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**AERODYNAMIC LEVITATION REACTOR STUDIES OF FLUORINE REACTIONS WITH REFRACTORY CERAMICS**

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## I. INTRODUCTION

In recent years, much progress (1-4, 6-8, 17-19, 33, 34, 36-39, 50, 52-3, 58-71) has been made towards one goal of this (19, 33, 37-9, 50, 53, 61-6) and other (17, 18, 34, 36, 52, 59, 60) research: to survey heterogeneous fluorine reactions in different families of materials. The present work has, therefore, placed a greater emphasis on our second goal, i.e., the detailed kinetic and mechanistic study of selected fluorine/ceramic reactions. The results of our program include work on fluorine reaction with  $Al_2O_3$  (38, 39),  $B_4C$  (33,37), Re (61, 64), Gd (61, 65),  $LaB_6$  (37, 50, 61, 63) and  $LaB_6-C$ ,  $LaB_6-MoSi_2$  composites (61, 63).

One application of materials resistant to fluorine attack at high temperature is the HF chemical laser. Nickel and nickel alloys are useful in fluorine to ca. 1000K, but higher temperatures are required in CW HF lasers. Since the number of candidate materials decrease and fluorine corrosion rates increase with temperature it is useful to set upper bounds on the temperatures required for this application. Our analysis of this problem (61, 66) is presented, in Section II below.

Given the temperature range of interest, the mechanisms by which fluorine gasifies solids limit the number of possible fluorine resistant materials. These are discussed also in Section II.

In Sections III - IX we summarize the experimental results of this program. These results have already been presented (19, 37-9, 50, 53, 59, 61-2). Here we present a brief discussion of the essential results, along with abstracts of the papers that have been prepared for publication.

The list of references included here is a bibliography of work in the area of heterogeneous fluorine gas/solid reaction kinetics along with the additional references used in preparing this and previous reports. Titles are included to assist the interested reviewer of this subject.

## II. TEMPERATURE REQUIREMENTS AND CORROSION RATES IN EFFICIENT HF SUPERSONIC DIFFUSION LASERS (66)

Abstract - Design parameters for a  $(D_2 + F_2)$  combustion driven HF supersonic diffusion laser include the temperatures and pressures in the laser cavity  $(T, P)$  and the combustor  $(T_0, P_0)$ , the choked half width,  $w^*$ , of the supersonic expansion nozzle, and the fluorine stream half width,  $w$ , and  $F$ ,  $DF$  mole fractions,  $X_F$ ,  $X_{DF}$ . These eight quantities are constrained by i) an optimal cavity performance criterion, ii) the continuity equation, and iii)-v) combustor equilibrium, mass and energy balances. Also, vi) the characteristic temperature for cavity flow is determined mainly by  $X_F$ . Maximum power occurs at minimum  $w^*$ . With  $X_F = 0.1$ ,  $w^* \approx 0.01$  cm, and mixing by laminar diffusion between  $H_2$  and F (dilute in He) streams, the maximum required combustor temperature would be about 1240K. Much larger F-atom mole fractions would produce thermal choking ("thermal blockage") in the supersonic flow, but  $T_0 \leq 1300$  K at  $X_F = 0.20$

may be of interest. Corrosion of uncooled laser nozzles may be prevented if the construction material forms an involatile passivating fluoride coating. Due to rapid convective mass transfer at the nozzle throat, evaporation of a passivating fluoride would occur at nearly its vacuum sublimation rate. Evaporation from a nozzle passivated by the least volatile fluorides ( $\text{CaF}_2$ ,  $\text{SrF}_2$  and rare-earth trifluorides) would yield a 10% increase in  $w^*$  (initially 0.01 cm) in about 1 hour at 1300K.

Discussion - This paper shows that materials resistant to fluorine at temperatures up to ca. 1300K are of primary importance in the development of HFSDL's and that useful fluorine resistance at the throat of a laser nozzle will not be found with passivating metal fluorides unless the vacuum evaporation coefficient,  $\alpha$ , of the fluoride is small. For  $\text{LaF}_3$ ,  $\alpha = 1.0$ ; most other candidate fluorides have not been studied.

The conclusion that a passivating fluoride would evaporate from a laser nozzle throat at nearly its vacuum sublimation rate is based on the rates of transport of F-atoms to the surface of a cooled/laser nozzle computed by Ferrell, Kendall, and Tong (16).

Figure 1 shows our calculation of the combustor temperature - pressure relation, assuming adiabatic combustion of a  $\text{D}_2$  - excess  $\text{F}_2$  mixture whose initial temperature is 298K. The lines indicate the  $P_0$  ( $T_0$ ) relations for different  $X_{\text{F}}$  at which the fraction of total fluorine present as atomic fluorine equals 95% of its maximum possible value. This slight derating of combustor F-atom yield permits a substantial reduction in combustor temperature (ca. 100K).

Research to date has been guided by the belief that much higher temperatures would be of interest. Thus, a number of interesting candidate materials for HFSDL's have been rejected, but may yet find useful applications. Some of these are i) the heavier rare earth metals, whose melting points exceed 1500K and whose fluorides melt above 1400K. (However, see Section VIII for the F/Gd reaction kinetics; ii) yttrium metal or yttrium compounds, whose fluoride shatters when cooled through its phase transition temperature (14) (1350K); iii) MgO, which forms a MgO/MgF<sub>2</sub> eutectic at 1485K and exhibits fluoride film protection (61) to ca. 1360K.

Table I presents the vapor pressures of the least volatile fluorides. In many cases, these data were obtained by extrapolating measured results outside the range of measurement, and are, therefore, somewhat uncertain.

The melting points of the rare-earth metals and their trifluorides are illustrated in Fig. 2. The melting points of the heavier rare earth metals are sufficient for use as HF laser construction metals. However, we find (see Section VIII) that the fluorination of Gd to form solid  $\text{GdF}_3$  is not a passivated process.

