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16. Abstract

The reaction between zinc metal and fluorine gas can be described by a parabolic rate law This reaction is both temperature and pressure dependent. Simple kinetics are complicated by the considerable vaporization rate for zinc at temperatures above 300° C (573 K).

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KINETICS OF THE FLUORINATION OF ZINC

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SUMMARY

The reaction between zinc metal and fluorine gas was studied over the temperature range of 100° to 400° C (373 to 673 K) and at pressures from 6 to 83 kilonewtons per square meter (50 to 625 torr). At all temperatures and pressures the rate follows a parabolic equation. The parabolic rate constant is markedly pressure dependent. Above 300° C (573 K) simple kinetics are complicated by zinc vaporization. At low temperatures an activation energy of 11.7 kilojoules (2.8 kcal) per mole was calculated; however, a break was observed in the Arrhenius plot at $\sim 300^{\circ}$ C (573 K). There is a clear change in the nature of the temperature dependence due to a change in mechanism between the low temperature region and the high temperature region.

INTRODUCTION

The reaction of fluorine with zinc is reported by Haendler (ref. 1); he determined the structure and density of zinc fluoride (ZnF_2) from X-ray powder patterns. Some thermodynamic studies report calculated heats of formation of the transition halides and compare them with experimental results (ref. 2). A discussion of the entropies and enthalpies of gaseous metal dihalides is presented along with other thermodynamic properties by Brewer in reference 3. Although some corrosion studies have been reported (ref. 4), no kinetic studies have been reported on the reaction between fluorine and zinc. It is therefore of interest to study this reaction from a kinetic point of view and to elucidate the gas solid reaction mechanism (including the formation of ZnF_2, its temperature dependence, and its pressure dependence) and to compare the results with those for the zinc-oxygen reaction (refs. 5 and 6).

EXPERIMENT

The fluorination apparatus used in this study and shown in figure 1 is identical to that used previously (ref. 7). The samples consisted of zinc strips 0.152 by 0.012 by 0.0001 meter (6 by 0.5 by 0.005 in.) with a hole in one end to facilitate handling. An emission spectroscopic analysis (in ppm) of the strips is as follows: cadmium, 0.2; calcium, 0.1; chromium, 0.2; copper, 0.1; iron, 0.1; lead, 3; magnesium, <0.1; silicon, 0.1. The strips were used as received in an oxide-free condition, they were stored in an inert atmosphere dry box.

A strip is positioned in the furnace on its long side so that the fluorine exposure is uniform as shown in figure 1. The section is then closed, heated, and filled with fluorine. The pressure drop method used to follow the reaction is described in reference 8. This method is used to measure the pressure decrease with time in a vessel of known volume containing the zinc sample. The pressure is incrementally adjusted to its original value to eliminate an internal pressure effect. The amount of fluorine consumed during the course of the reaction can be calculated by assuming ideal gas behavior and by using the calibrated volume of the reaction chamber, the temperature, and the observed pressure drop values. Corrections are applied for the difference in density of the protecting oil floated on the mercury columns and the mercury in the manometers. Measurements are made at different temperatures and pressures and the results are recorded as a function of time with a strip chart recorder.

RESULTS AND DISCUSSION

The reaction between zinc and fluorine was studied at several conditions in order to determine the effect that both temperature and pressure had on the reaction. The temperature range studied was from 100° to 400° C (373 to 673 K). The reaction was run at several different pressures; the lowest pressure was 6 kilonewtons per square meter (50 torr) at 350° C (623 K), and the highest was 83 kilonewtons per square meter (625 torr) at 100° C (373 K).

