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EQUILIBRIUM RETENTION IN THE NOZZLE OF OXYGEN HYDROGEN PROPULSION SYSTEMS

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Abstract

Arguments are presented for the retention of vibrational equilibrium of species in the nozzle of the space shuttle main engine which are especially applicable to water and the hydroxyl radical. It is shown that the reaction OH + HH -> HOH + H maintains equilibrium as well. This is used to relate OH to H, the temperature, and the oxidizer-to-fuel ratio.

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INTRODUCTION

Spectroscopic examination of the exhaust gases of liquid oxygen-hydrogen propulsion systems is currently being considered as a non-intrusive method to perform engine diagnostics. (1) Emission or absorption methods yield number densities for specific states and in some instances, rotational vibrational and electronic "temperatures." Knowing which processes are at equilibrium greatly facilitates the use of such data to calculate overall species concentrations by use of the Boltzmann distribution for internal states and equilibrium constants for the chemical reactions.

The most promising species for spectroscopic measurements is the hydroxyl radical, OH. If complete equilibrium were maintained at the exit plane, then the OH number density and rotational "temperature" which can be deduced from its band structure could be used to calculate all other species concentrations and the oxidizer-to-fuel mass ratio, (O/F). It is well known, however, that complete chemical equilibrium is not maintained. It is the purpose of this report to identify those processes which are expected to be at or near equilibrium.

Chemical Model

Typical combustion chamber and exit plane conditions are displayed in Fig. 1 for the Space Shuttle Main Engine (SSME). It is generally assumed that combustion is complete and total equilibrium is achieved in the combustion chamber before the combustion products begin their expansion through the throat and nozzle. Justification of such an assumption is based on the high collision frequencies of the various species under the chamber conditions of high temperature and pressure, along with a relatively long resident time in contrast to the opposite conditions in the nozzle. Computer codes for engine performance calculations use this initial equilibrium assumption and perhaps spectroscopic studies can shed some light as the the extent to which it is valid.

For fuelrich engines, the chemistry is described as follows: an initial equilibrium mixture of high enthalpy water vapor and molecular hydrogen (with about 4-7 percent of the dissociation products OH and H) is rapidly expanded through the nozzle. The temperature and pressure dropping rapidly, new conditions for equilibrium are established and the internal and chemical states change to accommodate the new Boltzmann distributions and equilibrium constants. These changes are rate processes and are governed by the collision frequencies between the various species and the probabilities for the individual collisions to produce a change.

Table 1 gives the typical number of collisions required for readjustment to take place for the various types of energy modes at 300K. (2) As a "rule of thumb" then, it is expected that equilibrium is achieved very fast for rotation, more slowly for vibration and ever slower yet for chemical reaction. However, it must be cautioned that these collision numbers have a strong temperature dependence and may overlap depending on the specific systems under consideration. In the following, each kinetic process will be examined separately as it applies toward the hydrogen-oxygen reaction.

Translational - Rotational Relaxation

Translational and rotational equilibrium is generally thought to be extremely rapid even in strong shock fronts. It is therefore safe to assume that the rotational "temperature" of the OH bands will be the same as the translational temperature at the exit plane. This temperature can be determined by comparing various rotational transitions which occur simultaneously with the electronic transition in the region of 280 to 340 nm for the OH radical.

Vibrational Relaxation

A significant amount of energy resides in the vibrational modes of the HH, and OH molecules in the high temperature environment of the combustion chamber. During expansion, the temperature drops and the vibrational energy begins to relax toward a new equilibrium state dictated by the local translational temperature. This again is a rate controlled process and occurs almost exclusively during molecular collisions. Present computer codes assume that this relaxation process is fast and that vibrational equilibrium is maintained throughout the nozzle. At high expansion rotations, it is known that for molecules with long relaxation times such as N_2, and CO_2, and CO, significant deviations from the Boltzmann distribution can occur. (3) One approach that has been used to account for the final rate of vibrational relaxation along with the chemical reactions is to consider each vibrational state as a separate species. (3,4) There are, however, several serious difficulties with this approach:

1. The number of states goes up drastically. Present codes can handle effectively the kinetics of 150 to 250 species, but when each vibrational state is considered separately, the number of species increases to thousands instead of hundreds. This can be partially overcome by the somewhat arbitrary grouping of states.
2. Rate constants of the various vibrational relaxation processes have, for the most part, not been determined experimentally and theoretical predictions are at best tentative.
3. The most serious difficulty is that no one has been able to model the strong coupling which exists between the chemical reaction and the vibrational relaxation. It is known, for example, that molecular hydrogen in its first vibrationally excited state reacts with oxygen atoms 2600 times faster than hydrogen in the ground state at 300K. (5) Such data as this is sparce and then it is only given for one temperature. Also, the distribution of vibrational states among the newly formed products is

unknown except in some rather isolated cases.

In absence of a quantitative approach, we offer the following qualitive arguments for retention of vibrational equilibrium during the expansion of the exhaust gases of the liquid oxygen-hydrogen engines.

1. The vibrational modes of water are known to relax very rapidly - comparable to its rotational relaxation. (6) This is generally true of molecules which have large dipole movements. In contrast N_2, CO_2, and CO have zero or small dipole movements and relax much slower than water. As a rule, any strong intermolecular force assists vibrational relaxation. (7) Water forms hydrogen bonds which are very strong intermolecular forces.

(2) Water couples well with the other molecules present, OH and HH by forming hydrogen bonds.

3. The three vibrational frequencies of HOH are 1600,3600 and 3760 1/cm. The vibrational frequency of hydroxyl, OH, is 3730 1/cm which differs from the last frequency given for HOH by only 30 1/cm. Frequencies within 50 1/cm are said to be "resonant" and equilibrate quickly. (8) In summary, the exhaust gases of liquid oxygen-hydrogen engines are much more likely to be at vibrational equilibrium than hydrocarbon engines because of the predominance of water in the former. This could be verified by the OH spectrum. If non-equilibrium is observed it could indicate:

1. The above vibrational relaxation mechanisms, though fast, are not fast enough.

2. Chamber equilibrium may not be established. For example, the liquid oxygen may not be fully dispresed before it makes it to the throat.

3. Secondary oxidation of the excess hydrogen with atmospheric oxygen in the vicinity of the exit plane may have to be excluded or allowed for in the data analysis.

