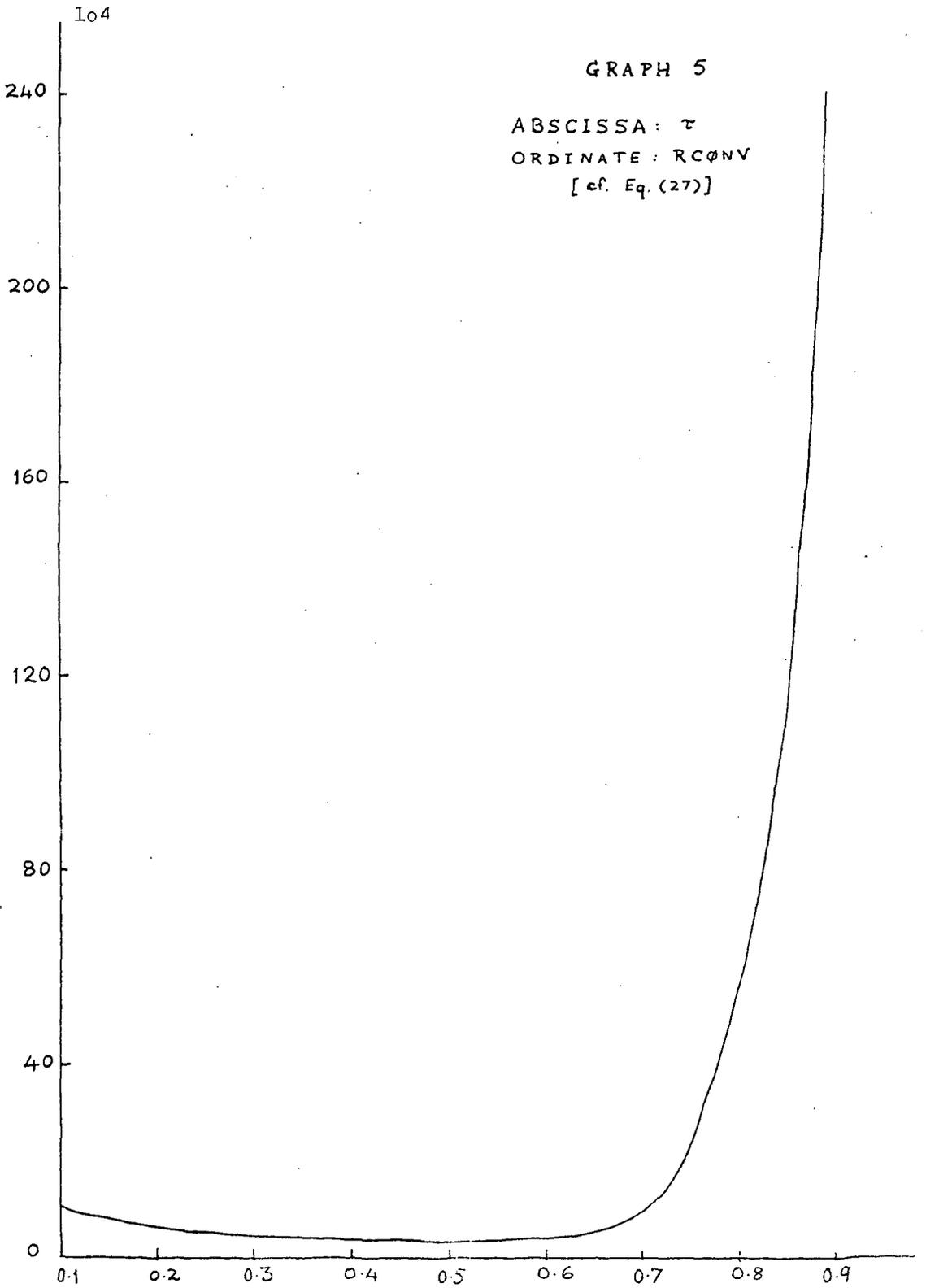
ORDINATE: $X_0 \times 10^4$

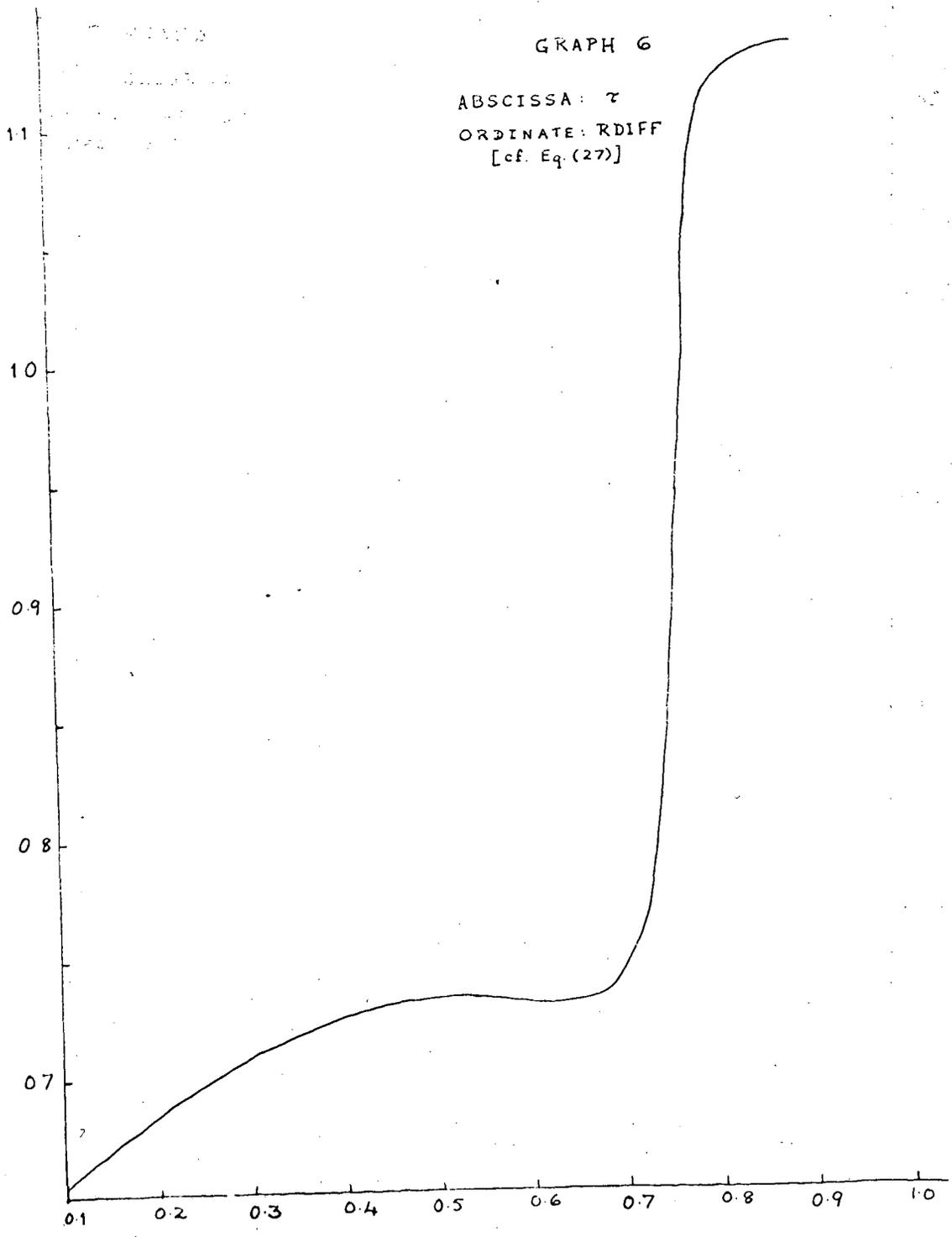


GRAPH 4

ABSCISSA : τ
ORDINATE : dt/dz ,
 $t = (T - T_{max})/T_{max}$







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GRAPH 7

ABSCISSA: τ
ORDINATE: RH
[cf. Eq. (29)]

