Heterogeneous Fluorine Atom Recombination/Reaction on Several Materials of Construction

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Heterogeneous F-atom recombination/reaction probabilities on several construction materials were computed from measurements of F-atom flow rates at the entrance and exit of a catalytic duct in a low-pressure reactor. Atom loss probabilities at 300 K and $p_F \approx 13 \mathrm{N} \cdot \mathrm{m}^{-2} (\sim 1.3 \cdot 10^{-4}$atm) are $6.4 \cdot 10^{-5}$ for Al_2O_3, $1.6 \cdot 10^{-4}$ for quartz and pyrex glass, $2.8 \cdot 10^{-4}$ for type-304 stainless steel, $4.2 \cdot 10^{-4}$ for molybdenum, $7.2 \cdot 10^{-4}$ for nickel, $1.8 \cdot 10^{-3}$ for aluminum, and $> 10^{-2}$ for copper, brass, and zinc. The values for steel and aluminum vary little with temperature up to 470 and 560 K, respectively. Application of these materials in gas dynamic hydrogen fluoride laser nozzles is discussed briefly.

Introduction

KNOWLEDGE of fluorine atom reaction kinetics has grown rapidly in recent years.[1-4] This growth is largely attributed to the discovery of many chemical lasers, which utilize fluorine reactions, as well as interest in fluorine-containing rocket propellants and fluorine corrosion problems. In both research and applications, heterogeneous F-atom recombination and/or reaction on the surfaces of the apparatus or device is often an important F-atom loss mechanism which must be avoided. Yet, F-atom loss rates have been reported only for materials most suitable for research (alumina,[5] quartz,[6] pyrex,[7] and teflon[8]), although F-atoms have been demonstrated[2] to react and/or recombine incompletely on the metals Mo, W, Ni, Au, Ag, Pt, Re, and Co near room temperature. The lack of data for materials, that are suitable in applications is especially important in the design of supersonic diffusion hydrogen fluoride lasers,[9] where, for lack of data, the nozzle surfaces are assumed to be fully catalytic in recombining F-atoms.[10-11] Here, the use of small nozzles to increase downstream mixing rates conflicts with the requirement for low surface catalyzed F-atom losses, which may be as high as 20%[10,11] on fully catalytic materials. Further, the evolution of heat and increase in average diffusion distance, which accompanies F-atom recombination, complicates laser design calculations.[11]

The few data that do exist suggest that heterogeneous F-atom loss usually occurs with small probability (ratio of F-atom loss rate to F-atom surface impingement rate). Reported loss probabilities include $2 \cdot 10^{-4}$ for fluorine-passivated alumina,[5] $1.2 \cdot 10^{-4}$ for quartz,[6] and $\leq 7 \cdot 10^{-5}$ for teflon,[1,8] as well as the previously mentioned observation that the F-atom loss rate is low on many metals.[2] F-atom loss on pyrex in the presence of various reactive gases is reported[7] to occur with a probability between $1.7 \cdot 10^{-4}$ and $3.7 \cdot 10^{-3}$. Also, fluorine poisons the rapid recombination of Cl-atoms on pyrex, with a resulting Cl-atom recombination probability of $< 8 \cdot 10^{-5}$ at room temperature.[5]

This paper presents measured heterogeneous F-atom loss probabilities on several materials of construction. These experimental results are obtained by use of the chemiluminescent titration of F-atoms with Cl_2[5,8,12] to measure F-atom flow rates at the entrance and exit of a catalytic duct in a low-pressure flow reactor. Commercial stainless steel (type 304) and aluminum tubing are shown to be poor atom loss catalysts at temperatures up to about 500K, as are nickel and molybdenum at room temperature. On the other hand, copper, zinc, and brass are highly catalytic, and will remove F-atoms at diffusion limited rates (fully catalytic) under most conditions of practical interest.

