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KINETICS OF THE REACTION OF ELEMENTAL FLUORINE WITH ZIRCONIUM CARBIDE AND ZIRCONIUM DIBORIDE AT HIGH TEMPERATURES

ZrC and ZrB_2

MASTER

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INTRODUCTION

Although there have been extensive studies of rates of oxidation and nitridation of metals and compounds, there have been very few studies of reaction rates with fluorine. Haendler et al[1-5] have, however, investigated the reaction of fluorine with several metals and some of their compounds in an attempt to synthesize and characterize metallic fluorides. They observed that fluorine reacts with zirconium metal above 190° and that the fluoride coating prevents complete reaction. They also noticed that zirconium dioxide does not react with fluorine at 100°, but converts to zirconium tetrafluoride above 250°C. There have also been several other reports[6-17] on the interaction of fluorine

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1. H. M. Haendler and W. J. Bernard, J. Am. Chem. Soc. 73, 5218 (1951).
2. H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, J. Am. Chem. Soc. 74, 3167 (1952).
3. H. M. Haendler, S. F. Bertram, R. S. Becker, W. J. Bernard, and S. W. Bukata, J. Am. Chem. Soc. 76, 2177 (1954).
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6. R. M. Gunzik and C. E. Feider, NACA-TN-3333, September, 1954.
7. L. Stein and R. C. Vogel, ANL-5441, May, 1955.
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11. G. L. Ericson, W. K. Boyd and P. D. Miller, NP-6729, April, 1958.
12. E. L. White and F. W. Fink, "Proceedings of the Propellant Thermodynamics and Handling Conference," pp. 161-81, Special Report 12, Engineering Experimental Station, The Ohio State University (1959).
13. C. F. Hale, E. J. Barber, H. A. Bernhardt, and K. E. Rapp, K-1459, September, 1960.

14. F. W. Fink, TID-5935, May, 1960.
15. R. B. Jackson, Final Report NP-8845, Allied Chemical Corporation, General Chemical Division, New York, 1960.
16. F. W. Fink, TID-13206, June, 1961.
17. A. P. Litman and A. E. Goldman, ORNL-2832, June, 1961.

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under different conditions, with various types of materials. As for kinetic studies with metals, the reaction of fluorine with copper[18,19]

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18. P. M. O'Donnell and A. E. Spakowski, NASA Technical Note D-768, April, 1961.
19. P. E. Brown, J. M. Crabtree, and J. F. Duncan, J. Inorg. and Nucl. Chem. 1, 202 (1955).

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and nickel[20-22] have been worked out in some detail.

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20. R. K. Steunenberg, L. Seiden, and H. E. Griffin, ANL-5924, (1958).
21. R. L. Jarry and W. H. Gunther, ANL-6477 (1961).
22. C. F. Hale, E. J. Barber, H. A. Bernhardt, and K. E. Rapp, AECD-4292, July, 1959.

The reactions between fluorine and ZrC and ZrB_2 are complicated because of the variety of possible solid and gaseous products. Also, ZrF_4 sublimes above 600°C.[23-25] Zirconium carbide is known to be

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23. K. A. Sense, M. J. Snyder, and J. W. Klegg, Rept. AECD-BMI 3708 (1953).
24. K. A. Sense, M. J. Snyder, and R. B. Filbert, J. Phys. Chem. 58, 995 (1954).
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decomposed by halogens and oxidizing agents,[26] in general, and hence,

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26. P. Schwarzkopf and R. Kieffer, in "Refractory Hard Metals," p. 95, MacMillan Company, New York, 1953.

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a rather vigorous exothermic reaction is to be expected with fluorine. However, no previous data are available on the rate of reaction of fluorine with ZrC and ZrB_2.

APPARATUS AND EXPERIMENTAL PROCEDURE

The arrangement of the fluorination furnace is shown in Figure 1. The reaction chamber consisted of a nickel tube 12" long with 1" I. D. and 1/8" wall thickness. Heating was done by a Kanthal wire-wound furnace, and the temperature measured with a Pt vs. Pt - 10% Rh thermocouple introduced from the bottom of the furnace tube through a 1/4" nickel tube, closed at the top end. The metal joints of the furnace tube were made gas-tight with teflon gaskets.

The flow of fluorine gas was regulated by a Matheson fluorine pressure reducing valve and metered by a Fisher-Porter borosilicate glass flowmeter containing a sapphire float which was calibrated periodically. The fluorine was mixed with purified dry helium gas, metered by another flowmeter, in various proportions to obtain the desired fluorine partial pressures. The unreacted fluorine from the exit was reacted with the ammonia fumes over a concentrated NH_4OH solution.

