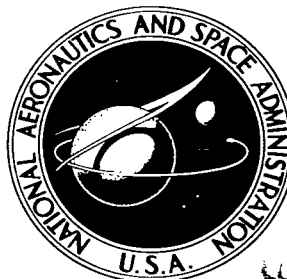


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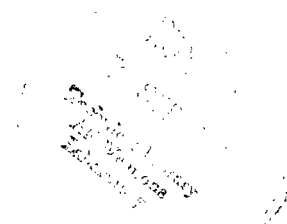
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KINETICS OF THE FLUORINATION OF IRON

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SUMMARY

The effect of temperature and pressure on the reaction of fluorine gas on solid iron samples was studied at various pressures up to 200 torr over the temperature range of 225^o to 525^o C. An activation energy of 2 kilocalories was calculated for the 60-torr pressure runs. The reaction was found to follow the logarithmic rate law, and logarithmic rate constants are reported. The probable mechanism of film growth is movement of fluorine through defects in the fluoride film to the iron surface.

INTRODUCTION

The purposes of this report are (1) to present the results of a kinetic study of the fluorination of iron in the temperature range of 225^o to 525^o C and (2) to propose a mechanism for this reaction. The kinetics of this reaction are interesting since the only data available in the literature are the corrosion type where the reaction of fluorine on iron has been observed by taking a few measurements at long incremental time periods and linearly extrapolating them to give results reported as inches of penetration per month or per year at varying temperatures (ref. 1). A linear extrapolation of this type does not give a detailed picture of the reaction but merely defines maximum gross effects. This kinetic study was, therefore, undertaken in order to observe the details of the reaction of fluorine on iron. A few detailed studies of the reaction of fluorine gas with other metals have been reported. By studying the reaction between copper powder and fluorine gas from room temperature up to 250^o C and at pressures up to 60 torr, Brown, Crabtree, and Duncan (ref. 2) found that the reaction obeys a logarithmic rate law and is not pressure dependent. This law is widely applicable to corrosion kinetics (ref. 3, pp. 829 to 835) and relates the amount of reaction y with time t by

$$y = K \log(at + 1) \quad (1)$$

where K and a are constants for a given system and temperature. In a study of the reaction of fluorine on plate copper (refs. 4 and 5), it was found that the reaction followed a logarithmic law above 538°C but that below that temperature a simple power law was applicable. The reaction was observed to be pressure dependent. Other studies have been made of the reaction kinetics of fluorine with copper (ref. 6), nickel (ref. 7), and zirconium compounds (ref. 8) under various conditions. Although there have been extensive kinetic studies of the rates of oxidation of iron, there are no similar studies on the rates of the fluorination of iron.

APPARATUS

The vacuum apparatus used to measure the rate of fluorination of iron is shown in figure 1. The reaction section is quartz heated by a Nichrome wound furnace. The temperature was measured with a Chromel-Alumel thermocouple. The ball joint connection on the end of the reaction section was nitrogen cooled. The analysis of the fluorine gas using the mercury reflux still method (ref. 9) was 100 percent fluorine after removal of 0.17 percent hydrogen fluoride in the methylcyclohexane slush cold trap. Soda lime traps were used to absorb residual fluorine left after a run. The mercury in the manometer was covered with a layer of fluorocarbon oil to protect the mercury from reacting with the fluorine gas. Ultra-dry argon, 99.998 percent pure as purchased, was used as the purge gas. All stopcocks and ground glass joints were lubricated with a fluorocarbon grease.

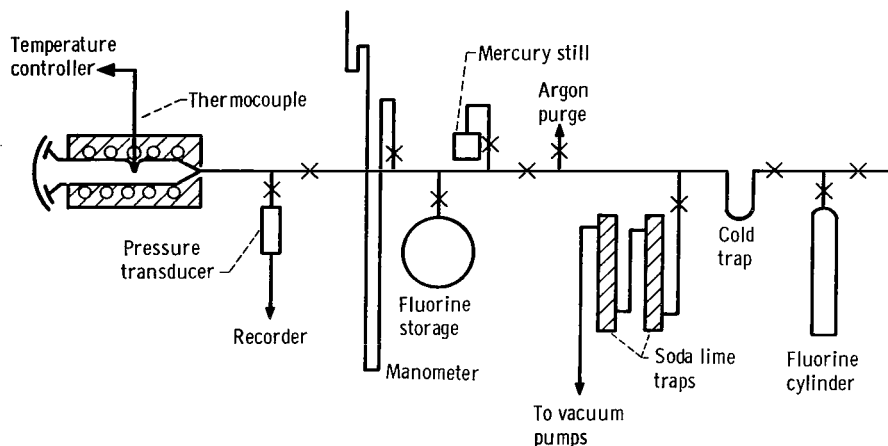


Figure 1. - Apparatus used for iron-fluorine kinetic studies.