### III. AERODYNAMIC LEVITATION OF LASER HEATED SOLIDS IN GAS JETS (62)

Abstract - Solid spheres were aerodynamically levitated in gas jets and laser heated to temperatures above 2000 K. Stable levitation in a supersonic jet from a 0.081 cm nozzle was demonstrated with 0.03 to 0.20 gram, 0.24 - 0.47 cm diameter specimens at a height between 0.7 - 2.0 cm above the nozzle and ambient pressures between 1.1 - 19 torr. An empirical model of supersonic jet levitation accurately predicts height vs. pressure over the full range of conditions that were investigated. The efficiency with which jet momentum is converted into levitation force decreases with the jet:specimen diameter ratio and the jet Reynolds number. The rate of jet spreading with distance from the nozzle deduced from levitation experiments agrees with that measured by pitot tube traverses of the jet. Pitot tube pressure measurements also reveal a transition from laminar to turbulent supersonic jet flow at a jet Reynolds number (ca. 1300) just above the maximum value at which stable levitation is observed. Laser heating reduces the jet momentum required for levitation at a given height and increases levitation stability. In experiments with subsonic jets, the required jet momentum flow rate exceeds the specimen weight by ca.  $2/C_D$  where  $C_D$  is the specimen drag coefficient at its terminal free fall speed under the ambient conditions. Exploratory studies of laser heated liquid levitation were unsuccessful.

Discussion - This technique was used for the F/LaB<sub>6</sub> kinetic study (See Section IX). Specimen mass measurements before and after reaction with fluorine or fluoride coating evaporation yield the flux of molecules produced by reaction to ca.  $10^{14}$  cm<sup>2</sup> sec<sup>-1</sup> or the effective thickness of a passivating coating to ca.  $10^{-5}$  cm. The apparatus is illustrated in Fig. 3.

### IV. KINETICS OF THE F/ALUMINA GASIFICATION REACTION (38)

Abstract - Intrinsic kinetics for the F/alumina gasification reaction were measured using a low pressure, transonic microwave discharge flow reactor technique, at  $p_p = 2.4$  Pa and  $1100 < T < 2000$ K. Rate measurements were obtained on polycrystalline alumina tubes or single crystal sapphire rods which were heated with a CW CO<sub>2</sub> laser and on alumina tubes heated internally by a tungsten filament electrical heating element.

Impurities greatly influence the rate of reaction, which is negligible below 1500K for uniformly heated specimens containing less than 1% Ca. The impurities diffuse from higher to lower temperature regions of specimens that are not uniformly heated. The F-atom reaction probability on pure alumina or sapphire at  $T > 1100$ K exceeds 0.5.

### V. SPECTRAL EMITTANCE OF POLYCRYSTALLINE ALUMINA (39)

Abstract - The spectral emittance of polycrystalline alumina was measured at  $T = 1660, 1830$ K. for  $0.37 \mu < \lambda < 0.85 \mu$ , and at  $\lambda = 0.66 \mu$ , between 1400-2100K. These measurements were obtained on 0.15cm diameter rods which were heated, in air, by a CW CO<sub>2</sub> laser. Emittances were obtained by alternately focusing an image of

the rod and of a black body hole in the rod onto the entrance aperture of a monochromator or by measuring the surface and black body temperatures with an optical pyrometer. The spectral emittance of alumina increases with temperature and is given, at  $0.66\mu$ , to ca.  $\pm 5\%$  by the expression  $\epsilon_{0.66} = 3.6 \times 10^{-4} T$ . At constant temperature  $\epsilon$  decreases with an increase of wavelength between  $0.37 - 0.6\mu$  and is nearly constant between  $0.6 - 0.85\mu$ . These and other data show the emittance of polycrystalline alumina is larger and the transmittance smaller than values estimated from specimen grain size and the absorbance, transmittance of sapphire crystal. A (weak) surface absorption process is suggested to explain this difference in the optical properties of single crystal and polycrystalline aluminum oxide.

## VI. KINETICS OF THE $F, F_2/B_4C$ REACTION

Abstract - Intrinsic kinetics for the  $F, F_2/B_4C$  reactions were measured using a low pressure, duct flow reactor technique. F-atom reaction was studied by use of a microwave discharge to dissociate  $F_2$ . Rate measurements were obtained from mass loss of a short  $B_4C$  duct through which the reactant flowed. The  $F/B_4C$  reaction probability<sub>3</sub> at  $P(F_2) = 4.6 - 14$  Pa depends only on temperature and increases from  $2 \times 10^{-3}$  at 570K to 0.35 at 1000K. The  $F_2/B_4C$  increases from  $4 \times 10^{-3}$  at 740K to 0.07 at 1000K.

Discussion - This study presents the kinetics of fluorine reaction with one of two phases in the La - B - C system (32) that can coexist with a mixture of  $LaB_6$  and carbon (see Fig. 4). Reaction of fluorine with the second phase,  $LaB_6C_2$ , has not been investigated but the F/carbon reaction has been studied (2, 52) in much detail. The kinetic data for  $F/B_4C$  reaction are presented in Fig. 5. The reaction probability is the fraction of F-atoms or  $F_2$ -molecules striking the  $B_4C$  surface which react to form  $BF_3$  and  $CF_4$  product molecules.

## VII. KINETICS OF THE F/Re GASIFICATION REACTION

The F/Re gasification kinetics have been measured by methods described elsewhere (1, 7) to obtain the results illustrated in Figure 6. The figure plots the logarithm of the rhenium gasification probability, defined as the rhenium removal : fluorine atom impingement flux ratio versus reciprocal temperature. Since the product of reaction is  $ReF_4$  (58), the F-atom reaction probability is 4 times greater than the rhenium gasification probability and the rate of reaction in the high temperature range where rate decreases with temperature is expected to increase with the 4-th power of the F-atom partial pressure. Rate measurements at  $P_F = 0.0023, 0.0048, \text{ and } 0.0086$  torr confirm this conclusion. It is apparent that rhenium displays no useful fluorine resistance at high temperature, except above ca. 1600K when the fluorine pressure is very small. These results agree with the expected kinetic behavior suggested by the trends among other third-row transition metal fluorine reactions (1), which are illustrated in Figure 7.

## VIII. HIGH TEMPERATURE KINETICS OF THE F/Gd REACTION

Gadolinium metal melts above 1600K (26), and its fluoride is involatile (11) and melts above 1500K (15). If it formed a passivating fluoride coat, gadolinium metal would be an interesting fluorine resistant material, especially

since it is stable in the atmosphere, easy to fabricate, and relatively inexpensive. A second reason for investigating the Gd/F reaction is to evaluate the effect of a large substrate metal activity on the passivating nature of rare-earth metal fluoride coatings.

