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MEASUREMENT AND CORRELATION OF INDUCTION TIMES FOR THE OXIDATION OF METHANE HYDROGEN MIXTURES

by

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Introduction

One of the prominent features of homogeneous auto-ignition in combustible mixtures is the strong ignition limit. In our systematic investigation of this limit in methane-hydrogen-oxygen mixtures[1], determined experimentally in combustion initiated by reflected shocks, we have obtained conventional induction time data for this binary fuel system. The objective of this communication is to present these data, together with a heuristic correlation formula we have developed for their application and generalization.

Experiments

The experiments were performed in a retangular cross-section, 3.8 cm by 4.4 cm, aluminum shock tube. The induction time was measured from the oscilloscope trace of a bar-type barium-titanite pressure transducer mounted on the end wall of the shock tube. As reported by us when this method was developed[2], the error in such measurements is about ±4 μsec. Eleven mixtures were used, two of methane and oxygen, two of hydrogen and oxygen, and seven of various combinations of methane, hydrogen and oxygen, all in 90% argon dilution. Mixture compositions were specified in terms of two parameters,

$$\zeta \equiv X_{H_2} \,/\, (X_{H_2} + X_{CH_4}) \tag{1a}$$

and

$$\phi = [\,(X_{H_2} + X_{CH_4}) \,/\, X_{O_2}] \,/\, [\,(X_{H_2} + X_{CH_4}) \,/\, X_{O_2}]_{\text{stoich}} \tag{1b}$$

where X_i ($i = H_2, CH_4, O_2$) is the mole fraction and ϕ is the equivalence ratio. In terms of ζ the stoichiometric equation for this binary fuel system is

$$(1-\zeta)CH_4 + \zeta H_2 + (2-1.5)\,\zeta O_2 \rightarrow (1-\zeta)CO_2 + (2-\zeta)H_2O \tag{2}$$

The corresponding values of mixture parameters are listed in Table 1. In all, some 800 viable experimental runs were performed. Initial conditions behind the reflected shock were determined on the basis of the measured incident shock velocity with the use of JANAF thermochemical data. The experiments covered temperature and pressure range of 1000 to 2200K and 1 to 3 atmospheres, respectively.

Results and Discussions

The data for the binary mixtures no. 1 and 2 for methane-oxygen and no. 10 and 11 for hydrogen-oxygen are shown in Figs. 1 and 2. These data are correlated by the Arrhenius expression:

$$\tau = A\,[\,\text{fuel}\,]^{x}\,[\,O_2\,]^{y}\ \exp\,(E/RT) \qquad (3)$$

the quantities in square brackets denoting concentrations in moles/cc, R - the universal gas constant, and E - the activation energy while A, x, and y are the correlation parameters. The latter were evaluated using a non-linear regression program of Marks[3]. The results, together with those reported in the literature [4,5,6,7,8], are listed in Table 2. In general our correlation parameters are in good agreement with others. Our data are compared in Figs. 1 and 2 with empirical correlations

$$\tau\,[\,CH_4]^{-0.48}\,[\,O_2\,]^{1.94} = 1.19\ \text{E-12}\ \exp\,(46.4/RT)$$

for CH_4 and

$$\tau\,[\,H_2]^{-.14}\,[\,O_2\,]^{0.56} = 1.54\ \text{E-4}\ \exp\,(17.2/RT)$$

for H_2, both represented by solid straight lines.

One of the most significant results we obtained was that the induction time for the CH_4-H_2-O_2 mixtures could be correlated simply by the following

formula:

$$\tau = \tau_{CH_4}^{(1-\varepsilon)} \; \tau_{H_2}^{(\varepsilon)} \tag{4}$$

where τ_{CH_4} and τ_{H_2} are the correlation formulae for the binary mixtures:

$$\tau_{CH_4} = 1.19 \text{ E-12} \, [CH_4]^{0.48} \, [O_2]^{-1.94} \exp(46.4/RT) \, \mu\text{sec} \tag{4a}$$

$$\tau_{H_2} = 1.54 \text{ E-4} \, [H_2]^{0.14} \, [O_2]^{-.56} \exp(17.2/RT) \, \mu\text{sec} \tag{4b}$$

while ε is a linear correlation parameter satisfying the conditions: $\varepsilon=0$ for $X_{H_2}=0$ and $\varepsilon=1$ for $X_{CH_4}=0$. The basic implication of Eq. (4) is that the induction times of the ternary system can be expressed with sufficient accuracy in terms of the corresponding induction times for binary mixtures. The formula was developed on the basis of the observation that the Arrhenius plots for the ternary system are linear with activation energies lying between those for methane and for hydrogen. Thus ε in the formula of Eq. (4) is essentially a weighing parameter for the evaluation of activation energy for the ternary system from those of binary mixtures.

