

THE OXIDATION OF CARBON BY
LEAD OXIDE-SILICA MELTS

by

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ABSTRACT

An investigation of the oxidation of carbon by lead oxide-silica melts was undertaken. The carbon specimens utilised in this investigation were spectroscopic graphite, petroleum coke (baked at 900°C) and spectroscopic carbon. The kinetics of the reactions were studied for different geometric surface areas over a wide range of concentrations of lead oxide and at different temperatures. In all cases the rate of oxidation was found to be directly proportional to the geometric surface area of the carbon sample used. The rate was also proportional to the square of the activity of lead oxide or equilibrium pressure of O_2 obtained from the dissociation of PbO in the melt. The experimental rate constant k values were calculated. The values of k for the oxidation of graphite, petroleum coke and carbon at 1000°C were found to be 1.35×10^{-2} , 1.31×10^{-2} and 0.97×10^{-2} gm.C/cm²/min. respectively.

The values of the experimental activation energies of the oxidation of graphite, petroleum coke and carbon were found to be 33, 28 and 22 kilocalories per mole respectively.

In all cases carbon dioxide was the product gas.

The results obtained in the present investigation indicated that the stoichiometry of the reaction is two molecules of lead oxide and an atom of carbon to produce metallic lead and carbon dioxide.

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THE OXIDATION OF CARBON BY LEAD OXIDE-SILICA MELTS

INTRODUCTION

The reactions between carbon and oxygen, and carbon and various metallic oxides are of considerable theoretical and industrial interest. For example, the reactions between metallic oxides and carbon are important in the case of blast furnace operation and in the anodic reaction occurring in the aluminium-reduction cell. In the past two or three decades much work has been done on the gaseous oxidation of carbon and much valuable information has been obtained concerning the nature and mechanism of these reactions. However, very little is known about the kinetics of the reaction of carbon with metallic oxides either in the solid or molten states. In view of this, the present work on the oxidation of carbon by lead oxide-silica melts has been undertaken.

The kinetics of the reactions of carbon with oxidizing gases such as oxygen, carbon dioxide have been studied by Langmuir, Hinshelwood, Sykes, Gulbransen and others.^{1,2,3,4,5} The entire reaction process can be divided into two main stages: (A) the oxidation or adsorption process and (B) the combustion or desorption process.

(A) The Oxidation or Adsorption Process

The work of Gulbransen and coworkers^{4,5} on the kinetics of the oxidation of graphite with gaseous oxygen provides some concept on the oxidation process. In their study, the effect of pressure of oxygen on the initial rate of reaction 'K' was found to follow the equation $K = A + Bp$, where A and B are constants and p is the pressure of oxygen. A first order

reaction was found for pressures of 10 cm. of mercury of oxygen or higher, while a zero order reaction was found at low pressures. The experimental activation energy for this oxidation reaction was found to be 36.7 kilo calories per mole.

A comparison of the experimental rate with those calculated from the absolute reaction rate theory, developed by Eyring,⁶ has shown that either (i) mobile adsorption or (ii) immobile adsorption with dissociation is a possible rate-controlling step.

(i) In the case of mobile adsorption, the activated complex-formed is mobile on the carbon surface with vibrational and rotational degrees of freedom similar to the reactant gas molecules. However, the activated complex has only two degrees of translational freedom over the surface. This is in contrast to three such degrees of freedom in the gaseous state. Where F_g and F^\ddagger are the partition functions for a cm^3 of gas and per cm^2 of activated complex respectively, the ratio, F^\ddagger/F_g reduces to $1/f_t$ where f_t is the contribution of one translational degree of freedom. The value of f_t is $\frac{(2\pi mkT)}{h}^{1/2}$, where k is Boltzmann's constant, h is Planck's constant, T is the temperature, m is the mass of the molecule. Eyring's equation applicable to mobile adsorption as the rate controlling step is as follows:

$$\begin{aligned} \text{Rate (atoms . C/cm}^2\text{/sec)} &= C_g \cdot \frac{kT}{h} \cdot \frac{F^\ddagger}{F_g} \cdot e^{-E/RT} \\ &= C_g \cdot \frac{kT}{h} \cdot \frac{h}{(2\pi mkT)^{1/2}} \cdot e^{-E/RT} \end{aligned} \quad (1)$$

where C_g represents the concentration of oxygen gas in molecules per c.c., R is the gas constant and E is the energy of activation. The rate of oxidation of graphite for an oxygen pressure of 7.6 cm^2 of mercury at 500°C calculated

from Equation (1) was 7.3×10^{11} atoms.C/cm²/sec compared to the experimental value of 7.2×10^{11} atoms.C/cm²/sec under the same conditions.

(ii) In the case of immobile adsorption with dissociation, the gas adsorbed on the surface forms an immobile layer. This means that the atoms obtained from the dissociation of reacting molecules are assumed to be attached to the sites until they are desorbed. Hence, their translational and rotational contributions to the partition function of the activated complex are unity. In this case the ratio of the partition functions of the activated complex and the reacting gas molecules F^*/F_g reduces to $\frac{1}{f_t^3 \cdot f_r^2}$ where f_r is the contribution of one rotational degree of freedom. Eyring's equation applicable to immobile adsorption with dissociation reduces to:

$$\text{Rate (atoms.C/cm}^2\text{/sec)} = C_g \cdot C_s \cdot \frac{kT}{h} \cdot \frac{h^5}{(2\pi mkT)^{3/2} (8\pi^2 I kT)} \cdot e^{-E/RT} \quad (2)$$

where C_s represents the number of sites per square centimeter and I is the moment of inertia and other terms have the same meaning as before.

