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METAL OXIDE STUDIES
IRON OXIDATION

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13. ABSTRACT

Iron pentacarbonly seeded CO-H_2/Air flames and $H_2/O_2/N_2$ flames were used to study the oxidation of iron. Iron and OH profiles were measured and the data interpreted on the basis of both kinetics and equilibration. A lower limit of 1×10^{-14} cm^3 molec.$^{-1}$ sec^{-1} was placed on the forward rate constant for:

$$Fe + O_2 \rightleftarrows FeO + O$$

The equilibrium constant for this reaction at 1600 °K was found to be $2 \pm 1 \times 10^{-2}$ in good agreement with existing results. In addition the equilibrium constant for:

$$Fe + H_2O \rightleftarrows FeOH + H$$

at 1600 °K was determined to be $3 \pm 1 \times 10^{-3}$. Evidence for particle formulation of both FeO and FeOH was also found and interpreted on the basis of a simplified bimolecular combination process. The forward rate appeared to be gas kinetic for both species. An initial concentration of FeO and FeOH of approximately 10^{12} molec. /cc appears to be necessary to initiate condensation from the super-saturated vapor.

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METAL OXIDE STUDIES
IRON OXIDATION

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FOREWORD

This study was performed at General Electric Company, Space Sciences Laboratory, King of Prussia, Pa., 19406, for the Advanced Research Projects Agency, Washington, D. C. Rome Air Development Center, Griffiss Air Force Base, New York, is monitoring the study for ARPA, under Contract F30602-69-C-0380, Project 1649. Mr. Vincent J. Coyne (OCSE) is the RADC Project Engineer.

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SUMMARY

Iron pentacarbonyl seeded CO-H_2/Air flames and $H_2/O_2/N_2$ flames were used to study the oxidation of iron. Iron and OH profiles were measured and the data interpreted on the basis of both kinetics and equilibration. A lower limit of 1×10^{-14} cm^3 $molec.^{-1}$ sec^{-1} was placed on the forward rate constant for:

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I. INTRODUCTION

This report describes a continuation of an experimental study aimed at obtaining information relevant to several ARPA programs. Of particular concern is the evaluation of the importance of certain metal oxides to Project IVY OWL and Project SECEDE.

During the past year the oxidation chemistry of iron has been investigated. In a previous report (ref. 1), a seeded flame technique was described in which iron was introduced into a low pressure CO-H_2/air by means of iron pentacarbonyl. Iron profiles throughout the flame were measured using the atomic resonance absorption of the 3719.9 Å of iron. The interpretation of these profiles could not be made since it was not clear whether changes in the iron concentration throughout the flame were due to true kinetic behavior via reaction of iron with oxygen or reflected a change in the steady state concentration because of changes in other flame components such as O atoms and H atoms. In order to clarify this situation, O atom and H atom profiles were determined throughout these same flames from measurement of OH profiles (in absorption). In addition iron and OH profiles were also measured in several seeded $H_2/O_2/N_2$ flames so that a fairly diverse set of conditions were obtained.

The iron profiles in these flames appeared to reflect a change in the equilibration with the species O_2, H_2O, O, H, FeO and FeOH. In addition it was observed that under certain conditions particularization of both supersaturated FeO and FeOH occurred leading to changes in the iron profile. It was possible to obtain approximate values for the equilibrium constant for:

$$Fe + O_2 = FeO + O \tag{1}$$

$$Fe + H_2O = FeOH + H \tag{2}$$

from the measured concentration profiles. It should be mentioned that the interpretation of the measured concentration profiles was extremely difficult in view of the complexity of the systems being studied. Indeed it often appeared that the interpretation of the iron profiles best fit a kinetic model and that simple first order kinetics for the disappearance of iron yielded the most consistent results. In fact, this interpretation has not been entirely rejected and the results obtained on this basis will also be given.

This study demonstrates the complexity that can occur in complicated systems involving metal atoms and the results may indeed be quite relevant to the understanding of the chemistry of disturbed environments.

II. FLAME STUDIES

1. Introduction

In a previous report (ref. 1) iron profiles (iron concentration vs distance above burner) were determined in several H_2-CO/Air flames. The iron concentrations appeared to decay approximately with first order kinetics, i.e.

$$Fe + O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} FeO + O \qquad (1)$$

$$\ln Fe/Fe^o = k_f \left[O_2\right] t$$

However, it could not be determined whether this apparent decay was the result of the kinetic loss of iron by the forward of reaction (1) or whether equilibration of reaction (1) had taken place very rapidly and the loss of iron simply reflected the change in O-atom concentration. In order to gain further insight into this problem O atom profiles were determined in these same flames. The method used has been described in detail by Kaskan (ref. 2, 3) and is based on the determination of OH profiles, by resonance line absorption techniques. Assuming partial equilibrium to be valid for the overall reaction:

$$2\,OH = H_2O + O \qquad (3)$$

O atom concentrations can be obtained directly from the OH concentration, the known equilibrium constant for (3) and the H_2O concentration, i.e.

$$[O] = K(3)\,[OH]^2/[H_2O] \qquad (4)$$

since these flames contain a significant amount of water, the possible reaction of iron with water cannot be ignored. Indeed, the reaction:

$$Fe + H_2O \rightleftarrows FeO\,H + H \qquad (2)$$

is estimated to be approximately + 20 kcal/mole endothermic. Therefore, it is expected that reaction (2) could be comparable in importance to that of reaction (1). For this reason H atom profiles were also obtained. This was again accomplished through the measured OH profiles and the assumption of partial equilibrium, i.e.:

$$O + OH = H + O_2 \qquad (5)$$

and

$$3OH = H + H_2O + O_2 \qquad (6)$$

so that

$$[H] = K(6)\,[OH]^3/[H_2O]\,[O_2] \qquad (7)$$

In addition several iron pentacarbonyl seeded $H_2/O_2/N_2$ flames were also burned in which iron and OH profiles were determined. As a result a fairly diverse set of conditions were obtained over which measurements were made.

