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SURFACE AREA EFFECTS ON THE OXIDATION KINETICS OF PYROLYTIC GRAPHITE

TECHNICAL REPORT

by

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SURFACE AREA EFFECTS ON THE OXIDATION KINETICS OF PYROLYTIC GRAPHITE

ABSTRACT

The oxidation kinetics of pyrolytic graphite was studied as a function of temperature, air velocity, and surface area. The transition temperature between chemical and diffusion control may be significantly increased or decreased by decreasing or increasing the surface area of pyrolytic graphite. Kinetic theory calculations showed that the maximum reaction rate in the diffusion-controlled region is 50,000 times the observed rate for specimens having the smallest surface area.

INTRODUCTION

Pyrolytic graphite is a specialized polycrystalline form of graphite deposited from a carbonaceous vapor at temperatures above 3635 F on a suitable substrate, resulting in a buildup of layers having the graphitic structure. According to the supplier, pyrolytic graphite is impermeable to both liquids and gases, has greater strength than normal commercial graphite, and exhibits a greater degree of anisotropy in its thermal and electrical properties than single-crystal natural graphite. The microstructure of pyrolytic graphite is typical of vapor-deposited materials (fibrous in nature) and shows an unusually high degree of preferred orientation.

Figure 1 illustrates the columnar structure of pyrolytic graphite. Localized regions within the grains have different preferred orientations which are due to the fact that the basal planes in the cones are not parallel to the specimen length but are curved instead. The varying degrees of curvature result in a grain structure of conical configuration. This curvature is indicative of strain. Frozen-in stresses exist because of the thermal expansion and contraction that occur in the deposition process. Although this is typical of other graphites it is so to a lesser degree because of the less preferred orientation in normal graphite. Pyrolytic graphite has a high density compared to commercial graphite and has been prepared with measured densities as high as 2.22 grams per cubic centimeter.

Figure 1. PYROLYTIC GRAPHITE MICROSTRUCTURE. Mag. 100X
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The susceptibility of graphite to oxidation, beginning at comparatively low temperatures and becoming progressively more severe with increasing temperature, limits its usefulness as a high temperature material in spite of its several very favorable properties.

Oxidation may be studied readily by observation of chemical composition, penetration rate, structure of the oxide layer formed, and by the change in weight of the material during oxidation. Graphite is less reactive to oxygen than many metals. However, its oxides are gaseous and provide no protective film or layer. The formation of these gaseous products produce a loss in weight which, when carefully recorded in relation to time, offers a means for studying the rate of oxidation.

Equilibria calculations may be made on several reactions to determine the thermodynamic feasibility of the secondary reactions and the stability of the reaction products.

The pertinent reactions involving graphite, oxygen, carbon dioxide, and carbon monoxide are contained in Table I along with values of the equilibrium constant K_R.

Table I. EQUILIBRIUM DATA FOR REACTIONS OF PYROLYTIC GRAPHITE

Temperature (deg)		$Log_{10} K_R$				
K	F	(1)	(2)	(3)	(4)	(5)
873	1112	11.27	23.64	12.37	-1.10	-11.725
1073	1472	10.05	19.25	9.20	+0.85	- 8.92
1273	1832	9.20	16.27	7.07	+2.13	- 6.97
1473	2192	8.55	14.04	5.49	+3.06	- 5.56

(1) $C(S) + 1/2\ O_2(g) \longrightarrow CO(g)$

(2) $C(S) + O_2(g) \longrightarrow CO_2(g)$

(3) $CO(g) + 1/2\ O_2(g) \longrightarrow CO_2(g)$

(4) $CO_2(g) + C(S) \longrightarrow 2CO(g)$

(5) $1/2O_2(g) \longrightarrow O(g)$

The equilibrium constants for reactions (1), (2), and (3) show that both carbon dioxide and carbon monoxide are stable to decomposition. Carbon monoxide can be oxidized at all temperatures between 1100 and 2200 F according to reaction (3), whereas the reaction of carbon dioxide with graphite (4) is possible anywhere above 1200 F. The dissociation of oxygen molecules, reaction (5), is not appreciable at all temperatures in Table I.

The overall heterogeneous reaction of O_2 and C may be envisaged as involving the transport of the gaseous reactants to the surface, the reaction on the surface, and the transport of the gaseous products from the surface. Thus, the controlling factors of the reaction would be diffusion or chemical reactivity, depending on which is the slower process.