Before commencing the reaction, the nickel furnace tube was passivated by reacting it with pure fluorine at 500 - 600°C to form a protective coating of nickel fluoride. The process was carried out during a period of three days by intermittently admitting fluorine for two or three hours each time. Also, before starting any run, a mixture of fluorine and helium was passed through the already passivated furnace tube, heated at the desired temperature for nearly half an hour to one hour as required, until fluorine was detected coming out of the combustion tube in large amounts, as indicated by use of KI paper. After passivation at the required temperature, the system was evacuated and flushed with helium several times, and the sample to be fluorinated was suspended from the helical spring by means of a 0.007" nickel wire, in the atmosphere of flowing helium gas. After about 10 minutes, fluorine was admitted, along with the helium, and a timer started simultaneously. The partial pressure of fluorine was calculated from the individual flow rates of fluorine and helium at atmospheric pressure. Any reaction of the fluorine with the nickel

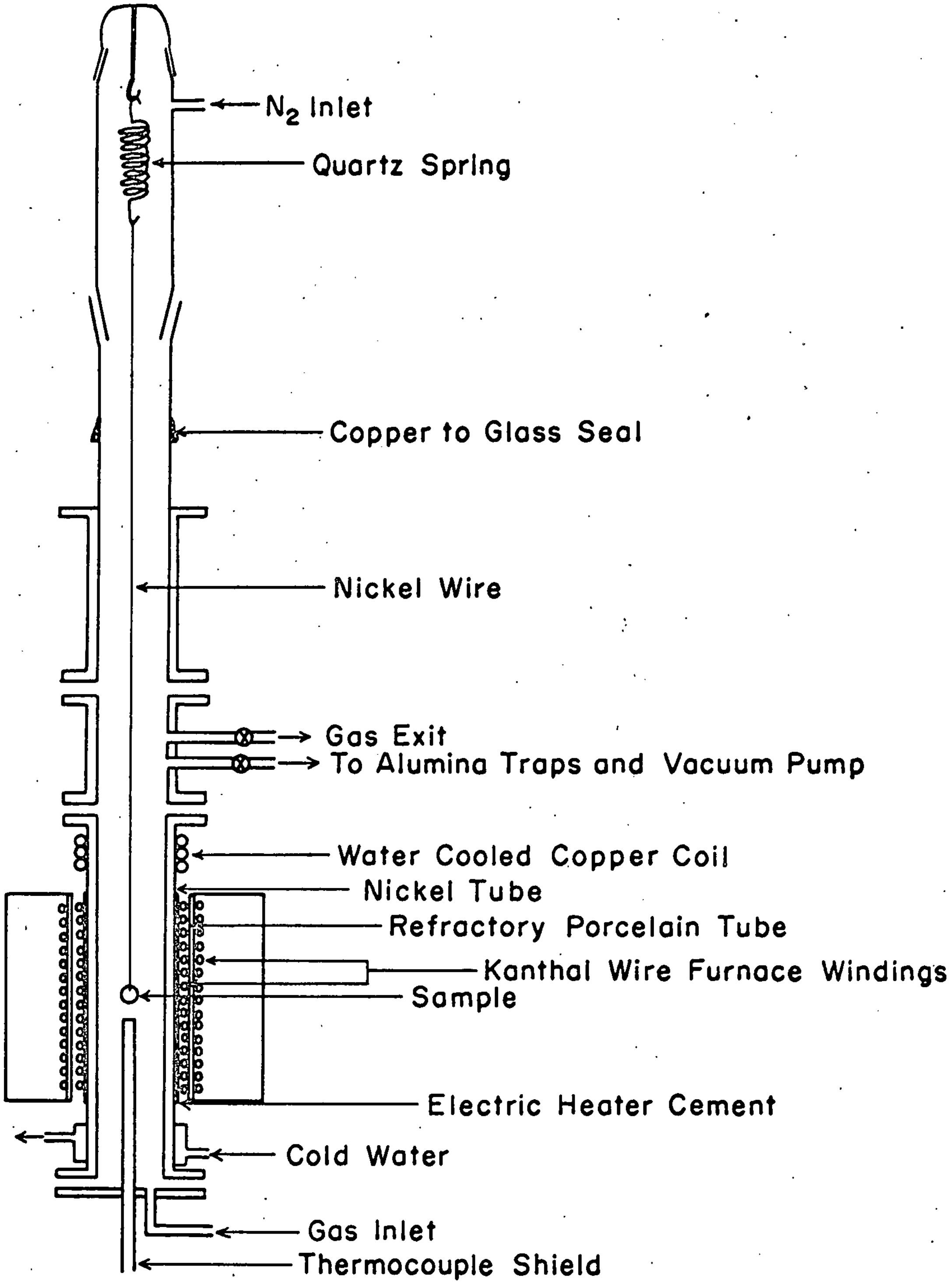

FIG. 1-FLUORINATION FURNACE SET-UP

suspension wire was neglected on the grounds that the surface area of the nickel wire exposed to the hot zone of the furnace was negligibly small compared to the relatively large area of the specimen. The change in extension of the spring was observed by means of a cathetometer and the smallest measurable weight change was 0.05 mg. Readings were taken at suitable intervals of time. The silica spring was protected from attack by fluorine by having a blanket of dry nitrogen in the form of a slow, steady stream sent from the top of the system. At the conclusion of the run, the fluorine was cut off and helium and nitrogen continued to flow until the exit gas was free from fluorine.