2. Experimental

The low pressure burner facility has been described in detail in a previous report (ref. 1). In the case of the $H_2/O_2/N_2$ flames, an inner 3.0 inch diameter porous-metal type burner surrounded by a 1 1/4 inch annular part was substituted for the larger burner used in the CO-H_2/Air flames. This enabled an approximate increase by a factor of two in the flow velocities and therefore, a doubling of the time resolution which could be attained. Iron was added to the inner burner, by premixing a mixture of nitrogen and gaseous iron pentacarbonyl with the bulk gases entering the burner base. Iron profiles were determined by measurement of the absorption of the Fe I 3719.94 A resonance line (ref. 4). Light from a liquid nitrogen cooled iron hollow cathode was passed through the flame and its intensity, as a function of distance above the burner surface (Z), was measured with a 1/2 meter JACO, using A. C. amplification. Similarly, OH concentrations were determined by measurement of the absorption of the P_1 (5) line of the OH $X^2\Pi$ - $A^2\Sigma$ system. As described in ref. 2 and 3, an OH line source was generated by passing a discharge through water vapor at several torr. The conditions of the discharge were approximately 3000 V at 12 ma. Light from the discharge was passed through the flame and monitored with the 1/2 meter JACO. In addition to the absorption measurements made on the P_1 (5) line, absorption measurements of the Q_2 (13), Q_1(13), Q_2 (12), Q_1 (9), Q_1 (8) R_2 (3), and R_2 (4) OH lines were also carried out at several fixed distances in the flames. This allowed the determination of OH rotational temperatures. Temperature profiles in all the flames were also measured by using a silica coated Pt - Pt 10% Rh thermocouple. Temperature corrections due to heat losses were made according to ref. (5).

Fe and OH concentrations were obtained from the measured line absorptions using the procedures given in references 1, 2, and 3. Corrections were made for changes in the Doppler width and partition functions of Fe and OH due to changes in temperature. O and H atom profiles were deduced from the measured OH concentrations by using the appropriate equilibrium constants [K (3) and K (6)] for reactions (3) and (6) as obtained from the JANAF Thermochemical Tables together with the known concentrations of H_2O and O_2 as deduced from the burned gas stoichiometry. These results for several CO-H_2/Air flames and several $H_2/O_2/N_2$ flames are given in Table I and Table II.

In order to check the method used above in obtaining O-atom concentrations, nitric oxide was added to the flames and the NO-O continuum intensity was monitored at 4300 A. Since the NO concentration throughout the flames was assumed to remain constant, the changes in the continuum intensity reflected changes in the O atom profiles. Comparison of the NO-O intensity against the O atom concentrations obtained from the OH measurements, on a relative basis, showed satisfactory agreement to approximately 20% except for flame #1 (P = 100 torr). In this case, deviations up to a factor of two were found. This is not surprising since both the pressure and temperature of flame #1 were low enough so that the assumption of partial equilibrium involving OH and O may indeed be invalid.

TABLE I.

CO-H_2 AND $H_2/O_2/N_2$ FLAME CHARACTERISTICS

Flame No.	ϕ[a]	P Torr	$\overline{T}$ °K	$\overline{V}$ mm/sec.	$O_2 \times 10^{-17}$ Part/cm^3	$H_2O \times 10^{-17}$ Part/cm^3	$CO_2 \times 10^{-17}$ Part/cm^3	$N_2 \times 10^{-17}$ Part/cm^3
1	.55	100	1420	669	.55	.29	1.2	5.1
2	.55	200	1550	661	.97	.52	2.3	8.9
3	.68	249	1625	1610	1.1	4.4	---	9.8
4	.75	258	1625	1575	.77	4.6	---	10.0
5	.89	254	1640	1525	.30	4.7	---	10.0

[a] ϕ = Equivalence Ratio = (Fuel/Oxident) Actual / (Fuel/Oxident) Stoichiometric

TABLE II.

CONCENTRATION PROFILES IN

CO-H_2/Air AND $H_2/O_2/N_2$ FLAMES

Flame No.	Height Z mm	Temp. ^oK	Fe x 10^{-11} Part/cc	OH x 10^{-15} Part/cc	O x 10^{-15} Part/cc	H x 10^{-15} Part/cc
1	10	1446	10.2	2.3	6.5	5.8
	15	1449	9.4	2.1	4.4	3.2
	20	1438	8.5	1.8	3.0	1.8
	25	1422	7.1	1.6	2.2	1.2
	30	1410	5.9	1.4	1.8	.88
	40	1375	3.4	1.1	1.2	.54
	50	1339	2.4	.80	.61	.20
	60	1303	2.1	.63	.087	.011
		T_{ROT} At Z = 25 mm = 1470 ± 25 ^oK				
2	5	1577	5.6	3.1	3.9	1.7
	10	1590	3.8	2.4	2.2	.72
	15	1584	2.7	1.8	1.3	.35
	20	1564	1.7	1.5	.89	.19
	25	1554	1.2	1.1	.52	.088
	30	1540	.88	.91	.37	.053
	40	1526	.57	.62	.18	.019
	50	1483	.48	.49	.13	.012
	60	1458	.40	.36	.077	.0057
		T_{ROT} At Z = 25 mm = 1560 ± 25 ^oK				

(Continued)

TABLE II. - Concentration Profiles in CO-H_2/Air and $H_2/O_2/N_2$ Flames (Continued)

Flame No.	Height Z mm	Temp. °K	Fe x 10^{-11} Part/cc	OH x 10^{-15} Part/cc	O x 10^{-15} Part/cc	H x 10^{-15} Part/cc
3	2	1573	13.6	7.8	2.9	2.6
	3	1609	9.0	7.1	2.1	1.6
	4	1625	4.9	5.9	1.4	.83
	5	1636	2.7	4.9	.96	.46
	6	1642	1.5	4.1	.66	.26
	7	1646	.82	3.6	.49	.17
	8	1647	.60	3.0	.35	.098
	9	1650		2.7		
		T_{ROT} At Z = 25 mm = 1650 ± 50°K				
4	2	1570	14.9	7.5	2.5	3.0
	3	1605	10.6	7.2	2.1	2.2
	4	1624	6.4	5.9	1.3	1.1
	5	1633	3.5	5.1	.97	.65
	6	1641	2.0	3.9	.58	.30
	7	1644	1.0	3.5	.44	.20
	8	1646	.60	3.1	.35	.41
	9	1647	.41	2.7	.26	.091
		T_{ROT} At Z = 10 mm = 1650 ± 50°K				
5	2	1536	15.2	6.5	2.0	5.8
	3	1586	13.5	6.3	1.7	4.0
	4	1613	10.8	5.9	1.3	2.9
	5	1628	8.7	5.1	.99	1.8
	6	1632	6.6	4.7	.80	1.3
	7	1646	4.9	4.0	.58	.77
	8	1648	3.4	3.6	.47	.56
	9	1652	2.4	3.2	.37	.38
	10	1657	1.6	2.9	.30	.28
	11	1658	1.1	2.7	.25	.22
	12	1660	.77	2.4	.21	.16
	13	1660	.51	2.2	.16	.11
		T_{ROT} At Z = 10 mm = 1670 ± 50°K				