The Gd/F reaction rate was studied by measuring the electrical resistance vs time of electrically heated Gd ribbon in atomic fluorine at temperatures ca. 1100-1500K. The rate of reaction is rapid, proportional to fluorine pressure, nearly independent of temperature, and independent of time, even after a fluoride coat, greater than 50 micron thick has formed. Thus, Gd metal is not a good fluorine resistant material because the fluoride coat formed on it is not passivating. The fluoride coat has a gray-black color, unlike  $GdF_3$ , suggesting that the solubility of Gd in  $GdF_3$  is substantial at high temperatures and unit metal activity. These observations imply that high metal activities are not conducive to formation of thin passivating fluoride coats, because rapid metal diffusion through the coating produces rapid reaction with fluorine at the fluoride-fluorine interface.

#### IX. HIGH TEMPERATURE KINETICS OF FLUORINE REACTION WITH $LaB_6$

$LaB_6$  reacts with atomic fluorine to form a passivating, white  $LaF_3$  coating. Further reaction then proceeds at the coating evaporation rate which can be calculated from the vapor pressure of  $LaF_3$  (35, 40) and the prevailing gas phase mass transfer coefficient. Rate data at  $p(F) = 0.12$  torr are given in Fig. 8.

The  $LaF_3$  coating thickness required to passivate F/ $LaB_6$  reaction is large for i) porous  $LaB_6$  specimens, ii) sample  $LaB_6-2$ , of low porosity (0.7%) and density equal to  $4.68$  g/cm<sup>3</sup> (99.3% of theoretical density), or iii)  $LaB_6/C$  and  $LaB_6/MoSi_2$  composites. Thin  $LaF_3$  coatings (less than 3 mg/cm<sup>2</sup>, or about 5 microns, at  $p(F) = 0.12$  torr) occur on sample  $LaB_6-4$ , of low porosity (0.7%) and 4.59 g/cm<sup>3</sup> density (97.5% of theoretical density).

The  $LaB_6$  phase exists over a considerable composition range (21, 22) as a result of La vacancy formation. The lattice parameter is essentially independent of composition. Therefore, the density measurements on  $LaB_6$  samples which form a thin passivating  $LaF_3$  coating in fluorine imply that the composition is actually  $La_{0.96}B_6$  (or  $LaB_{6.22}$ ). The lanthanum activity in this material would then be smaller by several orders of magnitude than it is in the more dense nearly stoichiometric substance (23).

The facts that thick  $LaF_3$  coatings occur on nearly stoichiometric  $LaB_6$  ( $a_{La} = 10^{-2}$ ) and on gadolinium metal ( $a_{Gd} = 1$ ), but not on La deficient  $LaB_6$ , imply that the coating growth process occurs by diffusion of dissolved La through the coating. Then  $LaF_3$  coating thickness should not increase much with fluorine pressure.

$LaF_3$  coating thickness has been measured on  $LaB_6$  specimens exposed to atmospheric pressure fluorine-rich  $H_2/F_2$  flames (17, 18, 34, 36, 52, 59, 60). The material which gave thicker coatings (ca. 30 microns, or 18 mg/cm<sup>2</sup>) at  $p(F) = 0.12$  torr produced a 100 micron thick coating in the flame tests (34). This relatively small change over a thousand-fold change in the F-atom pressure

supports the postulate that coating thickness depends on substrate lanthanum activity. However, flame test results are not available on the specimens that are passivated by thin  $\text{LaF}_3$  coatings.

Figure 9 reports our coating mass measurements, which may be converted to an effective coating thickness via the density of  $\text{LaF}_3$ ,  $5.9 \text{ g/cm}^3$ . The figure presents coating mass per unit area as a measure of coating thickness. Specimen area is taken as the area of a sphere of equal mass and does not include corrections for surface roughness. The results of three experiments with sample  $\text{LaB}_6$ -2 (open symbols) and two experiments with sample  $\text{LaB}_6$ -4 (filled symbols) are given. The figure plots  $\text{LaF}_3$ (s) mass per unit area after reaction for 20-50 minutes at the indicated temperatures, and  $P_p = 1.6 \times 10^{-4}$  atm. The abscissa is the number of times that the coating has been formed on the specimen. Evaporation of the coating at  $T = 1500\text{K}$  was carried out between each run.

Further details of our  $\text{F/LaB}_6$  work are given in Reference 61.



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Table 1  
Melting Points, Transition Temperatures, and Vapor Pressures of Refractory Fluorides

| Fluoride         | T <sub>m</sub> (K) | T <sub>t</sub> (K) | Vapor pressure, atm |          |           | T <sub>m</sub> | Refs. |
|------------------|--------------------|--------------------|---------------------|----------|-----------|----------------|-------|
|                  |                    |                    | 1400K               | 1500K    | 1600K     |                |       |
| MgF <sub>2</sub> | 1536               |                    | 6.71E-6             | 5.55E-5  | 1.11E-4   | 9              |       |
| CaF <sub>2</sub> | 1691               | 1424               | 2.73E-7             | 2.57E-6  | 1.81E-5   | 9              |       |
| BaF <sub>2</sub> | 1563               |                    | 5.03E-6             | 3.89E-5  | 1.22E-4   | 9              |       |
| SrF <sub>2</sub> | 1673               |                    | 5.64E-7             | 4.75E-6  | 3.00E-5   | 9              |       |
| LaF <sub>3</sub> | 1766               |                    | 9.14E-7             | 9.63E-6  | 7.56E-5   | 11,14          |       |
| PrF <sub>3</sub> | 1668               |                    | 1.87E-6             | 1.88E-5  | 1.42E-4   | 11,14          |       |
| NdF <sub>3</sub> | 1647               |                    | 1.56E-6             | 1.64E-5  | 1.28E-4   | 11,14          |       |
| SmF <sub>3</sub> | 1573               | 763                | 5.29E-6             | 5.38E-5  | 2.43E-4   | 11,15,40       |       |
| GdF <sub>3</sub> | 1505               | 1348               | 5.56E-7             | 6.39E-6  | 7.15E-6   | 11,15          |       |
| DyF <sub>3</sub> | 1430               | 1305               | 8.42E-7             |          | 1.79E-6   | 11,15          |       |
| ErF <sub>3</sub> | 1419               | 1390               | 7.53E-7             |          | 1.18E-6   | 11,15          |       |
| ScF <sub>3</sub> | 1825               |                    | 3.86E-5             | (3.24E4) | (2.08E-3) | 11,15          |       |
| YF <sub>3</sub>  | 1428               | 1350               | 1.45E-6             |          | 2.94E-6   | 12,14          |       |