Experimental

The apparatus and method for chemiluminescent titration of F-atoms with Cl_2 have been described previously.[5,12] Atomic fluorine was generated by passing F_2 (2-10% in Ar) through a 2450-MHz, 70-W, microwave discharge in a 0.95-cm-i.d. alumina tube at total flow rates of about 150 cm^3 (STP)/min. First, F-atom flow rates at the discharge tube exhaust were measured by titration with Cl_2 in a pyrex reactor maintained at 93-200 Pa‡ total pressure. Then, under nearly identical flow conditions, heterogeneous atom loss rates on several catalysts were obtained by measuring the atom flow rates with cylindrical catalyst tubes placed between the discharge tube and the titration region of the apparatus.

A few experiments were performed at an increased flow rate when atom loss on the material of interest was found to be very rapid. Atom loss on alumina was studied by measuring F-atom flow rates, with the microwave cavity located at different positions up to 83 cm from the discharge tube exhaust.

The chemiluminescent F/Cl_2 titration[5,12] makes use of the fast reaction

$$F + Cl_2 = ClF + Cl$$

to convert F-atoms into easily observed Cl-atoms. The Cl-atom concentration is measured vs Cl_2 flow rate by observing the slow three-body chlorine atom recombination afterglow with a phototube. The afterglow intensity increases (with the ~ 1.4 power of Cl-concentration) up to the titration end point, and then remains constant. The rate constant for reaction of Cl-atoms with undissociated F_2:

$$Cl + F_2 = ClF + F$$

is unusually small,[1,8] and this reaction does not interfere with the titration. It is convenient to locate the phototube close enough to the Cl_2 inlet so that termolecular recombination does not remove more than 10% of the Cl-atoms prior to their detection. Otherwise, corrections[5] to the titration end point must be made. Cl-atom losses were avoided by employing a 10-cm distance between the Cl_2 inlet and phototube. Com-

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‡1 Pa (pascal) = $1 \ \mathrm{n} \cdot \mathrm{m}^{-2} = 0.99 \cdot 10^{-5}$ atm.

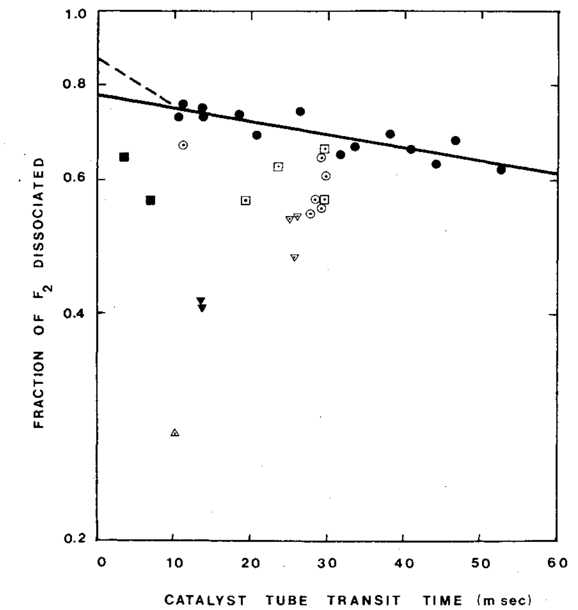

Fig.1 Measured fraction of dissociated fluorine vs catalyst tube mean transit time. ● -Al_2O_3, □ -pyrex, ○ -quartz, ▽ -steel, ■ -molybdenum, ▼ -nickel, △ -aluminum.

plete mixing of the F-atom and Cl_2 reactants was verified by measurements at different Cl_2 inlet-phototube distances.

The materials investigated are listed in Table 1. Prior to use, the catalyst tubes were degreased with reagent grade toluene and acetone, and rinsed with distilled water. Several catalysts also were studied after cleaning with dilute acid (HF or H_2SO_4) and distilled water. Measurements with copper, stainless steel, and aluminum were made before, during, and after heating the central 20 cm of the specimen tubes to 200-300°C in order to accelerate any possible reaction of the catalyst with fluorine.