The rate of oxidation of graphite for an oxygen pressure of 7.6 cm^2 of mercury at 500°C calculated from the above equation was found to be 2.1×10^{12} atoms.C/cm²/sec. whereas the rate value obtained experimentally was 7.2×10^{11} atoms.C/cm²/sec.

Like gaseous oxygen pure molten metallic oxides or their mixtures are also able to oxidise carbon. One might speculate on the fundamental difference between the oxidation of carbon by gaseous oxygen and that by molten oxides. In the gaseous oxidation of carbon, the oxygen goes from the state of a gaseous molecule to an activated complex. On the other hand in the oxidation of carbon by molten metal oxides, the initial reactant goes from the liquid state to an activated complex state on the carbon surface. It is not very likely that the

corresponding partition functions of the activated complex and the reactants in both the cases will be the same in magnitude. Therefore, by taking absolute reaction rate theory in to consideration, it appears that the rates of oxidation for both cases will also be quite different under similar experimental conditions.

(B) The Combustion or Desorption Process.

A large number of investigations in the field of carbon combustion has been carried out by Rhead, Sykes, Arthur, Gilliland, Bowring and others.^{7,8,9,10,11,12,13} These investigations indicate the following points with respect to the CO and CO₂ ratio desorbed from the carbon surface under conditions of gaseous oxidation of carbon with oxygen:

(1) CO and CO₂ are simultaneously produced by the desorption of the surface oxide of carbon.

(2) The observed ratio of CO to CO₂ desorbed covers a wide range of values and is dependent upon numerous factors such as (a) temperature, (b) pressure, (c) presence of halogens in the gas phase, (d) presence of hydrogen atoms on the carbon surface, (e) presence of transition metal atoms in the carbon.

Some valuable work on the reaction of carbon dioxide with carbon has also been done. Comments of R.F. Strickland-Constable¹⁴ on the work of Key,¹⁵ indicate that carbon dioxide reacts with coke by a two stage mechanism: in the first stage, a surface oxide is formed and in the second stage, the surface oxide decomposes to give CO. This reaction is retarded by CO. This is attributed to the reversal of stage 1, in that the CO is assumed to react with the surface oxide to reform CO₂. The studies of Bonner,¹⁶ Broom¹⁷ and Gadsby¹⁸ on the reaction of carbon dioxide with carbon and recently the work

of Gulbransen and Andrew¹⁹ on the reaction of carbon dioxide with artificial graphite, suggest the probability of a secondary reaction at the carbon surface:

$$\text{C} + \text{CO}_2 \rightleftharpoons 2 \text{CO}.$$

Recently J.D.S. Turnbull²⁰ has studied the oxidation of commercial graphite by a lead-borosilicate melt with and without the application of an electrical potential. His work was mainly focussed on the combustion products of carbon and the effect of temperature and current density on them. A rough value of 2×10^{18} atoms of oxygen per cm^2 per sec. at 1000°C , was found for the rate of the oxidation of commercial graphite in the above melt. In his work, there may be an error due to the secondary reaction of the exposed graphite surface with the product gas inside the apparatus.

Object and Scope of the Present Investigation.

The object of the present investigation has been to study the kinetics of the oxidation of (i) spectroscopic graphite, (ii) spectroscopic carbon and (iii) a petroleum coke mixture (National Carbon Company graphitizing stock, baked at 900°C) by lead oxide-silica melts at different temperatures.

Three different types of carbon and graphite were investigated because of the fact that they show a range of properties.^{21,22,23} For instance, with increase in temperature of heat treatment the nature of the carbonaceous material changes from a molecular solid through an aggregate of 'turbostratic' micro-crystallites to polycrystalline graphite. This polycrystalline graphite is obtained at temperatures greater than 2500°C .

It has been observed²¹ that as the heat treatment temperature is increased, the reactivity of carbon in the oxidation process progressively decreases. Thus the activation energy for the oxidation of carbon should increase with the increase in heat treatment temperature. Sebastian and Mayers²⁴

investigated the gaseous oxidation of a series of cokes having calcination temperatures from 400°C to 1000°C with varying rates of calcination. The activation energy of the oxidation varied directly with the calcination temperature and inversely with the rate of heating to temperature. Above 1000°C, the rate of calcination appeared to have no effect on the activation energy of the oxidation process. Gilliland and coworkers¹⁰ found that the activation energies of the oxidation of Ceylon graphite, metallurgical coke and hardwood charcoal in oxygen gas were 49, 29 and 16 kilocalories per mole respectively.

In view of the above results, in the present study the magnitudes of the experimental activation energy 'E' for the oxidation of graphite, petroleum coke and carbon should be in the order of $E_{\text{graphite}} > E_{\text{petroleum coke}} > E_{\text{carbon}}$.

In the present study, lead oxide in silica melts was selected as the oxidizing agent for the oxidation of carbon for the following reasons:

(1) In the oxidation of carbon in oxygen gas a relation between the reaction rate and the pressure of the reacting oxygen has been found. In order to establish a relation between the oxygen pressure of the oxidizing melt and the rate of oxidation of carbon in the present study, it was necessary to investigate the rates of oxidation in different lead oxide-silica melts since these melts have variable oxygen pressure. An examination of the phase diagram of the lead oxide-silica system²⁵ (Fig. 1) shows that a large number of low melting melts of lead oxide and silica can be obtained.