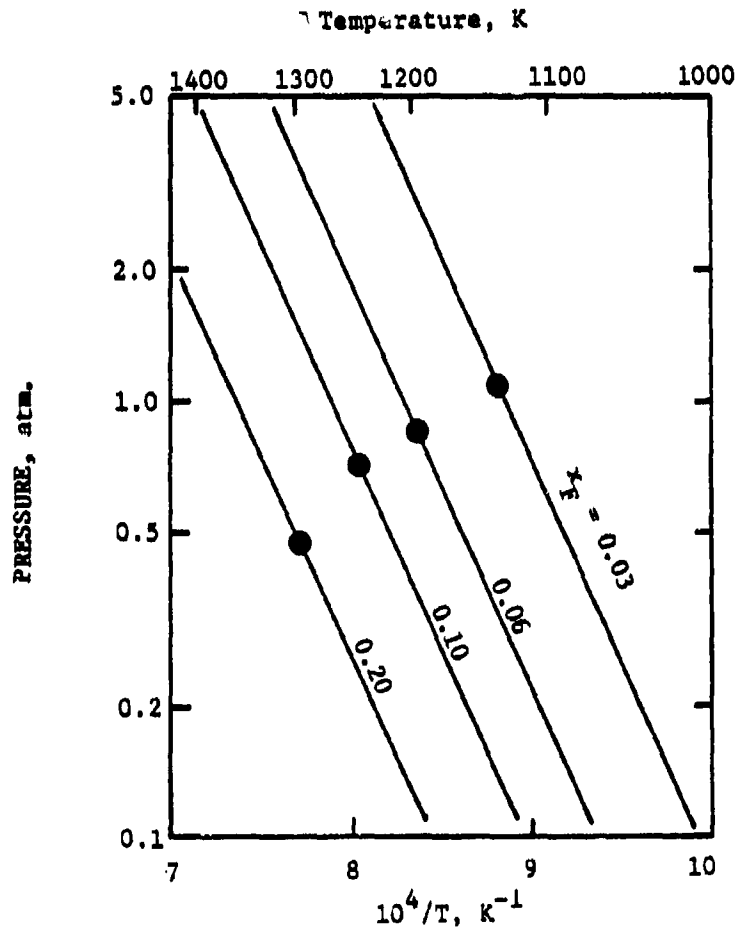


Figure 1.  $F_2/H_2/He$  adiabatic combustor temperature and pressure at  $\eta_c = 0.95 \cdot \eta_c(\max)$ .

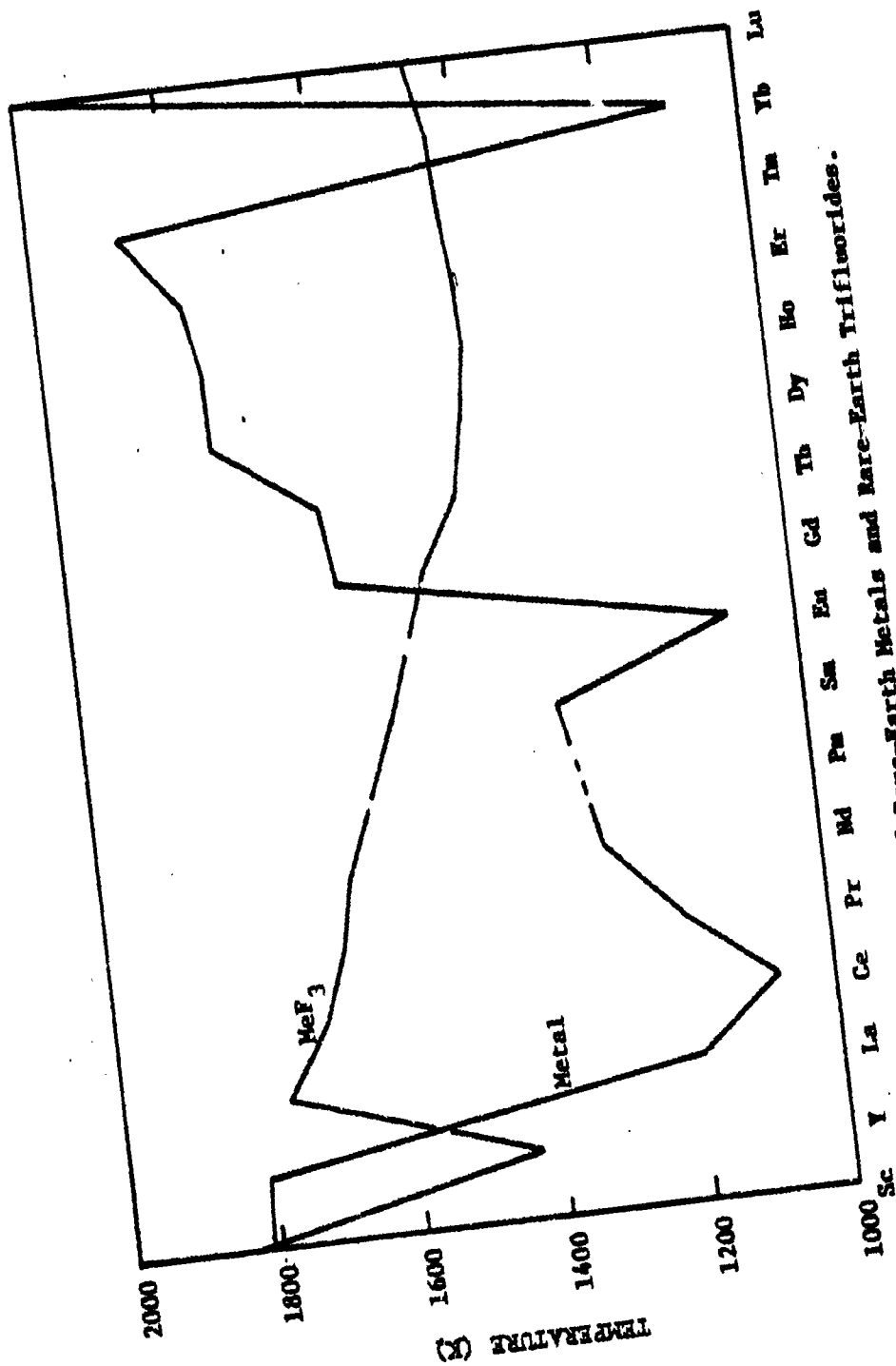


Figure 2. Melting Points of Rare-Earth Metals and Rare-Earth Trifluorides.