Interpretation

Fluorine atoms are consumed in passing through the catalyst tubes by heterogeneous reaction or recombination reactions. Homogeneous atom recombination may be neglected under the present conditions, because the termolecular F-atom recombination rate constant is too small.[8] Under the assumption that F-atom loss occurs via first-order surface catalyzed wall reactions, the sum of apparent F-atom recombination (γ_{app}) and reaction (ϵ_{app}) probabilities may be calculated from

$$Q/Q_o = \exp\{-(\gamma_{app} + \epsilon_{app})\bar{c}t/d\} \qquad (1)$$

where Q/Q_o is the ratio of F-atom flow rates with or without the catalyst tube, $\bar{c}$ is the F-atom mean thermal speed, and t is the mean transit time in the catalyst tube, whose diameter is d. In practice, Q and Q_o were measured at slightly different fluorine flow rates, but the fraction of F_2 molecules dissociated in the discharge is nearly independent of F_2 flow rate. Therefore, Q/Q_o was set equal to η/η_o, the ratio of apparent fractional dissociation of F_2 with or without the catalyst tube.

For sufficiently active catalysts, transverse diffusion limitations will reduce the F-atom concentration near the wall so that the apparent atom loss probability is less than its true value. However, it can be shown[13] that for first-order wall loss, with negligible pressure drop in the catalyst tube

$$(\gamma+\epsilon)/(\gamma_{app}+\epsilon_{app}) \cong \{1-(\gamma_{app}+\epsilon_{app})\bar{c}d/4D\overline{\mathrm{Nu}}\}^{-1} \qquad (2)$$

where D is the relevant Fick diffusion coefficient and $\overline{\mathrm{Nu}}$ is the prevailing axial-average Nusselt number for mass transfer ($\overline{\mathrm{Nu}} \cong 3.66$ for the present laminar Newtonian flow case). At a pressure of 133 Pa, $D \cong 300$ cm^2/sec, and Eq. (2) shows that diffusion corrections will be negligible (less than, say, 15%) if $(\gamma_{app}+\epsilon_{app}) < 10^{-2}$.

Table 1 Materials studied in heterogeneous F-atom loss experiments

Material	I.D. cm	Length cm	Remarks
Copper	1.1	57	Hard drawn copper tubing, new alloy no. 122, Anaconda Brass and Copper Co., Waterbury, Conn.
Brass	1.1	6-21	Common yellow brass tubing, source, composition unknown.
Zinc	0.8	2-13	Purity and source unknown. Fabricated from zinc sheet.
Steel	1.08	57	Type 304 18-8 stainless steel (18-20% Cr, 8-12% Ni, and max. of 2% Mn, 1% Si, 0.08% C, 0.045% P, 0.03% S).
Aluminum	1.10	57	Alloy 6061T6 aluminum tubing (1%Mg, 0.6%Si, 0.25%Cr, 0.25%Cu).
Molybdenum	0.62	33.4	"Industrially pure molybdenum," Climax Molybdenum Co.
Nickel	0.96	37.5	Fabricated from 0.005 cm nickel foil, 99.9% pure, Pfizer, Inc., Wallingford, Conn.
Alumina	0.95	17-83	Type AD998, 99.8% pure, dense alumina tubing, Coors Porcelain Co., Golden, Colo.
Quartz glass	0.95	25,57	...
Pyrex glass	0.95	57	...

Results

Figure 1 presents atom loss data that were not diffusion-limited. The measured fraction η of dissociated fluorine molecules is plotted vs catalyst tube mean transit time. The dashed line refers to earlier data[5] on alumina (discussed later), whereas the full line shows a least squares fit of the present alumina data to Eq. (1) from which the values $\eta_o = 0.773 \pm 0.017$ and $\gamma_F + \epsilon_F = 6.4 \pm 1.1 \cdot 10^{-5}$ were derived. The average deviation of measured values from the straight line is 3%, in good agreement with that expected from estimated uncertainties in Cl_2 (3%) and F_2 (1%) flow rates. Thus, it was concluded that discharge efficiency is constant within 3% over the range of fluorine flow rates [10.0-14.4 cm^3 (STP)/min], argon flow rates [139-201 cm^3 (STP)/min], and pressures at the discharge (161-307 Pa) which prevailed in the alumina experiments. The value of η_o for other catalysts accordingly was taken as $\eta_o = 0.74 \pm 0.02$, which includes the small correction for atom loss due to ~10 msec mean transit time in the discharge tube. Upper and lower limits on $\gamma + \epsilon$ were computed from the data in Fig. 1 (and their estimated uncertainities); average values are presented in Table 2. Lower limits on $\gamma + \epsilon$ also are given for copper, brass, and zinc. Specific observations for each catalyst are given below.