The zirconium carbide and zirconium diboride samples in the form of small discs, weighing about 0.2 to 0.4 gm., cut from electron-beam melted rods, were polished by grinding on abrasive cloth. The ZrC was 99.5%+ pure with traces of Ti, Si, B, Fe, N in the order of 0.1% and less and O, Al, Sn, Mg, Ca, Mn, Cu, Mo, Ag, Hf, and Pb in the order of 0.01 to 0.001%. The zirconium diboride was of composition $ZrB_{1.95}$ with 1.7% Hf and 200 ppm of carbon as impurities. The polished ZrB_2 had a shining mirror-like appearance while the ZrC had a shining metallic gray color. Surface areas of the specimens were determined by measuring the geometrical dimensions.

RESULTS AND DISCUSSION

A preliminary examination showed that ZrC would burn in fluorine or in an atmosphere rich in fluorine, at about 250 - 300°C. On the other hand, ZrB_2 did not catch fire in pure fluorine at a pressure of 1 atm., but it broke into bits at about the same temperature. Thus, the fluorination of these materials was examined at low fluorine partial pressures where the reactions could be effectively controlled.

REACTION BETWEEN ZrC AND FLUORINE AT 278 - 410°C

Initial experiments with ZrC and F_2 under a low partial pressure of F_2 (31 mm. of Hg) indicated that the reaction was rather smooth at about 300°C with a regular increase in weight. The reproducibility of the results was checked at 300°C and found to be within 20%. With the same fluorine partial pressure, the reaction was conducted at various temperatures ranging from 278 to 410°C. Above 410°C the reaction rate was too fast to measure by this technique. The weight increase per unit area of ZrC with time at the various temperatures is illustrated in Figure 2. There is no question regarding the linearity of the reaction with time. Abrupt breaks at and above 334°C indicate the crumbling away of part of the fluoride layer formed on the ZrC. Thick scales of ash-gray zirconium fluoride were observed on the surface of the ZrC after reaction. The adhesion of the scales was very poor and the material was soft and fluffy. The reacted samples had a sandwich appearance and their volumes had increased markedly because of the fluffiness of the ZrF_4 formed. The scales were apparently uniform and there were no visible cracks on them except at the edges, where the inner core was practically naked. Viewed under a microscope, the layers were made up of fine sugar-like crystals uniformly formed without any cracks. It appears that the unreacted ZrC was in direct contact with the fluorine atmosphere, in spite of the fluoride coating, and thus showed a linear rate of reaction.

It is not possible to say whether either zirconium or carbon in the system is preferentially attacked by fluorine, since the gaseous products were not analyzed. X-ray analysis of the inner core and the outer layer might show some evidence regarding this question; the coating gave an x-ray pattern characteristic of ZrF_4. The fact that the inner core is rough and black when once the fluoride scales are removed suggests the possibility that the Zr is reacting faster than the carbon.

From the slopes of the straight lines in Figure 2, the linear rate constants for the reactions were estimated, not taking into account the volatile products. The values obtained are displayed in Table II. The activation energy computed by a least square method is 22.1 ± 1.6 kcal/mole.

FLUORINATION OF ZrB_2 AND ZrC ABOVE 600°C

Zirconium diboride is apparently not attacked by fluorine under a low partial pressure (31 mm F_2; 709 mm helium) below 500°C. Since zirconium fluoride is very volatile above 700°C, practically no fluoride coating is formed on the boride or carbide surfaces above this temperature