Values of ε for each of the ternary mixtures were determined by the use of Mark's non-linear regression program[3]. The results are shown in Table 1. It can be seen that the values of ε are approximately equal to ζ. Furthermore, all values of ζ, except for one, fall within the 95% confidence limit prescribed for the corresponding value of ε. Consequently, ζ can be substituted for ε in Eq. (4), yielding the following straightforward correlation for the CH_4-H_2-O_2 system

$$\tau = \tau_{CH_4}^{(1-\zeta)} \; \tau_{H_2}^{\zeta} \tag{5}$$

The validity of Eq. (5) is displayed in Figs. 3, 4, and 5, showing the data

of mixtures no. 3 & 4 (ζ = 0.33), mixtures no. 5 & 6 (ζ = 0.5), and mixtures no. 7, 8 and 9 (ζ = 0.67) respectively. Again the straight line on each figure complies with the correlation:

$$\tau\,[CH_4]^{0.48\,(1-\zeta)\,+\,.14\zeta}\,[H_2]^{-1.94\,(1-\zeta)\,+\,.56\zeta} = (1.19E\text{-}12)^{(1-\zeta)}\,(1.54E\text{-}4)^{\zeta}\,\exp\frac{46.4\,(1-\zeta)\,+\,17.2\zeta}{RT} \qquad (6)$$

The activation energies of Eq. (6) compare very well with experimental data. Moreover, Eq.(5) served most satisfactorily in correlating the overall concentration (pressure) and stoichiometric dependency.

Representative experimental data from the present study, as well as those reported by others[4,5], were compared with prediciton derived by the use of Eq. (5) and with results obtained by numerical integration of chemical kinetic rate equations using rate constants compiled by Olsen et al.[9] for methane, and by Meyer et al.[10] for hydrogen. As demostrated in Table 3, induction times based on the correlation formula of Eq. (5) are in good agreement with all of the experimental data, while the results of numerical integration, including those for methane-hydrogen-oxygen mixtures, fall within a factor of two of the measurements.

Summary

The induction time data we measured for the methane-hydrogen-oxygen system, within an experimental range of temperatures between 1000 to 2200K and of pressures between 1 to 3 atm., can be correlated by a formula based on the correlation parameters of the binary mixtures. The most interesting implication of this formula is that the activation energies in the ternary system are directly proportional to the ratio of the concentrations of methane

and hydrogen. It should be pointed out that, at this juncture, we are offering this conclusion only for its practical merit, without attaching much theoretical significance to its possible chemical kinetic consequences.

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Figure Captions

Fig. 1 Comparison between data and correlation formula for methane mixtures, no. 1 (△) and no. 2 (◇).

Fig. 2 Comparison between data and correlation formula for hydrogen mixtures, no. 10 (△) and no. 11 (◇).

Fig. 3 Comparison between data and correlation formula for $\zeta = 0.33$ mixtures, no. 3 (△) and no. 4 (◇).

Fig. 4 Comparison between data and correlation formula for $\zeta = 0.5$ mixtures, no. 5 (△) and no. 6 (◇).

Fig. 5 Comparison between data and correlation formula for $\zeta = 0.67$ mixtures, no. 7 (△), no. 8 (◇), and no. 9 (○).

Table 3. Comparison of measured induction-times with those deducted from correlation formulae and evaluated on the basis of elementary chemical kinetic data.

Source	$CH_4:H_2:O_2:A$	P	T	τ	τ_1	τ_2
		(atm)	(K)	(μsec)	(μsec)	(μsec)
Serry and Bowman(4)	1:0:2 :8	2.24	1724	85	80	-
Serry and Bowman(4)	1:0:1 :4	1.81	1721	120	176	-
Liftshitz et al.(5)	1:0:1 :45	10.22	1905	95	98	-
Present Result	1:0:2 :27	2.5	2000	68	56	74
Present Result	1:0:2 :27	2.2	1750	350	297	352
Present Result	0:2:1 :27	1.95	1100	200	160	170
Present Result	0:2:1 :27	2.0	1312	48	50	44
Present Result	0:1:1 :18	2.0	1070	160	156	155
Present Result	0:1:1 :18	1.7	1200	80	73	80
Present Result	1:3:2 :54	2.0	1408	125	161	240

Note: τ_1 Induction time deducted from Eq.5

τ_2 Induction time evaluated on the sort of chemical kinetic data.