Quartz and Pyrex

Figure 1 shows that quartz and pyrex atom loss data are less reproducible than are data for other catalysts. Both also revealed a nonuniform activity for reaction with F-atoms by the appearance of spots where the glass is more severely etched. Quartz and pyrex develop a translucent etched appearance after about one-hour exposure to F-atoms, but pyrex appears to be etched more rapidly than is quartz. Etching is less rapid near the downstream end of the tubes, where F-atom pressure is reduced due to atom loss and viscous pressure drop in the catalyst tube. Despite the possibility that impurity effects may lead to increased etching and atom loss in some spots, the present result for quartz agrees with the published value[6] ($1.2 \cdot 10^{-4}$), and the value for pyrex is in

Table 2 Heterogeneous F-atom loss probabilities

Material	Temperature, K	F-atom Pressure, Pa	F-atom loss probability
Alumina	300	10-27	$6.4 \pm 1.1 \cdot 10^{-5}$
Quartz	300	9-24	$1.5 \pm 1.0 \cdot 10^{-4}$
Pyrex	300	7-26	$1.6 \pm 1.3 \cdot 10^{-4}$
Steel	300-470	7-21	$2.8 \pm 1.0 \cdot 10^{-4}$
Molybdenum	300	7-30	$4.2 \pm 0.9 \cdot 10^{-4}$
Nickel	300	6-20	$7.2 \pm 0.7 \cdot 10^{-4}$
Aluminum	300-560	4-34	$1.8 \pm 0.2 \cdot 10^{-3}$
Copper	300-570	7-21	$> 1.1 \cdot 10^{-2}$
Brass	300	1.3-13	$> 5 \cdot 10^{-2}$
Zinc	300	1.3-26	$> 2. \cdot 10^{-1}$

agreement with the lower value ($1.7 \pm 0.8 \cdot 10^{-4}$) obtained by Pollack and Jones.[7]

Alumina and Aluminum

The present atom loss probability on alumina is significantly less than the value $2 \cdot 10^{-4}$ reported in Ref. 5. The data from which this earlier value was derived are illustrated by the dashed line in Fig. 1. It would appear that more rapid atom loss occurs in the region immediatiely downstream of the discharge, where the alumina tube is at a higher temperature (up to 150°C) and where electrons, ions, and energetic particles produced in the discharge may affect its catalytic properties.

Atom loss on aluminum not cleaned with acid occurred with an initial probability of $5 \cdot 10^{-4}$, which increased to ca. 10^{-3} after one-hour exposure to F-atoms at room temperature. Further increase with time was noted, and the aluminum tube therefore was cleaned with dilute HF, after which the value in Table 2 was obtained. No change in atom flow occurred when the central 20 cm of the aluminum tube then was heated to 285°C.

Both alumina and aluminum are expected to form passivating aluminum fluoride coatings. Then their atom loss probabilities should be approximately equal. The larger observed catalytic activity for aluminum may be due to the alloying element, copper, which is highly catalytic. Indeed, the atom loss probability for aluminum is approximately equal to its atom fraction of copper (~ 0.0011). Use of high-purity aluminum therefore might yield a much lower F-atom loss probability.

Steel and Nickel

The rate of atom loss on steel was constant within experimental uncertainty, whether or not the steel tube was cleaned with dilute HF. Also, F-atom flow rate remained constant when the central 20 cm of the steel tube was heated to 200°C. Thus, it may be concluded that atom loss on steel is independent of temperature up to 200°C. Although the surface composition was not determined, it would be expected that cleaning with dilute HF exposes a surface whose composition is characteristic of the bulk material. Thus, the results on steel suggest low catalytic activity up to 200°C for the principal alloy components, iron, nickel, and chromium. This conclusion is supported by the data on pure nickel, which showed no time-dependence over a period of one hour. However, the effects of acid cleaning or F-atom exposure at elevated temperature were not investigated for nickel.