Since the molar volume ratio of ZnF_2 to zinc (V_{ZnF_2}/V_{Zn}) is 2.29, a protective layer should be formed on the surface of the zinc metal; thus, further reaction is inhibited (ref. 9). If a linear plot of the fluorine consumed in milliliters of fluorine per square centimeters of zinc against time in minutes is made (fig. 2), it can be seen that the reaction is in fact inhibited as the film forms over the range of temperature studied. Further analysis of this data shows that a power law of the form

$$y^n = kt \tag{1}$$

where

y fluorine consumed, ml/cm^2

t time, min

k rate constant, $(ml/cm^2)^n/min$

n exponent of reaction

is followed. In figure 3 the log of fluorine consumed (in ml/cm^2) against log time is plotted. The slopes of the low temperature lines are equal to 2±0.2; this indicates that the reaction follows a parabolic rate law at these temperatures and times up to 100 minutes. The dashed line in figure 3 indicates a transition from the parabolic rate law at long times. The fluorine pressure was varied for several temperatures to determine what effect pressure had on the reaction. The data are plotted in figures 4 and 5 for 100° and 350° C (373 and 623 K).

The reaction between fluorine and zinc forms only one fluoride which is an adherent film: it is the formation rate of this fluoride that is of interest. Since the law which describes the reaction has been determined, it is possible to calculate rate constants for the different temperature and pressure conditions studied. The rate constants calculated from the data at different fluorine pressures and temperatures are shown in table I. If the data at a specified temperature are plotted against pressure (fig. 6), the parabolic rate constant is found to be markedly pressure dependent according to the equation $K_p = aP^m$, which is similar in form to a generalized Langmuir isotherm. The value of m at 100° C (373 K) is ~5 while the value of m at 350° C (623 K) is ~2. Moore and Lee (ref. 6) found the reaction of zinc with oxygen to be pressure dependent with a value of $m = 1$ where an abrupt change in the temperature dependency of the parabolic rate constant is observed. The plot of 26 kilonewton per square meter (200 torr) rate constants according to an Arrhenius plot in which the logarithm of the rate constant k_p is plotted against the reciprocal temperature is shown in figure 7 for a constant pressure of 26 kilonewtons per square meter (200 torr) of fluorine. An interesting break is observed in the curve at approximately 300° C (573 K). This break indicates that the processes involved in the reaction change over the temperature range studied and that this change manifests itself in a significant change in the rate of the reaction.

A change was observed in the mechanism of the oxidation of zinc at about this same temperature (ref. 6). There is a low activation process with a ΔE_a of 11.7 kilojoules (2.8±0.7 kcal/mole) and a distinct change in the rate determining process of the reaction at higher temperatures. The temperature at which this break occurred was approximately 300° C (573 K). This temperature coincided with two other observed phenomenon. These were the loss of ductility of the metal strips and the formation of platelets during the reaction.

A microscopic examination indicated a surface variation between those strips fluorinated at low temperatures and those fluorinated at high temperatures. The metallographic pictures shown in figure 8 are (a) low temperature and (b) high temperature surfaces at a magnification of 100. On the high temperature runs the surface always had five- and six-sided platelet formation. The formation of platelets is attributed to a vaporization and recrystallization reaction (refs. 9 and 10). Weight loss data indicated that the rate of vaporization was approximately 0.1 gram per hour. Other samples of zinc were run using a pressure of argon to simulate the conditions of the zinc fluorine runs. Again from weight loss data the vaporization was shown to decrease as the argon pressure was increased. At a high enough pressure the vaporization was eliminated. The problem becomes a boundary layer diffusion problem, and the zinc vaporization becomes an important step. In the zinc fluorine studies the samples completely disintegrated at temperatures above 400° C (673 K).

The vaporization reaction was studied independently by running zinc strip blanks at several temperatures under vacuum. At approximately 300° C (573 K) the zinc strips showed a loss of ductility, and at 350° C (623 K) some of the zinc had actually vaporized and redeposited on the cool end plug of the furnace. The conclusion is that there is a complex pressure effect dependent on temperature which changes the simple gas-solid interface reaction to one involving several steps - mass transfer through a gaseous boundary layer surrounding the solid, diffusion through the product layer, and a chemical reaction step. This complexity is exhibited by a slope change as the temperature approaches the point where zinc vaporization becomes the predominent reaction. The reacting gas now not only has to react at the reaction surface but it must find its way through a vaporized layer at the surface to do so. Since an X-ray analysis of the surface of the metal after reaction indicated ZnF_2 on the surface and the microscopic examination showed platelet formation, the reacting species must condense on the surface as the reaction step.