In an earlier investigation, Levy[1] studied the oxidation of pyrolytic graphite in quiescent air between 1250 and 1850 F. A break in the Arrhenius plot occurred at 1550 F. This break may have been due to a change in controlling mechanism, but could not be ascertained in a quiescent system. Later, Levy and Wong[2] studied the oxidation kinetics of pyrolytic graphite between 1400 and 1800 F at air velocities of 25 to 100 cm/sec and atmospheric pressure and for a specimen area of 3.024 sq cm. A transition from chemical to diffusion control occurred between 1500 and 1600 F. The existence of a change in mechanism of reaction at approximately 1600 F was reported for normal graphite and carbon by Tu, Davis, and Hottel,[3] Kuchta, Kant, and Damon,[4] Blyholder and Eyring,[5] and Gulbransen, Andrew, and Brassart.[6] Gulbransen also found that the transition between chemical and diffusion control depends on pressure, sample size, and the nature of the reaction system. Since these earlier investigators also reported transition temperatures near 1600 F, their reaction system, specimen areas, and oxidation conditions were probably similar. This report presents a study of the effect of specimen surface area on the oxidation kinetics of pyrolytic graphite for a given reaction system.

APPARATUS AND EXPERIMENTAL PROCEDURE

An automatic weighing and recording reaction system (Aminco Thermograv) was used for obtaining the rates of oxidation of pyrolytic graphite. The weight sensitivity of the system was 0.2 mg. The furnace temperature was regulated by a calibrated chromel-alumel furnace thermocouple which controlled the power input to the furnace. An additional calibrated chromel-alumel thermocouple placed adjacent to the sample was used to maintain the desired temperature within ± 3.5 F during the oxidation runs. This assured that the difference between the temperature of the sample and the furnace would be minimized as much as possible under the experimental conditions.

Air was introduced at the bottom of the reaction chamber, dried with Drierite, and measured with flow meters.

According to the supplier (Raytheon Co., Waltham, Mass.), the pyrolytic graphite was deposited from methane on a synthetic graphite substrate at 3812 F and had a density of 2.20 g/cc. Specimens had surface areas of 6.27 sq cm, 0.927 sq cm, and 0.394 sq cm, were rinsed with ethyl alcohol, and dried to constant weight.

The oxidation of pyrolytic graphite was studied as a function of time, temperature, air velocity, and surface area. Runs were made at 1400, 1500, 1600, 1700, and 1800 F at air flow rates of 25, 50, 75 and 100 cm/sec for each temperature and surface area.

RESULTS AND DISCUSSION

A plot of reaction rate versus 1/T for four air velocities and a specimen surface area of 0.927 sq cm is shown in Figure 2. Limiting tangents at