3. Results and Discussion

As has been mentioned previously, the interpretation of the changes in the iron profiles throughout the flames has proven to be quite difficult. Other studies reported by Wray (ref. 6) and Fontijn (ref. 7) indicate that the forward bimolecular rate constant for reaction (1), i.e.

$$Fe + O_2 \rightleftarrows FeO + O \qquad (1)$$

at a temperature of approximately 1600 °K is expected to be approximately equal to 10^{-13} cc/molecule/sec. This would imply an activation energy for reaction (1) approximately equal to the endothermicity of the reaction and that the reverse rate constant would be approximately equal to 10^{-11} cc/molecule/sec. If this is indeed the case, under the conditions in the flames reported here it would be expected that equilibration of reaction (1) would take place very rapidly since the back reaction, at the O-atom concentrations observed, would not be negligible. It is estimated that equilibration would take place in less than a milisecond and therefore, the changes in the iron profiles would merely reflect changes in the equilibration due to changes in O-atom concentrations. A similar argument can be presented for the reaction of iron with water, i.e.

$$Fe + H_2O \rightleftarrows FeOH + H \qquad (2)$$

However, in this case no reported rate constants are available. If, however, the forward rates are smaller than that reported, kinetic behavior in the flames may have indeed been observed. For these reasons the flame data were treated both kinetically and on the basis of equilibrium.

If the changes in the iron concentration as a function of distance above the burner (Z) and therefore time, are assumed to be due to a simple first order kinetic process, then an exponential decay of the profiles is expected. The resulting psuedo-first order rate constant obtained should reflect contributions by both reactions (1) and (2) depending on their relative importance. Plots of log Fe vs Z are given in Figures 1 and 2. It is seen that rather good straight lines are obtained especially for the $H_2/O_2/N_2$ flames. The results for the CO-H_2/Air flames in fact may indicate a significant effect due to the back reactions since it appears that the iron concentrations are approaching a steady state value. Furthermore, the presence of CO_2 and CO in these flames may have an effect on the overall chemistry. If it is assumed that reaction (1) dominates the kinetics, rate constants of the order of 5 x 10^{-16} 5 x 10^{-16} cc/molecule/sec are obtained from the CO-H_2/N_2 flames and rate constants of the order of 1 x 10^{-14} cc/molecule/sec are obtained from the $H_2/O_2/N_2$ flames. On the other hand, if reaction (2) dominates these values become 10^{-15} for the CO-H_2/N_2 flames and vary between 2.5 x 10^{-15} and 6.4 x 10^{-16} cc/molecule/sec for the $H_2/O_2/N_2$ flames. Much better consistency is obtained in the $H_2/O_2/N_2$ flames where reaction (1) was assumed to dominate. It is felt that the results obtained on these latter flames may indeed reflect true kinetics and that the forward second order rate constant for reaction (1) is approximately 10^{-14} cc/molecule/sec at around 1625 °C.

The flame data were also analysed on the basis of equilibration of both reaction (1) and (2). The equilibrium concentrations of FeO and FeOH are related through the equilibrium constants and species concentrations by:

$$[FeO] = K(1)\,[Fe]\,[O_2]/[O] \tag{8}$$

and

$$[FeOH] = K(2)\,[Fe]\,[H_2O]/[H] \tag{9}$$

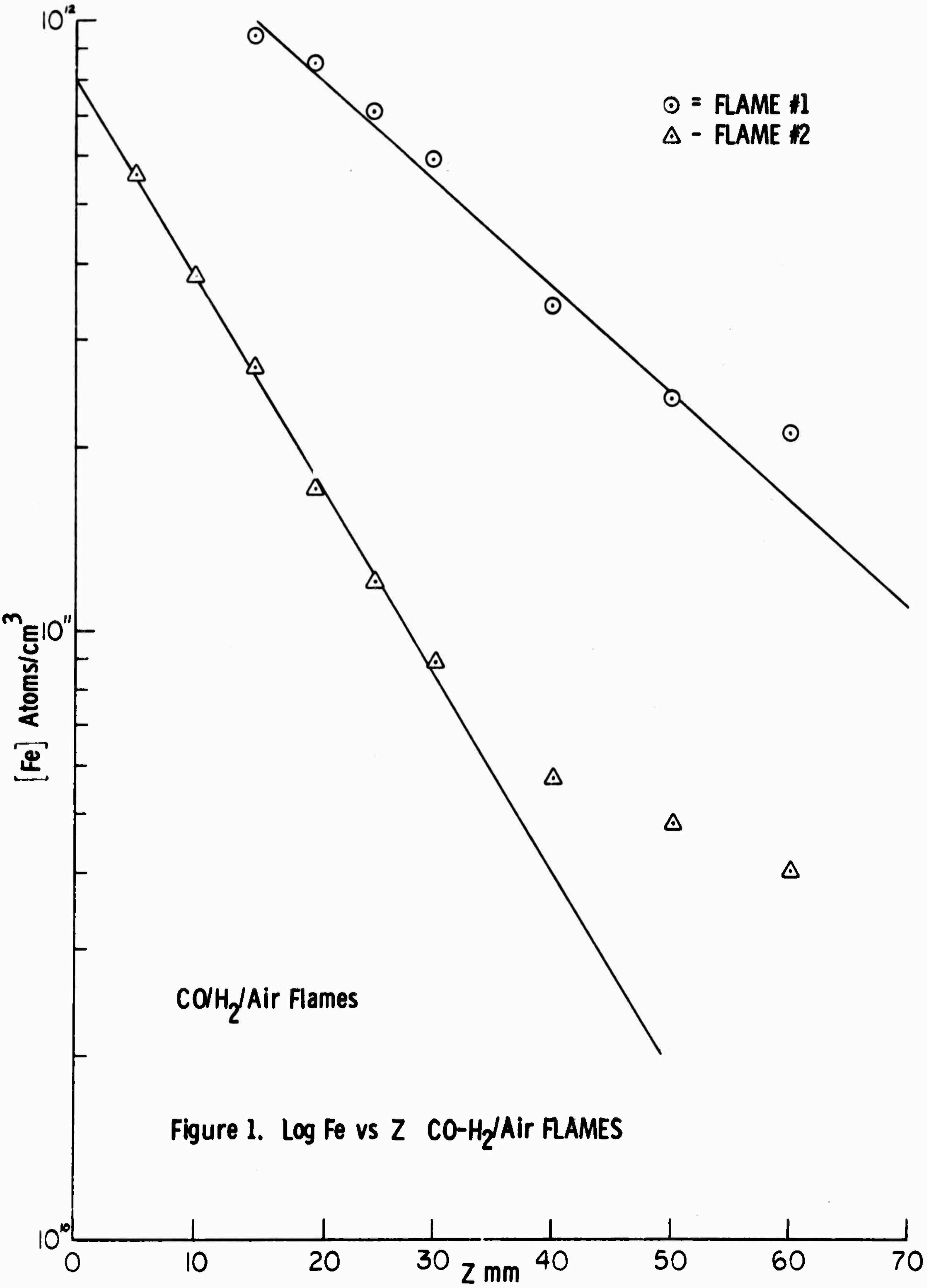

Figure 1. Log Fe vs Z CO-H$_2$/Air FLAMES

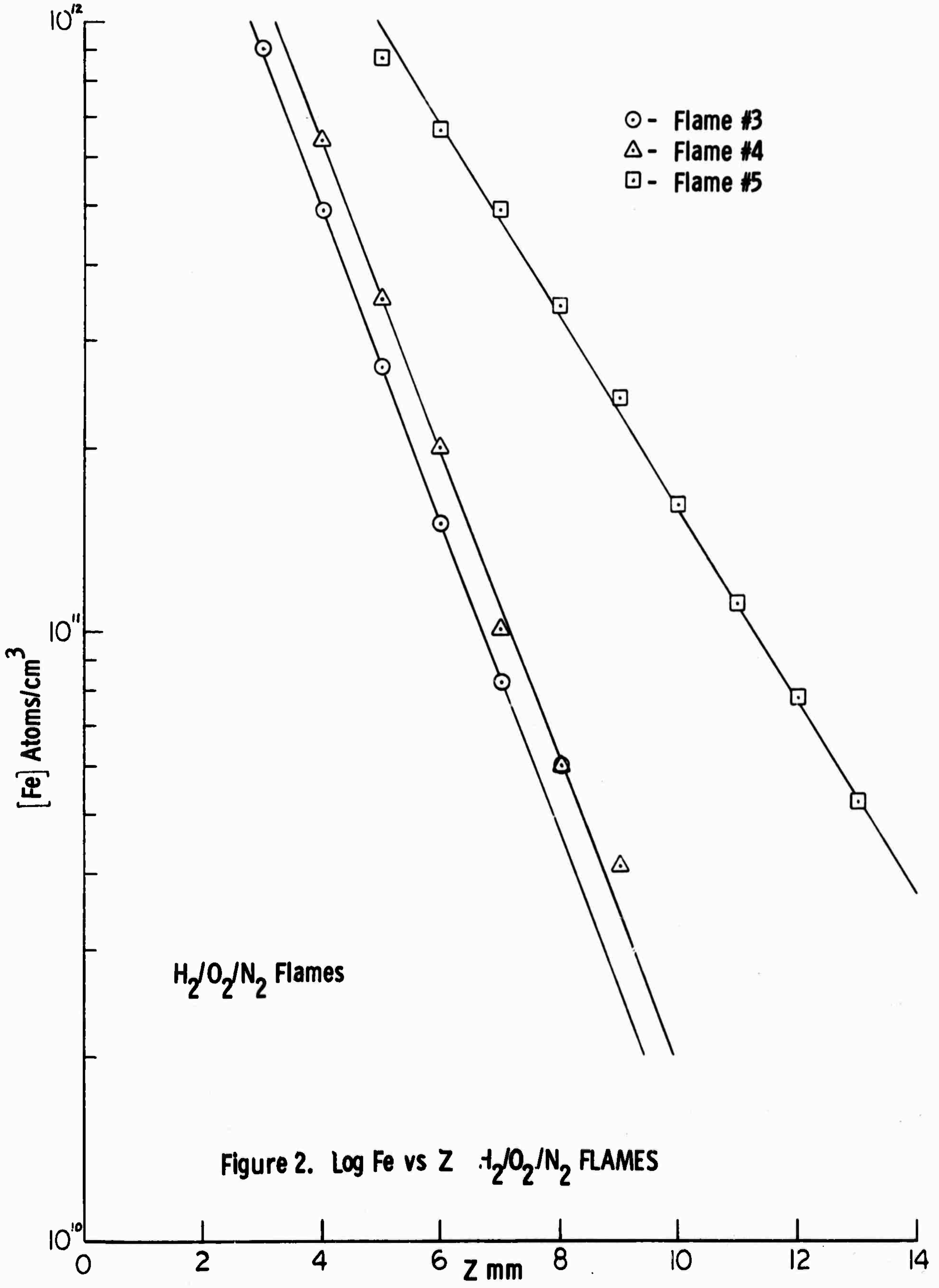

Figure 2. Log Fe vs Z $H_2/O_2/N_2$ FLAMES

Initially it was assumed that there were no condensed phase species present (no particle formation). Therefore, the total iron concentration at any point in the flame can be given by:

$$\left[Fe_T\right] = \left[Fe\right] + \left[FeO\right] + \left[FeOH\right] \qquad (10)$$

and

$$\left[Fe\right] = \left[Fe_T\right] - K(1)\left[Fe\right]\left[O_2\right]/\left[O\right] - K(2)\left[Fe\right]\left[H_2O\right]/\left[H\right] \qquad (11)$$

In principle it is possible to solve equation (11) for K(1), K(2) and Fe_T for each flame by a least square analysis using the concentration profiles obtained in the various flames. In order to correct for the change in equilibrium constant due to the change in temperature over a given flame profile, use was made of the vant Hoff relationship in such a way as to refer the equilibrium constants to a specific reference temperature, i.e.

$$K/K_{ref} = \exp\left(\frac{\Delta H\,\Delta T}{T\,T_{ref} \times 1.987}\right) = C(T) \qquad (12)$$

where T_{ref} was taken to be 1600 °K and ΔH = 20 Kcal/mole for both reaction (1) and (2). Equation (11) therefore becomes:

$$\left[Fe\right] = \left[Fe_T\right] - K(1)_{ref}\,C(T)\left[Fe\right]\left[O_2\right]/\left[O\right] - K(2)_{ref}\,C(T)\left[Fe\right]\left[H_2O\right]/\left[H\right] \qquad (13)$$

Attempts to obtain the equilibrium constants K(1) and K(2) by the above procedure using the concentration profiles for flames 2, 3, 4, and 5, were generally unsuccessful. Invariably, one of the constants obtained would be negative. In the case of flame #1, it was felt that the O-atom and H-atom profiles were unreliable because of the breakdown of the partial equilibrium assumption used in obtaining these concentrations.