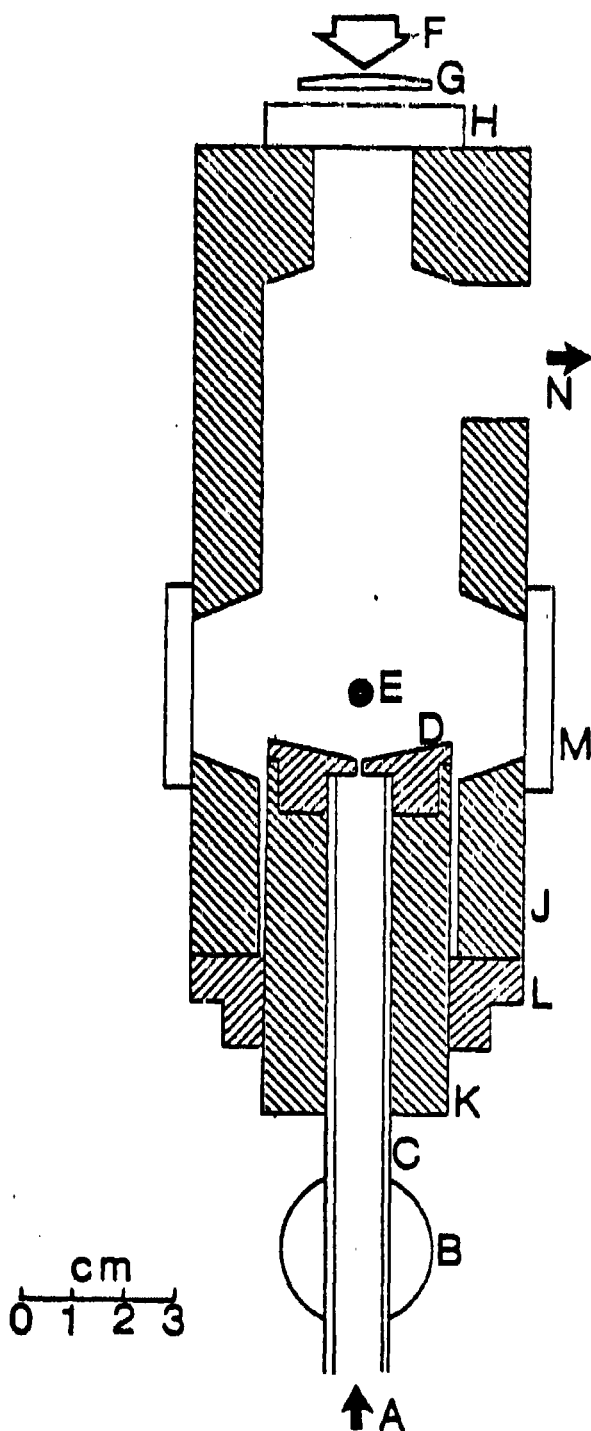


Figure 3. Aerodynamic Levitation Flow Reactor, A- Reactant gas flow ( $\text{Ar}/\text{F}_2$  mixture); B- 2450 MHz, 80 watt microwave discharge; C- Alumina discharge tube; D- Anodized aluminum nozzle; E- Aerodynamically levitated specimen; F- CW  $\text{CO}_2$  laser beam; G- ZnS lens (optional); H- NaCl window; J- Water-cooled aluminum housing; K- Water-cooled nozzle support; L- O-Ring coupling; M- Pyrex windows for optical pyrometer and sensor for laser power controller; N- to manometer, throttle valve, trap, and vacuum pump.