Chemical Relaxation

Computer programs are available which compute the performance of rocket engines taken into account finite ratechemical reaction. (9) The results of such a calculation are shown in Fig. 2 where number density is plotted versus area ratio. Also shown are the number densities which would result if chemical equilibrium had been maintained during the expansion. It is seen that the concentrations of the minor components, OH, H, O and O_2 are orders of magnitude different when finite rate chemistry is used. The water and hydrogen gives essentially the same result whether or not chemical equilibrium is assumed. This is because only a small amount of each was dissociated in the combustion chamber. The major reactions taken plan during the expansion are the following:

i $H + OH + M \rightarrow HOH + M$
ii $H + H + M \rightarrow HH + M$
iii $OH + HH \rightarrow HOH + H$
iv $O + HH \rightarrow OH + H$

M is a third body required to dissipate the energy of the newly formed water or hydrogen molecule and is likely to be either a water or hydrogen molecule. It is known from the study of the chemistry of flames, that away from the flame front, the exchange reactions iii and iv maintain equilibrium while coupled to the recombination reactions, i and ii, which are not at equilibrium. (10) Since equilibrium relationships can relate species concentrations to one other, it is worthwhile to examine whether iii and iv are in equilibrium in the nozzle expansion process as well. The extent to which equilibrium is maintained is shown by comparing the equilibrium constant Ke to the quantity K. K has the same form as Ke but uses the prevailing partial pressures of the species of the reaction instead of those that occur at equilibrium. Ke is a function of temperature only and may be determined by the thermodynamic relation:

$$-\Delta G^{o} = RT \ln Ke$$

and standard thermodynamic tables. K is calculated from the mole fraction and pressures computed at various area ratios using the NASA ODK code (9). Calculations were done for two engines. The smaller RL-10 engine has a 5 inch diameter throat, a chamber pressure of about 400 psi and a chamber temperature of about 3400K. The SSME has a 10 inch diameter thoat, a chamber pressure of about 3000 psi and a chamber temperature of about 3400K.

Examination of Figs 3-8 shows that the exchange reactions iii and iv are essentially at equilibrium i.e. K/Ke is close to one. Reaction iii appears to be closer to equilibrium than iv. The exchange reactions i and ii quickly fall out of equilibrium as is evidence by the rapid decline of K/Ke to zero. Equilibrium is more persistent for the larger SSME engine than for the smaller engine, presumably as a result of higher operating pressures.

One should use the ODK number densities and corresponding K/Ke values with caution. They are based on rate constants which are in many cases uncertain by an order of magnitude. Also, it appears that the smaller number densities may suffer from "computational scatter" especially at the large expansion ratios. I would suggest that they be used in a "soft" fashion, that is, to demonstrate trends and qualitative behavior.

Relating OH to Other Quantities

Using reaction iii as being essentially at equilibrium and the known equilibrium constant Ke(T), [H] can be calculated from:

$$[H] = \frac{[OH] \times [HH]}{Ke(T) \times [HOH]} \quad \text{where}$$

UV absorption measurements can give [OH] and T. [HH] / [HOH] can be calculated using the relation:

$$(O/F) = 8.0 \times (1 + [HH]/[HOH])^{-1}$$

The last equation comes from conserving O and H atoms and recognizing that at the exit plane, essentially all of the exhaust gas is HH and HOH. Alternately, if [H] and [OH] are both known, then (O/F) could be calculated. However, accurate temperatures must be used as Ke(T) is a strong function of temperature. (See table 2 and Fig 10.) A similar analysis can be made to estimate [O] from [OH] using reaction iv.

Fig. 9 shows how [OH] at the exit plan varies with (O/F). When (O/F) changes from 5 to 7, (8 being stoichiometric) [OH] increases by a factor of 150. This suggests that the hydroxyl number density can be a sensitive measure of the oxidizer-to-fuel ratio. Note also in Fig. 10, that the temperature at the exit plan increases substantially as (O/F) increases.

Conclusion

Arguments are presented suggesting that equilibrium is substantially maintained in the nozzle of the SSME with the exception of certain chemical reactions, notably the recombination reactions. Reaction iii and iv will maintain equilibrium enough to be used to estimate [H] and [O] from the [OH] measurement. Accurate measurements of the absorption spectra of OH in the exit plane will yield valuable information for engine monitoring and verification of models employed in various computer codes in use to predict rocket engine performance. The measurement of OH in the test study environment is a challenging experimental and engineering problem with the potential for giving a wealth of information.

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TABLE 1 - Collisions required for energy transfers.

Z(1-0) ------- vibrational to translational

Z(R) ------- rotational to translational

		T = 300 K	T = 2000 K
CO	Z(1-0)	1,000,000,000	100,000
	Z(R)	2	_
OO	Z(1-0)	100,000,000	10,000
	Z(R)	4	_
HH	Z(1-0)	10,000,000	10,000
	Z(R)	200	_
HOH	Z(1-0)	50	_
	Z(R)	4	_

TABLE 2 Equilibrium constants for various reactions of hydrogen and oxygen. K(x) is the equilibrium constant and x is the temperature in degrees Kelvin.

Reaction 1 ; O + HH -> OH + H
Reaction 2 ; O + HOH -> OH + OH
Reaction 3 ; OH + HH -> HOH + H
Reaction 4 ; OO + H -> OH + O
Reaction 5 ; HH -> H + H
Reaction 6 ; HOH -> H + OH
Reaction 7 ; OO -> O + O