(2) The activities of lead oxide (Fig. 2) over a wide range of compositions of the lead oxide-silica system have been determined accurately by Richardson.²⁶ The oxygen pressure in equilibrium with lead oxide in the melt is directly proportional to the square of the activity of lead oxide in the melt.

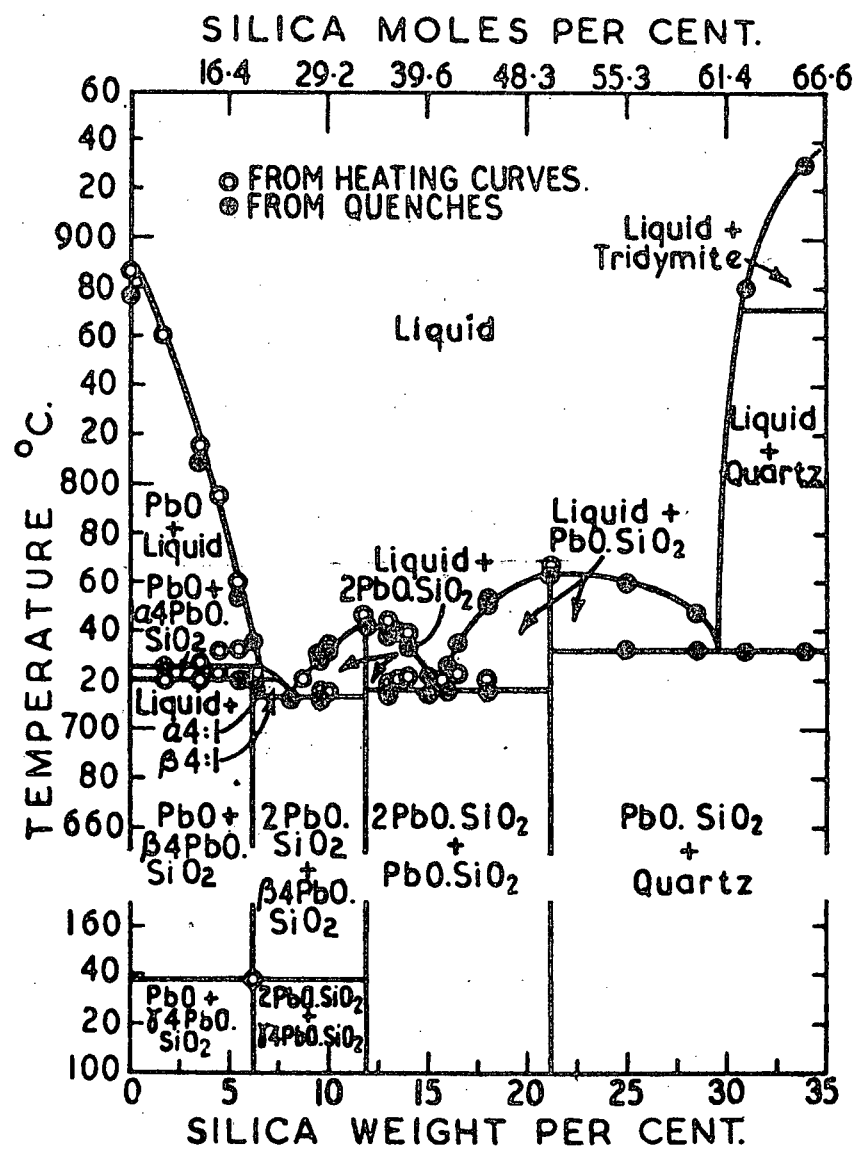


Fig. 1. PbO-SiO₂ Phase Diagram.