0.10

0.08

0.06

0.04

0.02

0.0

0.1

0.2

0.3

0.4

0.5

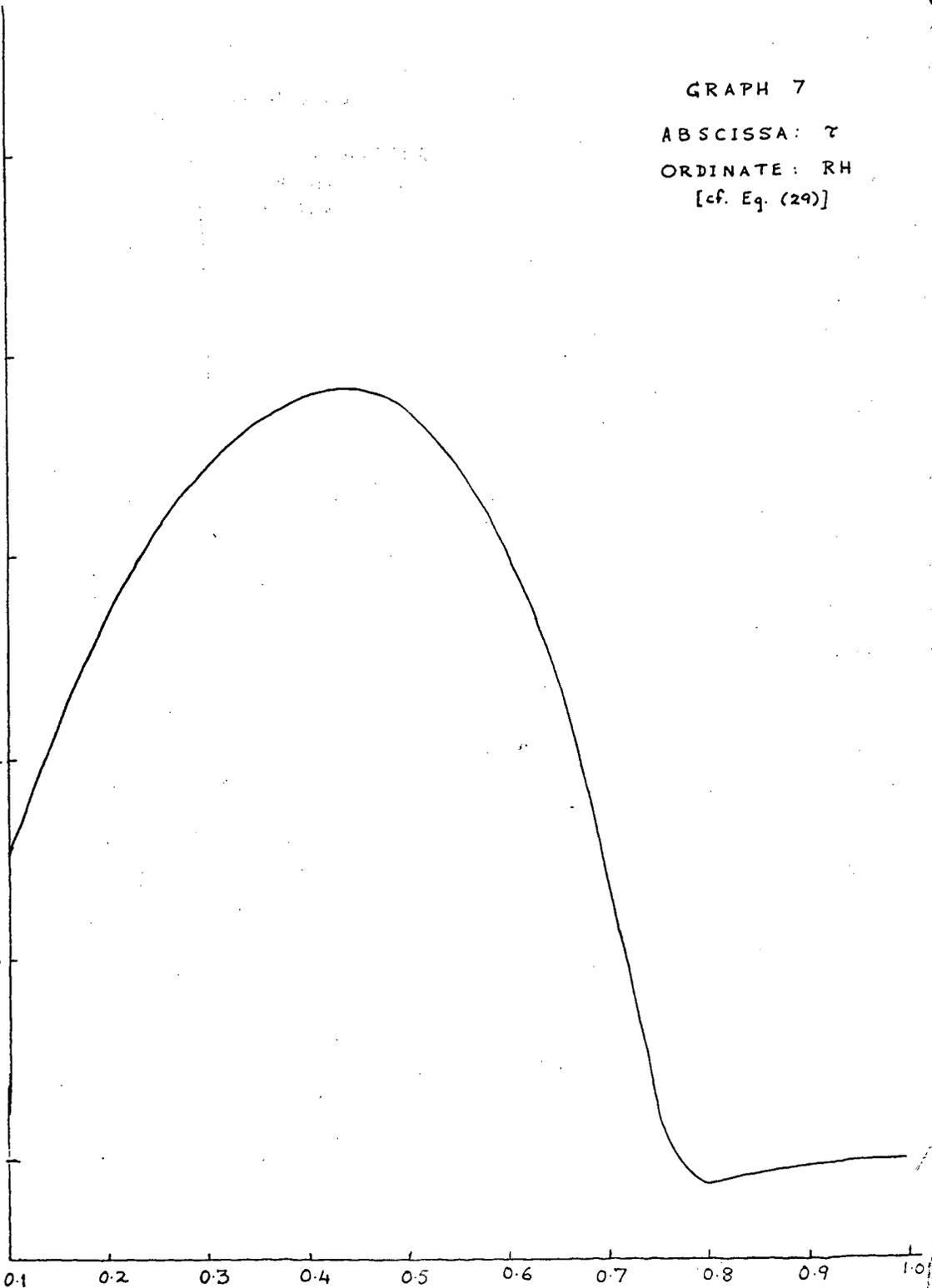