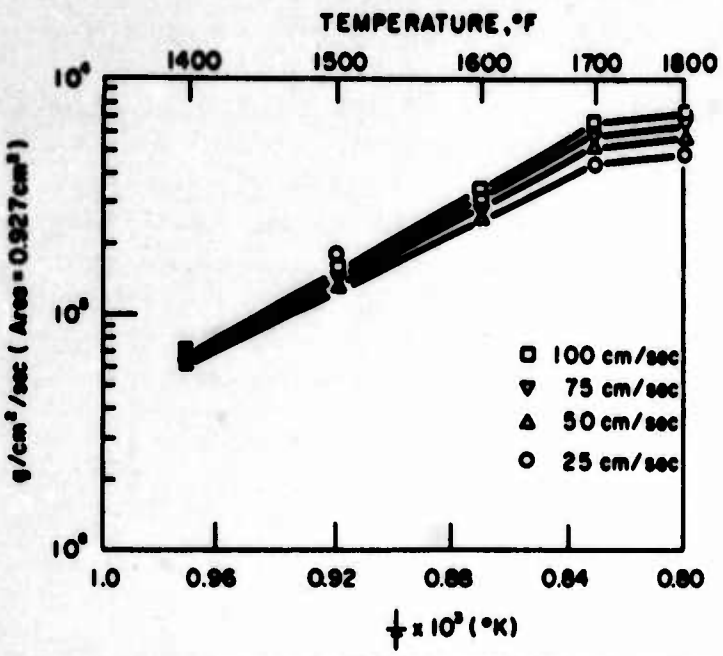

Figure 2. EFFECT OF TEMPERATURE ON REACTION RATE OF PYROLYTIC GRAPHITE
(Surface Area 0.927 sq cm)
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the longer exposure times were employed for the determination of reaction rate constants. The temperature of oxidation was then at constant value for each exposure. The initial portion of the curves between 1400 and 1700 F clearly represents a region in which chemical resistance is controlling, since the effect of velocity is overshadowed by that of temperature. For this region an energy of activation of 38 Kcal/mol was calculated. At 1700 F and above, a change is observed in oxidation kinetics at all gas velocities. In this region an energy of activation of 5 Kcal/mol was calculated.

The effect of velocity for several temperatures and a specimen surface area of 0.927 sq cm is shown in Figure 3a, both scales of which are logarithmic. Below 1700 F the curves are parallel to the velocity axis, showing a lack of dependence of rate on air velocity because of the predominant effect of chemical resistance at the surface. The slopes of the isotherms increase at 1700 F and above, where the rate is substantially independent of temperature. The substantial parallelism of the curves for this temperature region indicates that chemical resistance appears to have no importance between 1700 and 1800 F when the combustion rate is defined as containing two additive terms, the first of which corresponds to a diffusional resistance and the second to a chemical resistance.[3] If the reaction is in the diffusion-controlled region, one would expect the reaction rate to increase with increasing air velocity, which was the case at 1700 and 1800 F.

Figures 3b and 3c show similar curves for specimens having surface areas of 6.27 sq cm and 0.394 sq cm. By increasing the specimen surface area, the transition temperature between chemical and diffusion control decreases to 1600 F. Conversely, decreasing the specimen surface area increases the transition temperature to above 1800 F.

Figure 4 shows the effect of surface area on reaction rates at temperatures of 1400 to 1800 F and an air velocity of 25 cm/sec. It is important to note that the reaction rate is the highest for the small surface areas at the same temperature. This indicates that surface area itself has an effect on reaction rate independently of other variables. In other words, for the same air velocity and temperature a sample having a smaller surface area oxidizes more rapidly than one having a larger surface area. In the region of the smallest area, the curves become steeper and at 1800 F the curve was very steep, indicating an enormous reaction rate for a very small area. The effect of increasing air velocity on reaction rate is evidenced by a shifting of the curves upward for each increase in air velocity. For the reaction