Molybdenum

Although molybdenum showed a low catalytic activity that was constant over a period of one hour, the sample had not been cleaned with acid, and a higher activity might occur for samples that were prepared differently. Atom loss on molybdenum is expected to increase with temperature, since it has been demonstrated[2] that $\epsilon_F(\mathrm{Mo}) \sim 0.02$ at $T = 700\mathrm{K}$.

Copper, Brass, and Zinc

The initial atom loss probability on a new copper tube, which was not cleaned with acid, was small ($\sim 5 \cdot 10^{-4}$), but it increased with time, and was $\sim 4 \cdot 10^{-3}$ after two-hours exposure to F-atoms at room temperature and continued to increase with time. After heating to 300°C or cleaning with dilute HF or H_2SO_4, no F-atoms could be transmitted through the copper tube, even at increased flow rates. From estimated conversion $Q/Q_o < 0.01$ at $t \sim 0.008$ sec, one calculates $\gamma_F(\mathrm{Cu})_{\mathrm{app}} > 0.011$. Shorter catalyst tubes and high flow velocity were employed to obtain $\gamma_F(\mathrm{brass})_{\mathrm{app}} \sim 0.05$ and $\gamma_F(\mathrm{zinc})_{\mathrm{app}} \sim 0.2$. The correct values for these materials are clearly larger, because of the need for large diffusion corrections. However, such corrections are not attempted because the experimental conditions for copper, brass, and zinc deviate from those assumed in Eq. (2). For these active catalysts, atom loss occurs mainly by recombination; some reaction with the catalyst was observed, but reaction was insufficient to explain the large atom loss rates.

Discussion

The present F-atom loss probabilities on nickel, quartz, and pyrex are much smaller than those measured for other halogen atoms on these materials.[14,15] This result can be understood by considering the energetics of absorption and recombination. Chemisorbed F-atoms are expected to bind to the surface with energies greater than those for Cl-,Br-, or I-atoms. However, F_2 has a smaller dissociation energy than any other halogen, and recombination of chemisorbed atoms therefore may be endothermic for fluorine, but exothermic for other halogens. On the other hand, because of smaller Van der Waals forces for fluorine, the concentration of physisorbed F-atoms would be much smaller than that of other halogens. In either case, F-atoms would recombine more slowly than would other halogen atoms. The fact that fluorine poisons Cl-atom recombination on pyrex[5] also indicates that F-atoms are chemisorbed more strongly than are Cl-atoms. The same should be true for other halogens; thus, addition of small amounts of F_2 to discharges in Cl_2, Br_2, or I_2 probably would increase atom yield by reduction in heterogeneous atom losses.

Our results for aluminum and steel cover most of the surface temperature range of interest in water-cooled chemical laser nozzles (up to ca. 520K).[11] The use of these materials would reduce atom loss in these nozzles to a negligible value. For example, whereas Ferrell, Kendall, and Tong[10] compute an F-atom loss rate of 1.3 $\mathrm{lb/ft^2 \cdot sec}$ (6.4 $\mathrm{Kg/m^2 \cdot sec}$) at the throat of their fully catalytic "baseline" nozzle (where $p_F \sim 0.14$ atm), the kinetic theory permits a maximum F-atom loss rate of only $2.4 \cdot 10^{-3}$ $\mathrm{lb/ft^2 \cdot sec}$ ($1.2 \cdot 10^{-2}$ $\mathrm{Kg/m^2 \cdot sec}$) if $\gamma = 10^{-3}$, and the surface temperature is assumed to be 500K.

The potential benefits of reduced F-atoms losses in hydrogen fluoride chemical laser nozzles would include: 1) improved performance (higher efficiency, shorter mean reactant diffusion distances), 2) reduced complexity of design calculations (no recombination heat effects, uniform concentration at nozzle exit), and 3) simplified construction (use of contoured nozzles[10] to reduce atom loss would be unnecessary).

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