EXPERIMENTAL

The general experimental method used to determine the rate of fluorine consumption by the iron was to measure the pressure decrease in a vessel of known volume containing the iron sample. In order to maintain approximately constant fluorine pressure, the pressure was allowed to drop only about 2 torr, whereupon additional fluorine was admitted to return the pressure to its initial value. The perfect gas law was used to calculate the amount of fluorine consumed after each of these steps, from the incremental pressure drop, the vessel volume, and the temperature. Fluorine consumed was expressed in milliliters at standard temperature and pressure. Standard volumetric procedures were used to calibrate the volume of the furnace, storage vessel, and connecting lines. The glass system was passivated by introducing fluorine at increasing pressures and temperatures until further reaction of fluorine with the system was insignificant. The blank after passivation represented a correction of less than 1 percent.

To determine the temperature gradient along the iron strip, a special strip was made with eight Chromel-Alumel thermocouples attached along it. The leads came through a special end plug to a recording system. The temperature profile along the strip varied $\pm 0.5^{\circ}\text{C}$ at the low temperatures and $\pm 3^{\circ}\text{C}$ for the 525°C temperature in a nitrogen atmosphere.

The iron samples were machined from spectrographically pure iron having the following impurities in parts per million: manganese, 2; silicon, 2; magnesium, 1; nickel, 1; silver, 1; and copper, 1. The samples were 1.27 by 15.24 by 0.012 centimeter with a 0.5-centimeter hole drilled in one end to facilitate handling. All samples were degreased in trichloroethylene, cleaned in 20 percent hydrochloric acid for 3 minutes, and washed in distilled water, acetone, and alcohol. The samples were immediately inserted into the furnace under flowing argon and were positioned the same for each run. The system was sealed and pumped down to about 0.1-micron pressure. All samples were preheated 0.5 hour at 525°C under vacuum before running. After the pretreatment, the temperature was adjusted to the operating temperature and fluorine was introduced to the desired pressure.

When the consumption of fluorine had decreased to a negligible value, the heaters were turned off, the system was allowed to cool to 25°C , and the fluorine was pumped out of the system through the soda lime traps. The test sample was removed to a glass tube holder, which was attached to the end of the reaction section, and was sealed under flowing argon for later visual and instrumental analysis. Some of the films scraped from the strips were analyzed by X-ray diffraction.

For cross-sectional analysis, samples were embedded in plastic, cut, and polished. They were then examined on a metallograph and photographed. The cross section was etched and dyed in order to determine if there was any grain boundary attack. Micro-

TABLE I. - SUMMARY OF TEMPERATURE AND PRESSURE CONDITIONS AND CALCULATED LOGARITHMIC RATE CONSTANTS

Temperature, °C	Pressure, torr	Logarithmic rate constant, ml/sq cm
225	60 ↓	0.024
275		.026
325		.029
375		.031
425		.057
525	↓	.064
225	20	.016
225	60	.024
225	200	.046
525	15	0.022, 0.013
525	60	.064
525	100	.089

scopic analysis was performed to reveal the topology of the samples.

RESULTS AND DISCUSSION

The fluorine consumption by the iron samples was measured at several temperatures and pressures (table I). Figures 2 and 3 illustrate the results; the milliliters of fluorine consumed per square centimeter of iron surface are plotted against the time in minutes. Some duplicate runs (solid symbols) have been plotted in order to show the reproducibility of the data. The effect of temperature on the reaction is shown in figure 2 where the data are plotted at temperatures from 225° to 525° C at a constant pressure of 60 torr. Figures 3(a) and (b) show the effect of pressure on the reaction. In figure 3(a) the pressure effect is plotted at a constant temperature of