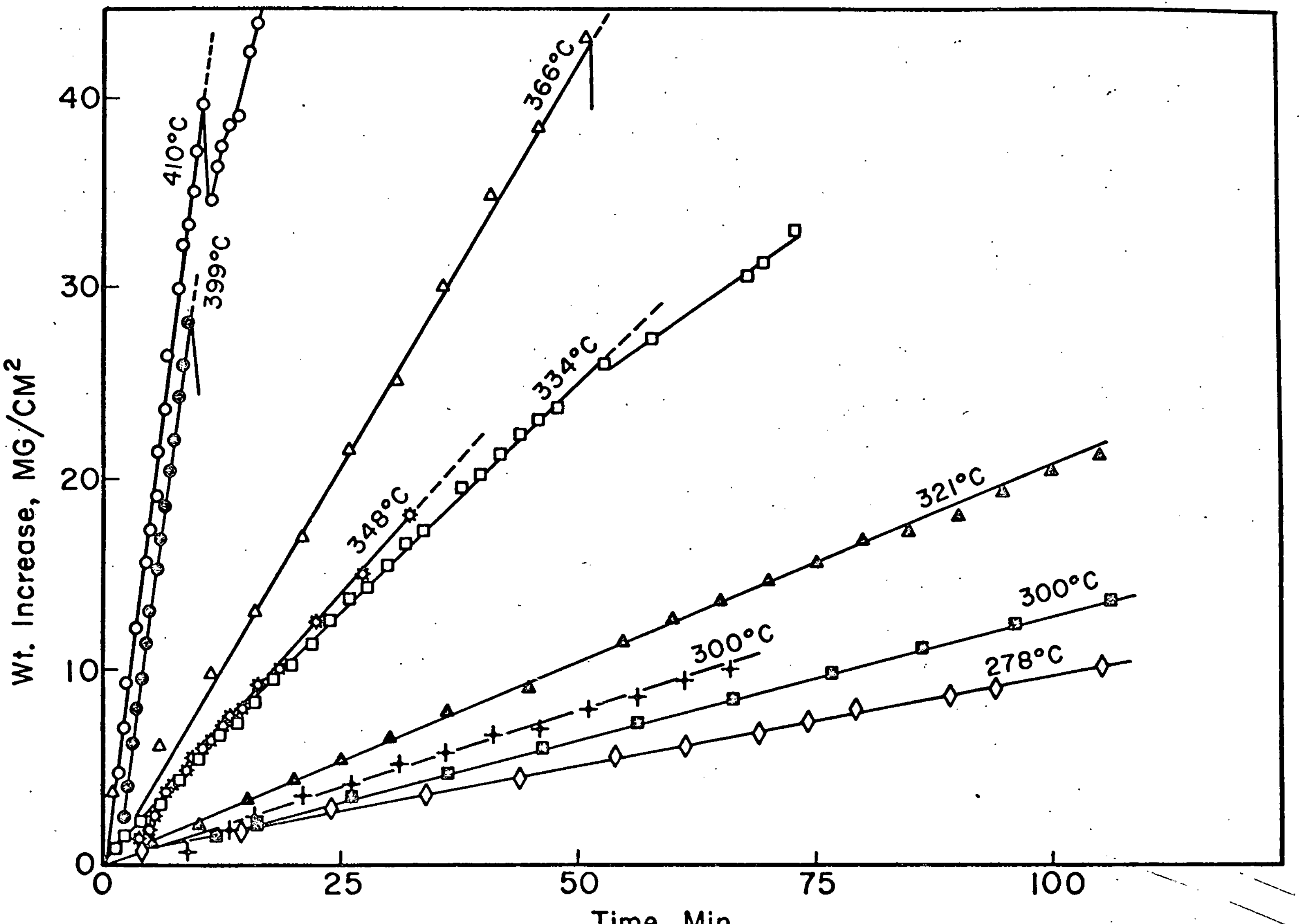

FIG. 2 – LINEAR PLOT FOR $ZrC-F_2$ REACTION. FLUORINE PARTIAL PRESSURE, 31 mm.

and hence the samples are found to lose weight during fluorination. The loss in weight can be measured and used for calculating the rates of the reactions. Figures 3 and 4 present plots of the weight loss/cm^2 of the samples with time in minutes, at 600 - 900° for ZrB_2 and 700 - 950°C for ZrC respectively, with a fluorine partial pressure of 2.7 mm of Hg (736 mm helium). The slight curvature in the lines is assumed to be due to the change in surface area of the specimens with the extent of corrosion. The rate constants for these reactions were, hence, calculated at zero-time on the basis of a linear rate law, using the equation

$$\Delta w/A = B + Ct - Dt^2 + Et^3 \quad \text{..........} \quad (1)$$

where:

Δw is the weight loss; A, the initial surface area; t, the time; and B, C, D, and E are constants with C being the linear rate constant $k_{1,t=0}$.

Equation (1) was derived assuming that the length and radius of the cylindrical specimen vary linearly with time, as treated below:

The linear rate of reaction at the surface of a cylinder may be expressed by the equation:

$$\frac{d(\Delta w)}{dt} = k\, 2\pi r(r + l) \quad \text{.......} \quad (2)$$

where:

Δw represents the weight change; k, the linear rate constant; and r and l, the radius and length of the cylinder respectively.

Assuming that the cylinder is corroded at constant rate from all sides,

$$\frac{dr}{dt} = 1/2\,\frac{dl}{dt} = k' \quad \text{.......} \quad (3)$$

where k' is the rate constant for the change in radius and length.

Integrating (3),

$$r = r_o - k't \quad \text{.................} \quad (4)$$

$$l = l_o - 2k't \quad \text{.................} \quad (5)$$

where r_o and l_o represent the initial radius and length of the cylinder.

Substituting (4) and (5) in (2)

$$\frac{d(\Delta w)}{dt} = k\, 2\pi(r_o - k't)\,(r_o + l_o - 3k't) \quad \text{....}(6)$$

Integrating (6) with respect to t,

$$\Delta w = k\left[2\pi r_o\,(r_o + l_o)t - \pi k'\,(4r_o + l_o)t^2 + 2\pi k'^2 t^3\right] + B \ (7)$$

where B is a constant.