Table 1. Mixture Parameters

NO.	$CH_4:H_2:O_2:A$	ζ	ϕ	ε
1	1:0:2:27	0.	1.0	0.
2	1:0:4:45	0.	0.5	0.
3	2:1:4:63	0.33	1.125	0.312
4	2:1:8:99	0.33	0.562	0.326
5	1:1:2:36	0.5	1.25	0.453
6	1:1:4:54	0.5	0.625	0.514
7	1:2:2:45	0.67	1.5	0.689
8	1:2:3:54	0.67	1.1	0.712
9	1:2:4:63	0.67	0.75	0.718
10	0:2:1:27	1.0	1.0	1.0
11	0:1:1:18	1.0	0.5	1.0

Table 2. Induction Time Correlation Formulae for CH_4-O_2 & H_2-O_2

$$\tau_{CH_4} = A_1 [CH_4]^{x_1} [O_2]^{y_1} \exp(E_1/RT)$$

Source	x_1	y_1	A_1 (cc/mole)$^{x_1+y_1}$ μsec	E_1 kcal/mole
Serry & Bowman[4]	0.4	-1.6	7.65×10^{-18}	51.5
Lifshitz et al.[5]	0.33	-1.03	3.62×10^{-14}	46.5
Tsuboi & Wagner[6]	0.32	-1.03	2.5×10^{-18}	53.0
Present Result	0.48	-1.94	1.19×10^{-12}	46.4

$$\tau_{H_2} = A_2 [H_2]^{x_2} [O_2]^{y_2} \exp(E_2/RT)$$

Source	x_2	y_2	A_2 (cc/mole)$^{x_2+y_2}$ μsec	E_2 kcal/mole
Asaba et al.[7]	0.4→0.8	-0.5→-0.8	constant	0.
White & Moore[8]	-0.33	-0.66	1.58×10^{-11}	17.19
Present Result	0.145	-0.56	1.54×10^{-4}	17.20