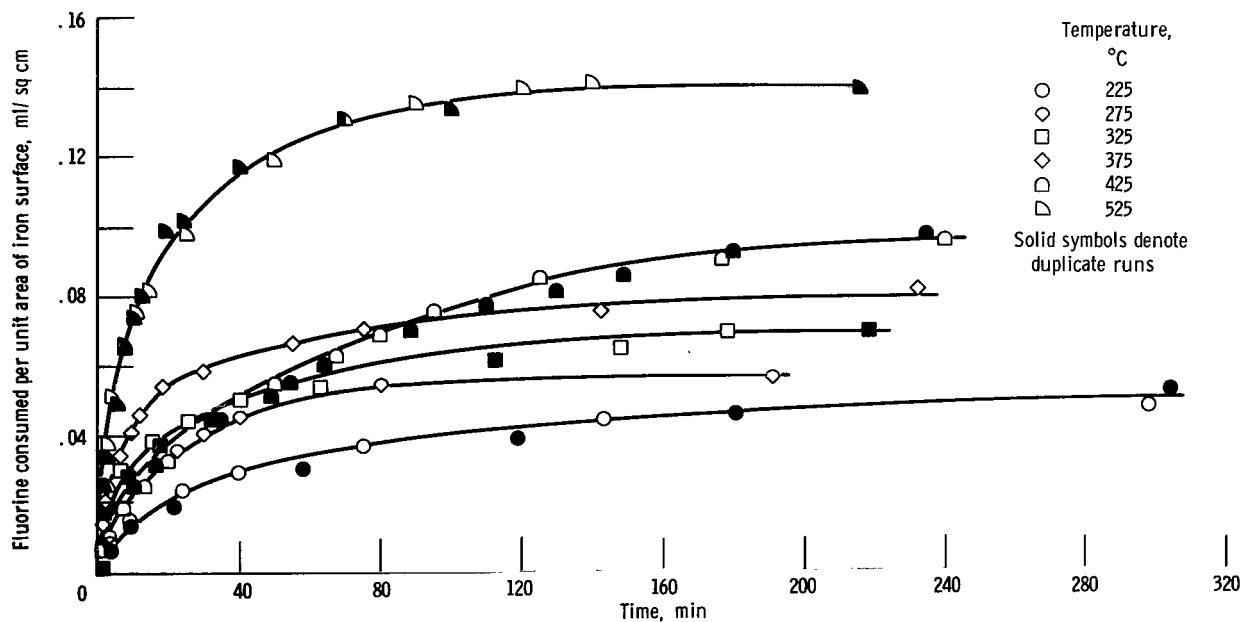


Figure 2. - Effect of temperature on fluorination of iron at 60 torr.

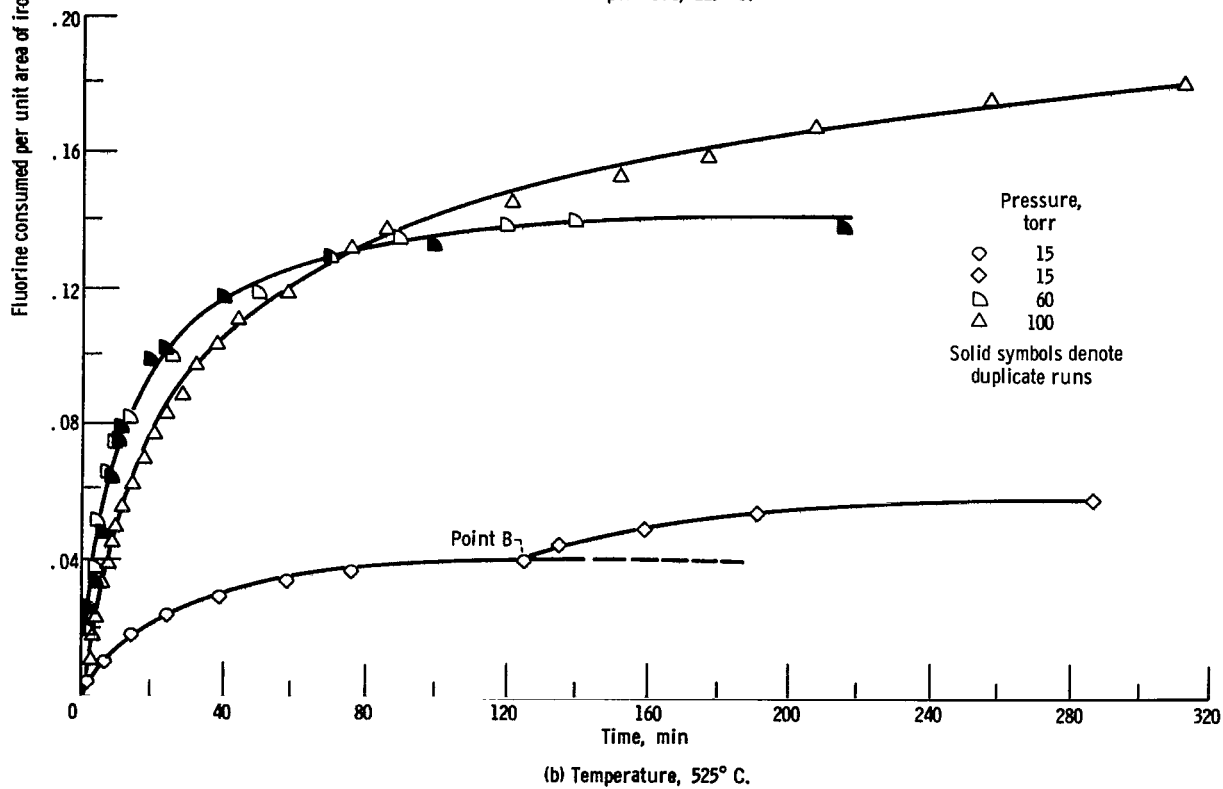
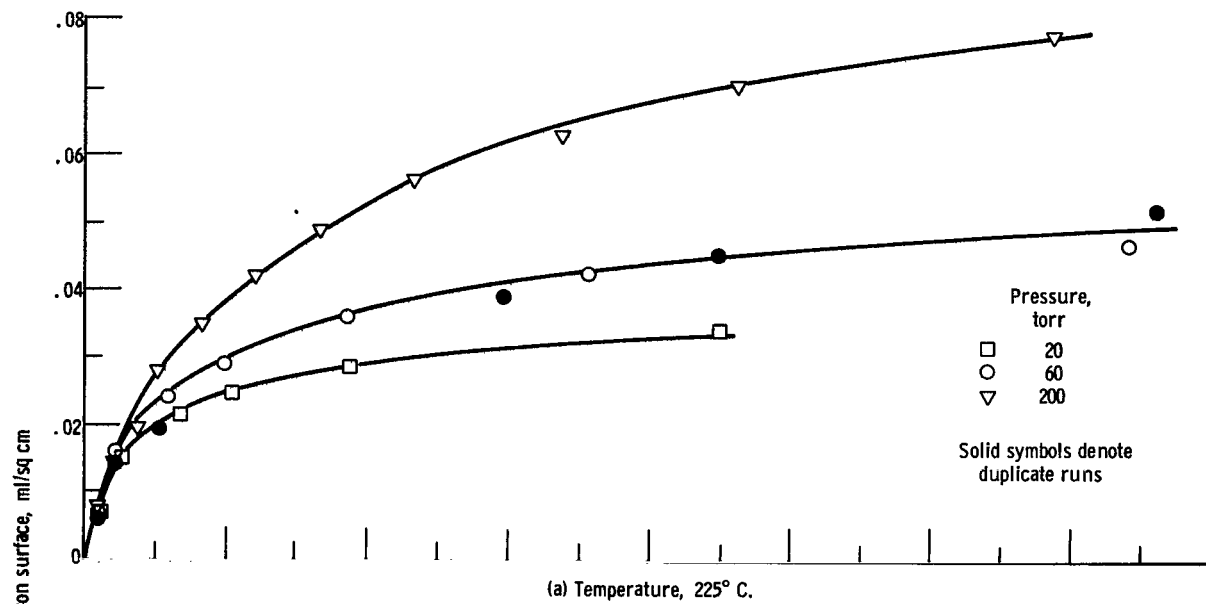