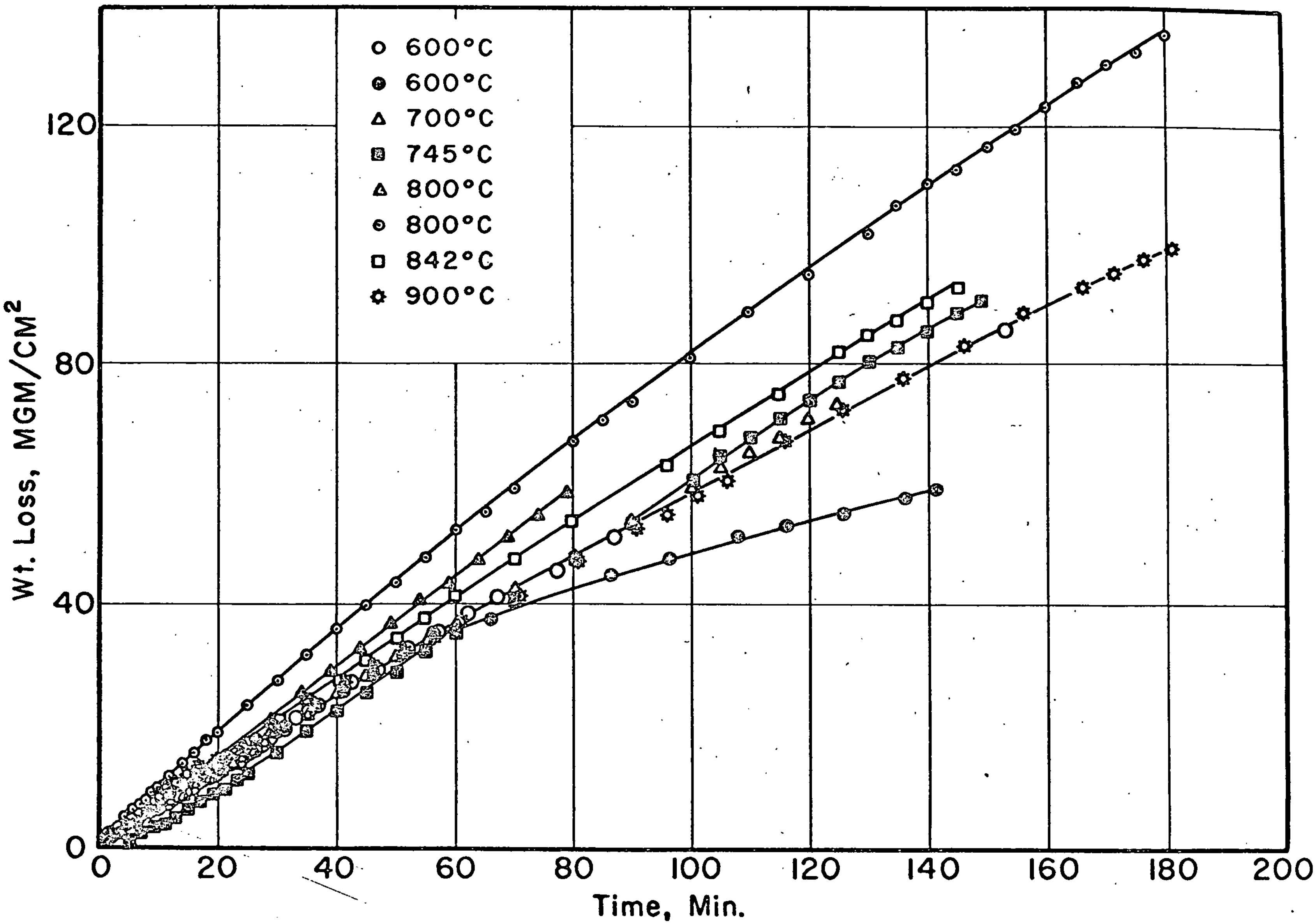

FIG. 3 — ZrB_2-F_2 REACTION AT VARIOUS TEMPERATURES, LINEAR PLOT. FLUORINE PARTIAL PRESSURE = 2.7 mm.