Comparing the reaction between zinc and fluorine with that reported between zinc and oxygen up to 400° C (673 K) shows that both follow a parabolic reaction (ref. 11). However, the rate of the zinc oxygen reaction is considerably lower; reported rate constants were of the order of 10^{-14} $ml^2cm^{-4}min^{-1}$ (ref. 5) and an activation energy of 167.3 kilojoules (~40 kcal/mole (ref. 6)) for the oxygen zinc reaction. The reaction of zinc with oxygen has been explained by the diffusion of interstitial zinc ions. At low temperatures the reaction has been reported to be logarithmic rather than parabolic. A break in the temperature-rate curve was observed in the oxidation reaction (ref. 12) at about 225° C. This was attributed to a change in the nature of the zinc oxide from amorphous to crystalline with an increase in compactness. Whether a similar explanation is applicable with the fluorine reaction cannot be said.

CONCLUSIONS

The formation of zinc fluoride can be described by a parabolic reaction. It is both pressure and temperature sensitive and at temperatures above 300° C (573 K) a complex reaction due to zinc vaporization is involved. The rates of reaction are considerably higher than those reported for the oxidation of zinc by molecular oxygen.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 2, 1975,
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TABLE I. - CALCULATED PARABOLIC RATE

CONSTANTS FOR THE REACTION

BETWEEN ZINC AND FLUORINE

Temperature		Pressure		K_p, $ml^2\text{-}cm^{-4}\text{-}min^{-1}$
^oC	K	kN/m^2	torr	
100	373	26	200	$1.3\times10^{-6} \pm 0.1\times10^{-6}$
↓	↓	52	400	$3.7\times10^{-5} \pm .1\times10^{-5}$
↓	↓	83	625	$1.2\times10^{-4} \pm .2\times10^{-4}$
200	473	26	200	$3.8\times10^{-6} \pm .2\times10^{-6}$
300	573	26	200	$4.7\times10^{-6} \pm .7\times10^{-6}$
350	623	6	50	$2.4\times10^{-5} \pm .2\times10^{-5}$
350	623	26	200	$3.5\times10^{-4} \pm .3\times10^{-4}$