Figure 3. - Effect of pressure on fluorination of iron.

225° C and in figure 3(b) at a constant temperature of 525° C. In the 525° C 15-torr run (fig. 3(b)), the fluorine was pumped out after 125 minutes while the sample was kept at 525° C in order to determine the effect of heat and vacuum on the reaction. New fluorine was introduced to 15 torr (point B) and the reaction appeared to start again. Copper plate and fluorine showed similar behavior (ref. 5); however, the reaction between copper powder and fluorine did not start again under similar conditions (ref. 2).

Product Identification and Volume Ratio

X-ray diffraction patterns were run on both the low and high temperature films and the product was identified as ferric fluoride (FeF₃); no ferrous fluoride (FeF₂) was detected. The overall reaction may be described by



In this reaction, the fluoride occupies a larger volume than the metal destroyed. The volume ratio (ref. 10) is defined as $\Phi = Wd/wD$ where W is the molecular weight of the film formed, w the formula weight of the metal, D the density of the film formed, and d the density of the metal. The volume ratio Φ for this reaction has a value of 4.9 at 25° C.

The Logarithmic Equation

The data from figures 2 and 3 are replotted in figures 4 and 5 in the form log time as a function of fluorine consumed. The straight lines shown on figures 4 and 5 fit a logarithmic equation that is similar to equation (1). This equation is