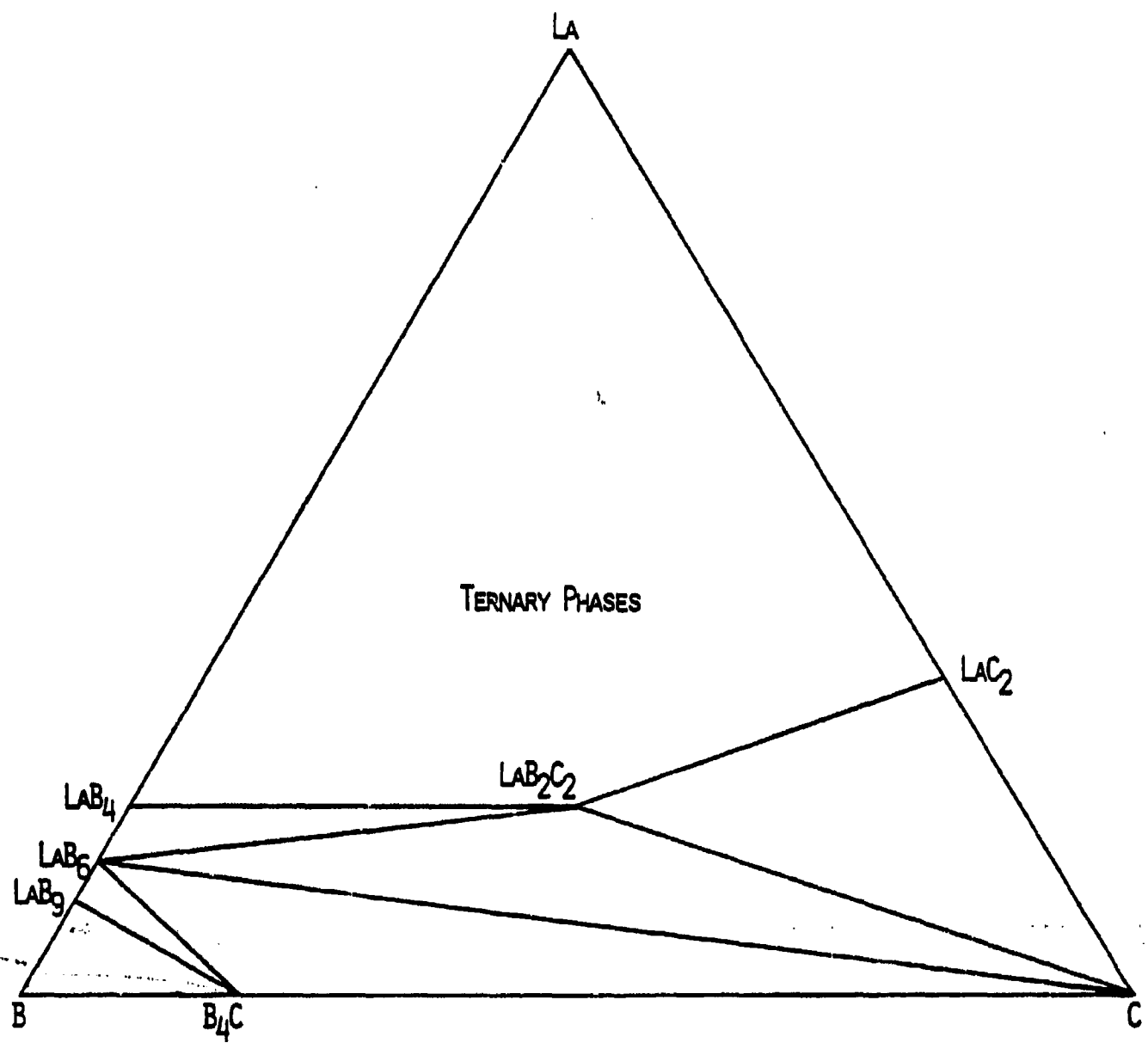


FIGURE 4. LANTHANUM-BORON-CARBON TERNARY PHASE DIAGRAM.

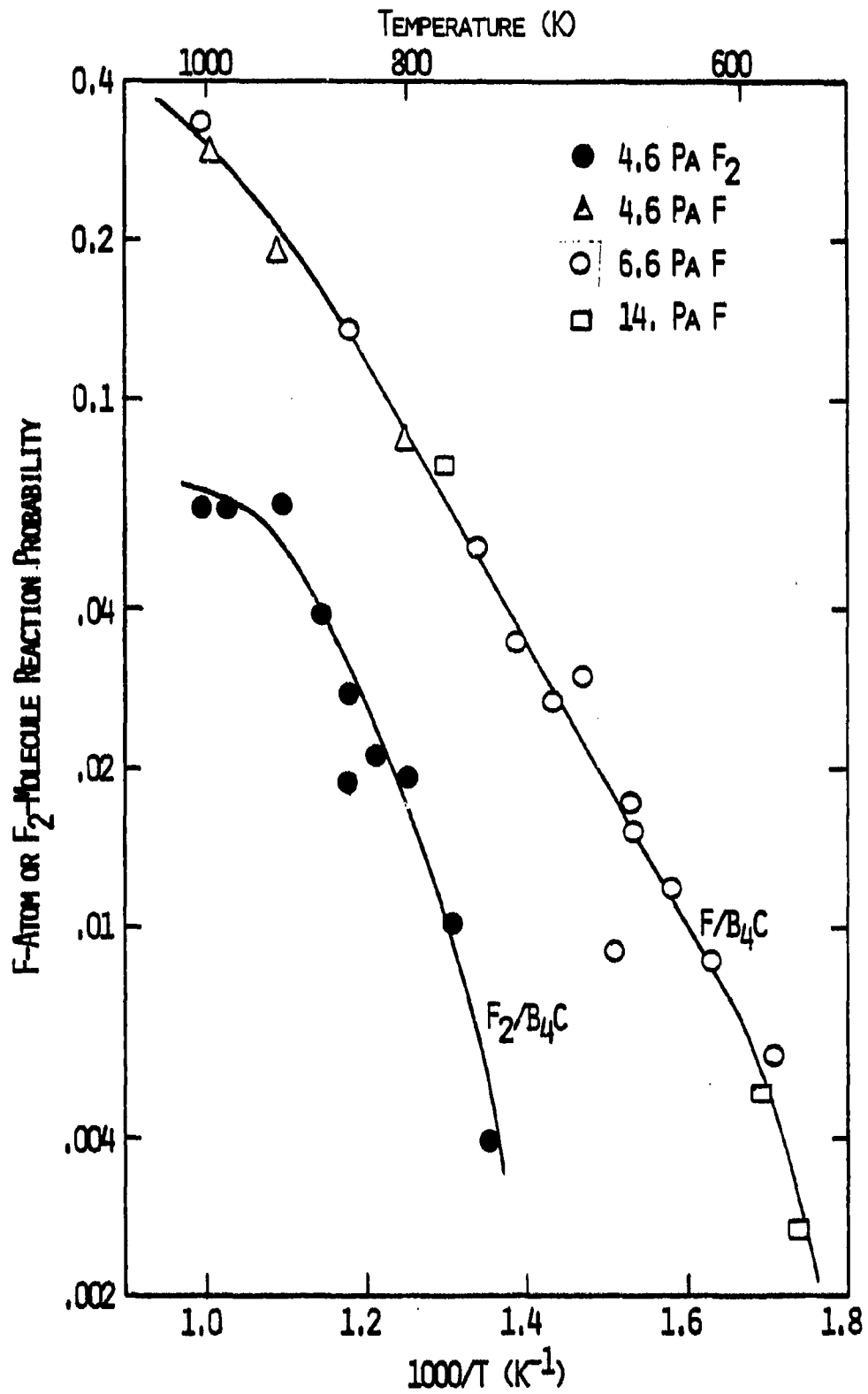


FIGURE 5. F, F<sub>2</sub>/B<sub>4</sub>C GASIFICATION KINETICS.