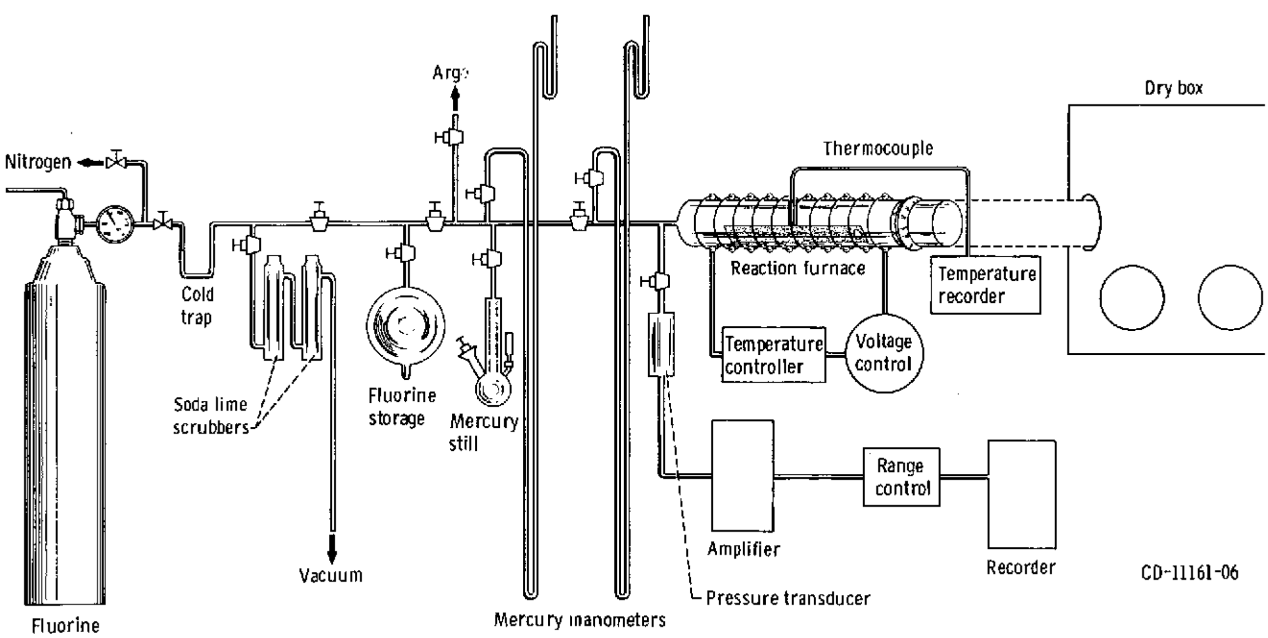


Figure 1. - Fluorination apparatus.

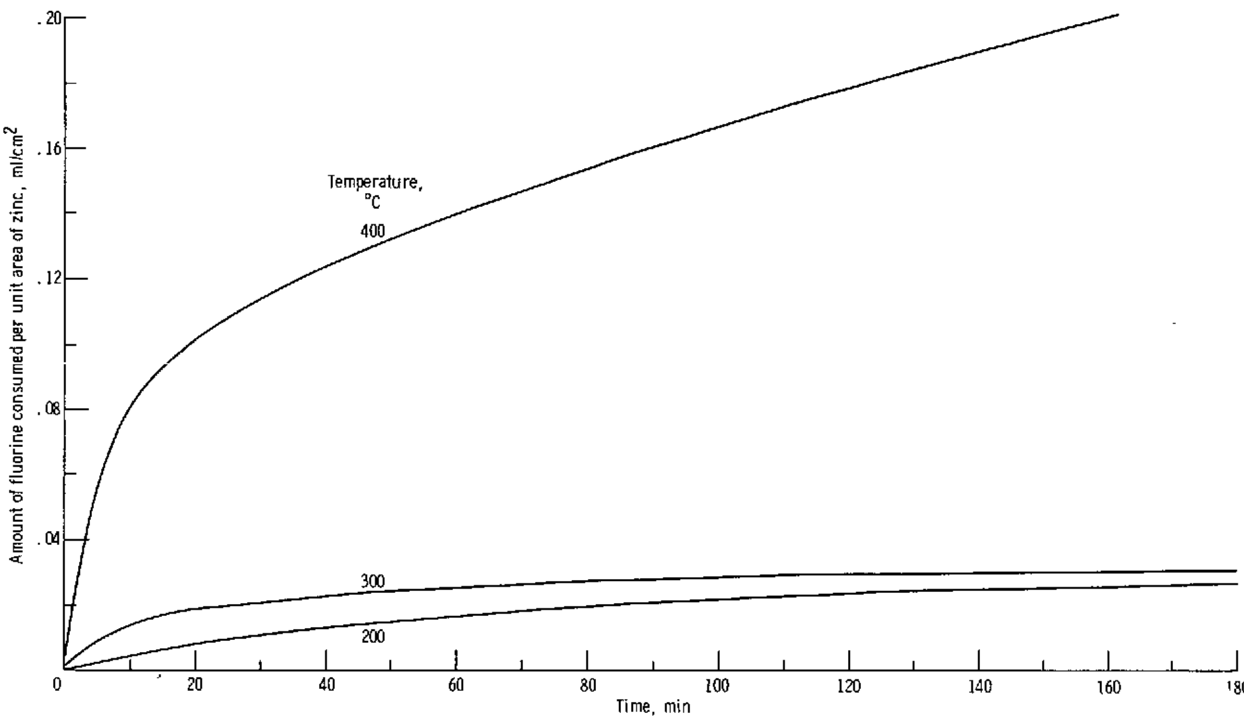


Figure 2. - Fluorination of zinc at constant pressure of 26 kiloneutons per square meter.