$$y = K(\log at) + c \quad (3)$$

where

y fluorine consumed (at STP), ml/sq cm

t time, min

K logarithmic rate constant

a constant with dimensions of reciprocal min

c intercept

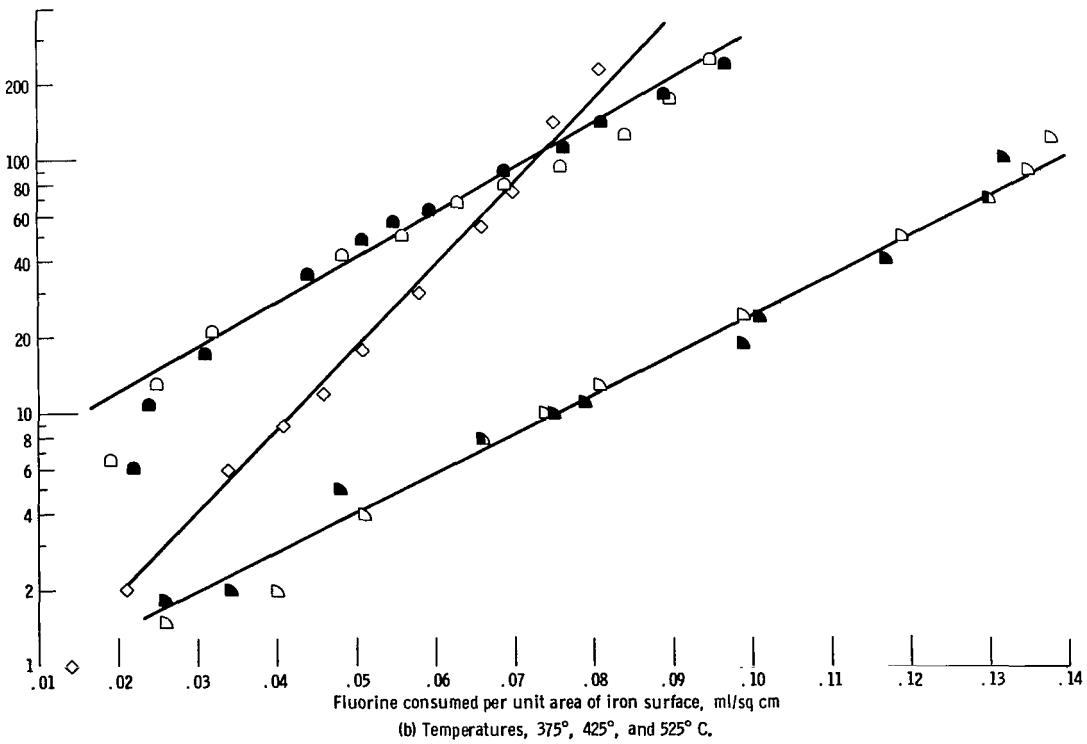
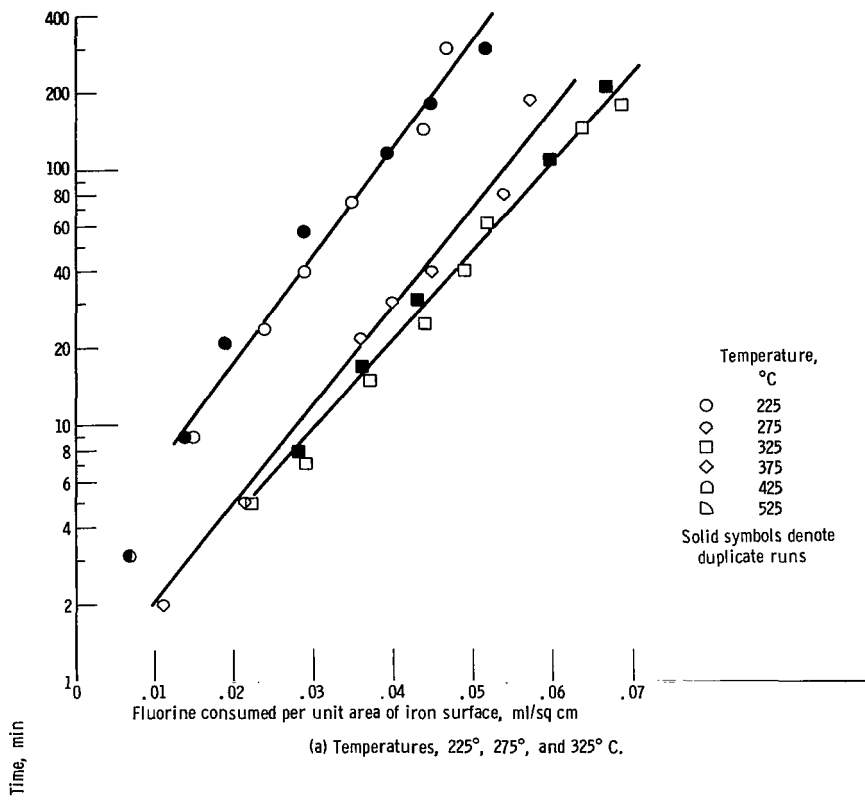


Figure 4. - Temperature effect at 60 torr.