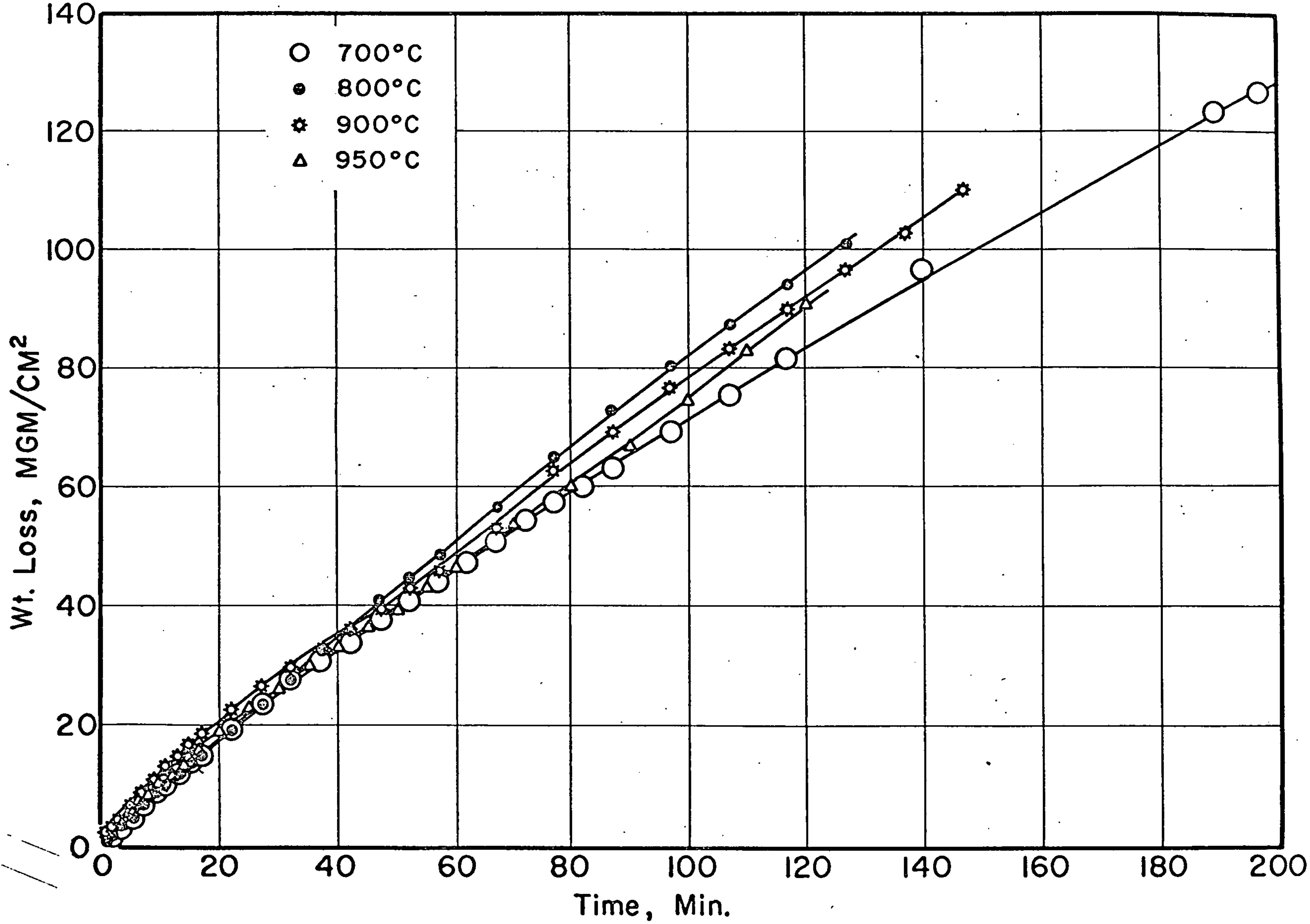

FIG. 4 – ZrC–F_2 REACTION AT 700–950°C. FLUORINE PARTIAL PRESSURE, 2.7 mm.

Equation (7) is of the same form as (1) and

$$\frac{d(\Delta w)}{dt_{t=0}} = k\left[2\pi r_o(r_o + l_o)\right] \quad \ldots\ldots (8)$$

and the value within the square bracket in (8) is the initial surface area of the cylinder.

The values for the zero-time rate constants were calculated with a Control Data 1604 computer and they are presented in Tables II and III. The reactions of both ZrB_2 and ZrC with fluorine are not strongly temperature dependent above 600°C and the activation energies calculated are essentially zero for both ZrB_2 and ZrC. The reaction rates depend on the fluorine partial pressure at temperatures above 600°C and probably appear to be very fast largely because of the rapid temperature rise produced at the surface by the highly exothermic fluorination process which produces more energy than the small sample can dissipate by combined radiation and conduction to the flow gas.

The Temp. rise, however, was only in the order of 15-20°C as observed by optical pyrometer above 700°C.

THE EFFECT OF FLUORINE PARTIAL PRESSURE ON THE FLUORINATION OF ZrC AND ZrB_2

The nature of the dependence of the rate of reaction of fluorine with ZrC was investigated at two temperatures, 350° and 700°C, since the mechanism of fluorination at these two temperatures is distinctly different. For ZrB_2, the effect of fluorine partial pressure was studied only at 700°C. The rate constants for the reactions were calculated as indicated earlier, and the results are graphically presented in Figures 5 and 6 for ZrC and ZrB_2 respectively. For ZrC at 350°C and for ZrB_2 at 700°C, the rate of fluorination is approximately proportional to the square root and for ZrC at 700°C, it is proportional to the 1.5 power of the fluorine partial pressure, in the range studied.