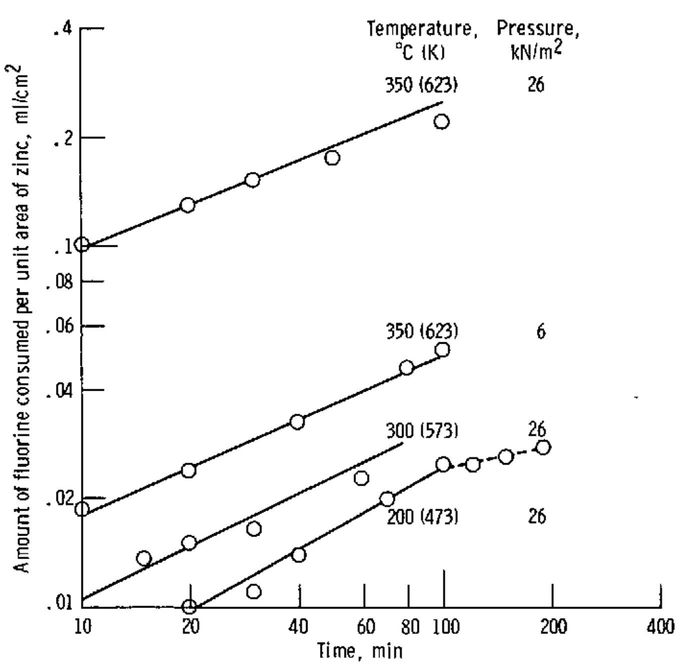


Figure 3. - Fluorination of zinc at 200° to 350° C.

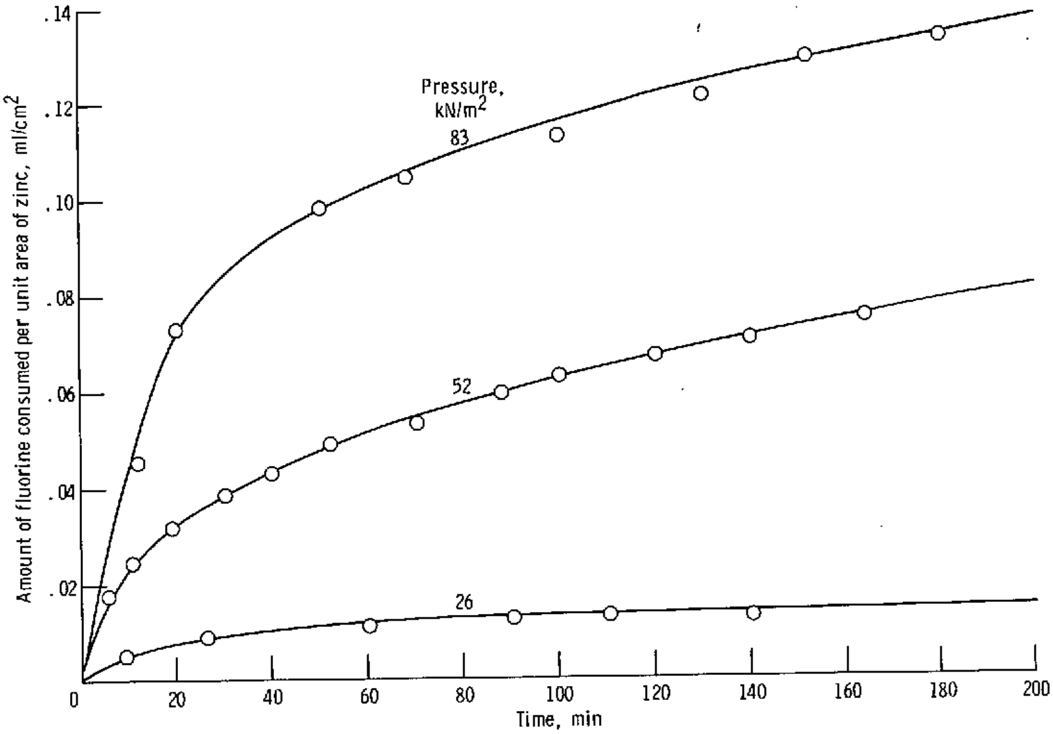


Figure 4. - Fluorination of zine at 100° C.