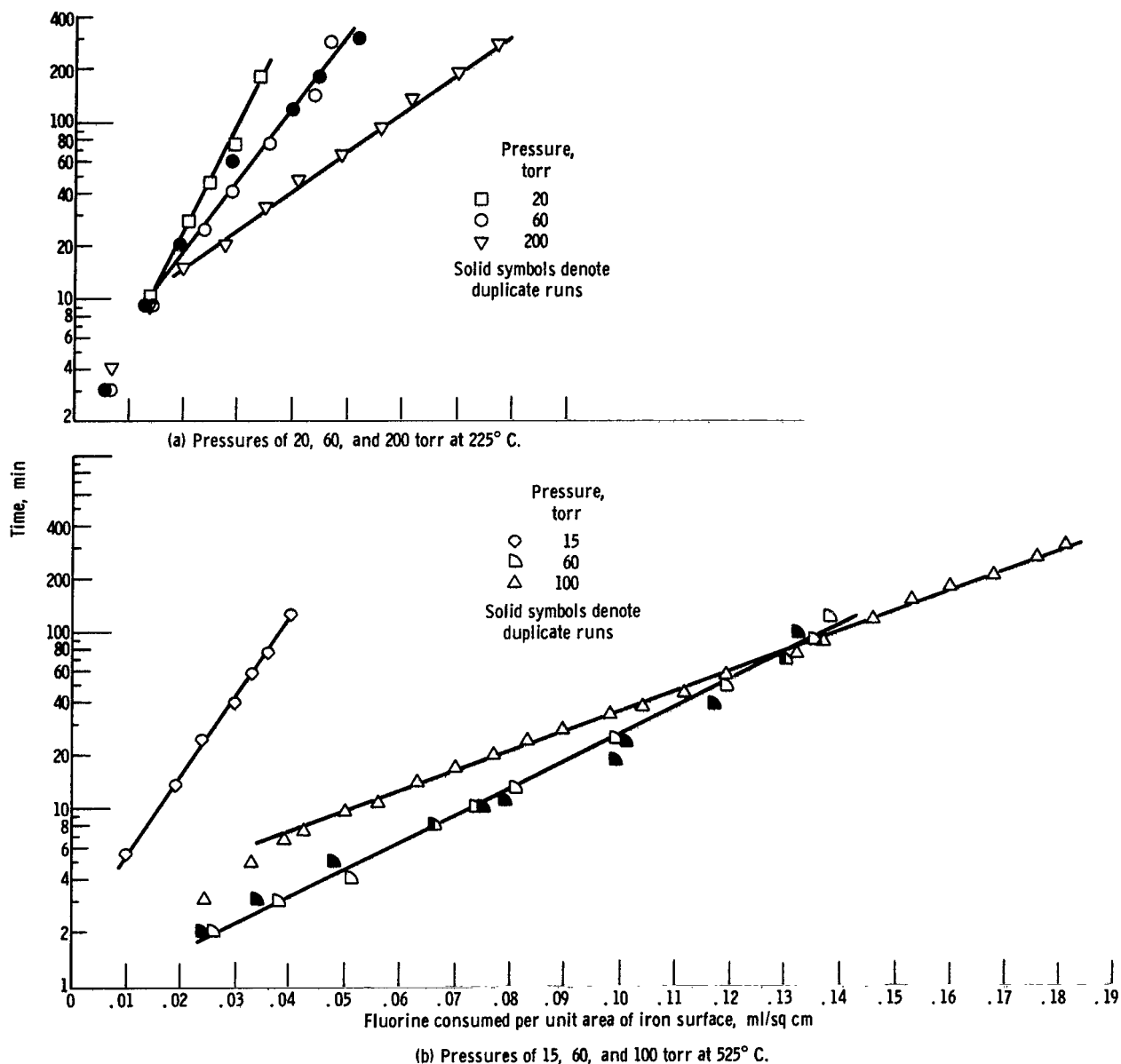


Figure 5. - Pressure effect.

The constant a is unity for the lines drawn on figures 4 and 5. The intercept c implies a finite induction period, but the data at short times deviate from the straight line so that a measurable induction period does not really exist. Figure 4 shows the data at constant pressure of 60 torr for various temperatures. In figure 5(a) the 225° C data are plotted at 20, 60, and 200 torr, and in figure 5(b) the 525° C data are plotted at 15, 60, and 100 torr showing the effect of pressure at constant temperature. It can be seen that the logarithmic equation fits all the data within the experimental error except at short times. Figure 3 indicates that heat and vacuum have an effect on the passivity of the metal strip.

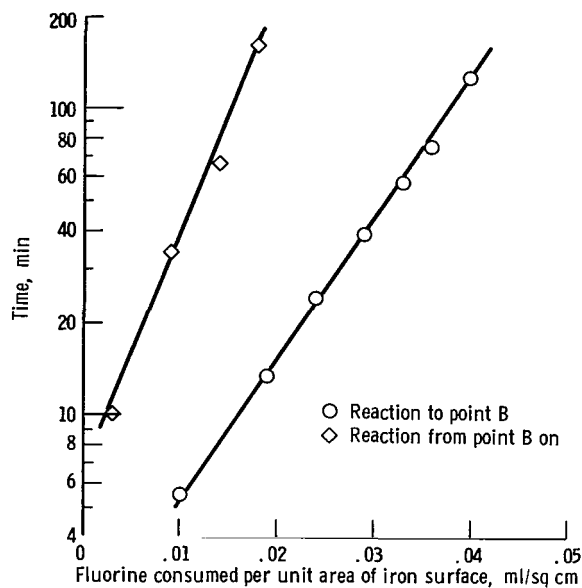


Figure 6. - Interrupted fluorination of iron at 525° C and 15 torr.