If the initial assumption of no particles was incorrect, the above treatment would be invalid since the total iron concentration would not be given by (11). In order to check this assumption, the relative equilibrium gaseous concentrations of FeO and FeOH, i.e. $C(T)\left[Fe\right]\left[O_2\right]/\left[O\right]$ and $C(T)\left[Fe\right]\left[H_2O\right]/\left[H\right]$, respectively, were calculated as a function of distance above the burner for the various flames. If no particles of FeO or FeOH were formed, these species in general should be monotonically increasing with distance above the burner since the iron concentration monotonically decreases. However, it was found that in most cases either or both species appear to decrease after a certain point is reached in the flame. Typical results are given in Figures 3, 4, and 5. It is believed that the decreases in concentration represent particularization of either FeO or FeOH from the super-saturated vapor. For example, in Figure 3 for flame #5, it is apparent that both FeO and FeOH at first increase and at different positions in the flame suddenly begin to particularize. Similarly in Figure 4 for flame #4, it is evident that FeO is always particularizing whereas FeOH begins to nucleate at approximately 7 mm above the burner base. In the case represented in Figure 5, flame #2, it appears that no particles are formed over the entire profile. Since it is impossible to inventory the total iron content, if particles are being formed, the simple equilibrium treatment used above can not hold in regions of the flame when particularization is taking place. Therefore, the least squares analysis was used over regions of those flames in which it was apparent that only gaseous species were present. This was done in the case of flame #2 and over the first 6 mm of flame #5. The resulting equilibrium constants are given in Table III.