0.6

0.7

0.8

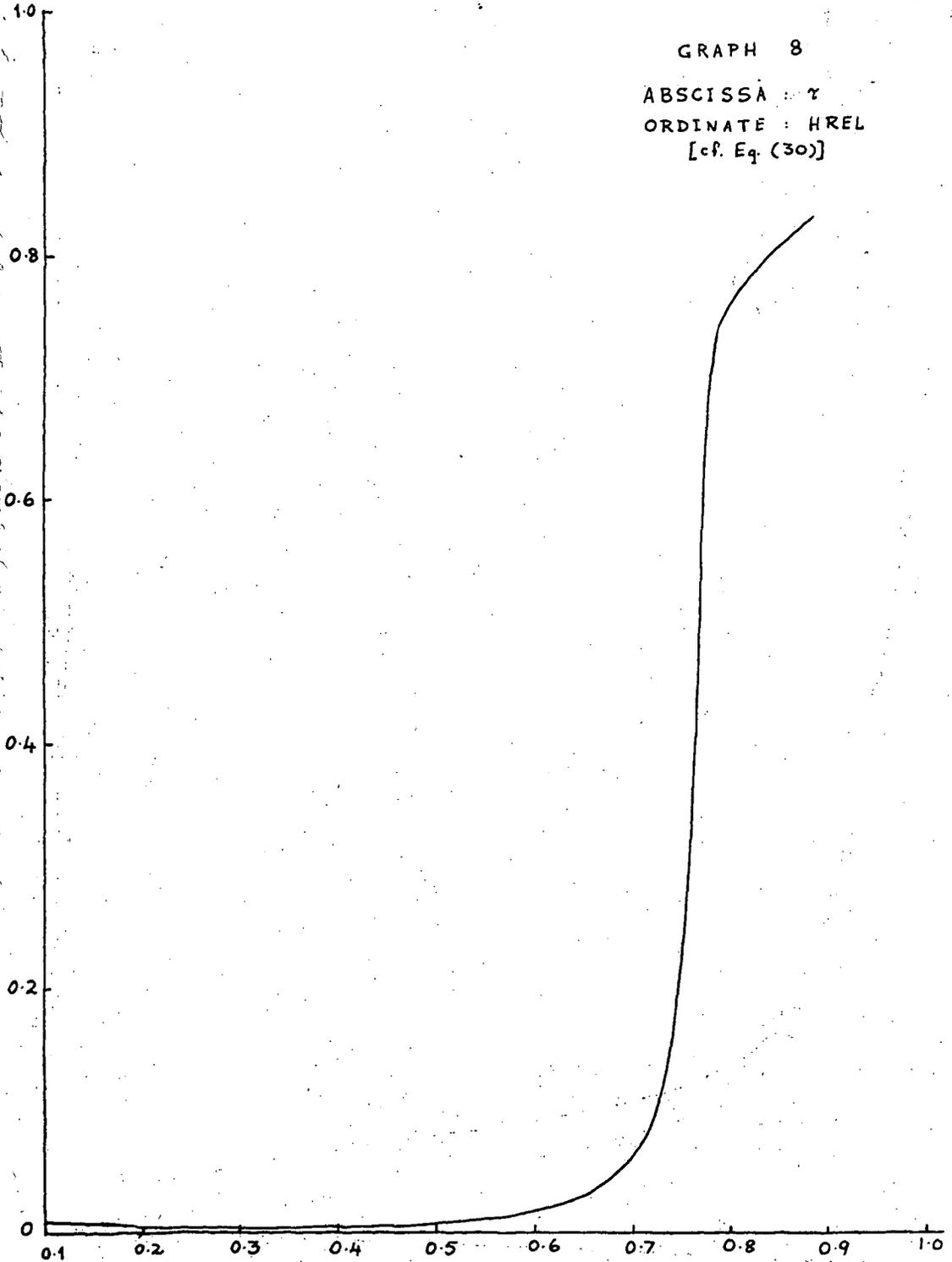
0.9

1.0