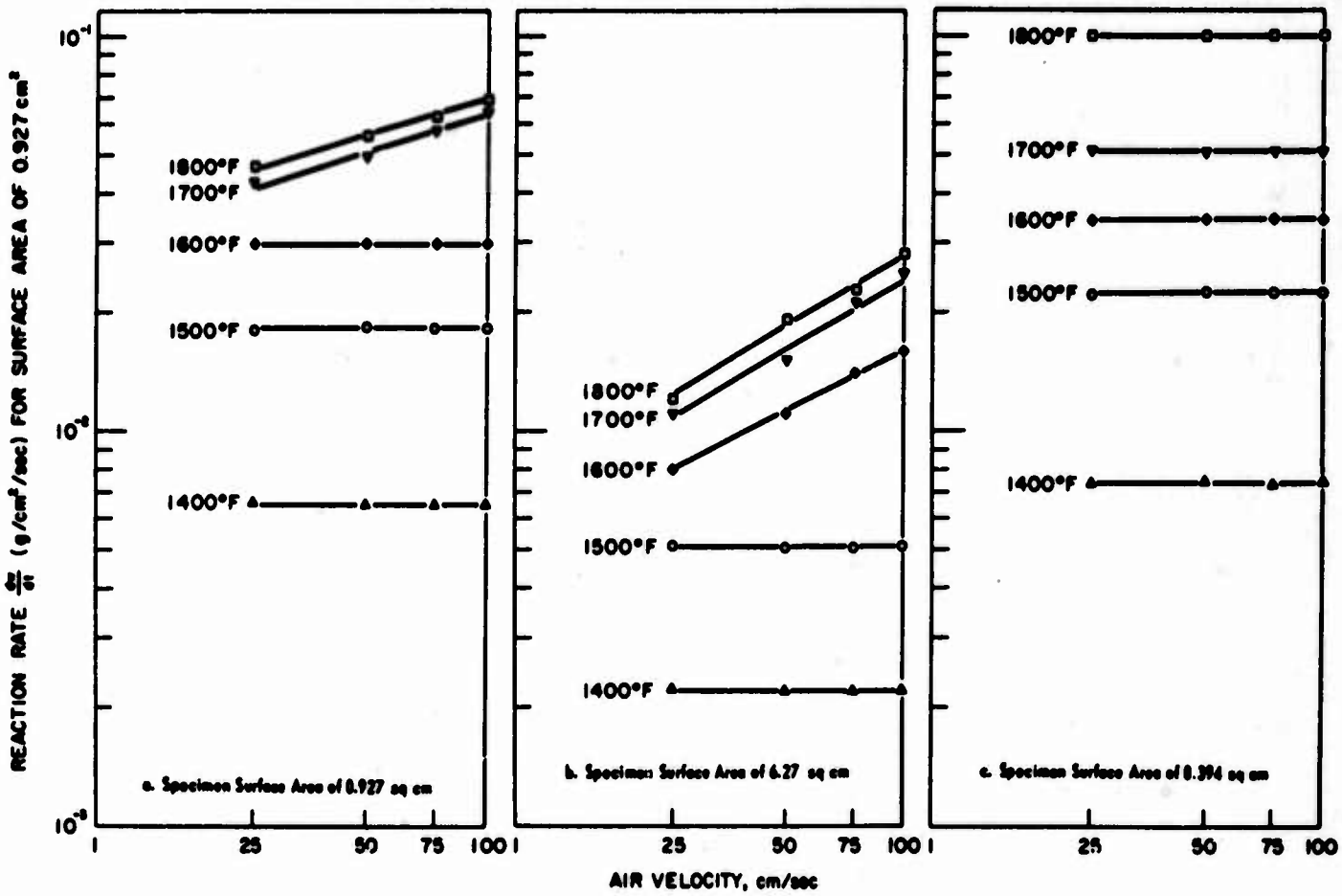

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Figure 3. EFFECT OF AIR VELOCITY ON REACTION RATE FOR SEVERAL TEMPERATURES

rates at higher velocities, the slopes of the curves were similar; however, the reaction rate curves begin to rise sooner than for the lower velocities.

Studies on the diffusion-controlled oxidation of graphite are more meaningful when the rates of reaction are related to the chemical-controlled reaction and to the values calculated from kinetic theory. Table II contains the number of impacts (n) of oxygen molecules with a square centimeter of surface area per second at temperatures of 1400 to 1800 F and atmospheric pressure, calculated from kinetic theory. If CO is formed, each collision results in reaction with two atoms of C. Therefore, the theoretical value

Table II. MOLECULAR COLLISION DATA CALCULATED FROM KINETIC THEORY

Temperature (deg) F	K	n (number of collisions of oxygen/sq cm/sec)	dn/dt (atoms C/ sq cm/sec)
1400	1033	1.47×10^{23}	2.9×10^{23}
1500	1089	1.44×10^{23}	2.9×10^{23}
1600	1144	1.40×10^{23}	2.8×10^{23}
1700	1200	1.37×10^{23}	2.7×10^{23}
1800	1255	1.33×10^{23}	2.7×10^{23}