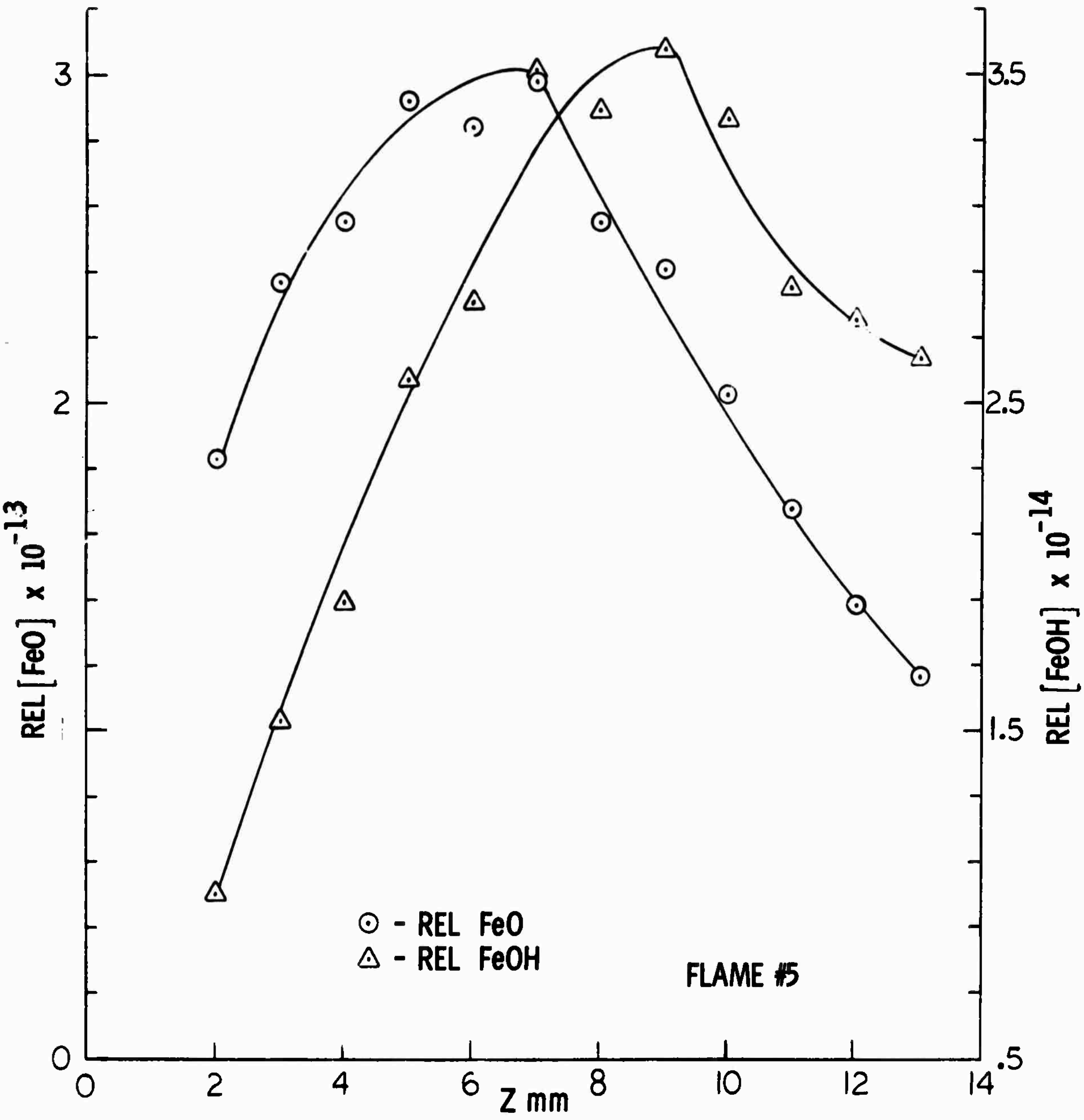

Figure 3. RELATIVE [FeO] & [FeOH] vs Z FLAME #5

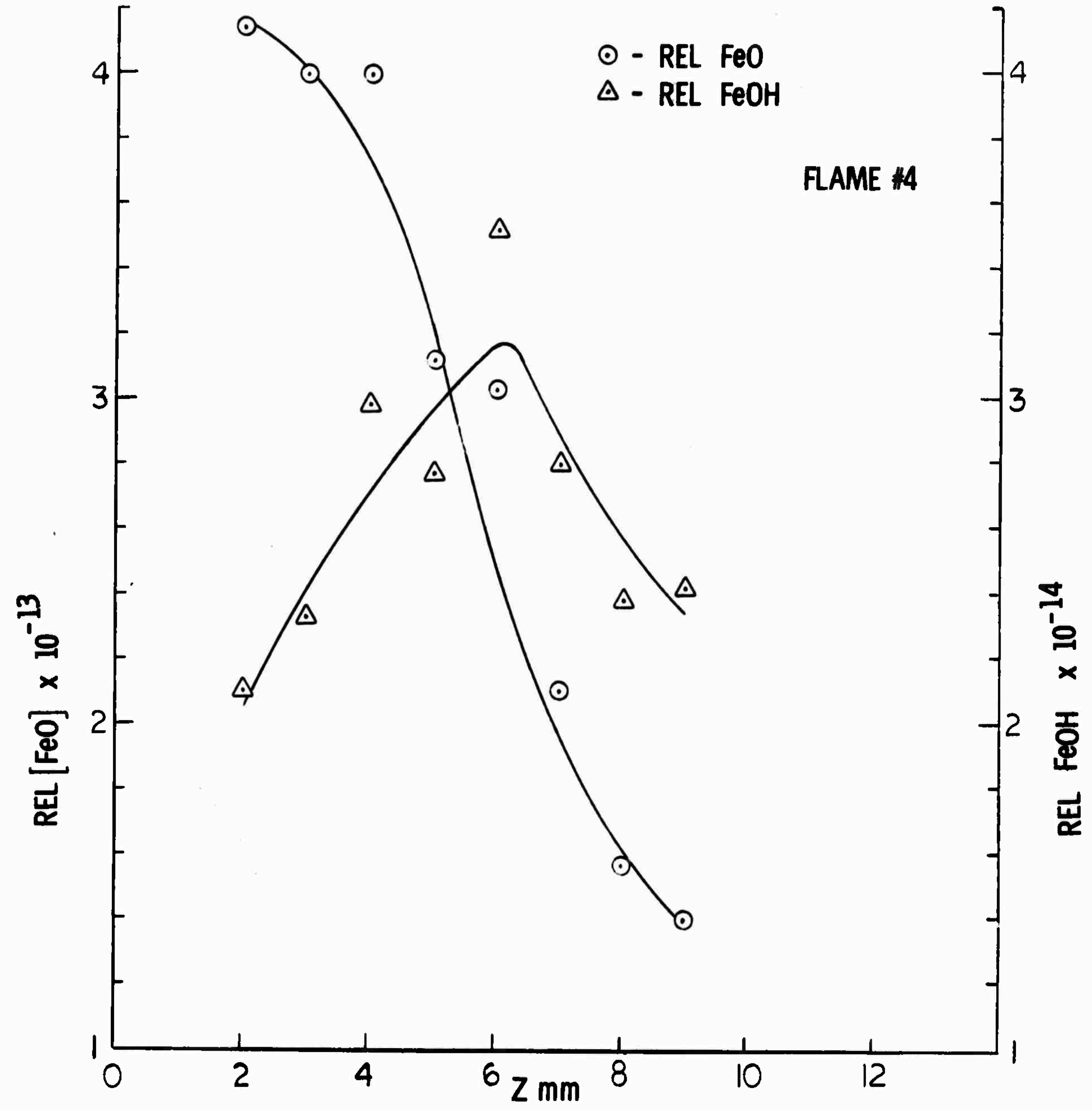

Figure 4. RELATIVE [FeO] & [FeOH] vs Z FLAME # 4.