x	K1(x)	K2(x)	K3(x)	K4(x)	K5(x)	K6(x)	K7(x)
1000.0	.79289669	.0016801417	471.92250	.0038066521	5.0808670e-18	1.0766316e-20	2.4392955e-20
1050.0	.83259451	.0025534418	326.06755	.0056608269	6.4898589e-17	1.9903419e-19	4.4124681e-19
1100.0	.87049220	.0037348662	233.07186	.0081113996	6.5951001e-16	2.8296424e-18	6.1454305e-18
1150.0	.90668913	.0052838664	171.59577	.011254331	5.4925323e-15	3.2008552e-17	6.8176371e-17
1200.0	.94128253	.0072603382	129.64720	.015181793	3.8426057e-14	2.9638940e-16	6.1976762e-16
1250.0	.97436592	.0097230825	100.21163	.019979847	2.3057145e-13	2.3008453e-15	4.7279796e-15
1300.0	1.0060282	.012728442	79.037812	.025726622	1.2076820e-12	1.5279800e-14	3.0883406e-14
1350.0	1.0363533	.016329158	63.466427	.032491018	5.6050548e-12	8.8315272e-14	1.7572572e-13
1400.0	1.0654198	.020573456	51.786135	.040331866	2.3349268e-11	4.5087874e-13	8.8389528e-13
1450.0	1.0933012	.025504377	42.867198	.049297525	8.8277738e-11	2.0593307e-12	3.9804896e-12
1500.0	1.1200659	.031159311	35.946426	.059425817	3.0583853e-10	8.5081765e-12	1.6226461e-11
1550.0	1.1457774	.037569747	30.497342	.070744256	9.7912446e-10	3.2105240e-11	6.0454527e-11
1600.0	1.1704949	.044761182	26.149776	.083270487	2.9179422e-09	1.1158575e-10	2.0758611e-10
1650.0	1.1942730	.052753178	22.638882	.097012898	8.1472724e-09	3.5987962e-10	6.6181728e-10
1700.0	1.2171625	.061559537	19.772120	.11197133	2.1434823e-08	1.0840933e-09	1.9718694e-09
1750.0	1.2392107	.071188565	17.407440	.12813784	5.3406425e-08	3.0680230e-09	5.5223736e-09
1800.0	1.2604610	.081643401	15.438614	.14549757	1.2658561e-07	8.1992859e-09	1.4612034e-08
1850.0	1.2809541	.092922396	13.785203	.16402947	2.8657206e-07	2.0788381e-08	3.6696290e-08
1900.0	1.3007277	.10501952	12.385581	.18370719	6.2187214e-07	5.0209365e-08	8.7829592e-08
1950.0	1.3198167	.11792478	11.192022	.20449978	1.2977354e-06	1.1595183e-07	2.0107838e-07
2000.0	1.3382538	.13162464	10.167198	.22637243	2.6118599e-06	2.5689083e-07	4.4180939e-07
2050.0	1.3560691	.14610248	9.2816299	.24928718	5.0831250e-06	5.4765436e-07	9.3443460e-07
2100.0	1.3732911	.16133892	8.5118398	.27320348	9.5886989e-06	1.1265131e-06	1.9075824e-06
2150.0	1.3899460	.17731230	7.8389709	.29807878	.000017570010	2.2413669e-06	3.7679502e-06
2200.0	1.4060584	.19399897	7.2477625	.32386905	.000031334209	4.3232942e-06	7.2174670e-06
2250.0	1.4216515	.21137366	6.7257742	.35052920	.000054484839	8.1009023e-06	.000013434043
2300.0	1.4367467	.22940981	6.2627956	.37801351	.000092523406	.000014773499	.000024343259
2350.0	1.4513643	.24807982	5.8503925	.40627597	.00015367224	.000026266997	.000043017001
2400.0	1.4655232	.26735534	5.4815558	.43527059	.00024997830	.000045603531	.000074245295
2450.0	1.4792413	.28720749	5.1504271	.46495166	.00039876699	.000077424062	.00012533951
2500.0	1.4925352	.30760709	4.8520832	.49527398	.00062452464	.00012871268	.00020723854
2550.0	1.5054208	.32852480	4.5823657	.52619305	.00096129739	.00020978190	.00033600440
2600.0	1.5179129	.34993134	4.3377450	.55766523	.0014557024	.00033558967	.00053480975
2650.0	1.5300256	.37179759	4.1152113	.58964787	.0021706552	.00052747116	.00083653647
2700.0	1.5417722	.39409476	3.9121865	.62209944	.0031899220	.00081538086	.0012871219
2750.0	1.5531652	.41679443	3.7264537	.65497959	.0046236113	.0012407537	.0019498062
2800.0	1.5642164	.43986871	3.5560984	.68824921	.0066147205	.0018601062	.0029104516
2850.0	1.5749372	.46329028	3.3994609	.72187051	.0093468537	.0027495106	.0042841188
2900.0	1.5853382	.48703245	3.2550978	.75580706	.013053225	.0040100870	.0062231009
2950.0	1.5954297	.51106922	3.1217487	.79002375	.018027059	.0057746669	.0089266265
3000.0	1.6052212	.53537533	2.9983099	.82448689	.024633484	.0082157900	.012652453

FIG. 1 Representative conditions in the combustion chamber and exit plane of the SSME.