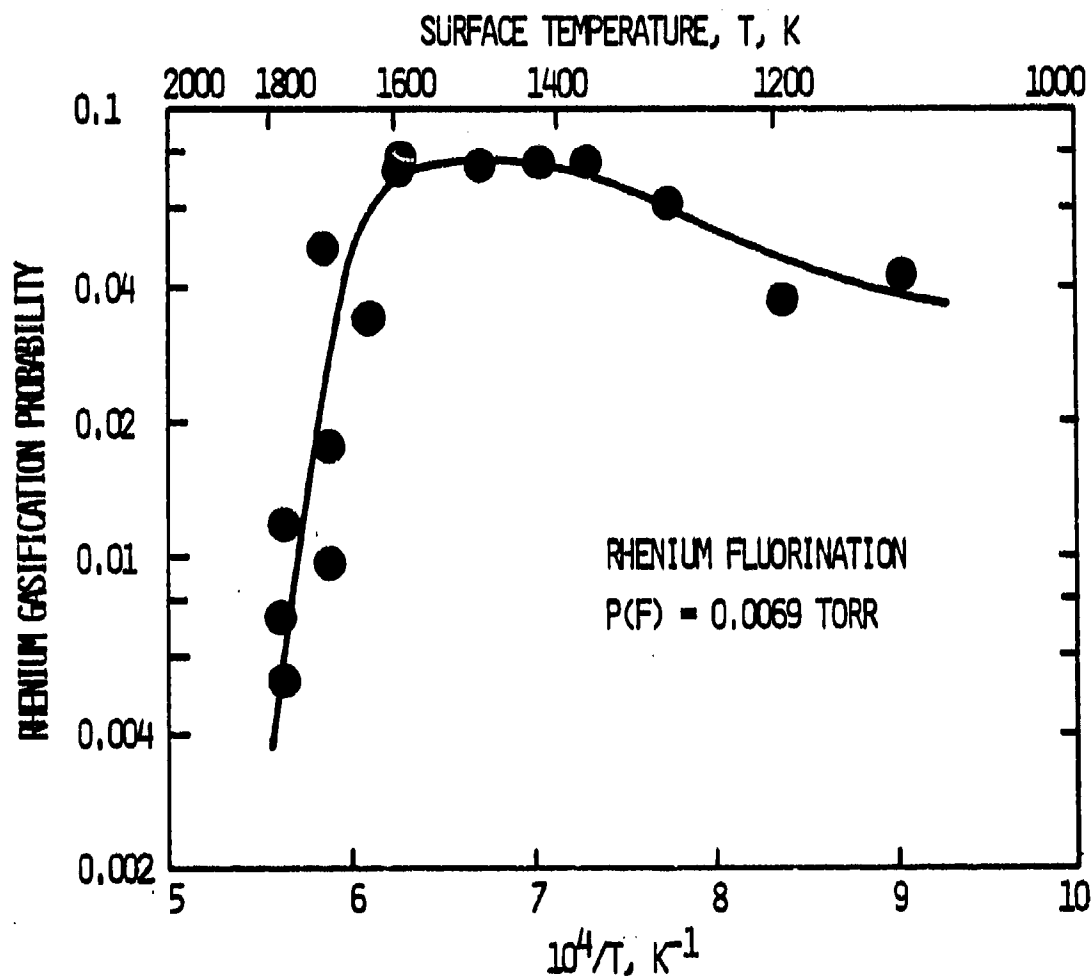


Figure 6. Rhenium fluorination kinetics.

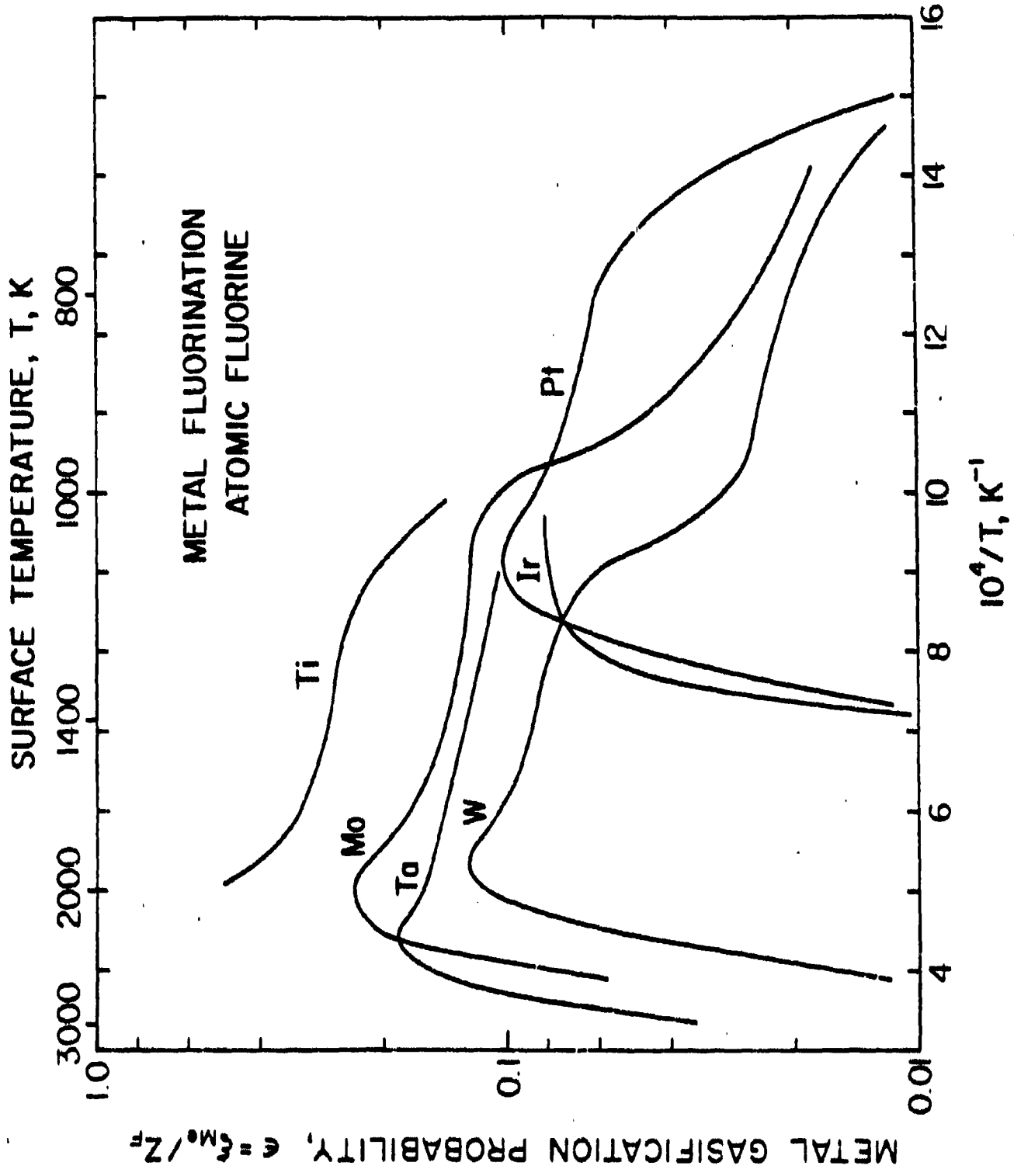


Figure 7. Transition metal fluorination kinetics.