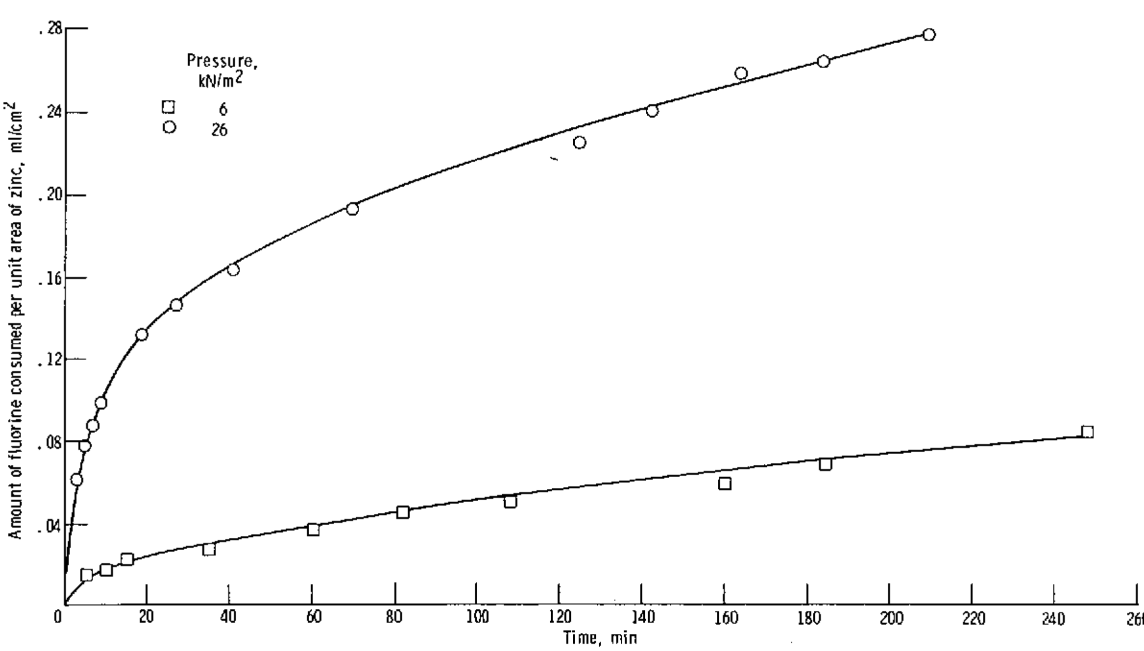


Figure 5. - Fluorination of zinc at 350° C.