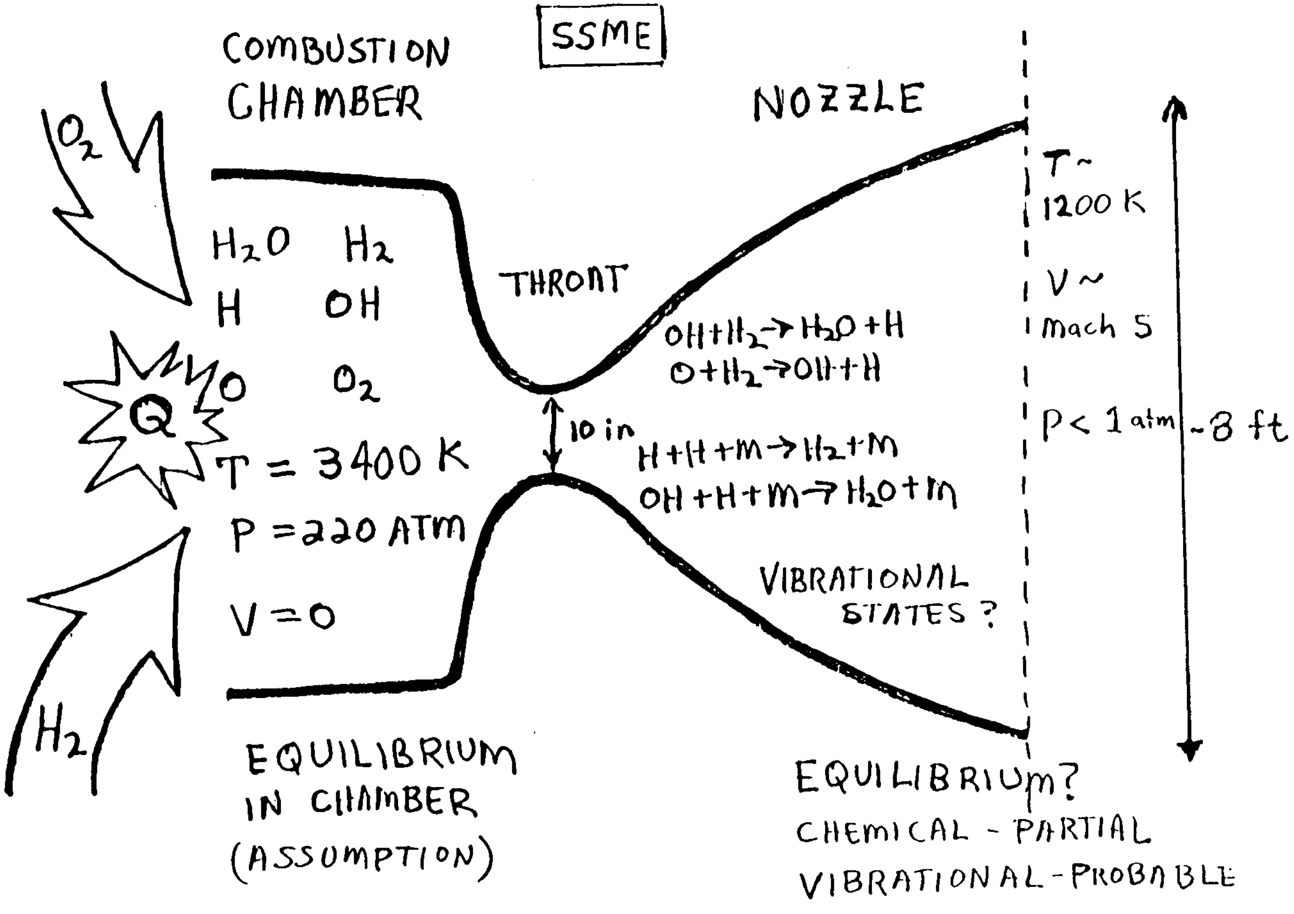


FIG. 2 Number density versus area ratio for RL-10 engine. Solid lines are for finite rate chemistry and dotted lines are for equilibrium.