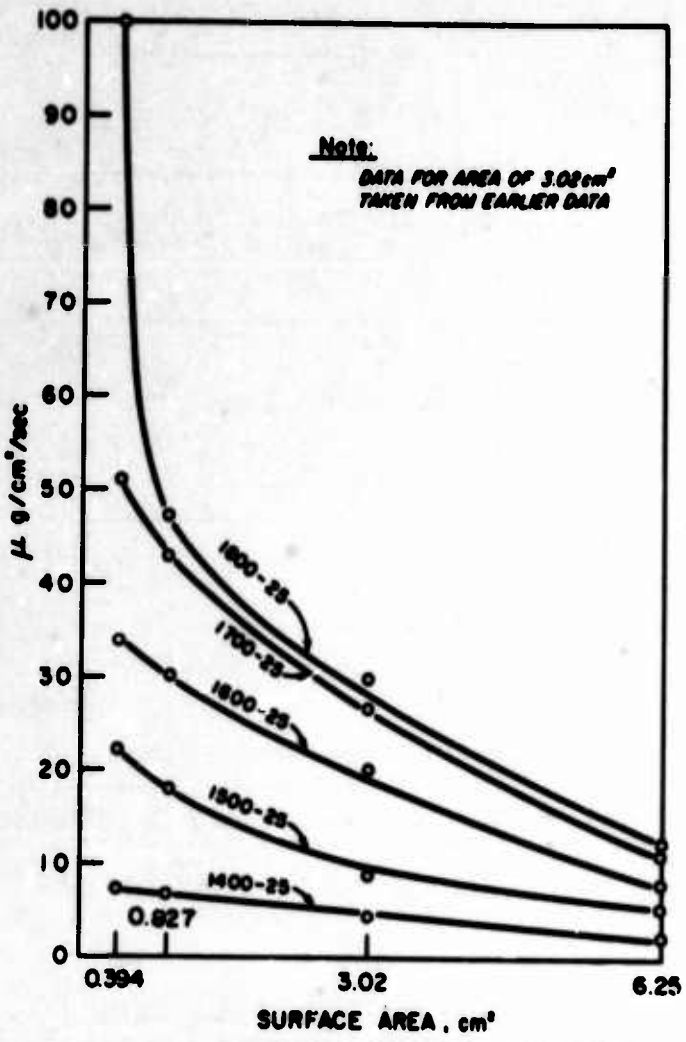

Figure 4. EFFECT OF SURFACE AREA ON REACTION RATES AT TEMPERATURES OF 1400 TO 1800 F AND AN AIR VELOCITY OF 25 cm/sec

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of dn/dt, expressed as atoms of carbon per square centimeter per second, will be twice the number of collisions per square centimeter per second. The values for dn/dt are also contained in Table II.

Table III shows the effect of surface area on the rates of oxidation which are expressed as dw/dt (g/sq cm/sec) and dn/dt (atoms C/sq cm/sec) calculated by using Avogadro's number (for air velocity of 25 cm/sec). The sample area was varied by a factor of 16 to determine the transition between chemical and diffusion control. Since the value of dn/dt increased on reducing the specimen size, the reaction is still under diffusion control for the smaller sample. Reaction rates up to 5.00×10^{18} atoms C/sq cm/sec were measured.

Figure 5 contains a plot of log dn/dt versus 1/T (K) at an air velocity of 100 cm/sec for samples having surface areas of 0.394, 0.927, and 6.27 sq cm. The linear portions of the curves represent chemical-controlled oxidation with an energy of activation of 38 Kcal/mol. Reaction rates to the right of these linear portions represent diffusion-controlled oxidation

Table III. EFFECT OF SURFACE AREA ON RATES OF OXIDATION
Air Velocity - 25 cm/sec

Temp. (deg F)	Sample Area (sq cm)	dn/dt (atoms C/sq cm/sec)	dw/dt (g/sq cm/sec)
1400	6.270	1.10×10^{17}	2.2×10^{-6}
1400	0.927	3.31×10^{17}	6.6×10^{-6}
1400	0.394	3.66×10^{17}	7.3×10^{-6}
1500	6.270	2.56×10^{17}	5.1×10^{-6}
1500	0.927	9.04×10^{17}	1.8×10^{-5}
1500	0.394	1.10×10^{18}	2.2×10^{-5}
1600	6.270	4.02×10^{17}	8.0×10^{-6}
1600	0.927	1.51×10^{18}	3.0×10^{-5}
1600	0.394	1.71×10^{18}	3.4×10^{-5}
1700	6.270	5.54×10^{17}	1.1×10^{-5}
1700	0.927	2.16×10^{18}	4.3×10^{-5}
1700	0.394	2.56×10^{18}	5.1×10^{-5}
1800	6.270	6.025×10^{17}	1.2×10^{-5}
1800	0.927	2.36×10^{18}	4.7×10^{-5}
1800	0.394	5.00×10^{18}	1.0×10^{-4}