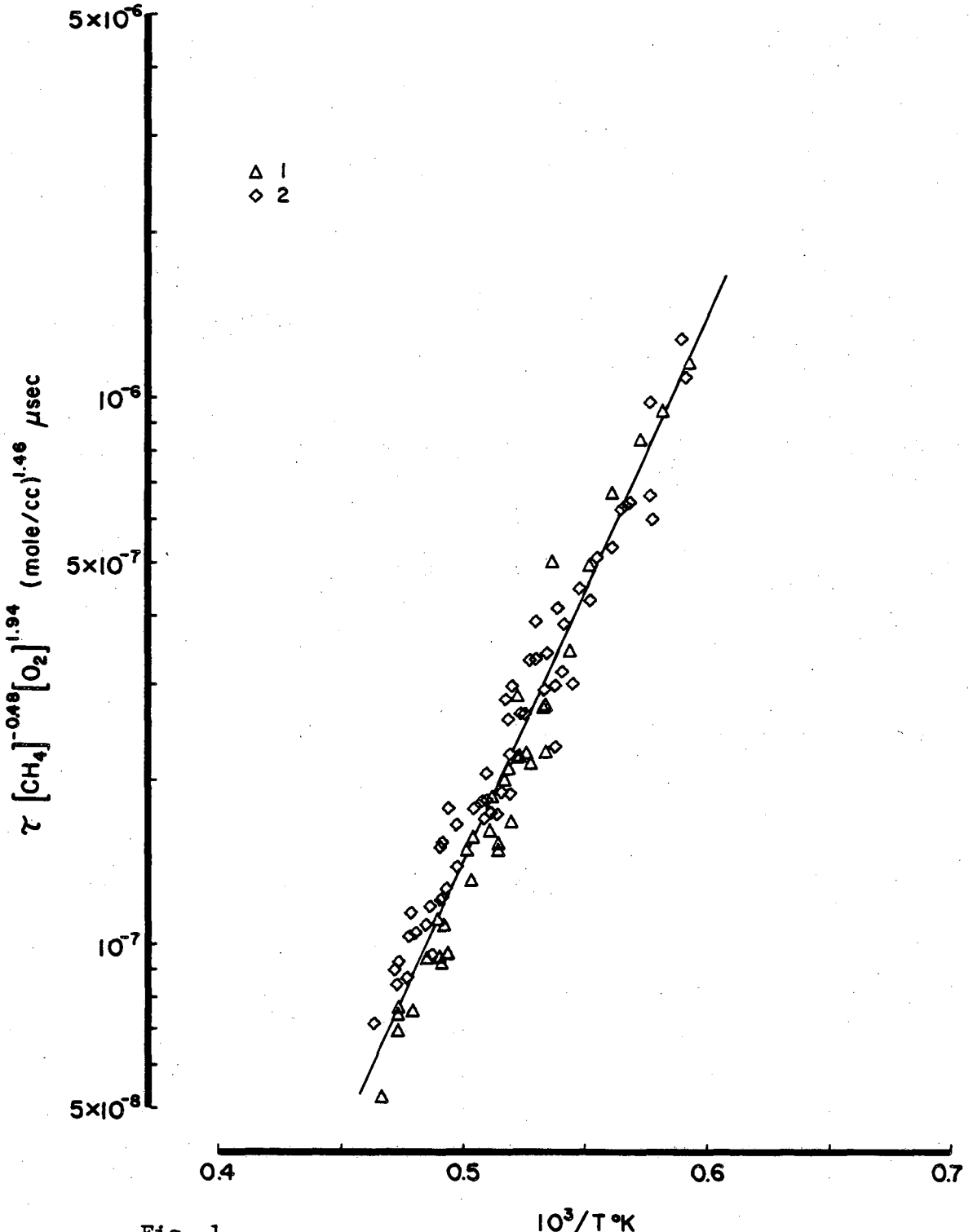

Fig. 1

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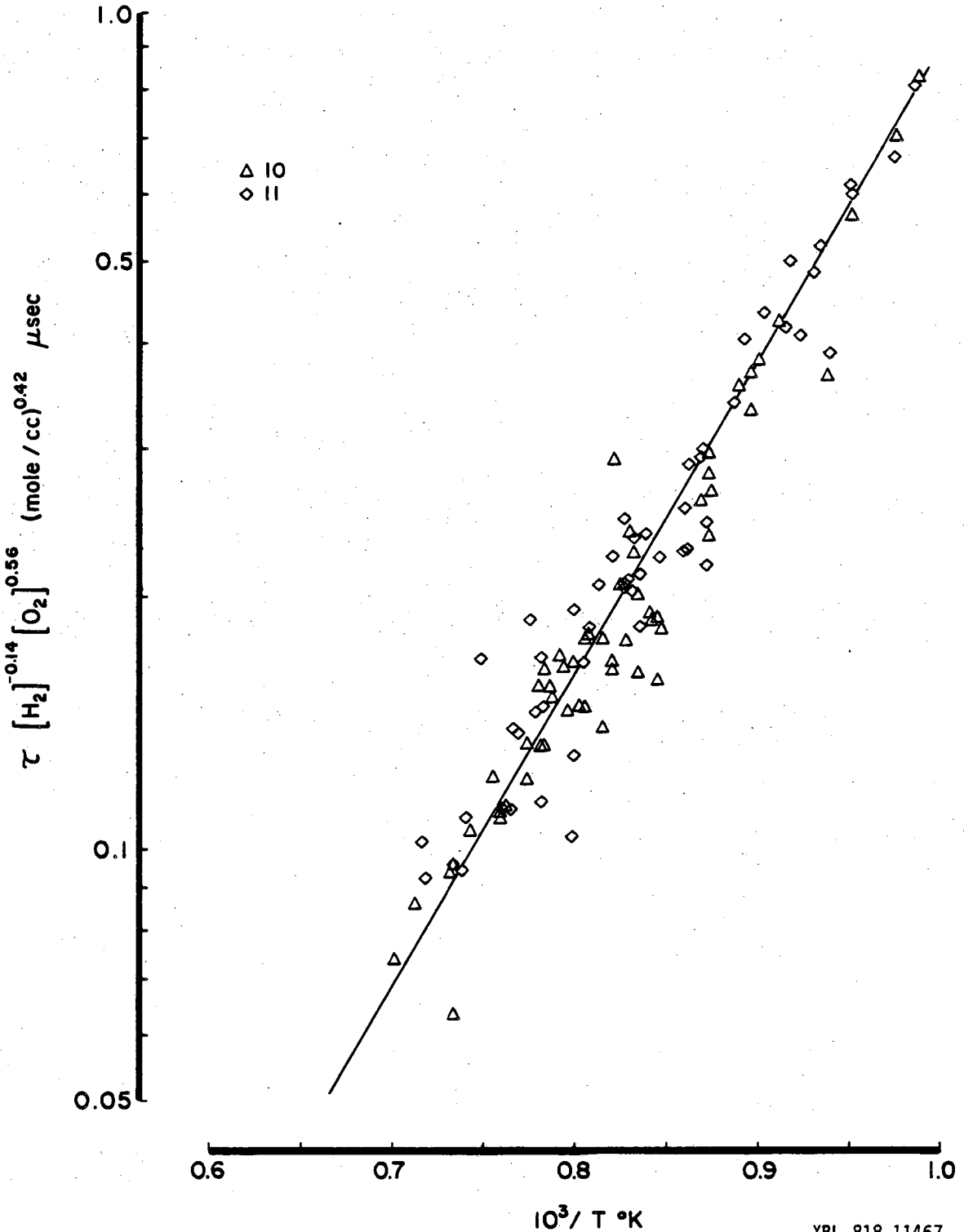