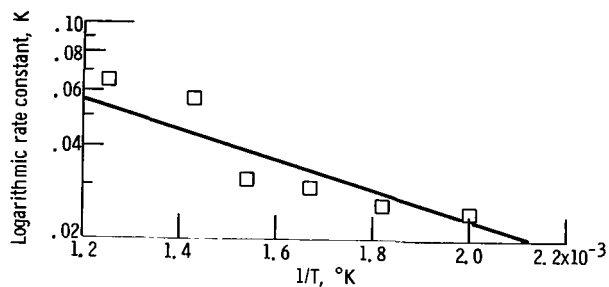


Figure 7. - Effect of temperature on rate constant at 60 torr.

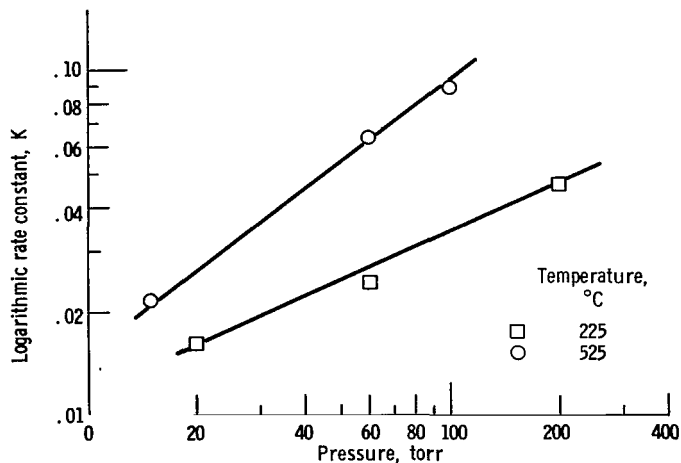


Figure 8. - Effect of pressure on rate constant.

At point B the metal strip had reached a point of negligible reactivity (passivation); however, when subjecting it to heat and vacuum and then to fluorine again it appears to lose some of its passivation. Figure 6 shows both parts of the 525° C run at 15 torr plotted according to the logarithmic equation. The two lines on figure 6 were obtained by plotting the fluorine consumption against log time for the reaction to point B (fig. 3(b)) and by plotting the reaction from point B on by considering the fluorine consumption for this second part of the reaction as the difference between reaction 1 (dashed line) and reaction 2 and B as the zero time point for reaction 2. The rate for this second reaction is, however, lower than the original rate. The values of K for these reactions are 0.022 and 0.013 milliliter per square centimeter, respectively, and are listed in table I (p. 4) along with the values of the other rate constants.

From the data of figures 2 and 3 (pp. 4 and 5), the reaction between iron and fluorine is seen to be both temperature and pressure dependent. The activation energy plot is shown in figure 7, where the logarithm of the logarithmic rate constant at 60 torr is plotted against the reciprocal of the absolute temperature. An activation energy of 2 kilocalories was calculated for the reaction at 60 torr.

The effect of pressure on the logarithmic rate constant is shown in figure 8, where the log of this constant is

plotted as a function of pressure at constant temperature according to the equation $\log K = m \log P + B$. The slope m is the order of the reaction with respect to the fluorine pressure. At 525°C , m has a value of 0.87, and at 225°C m is 0.48.

Metallographic Studies

Cross sections of the fluorine-corroded iron strips were prepared by standard metallographic techniques. Photomicrographs of typical cross sections are shown in figure 9.