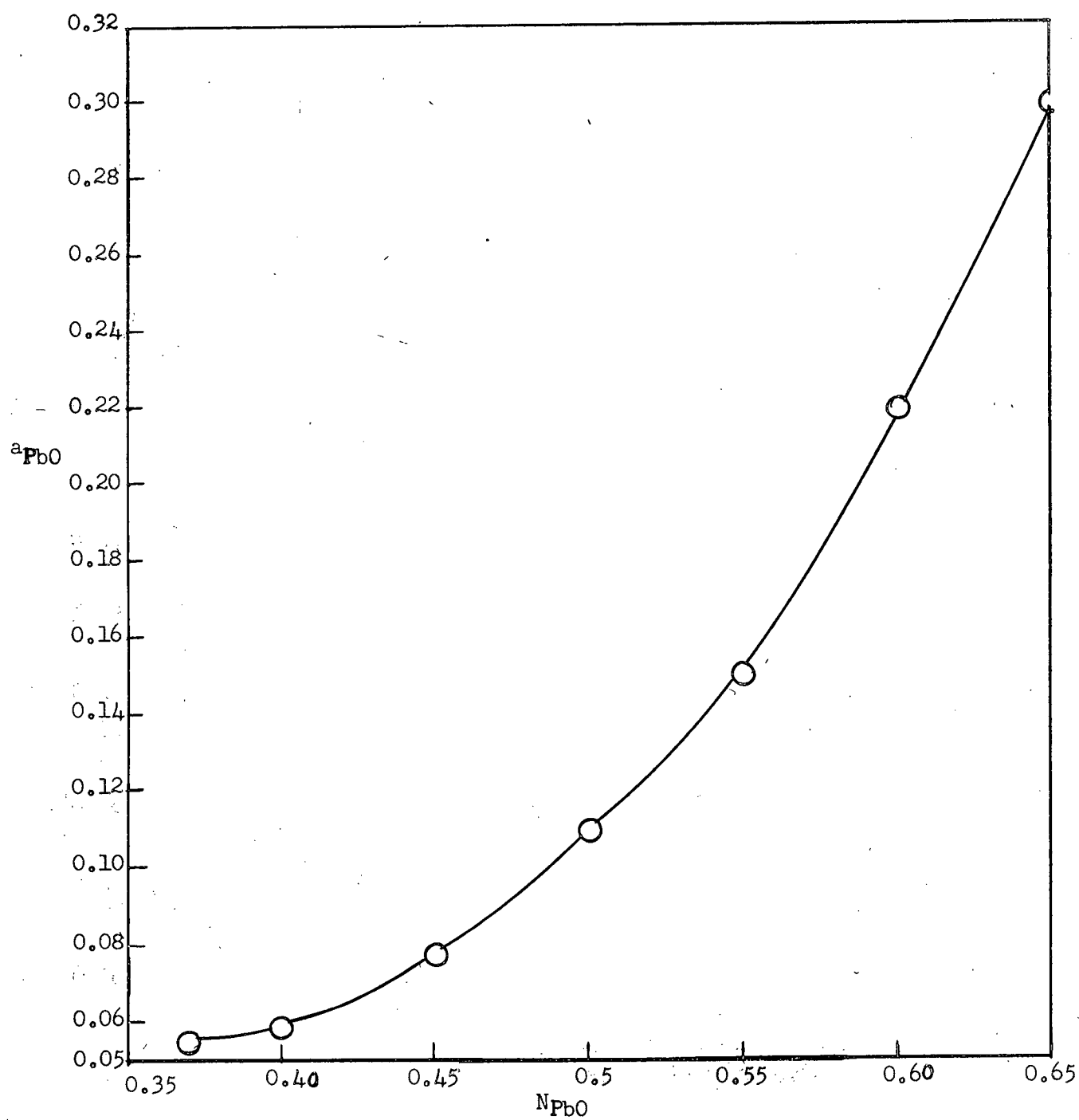


Fig. 2. Activity-mol fraction relation of lead oxide.

(3) It was also found that the rate of oxidation of carbon in most of these melts was measurable at the present experimental temperatures.

EXPERIMENTAL

Apparatus.

A diagram of the apparatus in which the chemical oxidation of carbon by lead oxide-silica melts has been performed, is given in Fig. 3. In that sketch,

A = Globar furnace

B = Chromel-Alumel Thermocouple to control the temperature of the furnace (± 2 to 3°C) through a Leeds and Northrup Micromax controller.

C = a fireclay crucible containing the lead oxide-silica melt.

D = a funnel. The stem of the funnel was a high temperature porcelain protection tube (supplied by McDanel Refractory Porcelain Co., Pennsylvania) and the cone portion was made of fired 'synthetic lava'. The cone was machined from a grade 'A' synthetic lava block (supplied by American Lava Corporation, Tennessee) and then fired slowly up to approximately 1150°C . The cone and the stem portions were joined by 'Sersit' cement. The cone portion of the funnel was then coated completely with lead oxide and silica paste (containing approximately 78.8% of PbO by weight) and then fired slowly nearly up to 1050°C in order to coat the funnel uniformly. It was found from preliminary experiments that when the portion of the funnel was dipped into the reacting melt (nearly 200 grams), the thin coat on the funnel did not cause a measurable change in the composition of the reacting melt. The purpose of the coating on the funnel was to avoid any diffusion of the product gas through its wall during the reaction of carbon with the lead oxide-silica melt. Synthetic lava, fireclay, vitreosil and inconel were tried as funnel materials and the fired synthetic