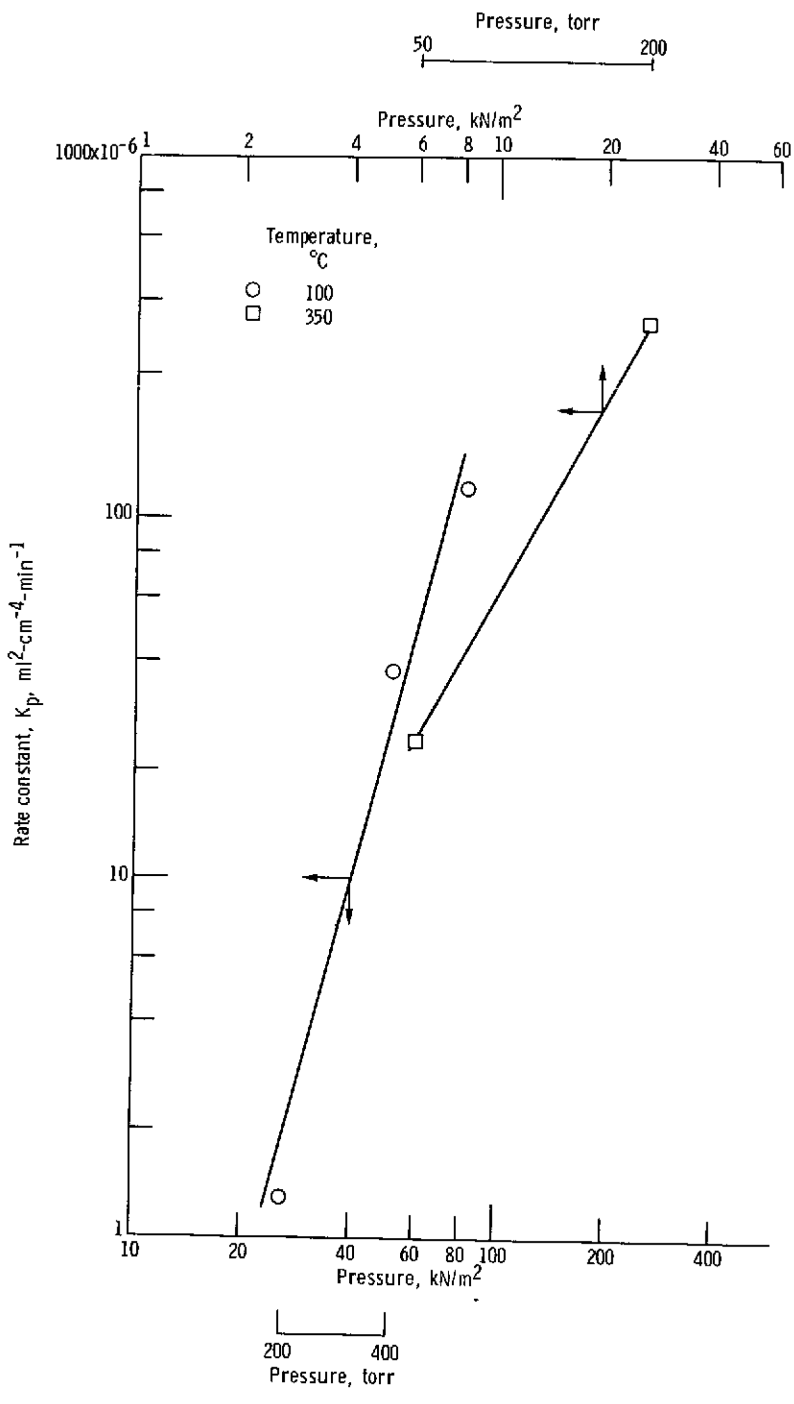


Figure 6. - Effect of pressure on rate constant.