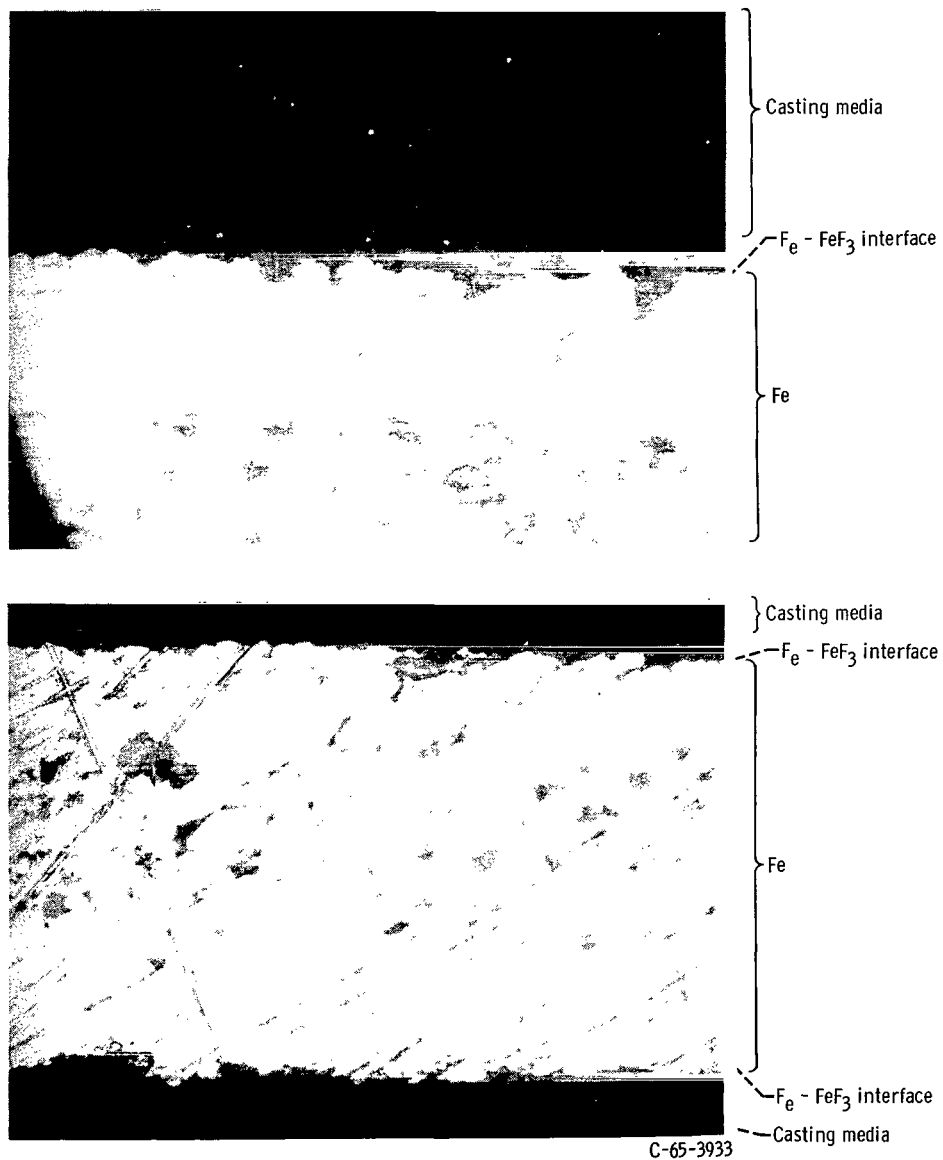


Figure 9. - Cross-section views ($\text{Fe} + \text{F}_2$ at 525°C). X500.

These photographs show that the boundary between the fluoride and the iron is very sharply defined. The fluoride film does not grow preferentially along grain boundaries in the iron. This was confirmed by etching and staining of polished cross sections. Near the iron - fluoride interface, the fluoride appears to be uniformly dense. Near the surface of the fluoride film, the fluoride appears somewhat broken and imperfect. This is to be expected, since the fluoride film occupies a volume 4.9 times larger than the iron from which it is formed, and this volume expansion must result in stresses which can fracture the film when it is thick enough.

Mechanism of Fluorine Attack

The rate-determining process in growth of corrosion films on metals can be deduced by consideration of the growth law of the film. For example, if the film grows by diffusion of lattice vacancies through the film, the film thickness will increase with the square root of time. In the experiments reported here, the fluorine uptake, and hence the film thickness, varied directly with the logarithm of time except at short times, where the film thickness is less than about 350 Å. Theoretical analyses (ref. 3) have shown that such a direct logarithmic dependence can arise from either of two mechanisms: (1) when the growth rate is controlled by tunneling of electrons through the film, or (2) when the growth rate is controlled by passage of gas through pores or other defects in the film to the metal surface. Tunneling is important only for films thinner than a few hundred angstroms. The film thicknesses in this research were much larger, so that this mechanism can be discarded. The second mechanism, that of passage of gas through pores in the film, is the most likely process. The pores through which the gas moves may be the intersection of three grains, the intersection of two slip-planes, screw and edge dislocations, or simply fractures in the film. When the compressional stress in one pore exerts a pressure on neighboring pores, some of these will be blocked as the film grows. This is the case of mutually blocking pores, and leads to the direct logarithmic growth law as found in this research. At low temperatures, the logarithmic law is found to be obeyed for the oxidation of iron and copper, where the expansion which occurs when metal is transformed to oxide tends to close up neighboring pores. In this research, the fluoride occupies a volume 4.9 times that of the metal from which it is formed, so that mutual blockage by compression can be expected. It is concluded that above a film thickness of about 350 Å the fluoride film on the iron grows by passage of fluorine through pores in the film, and that these pores tend to block one another as the film thickness increases.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 25, 1966.

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