ACKNOWLEDGEMENT

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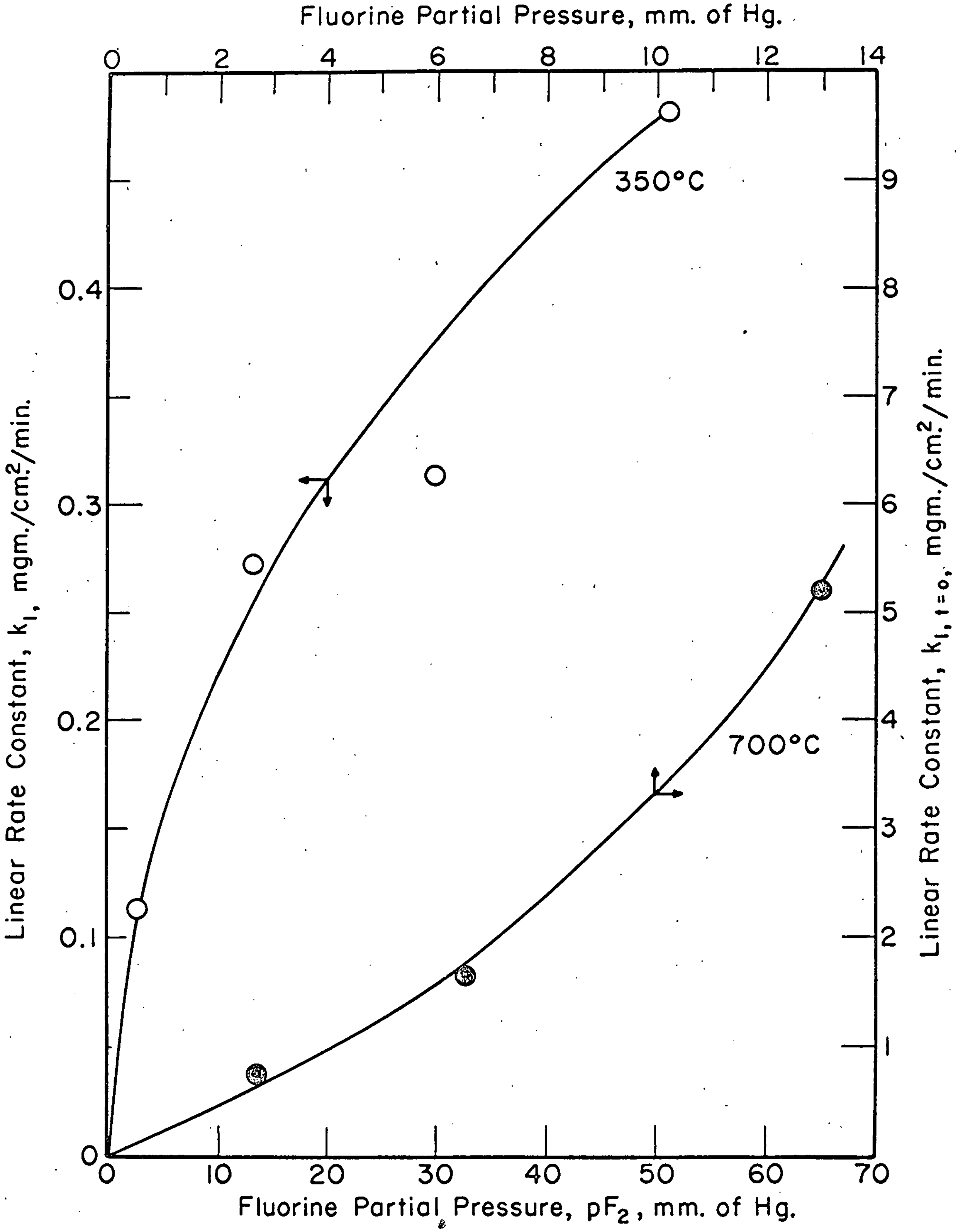