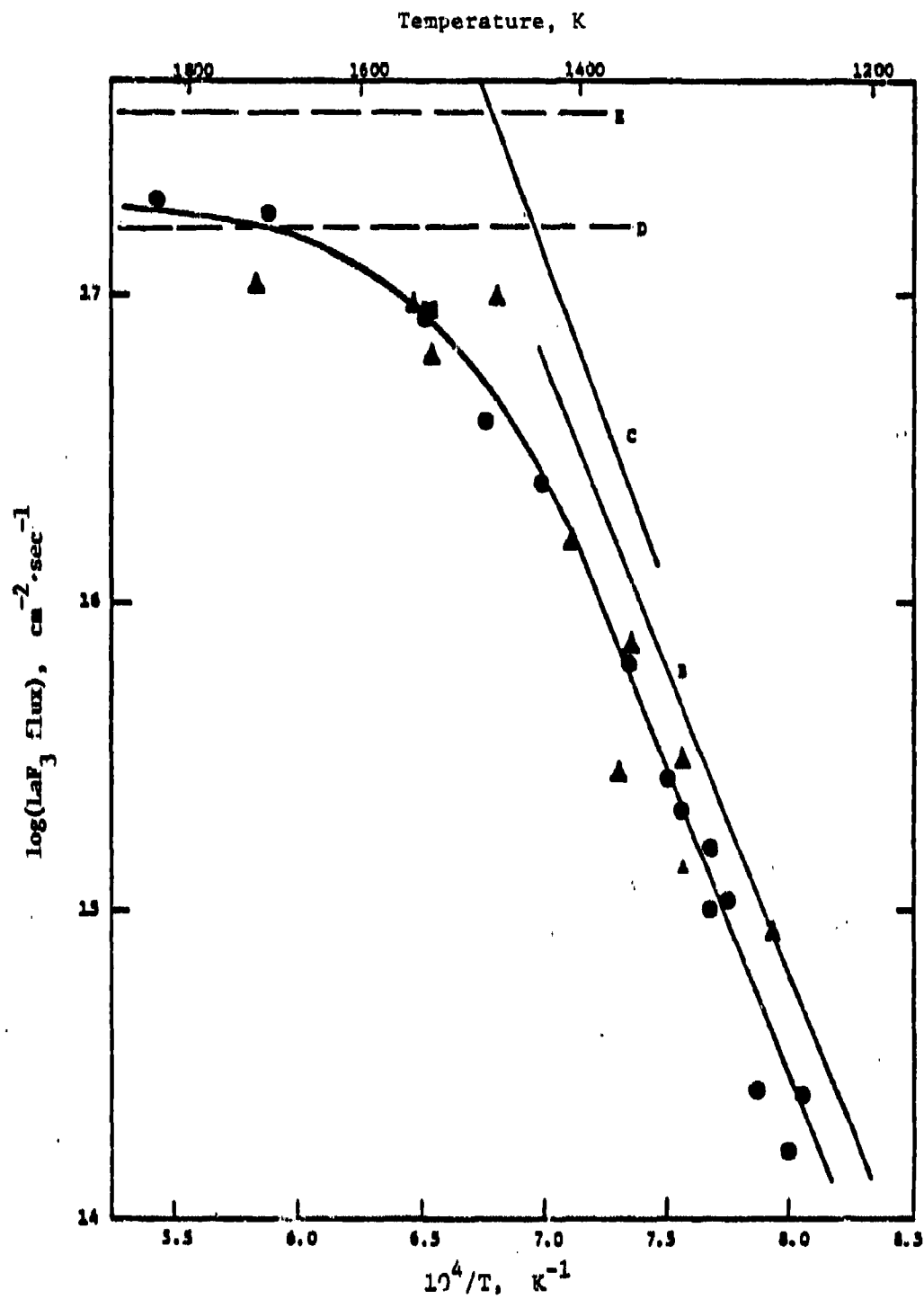


Figure 8.  $\text{LaB}_6/\text{F}$  reaction kinetics.

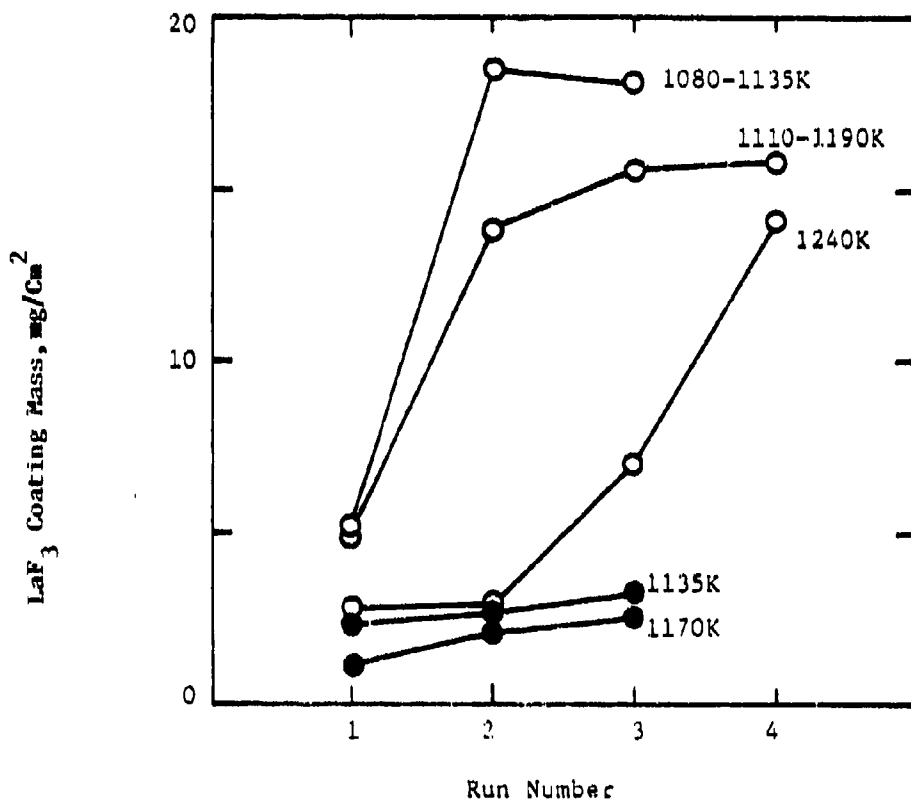


Figure 9. LaF<sub>3</sub> coating mass measurements.

Open symbols - LaB<sub>6</sub>-2.

Filled symbols - LaB<sub>6</sub>-4.