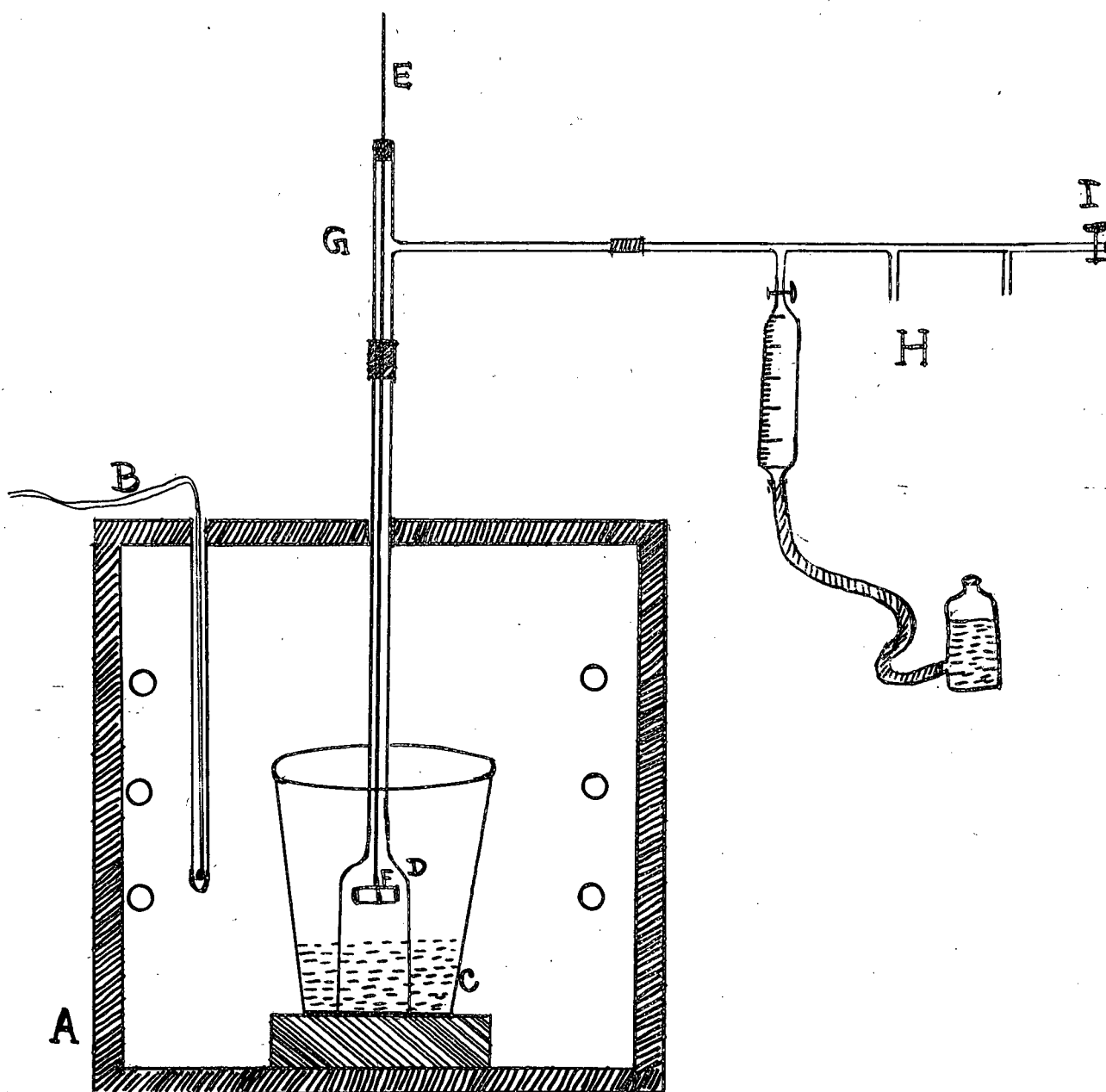


Fig. 3 Apparatus for study of chemical oxidation.

lava was found to be the most suitable material.

E = a thin chromel rod holding in a loop a piece of carbon sample 'F'.

G = a glass tube. This was joined to the stem of the funnel. This glass tube had a side tube which was joined to the gas collecting cylinders 'H' which were themselves joined in series.

I = a stopcock.

Materials.

Special spectroscopic carbon and graphite electrodes were supplied by National Carbon Company in the form of rods of different diameters. Petroleum coke mixture (the sample from the 500 ampere cell carbon) was National Carbon Company graphitising stock, baked at 900°C and supplied in blocks, from which rods of different diameters were machined.

The materials for the melt were reagent grade lead oxide (mono) (Baker and Adamson) and pure silica powder (supplied by Cave and Company Limited).

Procedure.

Weighed amounts of lead oxide and silica were placed in crucible 'C'. This crucible and the funnel 'D' (without the chromel rod holding the carbon) were then assembled in the electric furnace. The funnel was not dipped into the melt until the experiment was started. The furnace was maintained at the desired experimental temperature by a controller. After half an hour at temperature, the cleaned chromel rod 'E' holding a piece of carbon (whose geometric surface area was measured previously by a micrometer) was rapidly introduced into the funnel. The funnel was then dipped into the molten lead oxide-silica so that the carbon piece was completely immersed in the melt and

the oxidation process began. After this the side tube of the glass tube 'G' in Fig. 3 was joined to the burettes 'H'. Then the pinch cock 'I' was closed. This time was considered as the zero time. The interval from the immersion of the carbon to closing of the pinch cock was of the order of one minute. Time was read by means of a stopwatch. The gases evolved for different reaction times were collected by displacement of acidulated water (5-6 volume percent of concentrated sulphuric acid in distilled water) in gas collecting graduated burettes 'H' under atmospheric pressure and the gas volumes were simultaneously measured. After the experiment, the collected gases were analysed in an Orsat apparatus for carbon dioxide, oxygen and carbon monoxide. The absorbants for these gases were respectively potassium hydroxide solution, alkaline pyrogallol and Frantz reagent. Potassium hydroxide solution contained 500 grams of pure potassium hydroxide per litre. Alkaline pyrogallol was a mixture of one volume of a solution containing 300 grams of pure pyrogalllic acid per litre of solution with 4 to 6 volumes of the above potassium hydroxide solution. One gallon of Frantz reagent solution contained 910 grams of cuprous chloride, 1700 cc. of monoethanolamine, 60 grams of ammonium chloride and water.

Analysis by this method in all cases showed the product gas to consist of carbon dioxide and 0.0 to 0.5 percent of carbon monoxide. It was likely that some of the carbon dioxide would dissolve in the acidulated water during collection and hence there might be some error in the measurement of the volumes for different reaction times. Thus, in some separate experiments, pure carbon dioxide was collected in the usual way and it was found that less than 1.5 percent of total carbon dioxide went into solution over a time period of an experimental run.