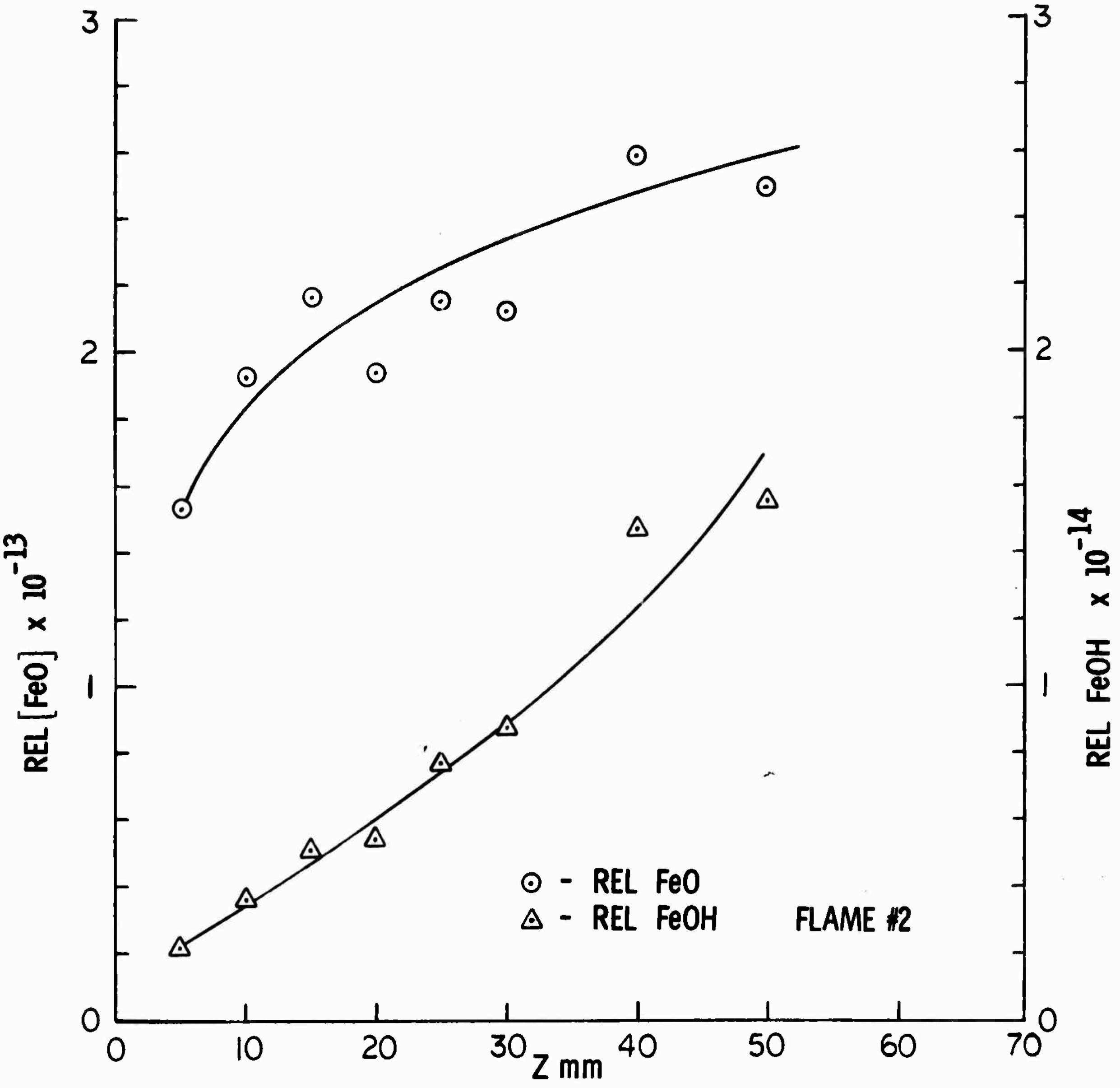

Figure 5. RELATIVE [FeO] & [FeOH]vs Z FLAME #2

TABLE III.

DERIVED EQUILIBRIUM CONSTANTS FROM FLAME DATA

FLAME	$K(1)^a$ $T = 1600\ ^\circ K$	$K(2)^b$
2	3×10^{-2}	2×10^{-3}
3	1×10^{-2}	4×10^{-3}
Ave.	$2 \pm 1 \times 10^{-2}$	$3 \pm 1 \times 10^{-3}$

[a]
$$K(1) = \frac{[FeO][O]}{[Fe][O_2]}$$

[b]
$$K(2) = \frac{[FeOH][H]}{[Fe][H_2O]}$$

For reaction (1), the equilibrium constant obtained from JANAF at 1600 °K was found to be:

$$K(1) = 1.4 \times 10^{-2}$$

This value is in excellent agreement with the flame results. Indeed this may imply that equilibration is in fact the situation existing in the flames. Furthermore, it also implies that the heat of reaction (1), viz., 20 Kcal/mole, given by JANAF, is substantiated. No information appears to be available on the thermodynamic properties of FeOH. The free energy function for this molecule can be estimated very approximately by use of the third law and by guessing a structure and vibrational frequencies. By comparison with similar molecules, the structure and vibrational assignment, assuming a linear model, was taken as: r(OH) ~ .96 A, r(FeO) ~ 1.8 A, ν_1 = 3500 cm^{-1}, ν_2 = 1000 cm^{-1}, and ν_3 = 900 cm^{-1}. The statistical weight was taken as 10. This leads to a free energy function, $-(G^o - H_o^o)/T$ at 1600 °K of approximately 66.0 gibbs/mole. Using this value and the deduced equilibrium constant of 3×10^{-3} for reaction (2), the heat of reaction (2), ΔH_{298}^o is found to be approximately 16.0 Kcal/mole. This implies that the heat of formation of FeOH, ΔH_f^{298}, is approximately 5.6 Kcal/mole. Perhaps the largest error in the above treatment is the assumption regarding ν_2. The value selected assumes that FeOH has a high degree of covalent bonding similar to BeOH. However, if the molecule is more like the alkali metal hydroxides, the bending frequency, ν_2, would be lower, i.e. approximately 350 cm^{-1}. If this is the case, the resulting heat of reaction (2) becomes approximately 21 Kcal/mole. Until more reliable free energy functions become available, these results must be taken as very approximate.

It is possible in a very approximate fashion to gain further insight into the nucleation kinetics of both FeO and FeOH. As is apparent from Figures 3 - 5, particle formation appears to be important in the $H_2/O_2/N_2$. Using the derived equilibrium constants for reactions (1) and (2) as obtained above, it is possible to deduce FeO and FeOH concentrations, on an absolute basis, from the relative quantities given in Figures 3 - 5. If it is assumed that the initial step of nucleation is a two body combination process such as:

$$2\,FeO \xrightarrow{k_n} (FeO)_2 \qquad (14)$$

and

$$2\ \mathrm{FeOH} \xrightarrow{k'_n} (\mathrm{FeOH})_2 \qquad (15)$$

The disappearance of FeO or FeOH can be described in terms of a simple bimolecular kinetic equation. Therefore, a plot of 1/FeO or 1/FeOH vs t should yield a straight line whose slope is equal to k_n. Smoothed values for FeO and FeOH were obtained from Figures 3 - 5 and the appropriate equilibrium constants. Zero time was measured from the point at which nucleation appeared to start. Plots of 1/FeO and 1/FeOH vs Z (~ t) are given in Figure 6. The resulting rate constants are given in Table IV.

TABLE IV.

NUCLEATION RATE CONSTANTS FOR FeO AND FeOH

FLAME	k_n (FeO) $\mathrm{cm^3\ molec^{-1}\ sec^{-1}}$	k'_n (FeOH) $\mathrm{cm^3\ molec^{-1}\ sec^{-1}}$
3	5×10^{-10}	---
4	8×10^{-10}	3×10^{-10}
5	8×10^{-10}	2×10^{-10}
Ave.	$7 \pm 1 \times 10^{-10}$	$2.5 \pm 1 \times 10^{-10}$

It is seen that the above over-simplified model leads to a reasonable second order kinetic fit of the data, as evidenced from Figure 6. The magnitude of the resulting rate constants indicate that the initial step of condensation