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Fig. 2

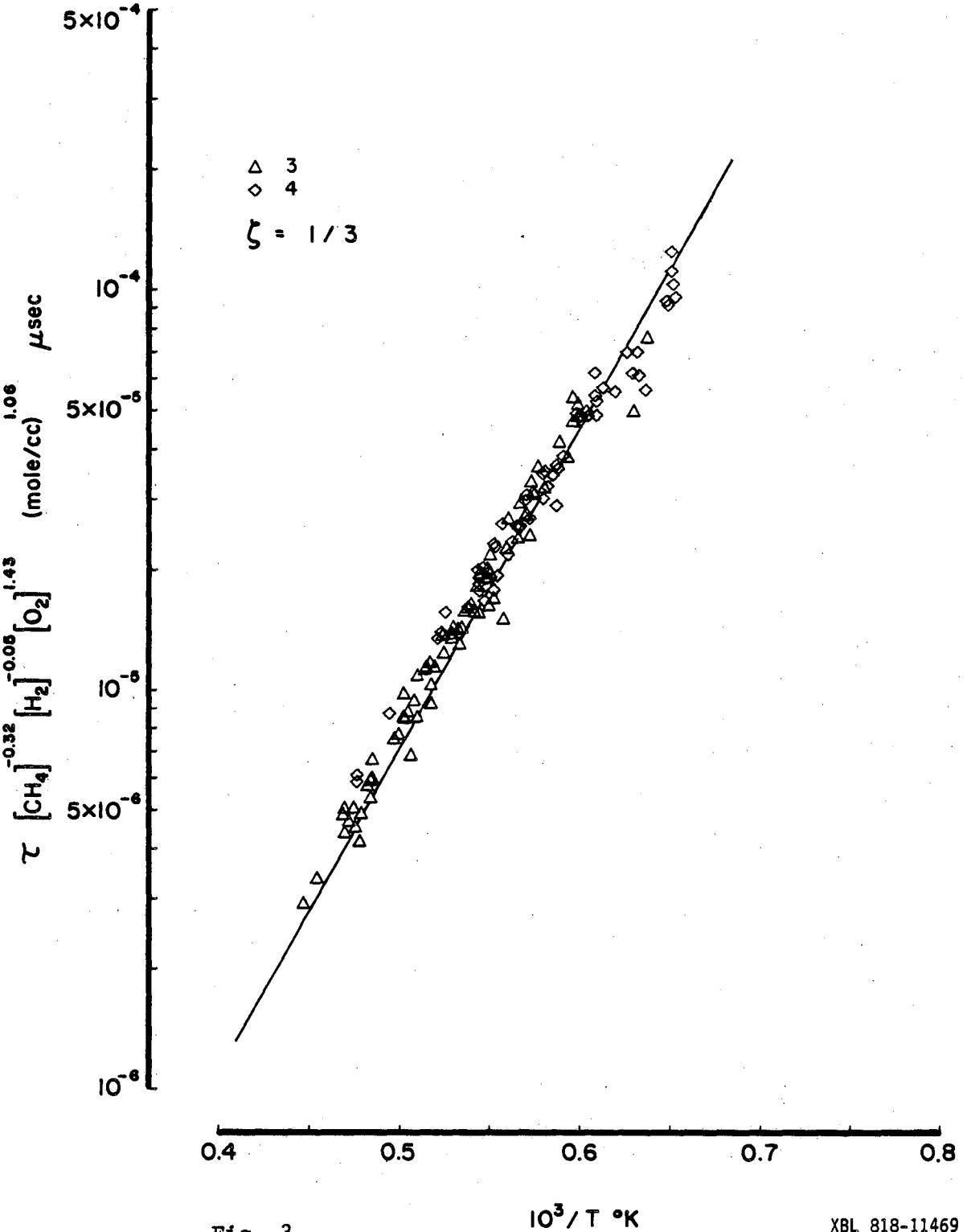