Reproducibility

For a particular set of experimental conditions the amount of carbon

oxidized was found to bear a linear relationship with the reaction time. The rate of oxidation was obtained from the slope of the above curve. The reproducibility of the experimental technique was checked by a series of experiments under identical conditions. It was found that the rates were reproducible to within ± 4 to 5%.

Diffusion

In three experiments under otherwise identical conditions the melts were stirred with the chromel rod 'E' in an electric stirrer at the rate of 1, 2 and 3 revolutions per second respectively. The rate of oxidation was found to be independent of the stirring rates. This indicated that under the present experimental conditions, diffusion of the reactants to the carbon surface was not rate controlling.

RESULTS

(A) Oxidation of Graphite.

(1) Oxidation rate as a function of geometric surface area (G.S.A.)

Special graphite spectroscopic electrodes of different diameters were machined to different sizes. The G.S.A. of each graphite piece, which varied from 5.1 cm^2 to 12.7 cm^2 , was measured with a micrometer. Separate experiments were carried out with these at 1000°C in lead oxide-silica melt (containing 78.8% of lead oxide by weight). For each piece of graphite the amount of carbon oxidized per unit time was determined (given in Fig. 4 and Table I). A plot of these values (gm. of C oxidized per piece of graphite per minute) against their respective G.S.A. values (in cm^2) is given in Fig. 5. It was found that the rate of oxidation of graphite was directly proportional to the G.S.A. of graphite. The rate of oxidation of graphite by a lead oxide-silica melt,

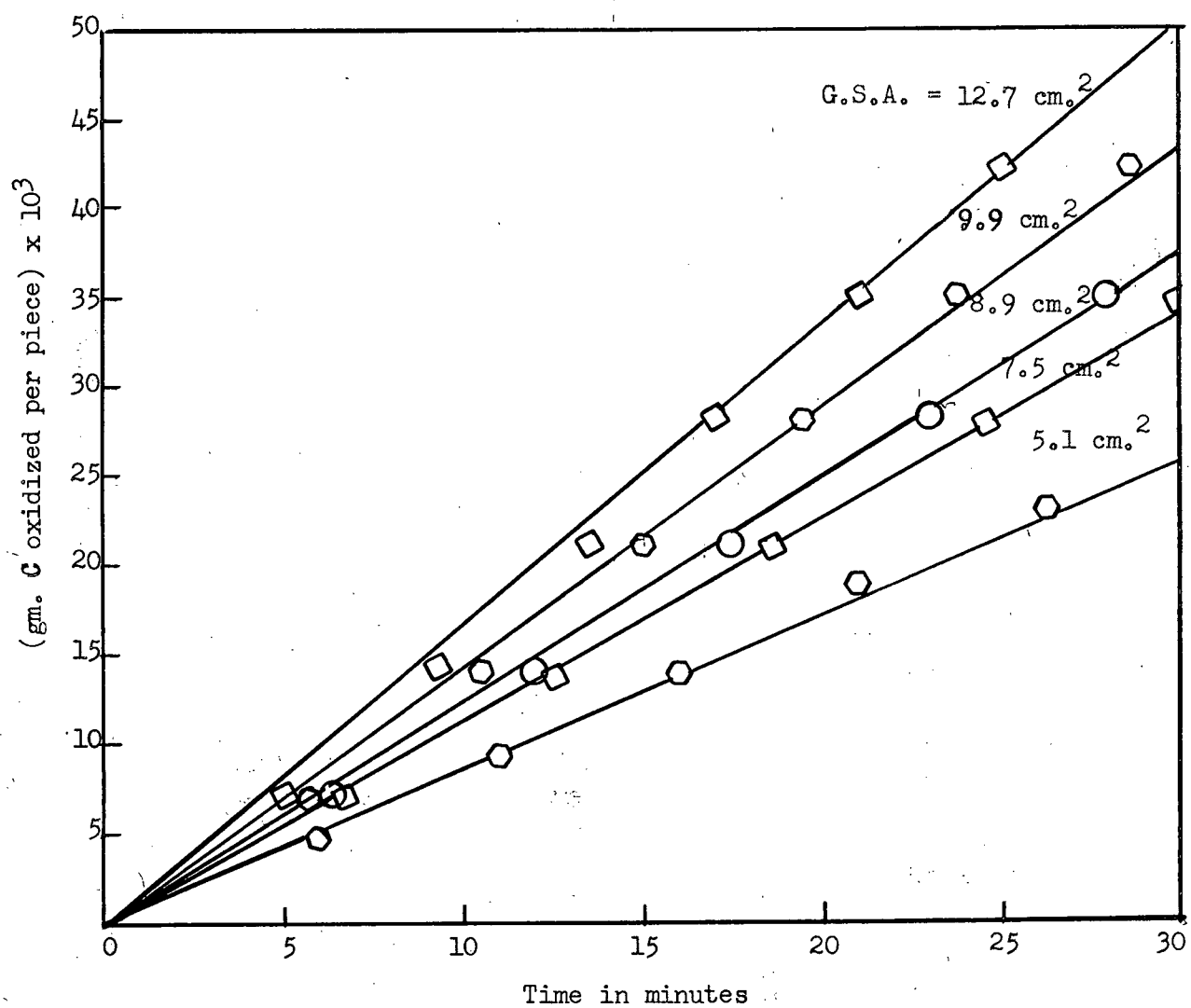


Fig. 4. Rate curves for oxidation of graphite having different geometric surface areas.