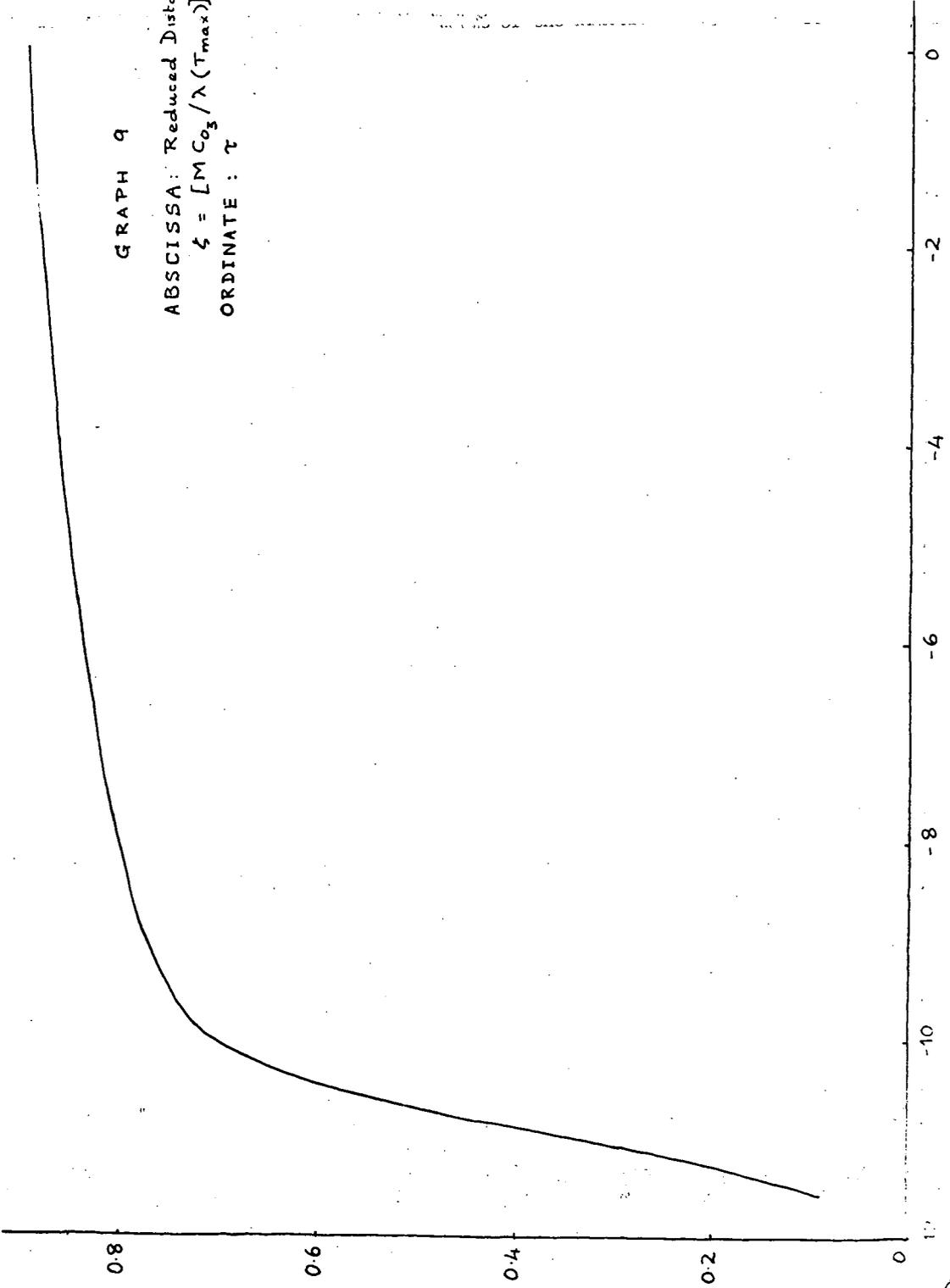
GRAPH 8

ABSCISSA : γ
ORDINATE : HREL
[cf. Eq. (30)]