Fig. 3

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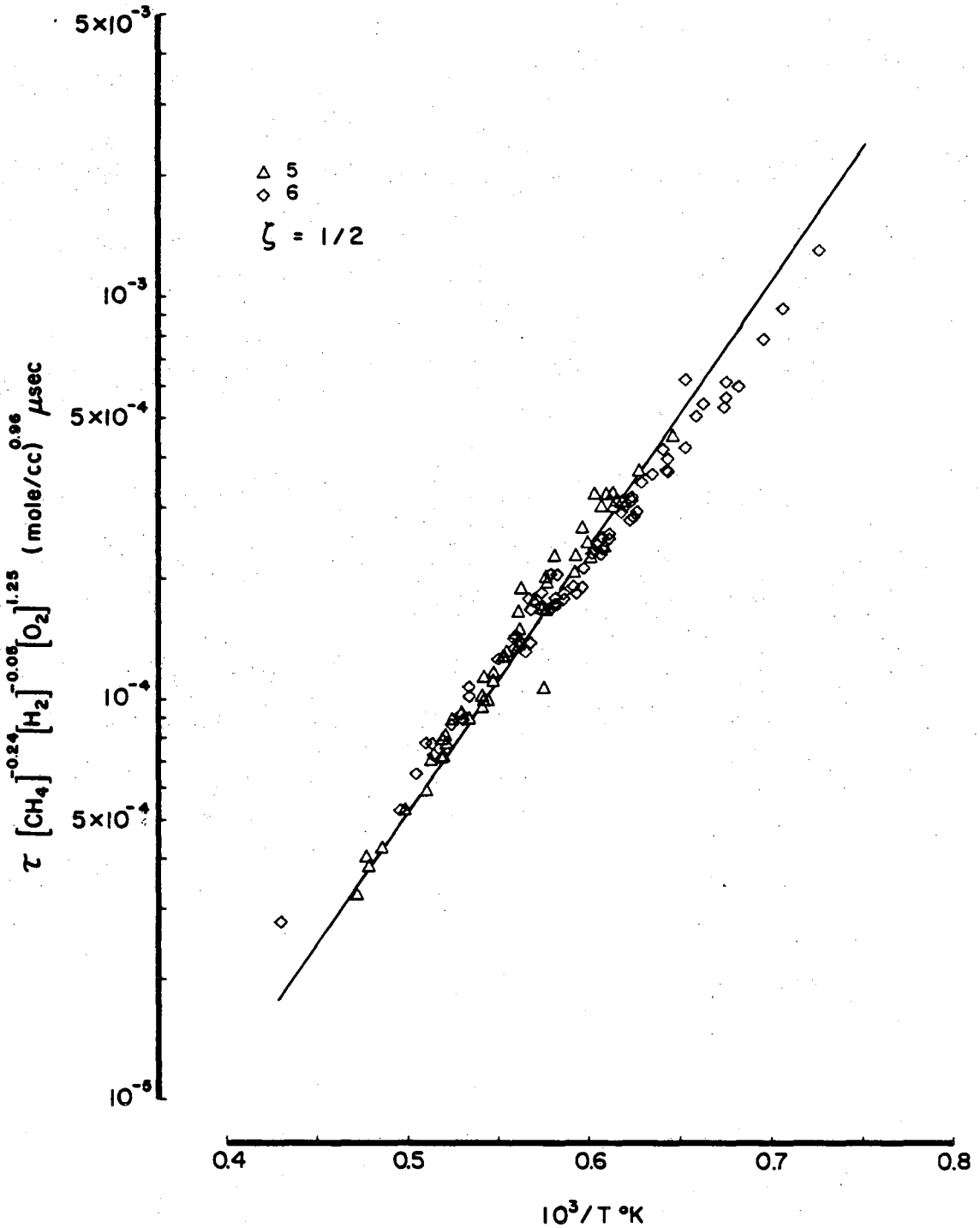