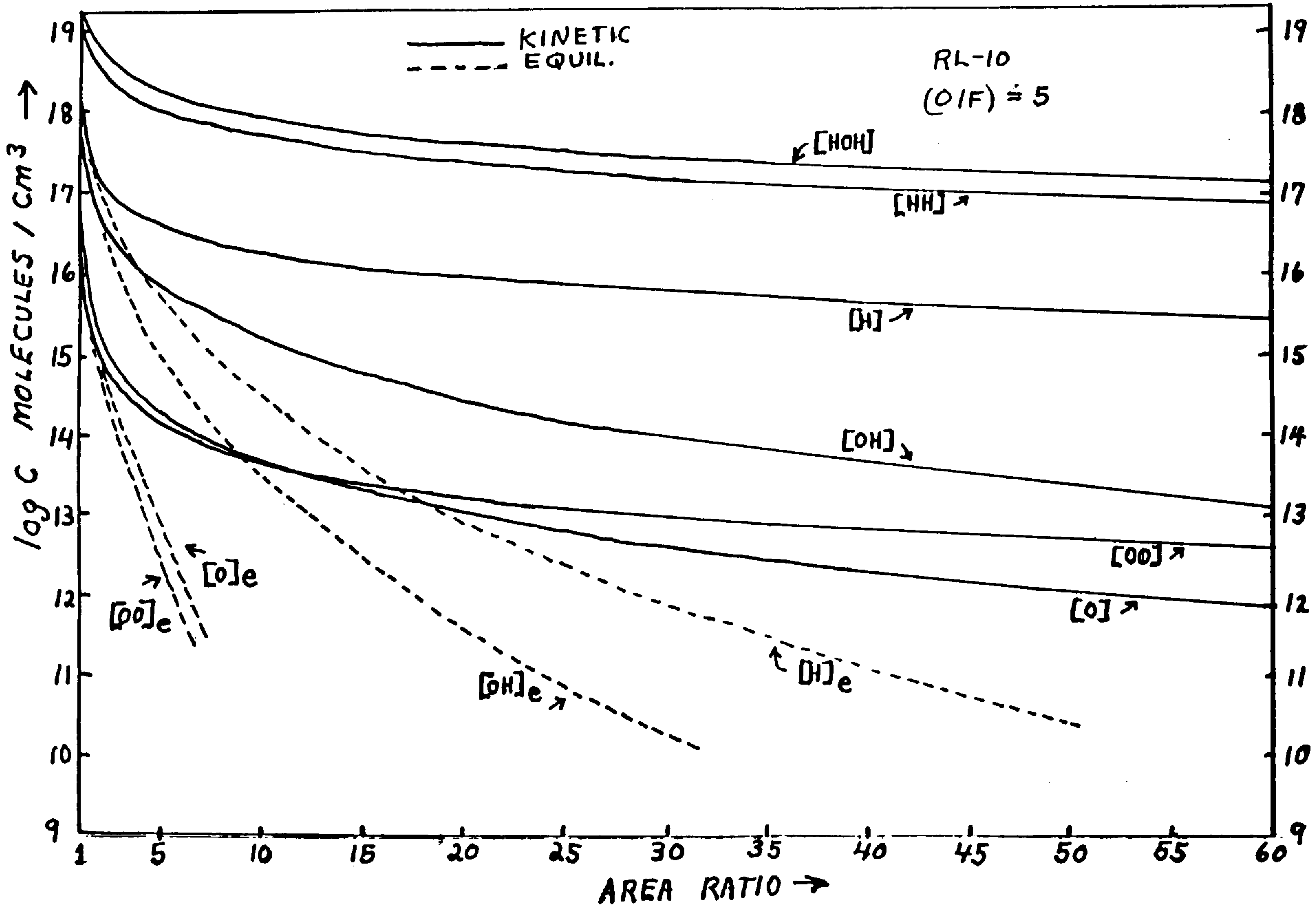


FIG. 3 K/Ke versus area ratio. Shows lack of equilibrium for

H + H -> HH

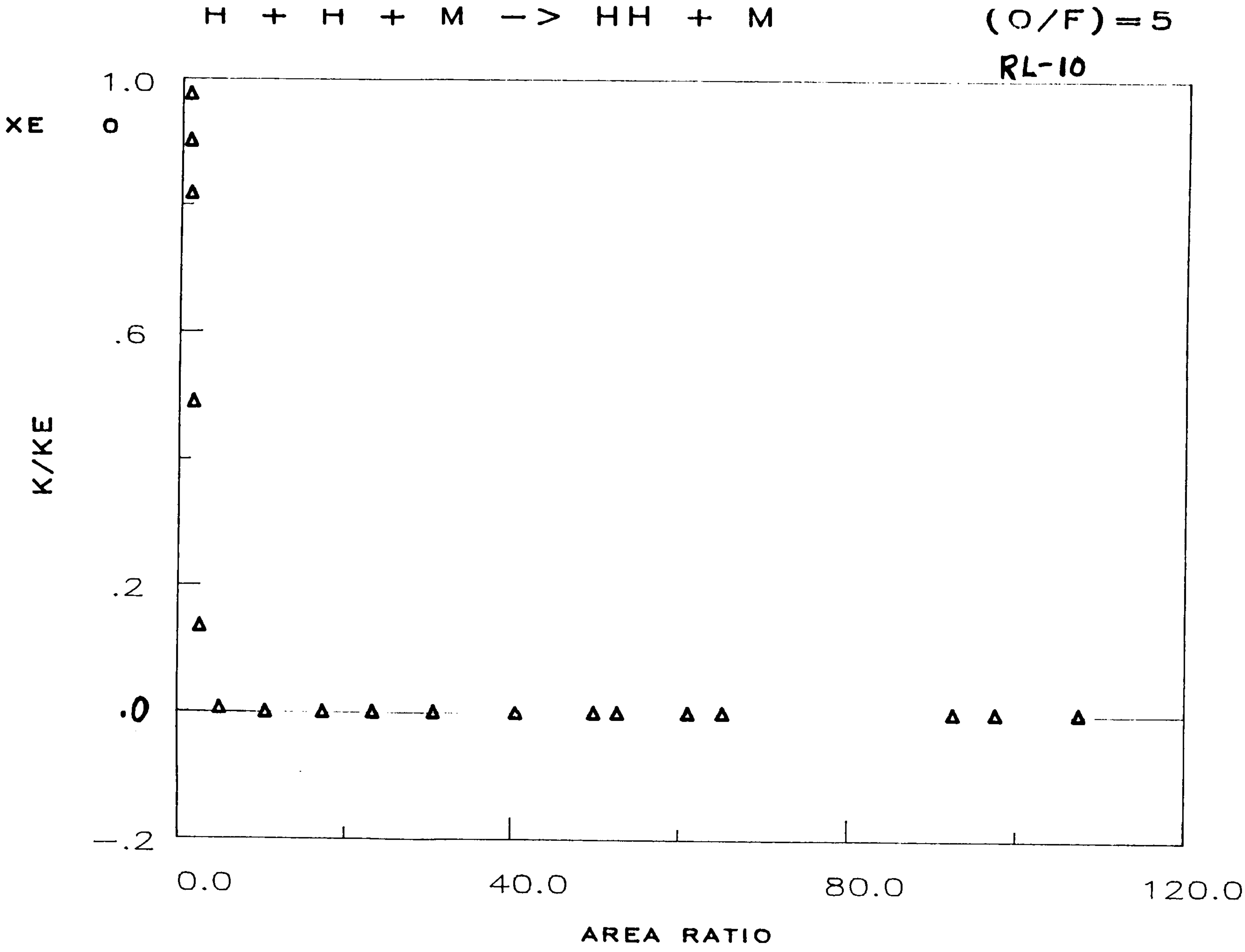


FIG. 4 K/Ke versus area ratio. Shows lack