TABLE I

Effect of geometric surface area of graphite
on the rate of oxidation.

Experimental temperature = 1000°C.

Percentage of PbO by weight in the melt = 78.8

| Geometric surface area of graphite in cm. ² | (Gram of C oxidized per piece of graphite per min.) x 10 ³ | Rate of oxidation (R) x 10 ⁴ (in gm.C/cm ² /min.) |
|---|--|---|
| 5.1 | 0.84 | 1.64 |
| 7.5 | 1.14 | 1.63 |
| 8.9 | 1.29 | 1.45 |
| 9.9 | 1.45 | 1.47 |
| 12.7 | 1.78 | 1.40 |

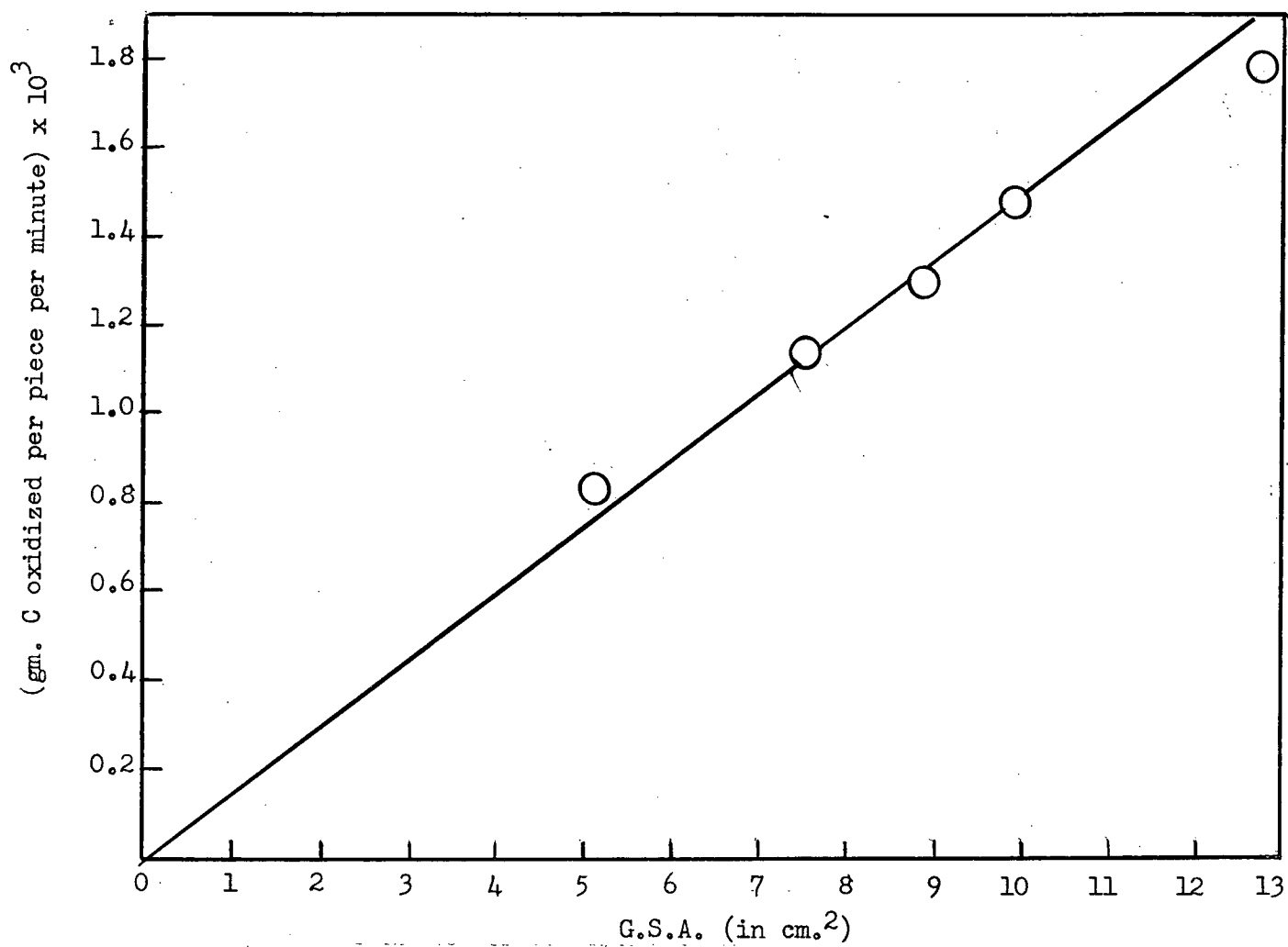


Fig. 5. Dependence of the reaction rate on the geometric surface area of graphite.

containing 78.8% of lead oxide by weight was found to be 1.63×10^{-4} gm.C/cm²/min. at 1000°C.

(2) Effect of the composition of the lead oxide-silica melt on the rate of oxidation.