Fig. 4

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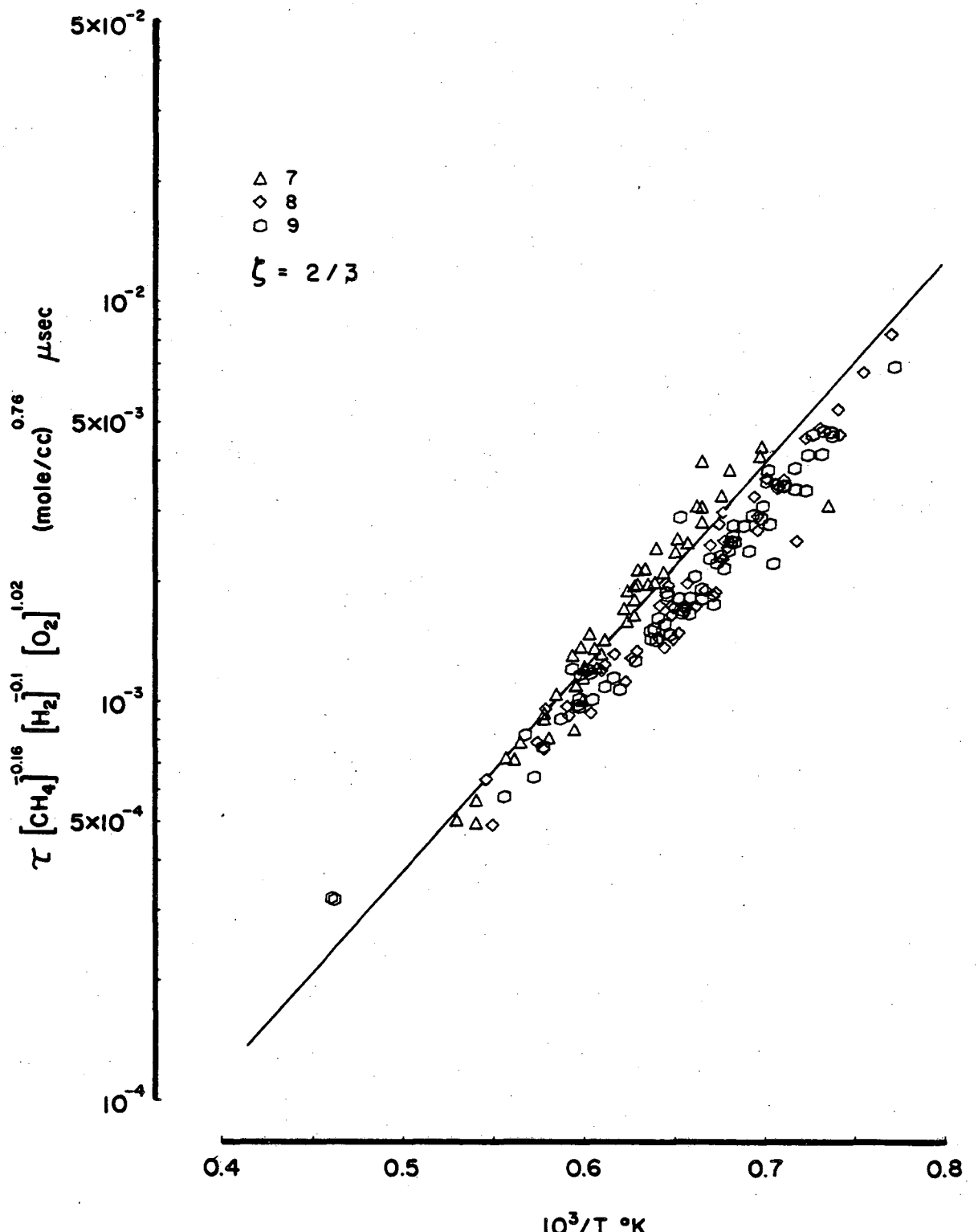

Fig. 5

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