of equilibrium for $H + OH \rightarrow HOH$.

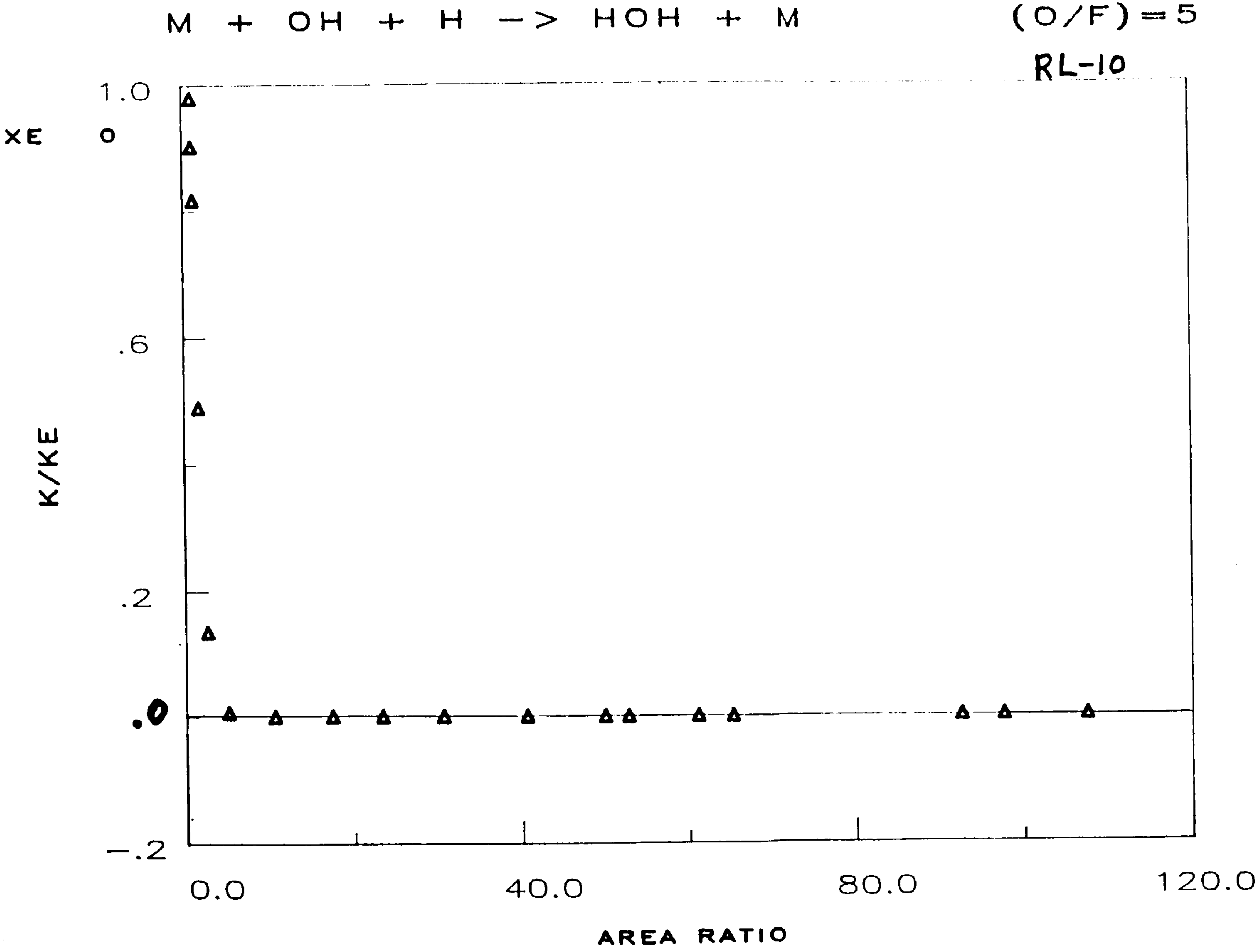


FIG. 5 K/Ke versus area ratio. Shows partial equilibrium for $O + HH \rightarrow OH + H$ and a dependence on (O/F).