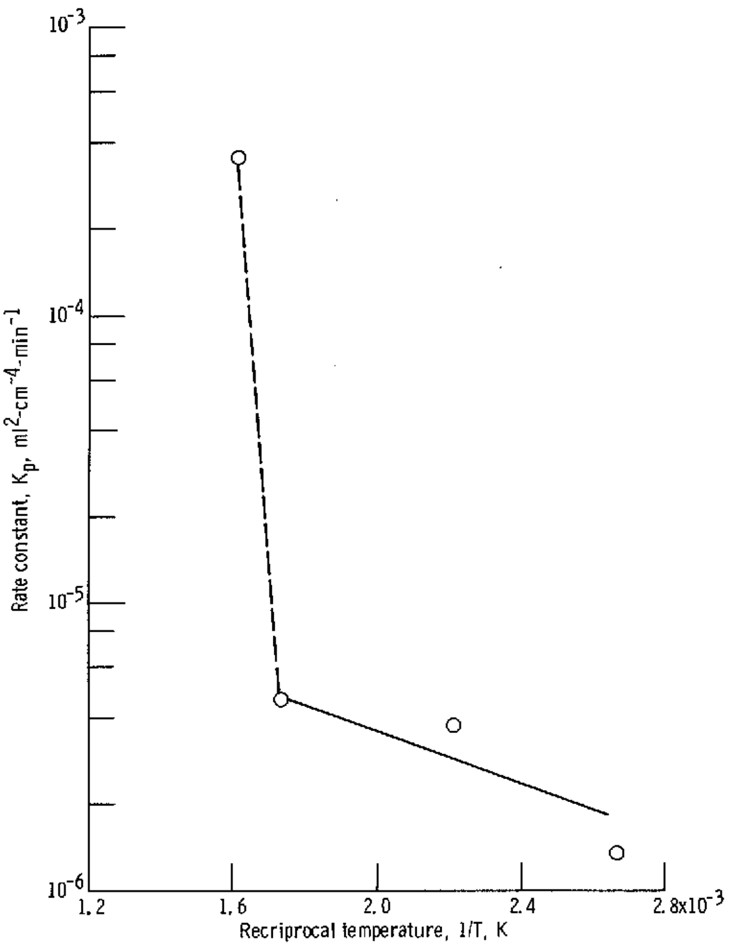
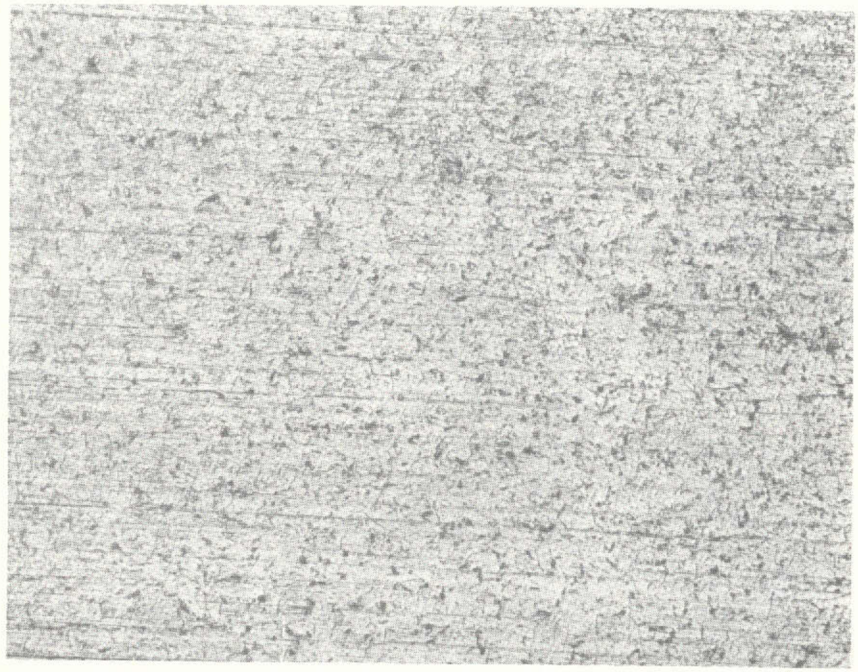
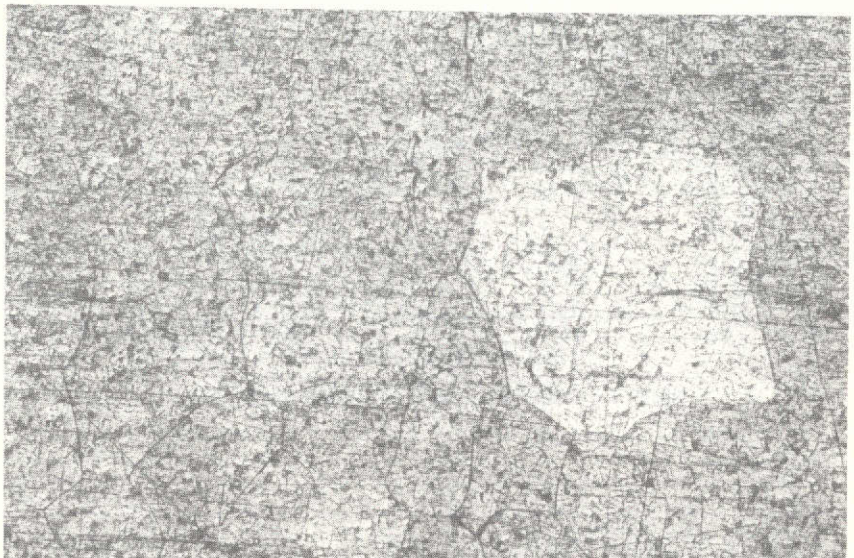


Figure 7. - Effect of temperature on parabolic rate constant.



(a) Temperature, 100° C (373 K).



(b) Temperature, 350° C (623 K).

Figure 8. - Zinc surface after reaction. X100.