GRAPH 9

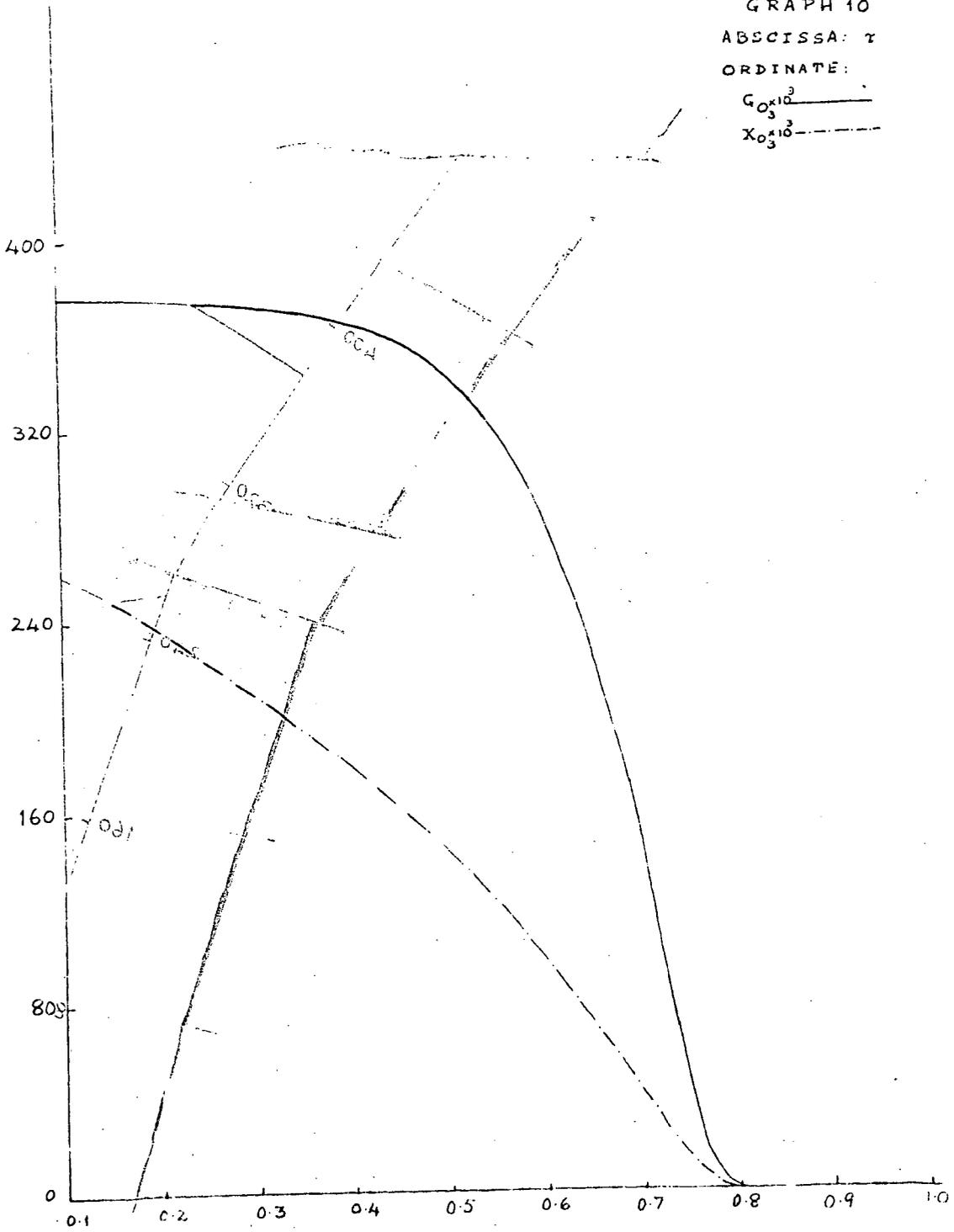
ABSCISSA: Reduced Distance,
 $\xi = [M C_{O_3} / \lambda (T_{max})] Z$
ORDINATE: τ