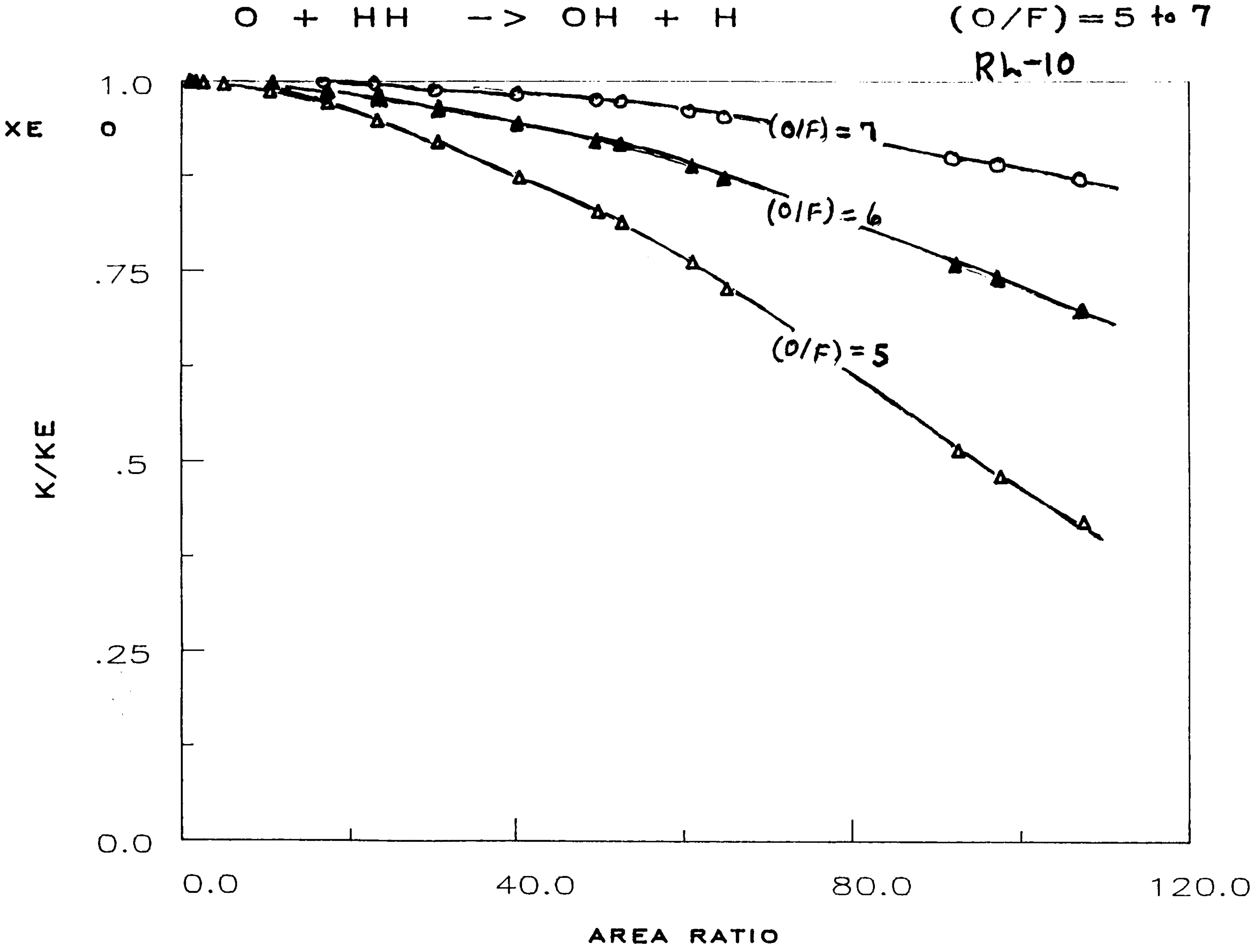


FIG. 6 K/Ke versus area ratio. Shows substantial equilibrium

for $HH + OH \rightarrow HOH + H$

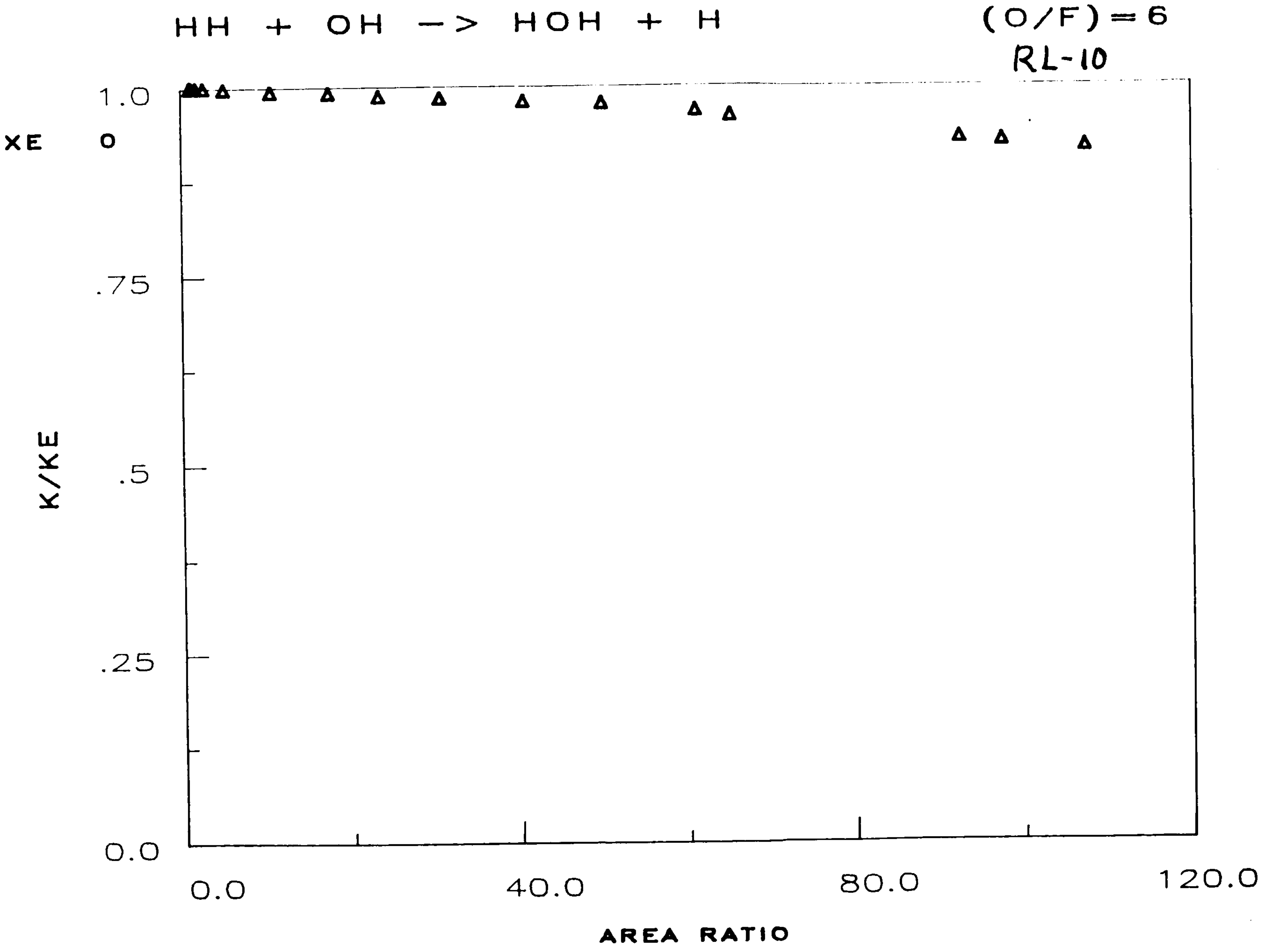
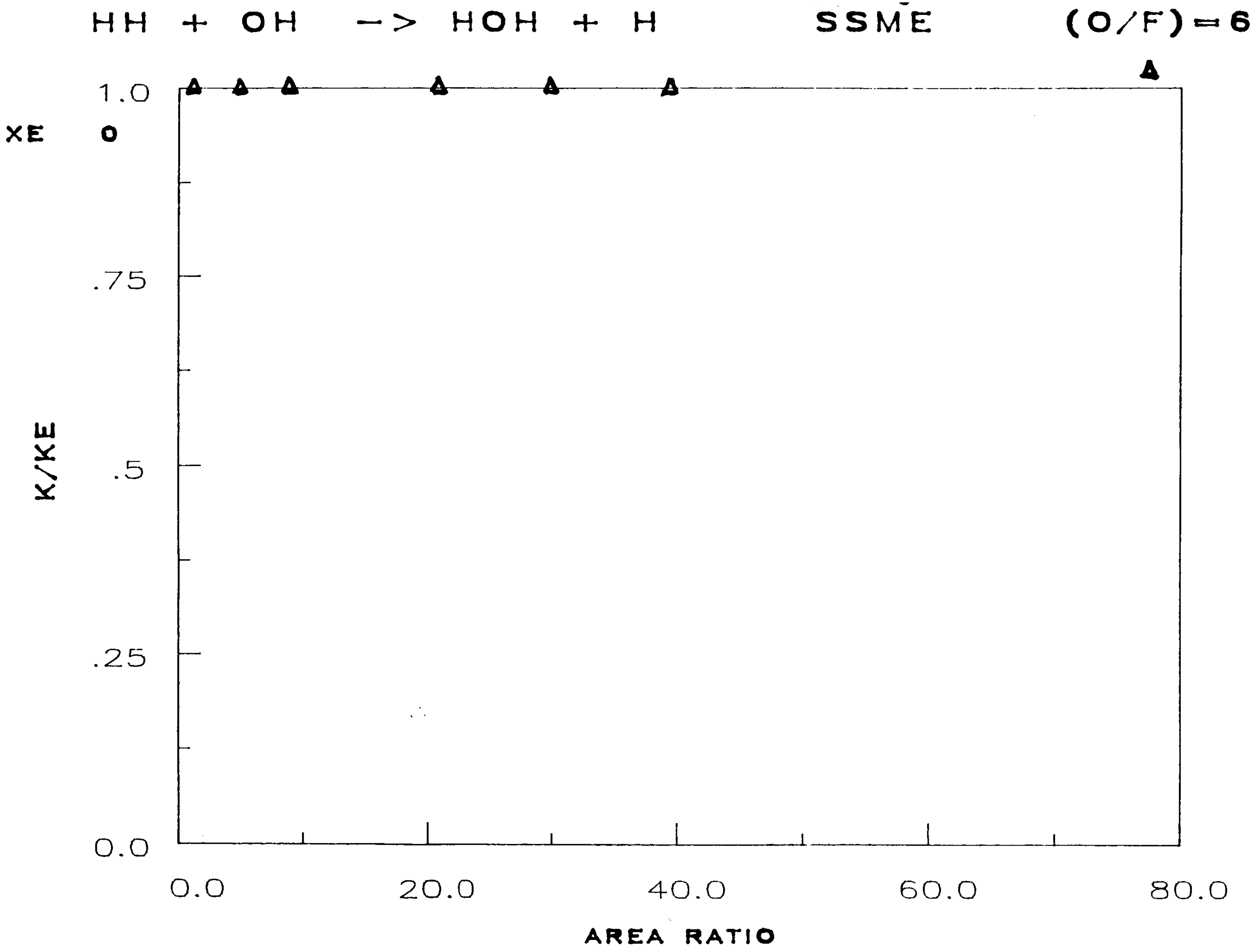


FIG. 7 K/Ke versus area ratio. Shows equilibrium for the reaction HH + OH -> HOH + H in the SSME.