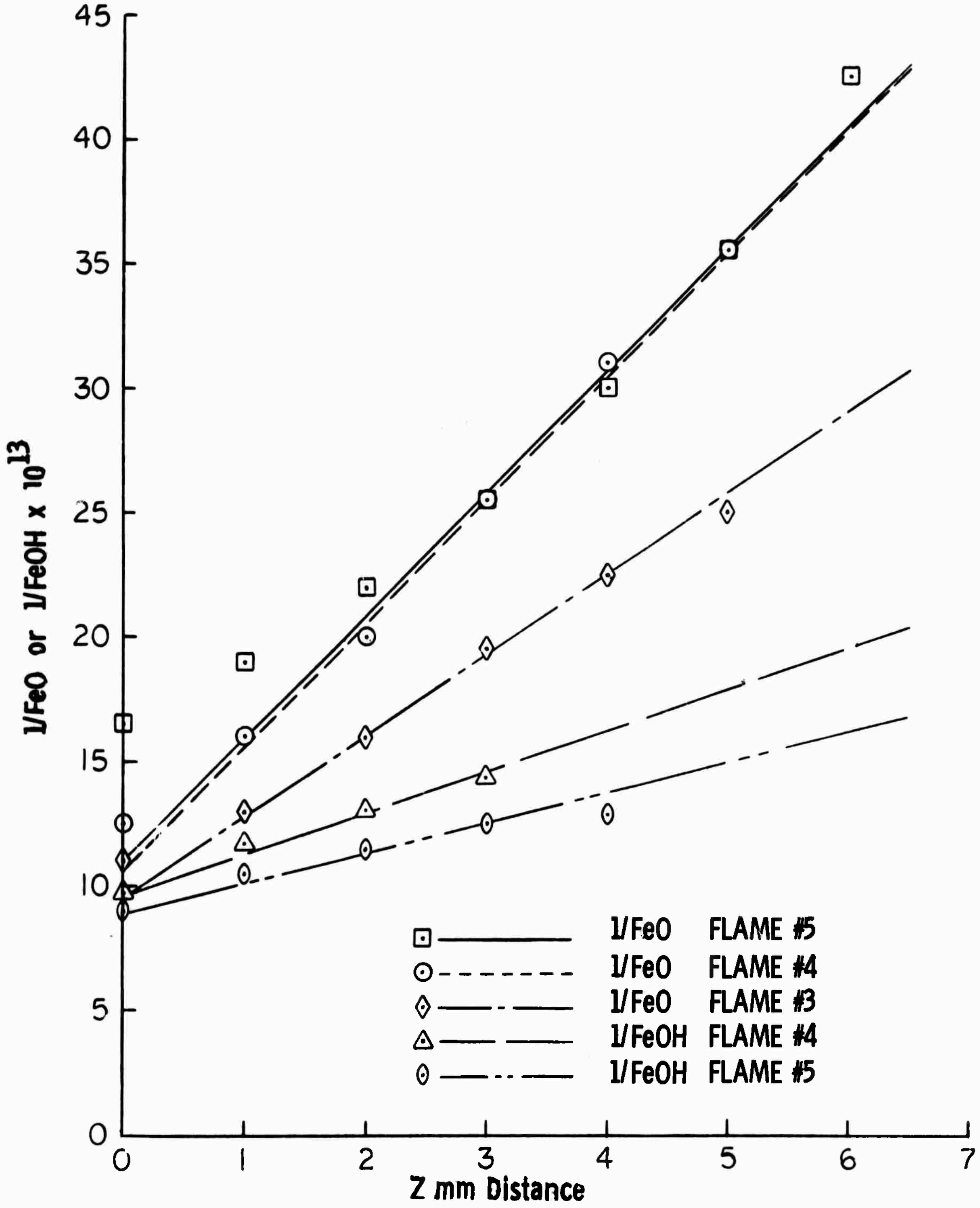

Figure 6. 1/FeO & 1/FeOH vs Z $H_2/O_2/N_2$ FLAMES

appears to proceed at a gas kinetic rate if not faster. In reality the condensation processes probably takes place heterogenously on nucleating sights. Such processes most likely involve strong electrostatic effects and can lead to rate constants seemingly greater than gas kinetic. It is interesting to note that the initial concentration at which particle formation begins, appears to be approximately the same (i.e. $\sim 10^{12}$ part/cc) for both FeO and FeOH.

III. CONCLUSIONS

Although the disappearance of iron in several different flame environments appears to proceed kinetically, it is felt that the reactions, under the experimental conditions in the flames, are in fact in partial equilibrium throughout the flame profiles. The apparent derived rate constant for the reaction of iron with O_2, viz around 10^{-14} cm^3 $molec.^{-1}$ sec^{-1} as obtained from the $H_2/O_2/N_2$ flame studies, most likely represents a lower limit. Indeed, it appears that the forward rate of reaction (1) is gas kinetic with an activation energy given by the endothermicity.

Treatment of the flame data on the basis of partial equilibrium involving reactions (1) and (2), although complicated by what appears to be particle formulation, yields equilibrium constants which are quite reasonable. The third law heat of reaction (1), (i.e. ΔH^{o}_{298} = 19 ± 2 Kcal/mole), derived from the resulting equilibrium constant at 1600 °K of $2 \pm 1 \times 10^{-2}$, when combined with the known heat of dissociation of oxygen, yields a heat of dissociation for FeO equal to 100 ± 2 Kcal/mole at 298 °K. This value is in excellent agreement with that selected by JANAF, viz 99 ± 5 Kcal/mole and in good agreement with a recent measurement by DeMaria, et al, (ref. 8) of 98 ± 2 Kcal/mole. In the case of reaction (2), the measured equilibrium constant at 1600 °K of $3 \pm 1 \times 10^{-3}$ again appears to be quite reasonable. However, since no free energy functions are available for FeOH, it was necessary to calculate this quantity from an estimate of the structure and vibrational frequencies based on analogous molecules. This leads to a derived heat of dissociation of FeOH to Fe and OH of approximately 98 - 103 Kcal/mole depending on the vibrational frequencies used. It is apparent that this agrees well with the FeO bond dissociation energy.

Perhaps the most interesting aspect of the flame studies is the observation of particle formation of both FeO and FeOH in certain of the flames.

Based on an oversimplified two body combination model, it was found that the rate of particle formulation for both FeO and FeOH appeared to be gas kinetic (if, indeed, not somewhat faster) and that a minimum concentration of gaseous FeO and FeOH of approximately 10^{12} molecules/cc was necessary to initiate particle formulation under the conditions in the flames. Estimates of the vapor pressures of FeO and FeOH reveal, that at this concentration, both species are supersaturated by at least an order of magnitude over the saturated vapor. Why a critical concentration of 10^{12} is necessary to initiate condensation, is not presently understood.

The present study clearly indicates the complexities that can arise in complicated systems represented by flames and may indeed be quite relevent to the understanding of even more complicated systems encountered in disturbed environments.

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