FIG. 5 – THE EFFECT OF FLUORINE PARTIAL PRESSURE ON THE ZrC–FLUORINE REACTION

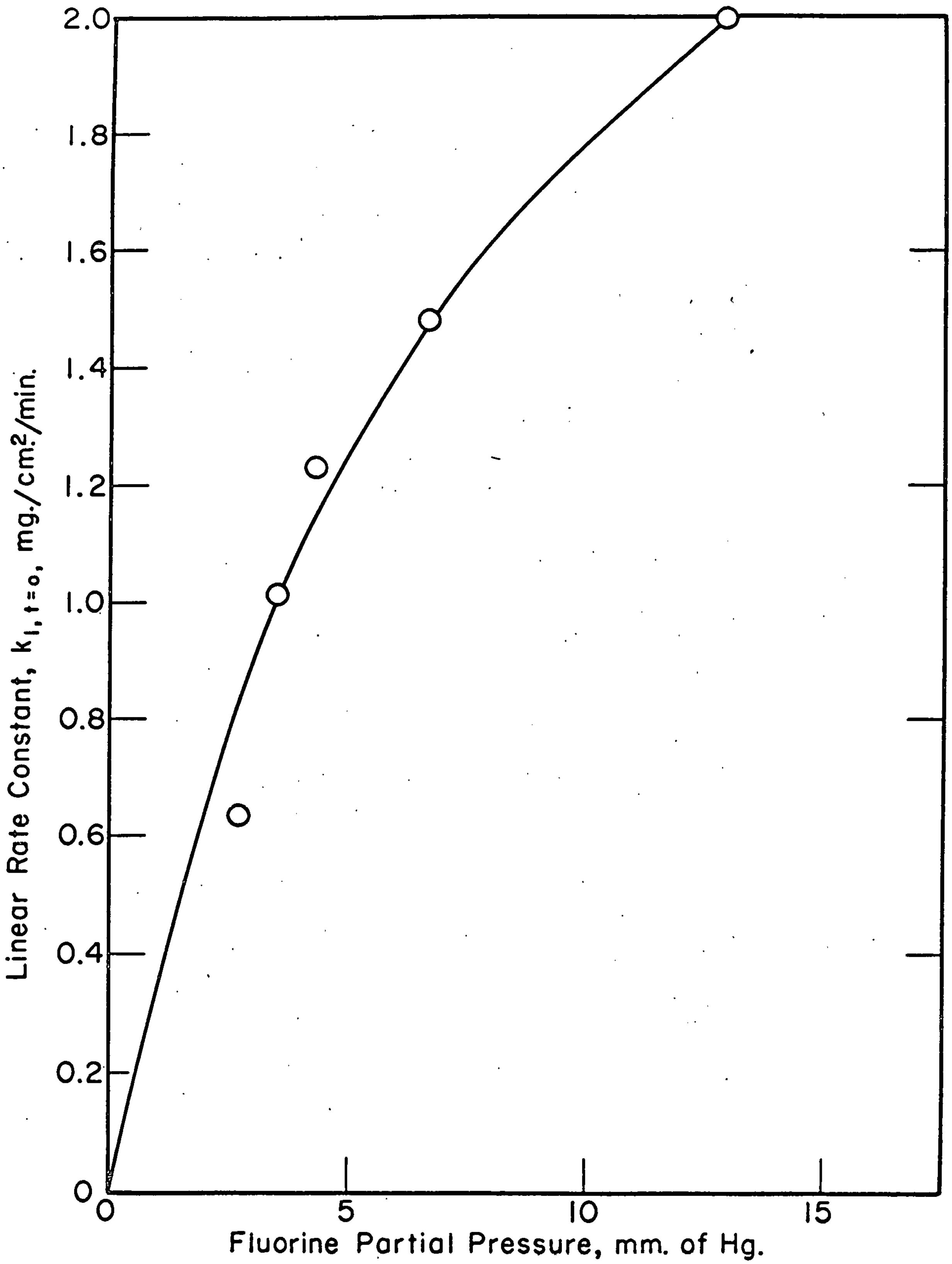

FIG. 6 – EFFECT OF F_2 PARTIAL PRESSURE ON THE ZrB_2-F_2 REACTION: 700°C

TABLE I.

LINEAR RATE CONSTANTS FOR THE $ZrC-F_2$ REACTION AT VARIOUS TEMPERATURES

(FLUORINE PARTIAL PRESSURE: 31 mm. of Hg)

Temperature (^{o}C)	Linear Rate Constant, k_1 ($mg/cm^2/min.$)
278	0.0995
300	0.1282
300	0.1515
321	0.2010
334	0.5069
348	0.5526
366	0.8450
399	3.4545
410	3.6786

$$\Delta E_a = 22.1 \pm 1.6 \text{ kcal/mole}$$

TABLE II.

LINEAR RATE CONSTANTS AT ZERO-TIME ($k_{1,t=0}$)

ZrB_2-F_2 REACTION AT $\overset{600}{\underline{700}}$ - 900°C

$P_{F_2} = 2.7$ mm. of Hg

Temperature (°C)	$k_{1,t=0}$, $mgm/cm^2/min$
600	0.6028
600	0.7734
700	0.6354
745	0.5313
800	0.9435
800	0.6842
842	0.7265
900	0.5916

$\Delta E_A = 0 \pm 1$ kcal/mole

TABLE III.

LINEAR RATE CONSTANTS AT ZERO-TIME ($k_{1,t=0}$)
FOR THE ZrC-F_2 REACTION AT 700 - 950°C
P_{F_2} = 2.7 mm. of Hg

Temperature (°C)	$k_{1,t=0}$, mgm/cm^2/min
700	0.7565
800	0.8764
900	0.9058
950	0.9697

ΔE_A = 2.2 ± 0.4 kcal/mole