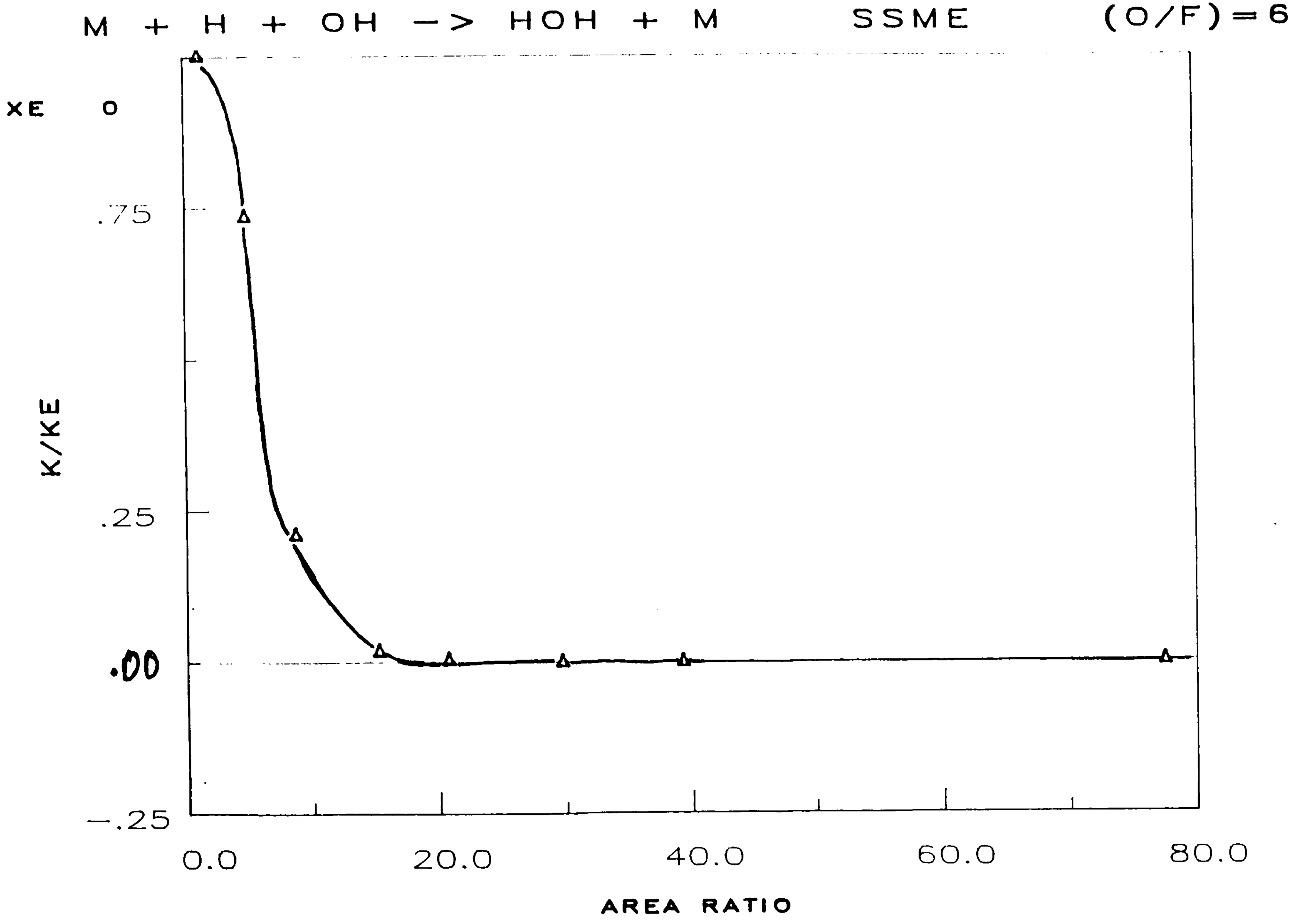


FIG. 8 K/Ke versus area ratio. Demonstrates a feeble attempt to maintain equilibrium for the reaction H + OH -> HOH in the SSME

FIG. 9 Variation of log[OH] and other species with (O/F).

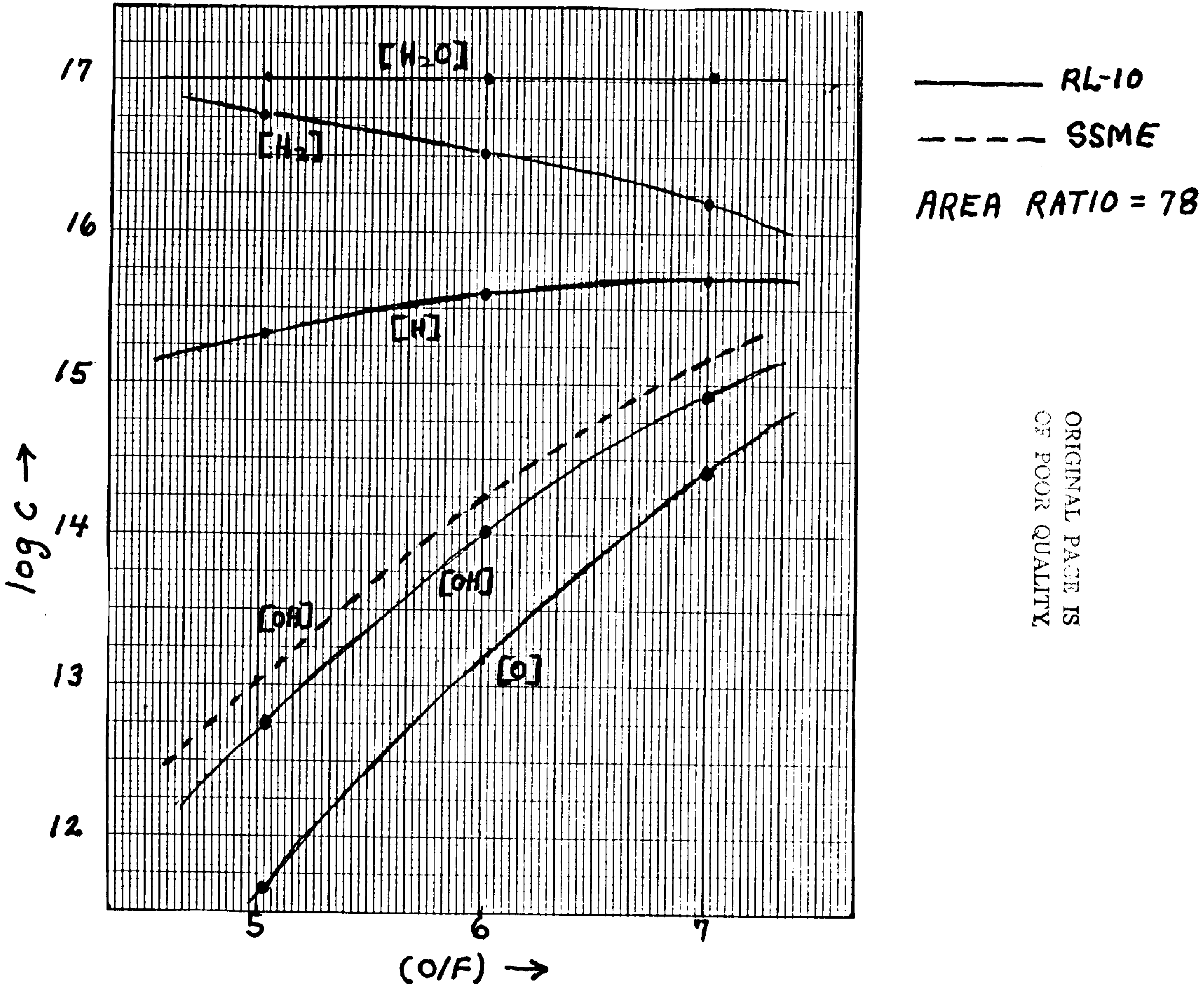


FIG. 10 Variation of the temperature (degrees Kelvin) at the exit plane with (O/F).