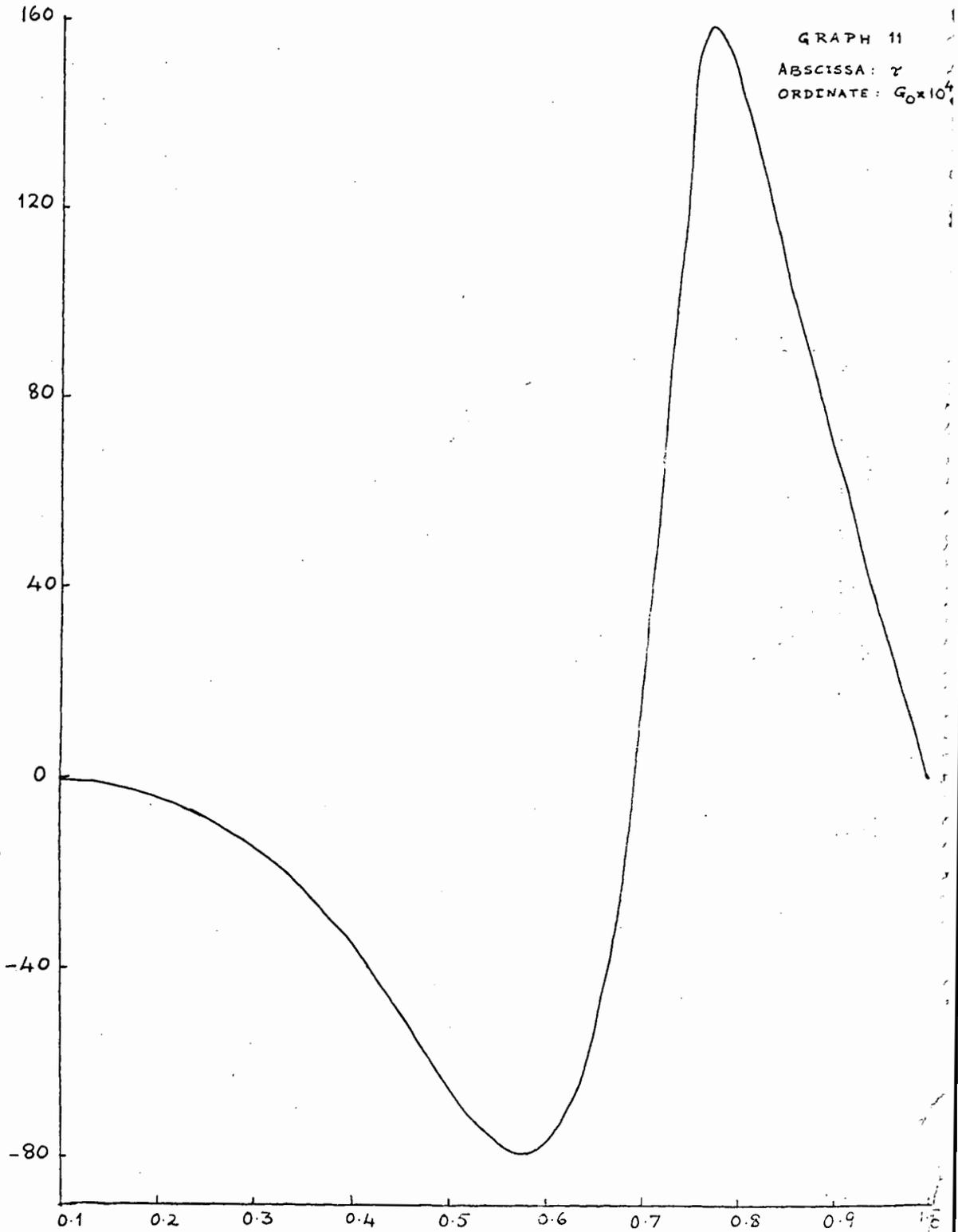
100

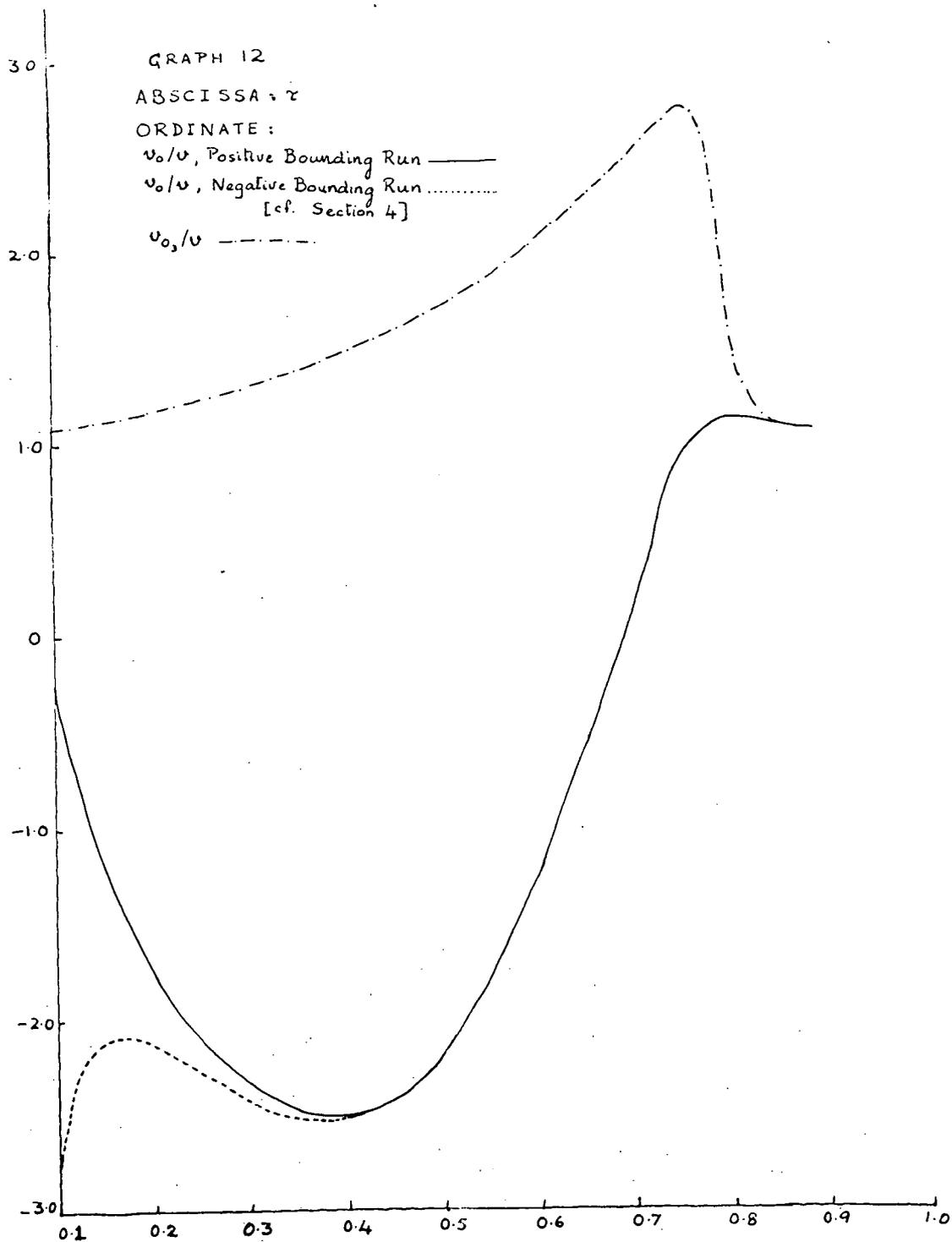
GRAPH 10
ABSCISSA: τ
ORDINATE:

$G_{O_3} \times 10^3$ ———
 $X_{O_3} \times 10^3$ - - -



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GRAPH 13