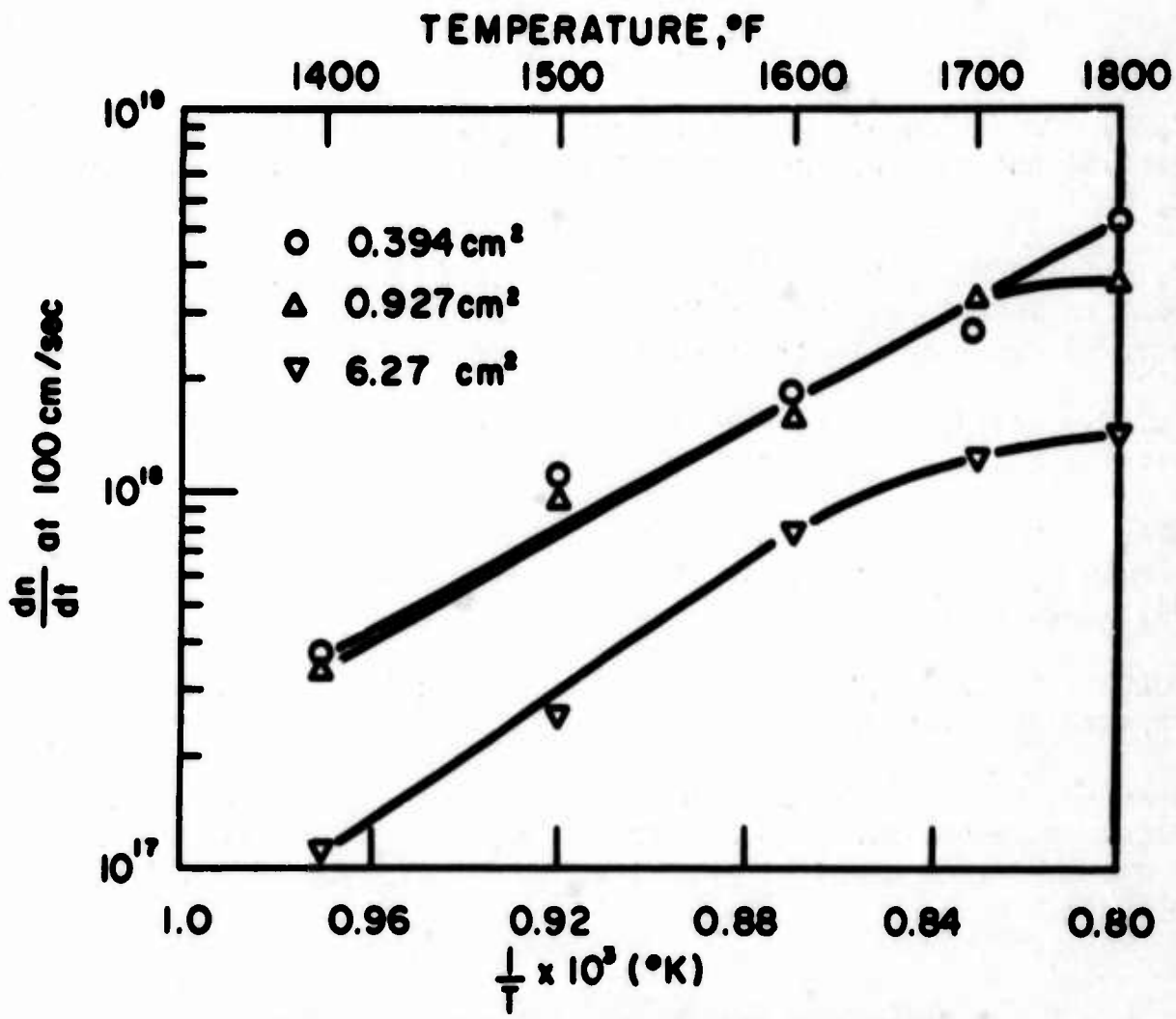

Figure 5. EFFECT OF SURFACE AREA ON REACTION RATES AT SEVERAL TEMPERATURES AND AN AIR VELOCITY OF 100 cm/sec

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where temperature has a minor effect on the reaction rate. The important variable is the surface area. The maximum measured rate of oxidation for a 0.394 sq cm sample at a furnace temperature of 1800 F was 5.00×10^{18} atom C/sq cm/sec. Kinetic theory calculations contained in Table II indicate a maximum reaction rate of 2.7×10^{23} atoms C/sq cm/sec at 1800 F. This value is 50,000 times the observed value for a 0.394 sq cm specimen area.

The transition temperature between chemical and diffusion control depends on the specimen area and the nature of the reaction. By decreasing the specimen area it was possible to increase the transition temperature from 1600 F to above 1800 F.

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