The rates of oxidation of graphite at 1000°C were determined in different compositions of lead oxide-silica melts (varying from 77 to 86 percent of lead oxide by weight) using graphite specimens of 7.5 cm² of G.S.A. It was found that the rate of oxidation of graphite in lead oxide-silica melts was proportional to the square of the activity of lead oxide, a_{PbO}^2 (given in Fig. 8). A plot of the rate against a_{PbO} resulted in the parabolic curve (given in Fig. 7). The a_{PbO} values corresponding to the different melt compositions were obtained from Fig. 2 (Richardson's data). The results are summarized in Figs. 6, 7 and 8 and in Table II. From the above relation the rate equation can be expressed as

$$R = k a_{\text{PbO}}^2 \quad (3)$$

where k is the experimental rate constant.

(3) Determination of the experimental activation energy of the oxidation of graphite.

The rates of oxidation of graphite in lead oxide-silica melt (containing 78.8% of PbO by weight) were measured for different experimental temperatures varying from 961°C to 1060°C using graphite specimens of 7.0 cm² of G.S.A. From the values of the rate of oxidation, the corresponding experimental rate constants ' k ' were calculated from equation 3, $\text{rate} = k a_{\text{PbO}}^2$. The effect of temperature on the activity of lead oxide in a lead oxide-silica melt (78.8% of PbO by weight) was obtained from Richardson's²⁶ data. The activities of lead oxide in the above melt at 1000°C and 1100°C were found to be 0.11 and 0.12 respectively, indicating that the effect of temperature on the activity of PbO

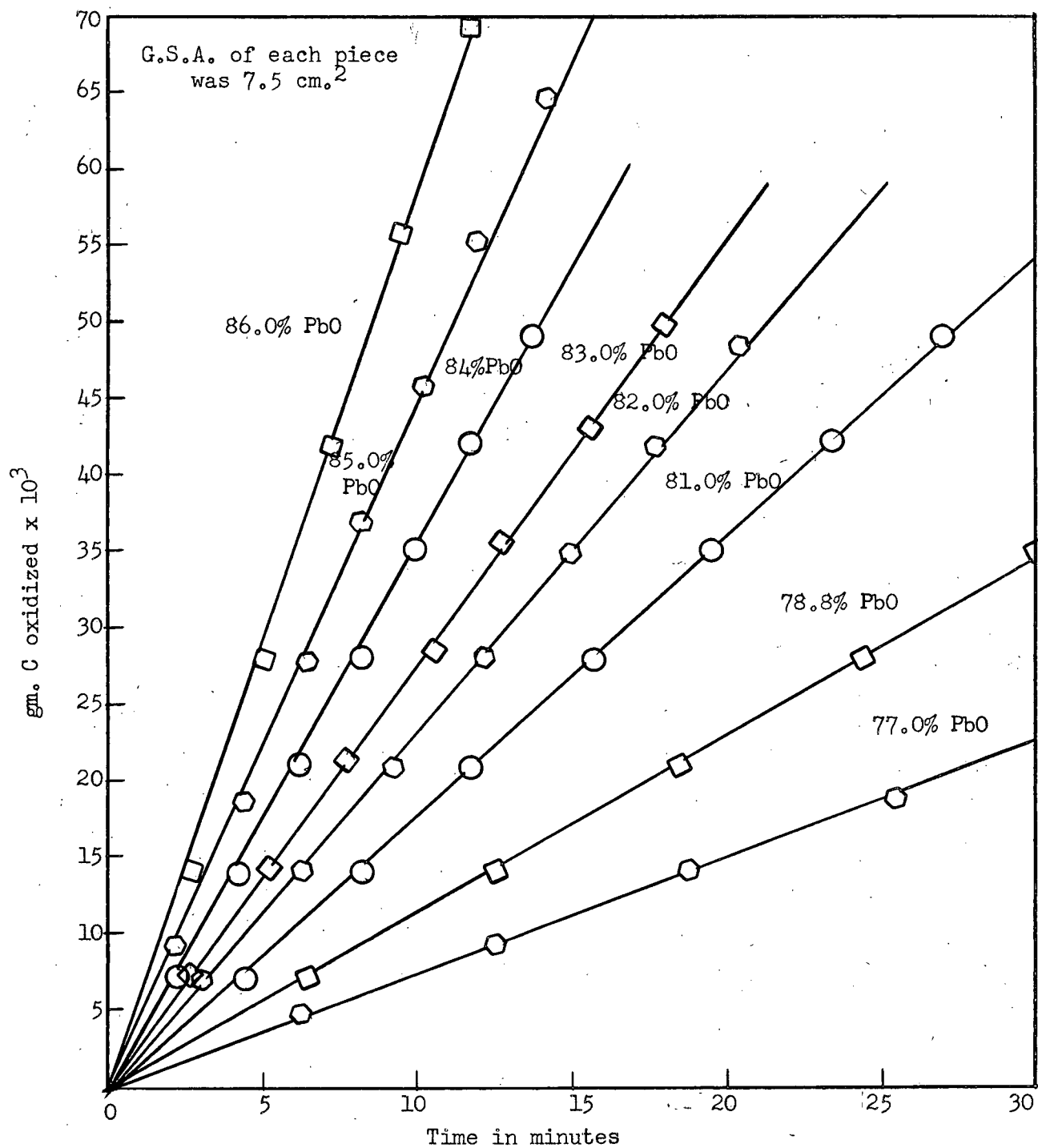


Fig. 6. Rate curves for oxidation of graphite by PbO-SiO_2 melts of different compositions.

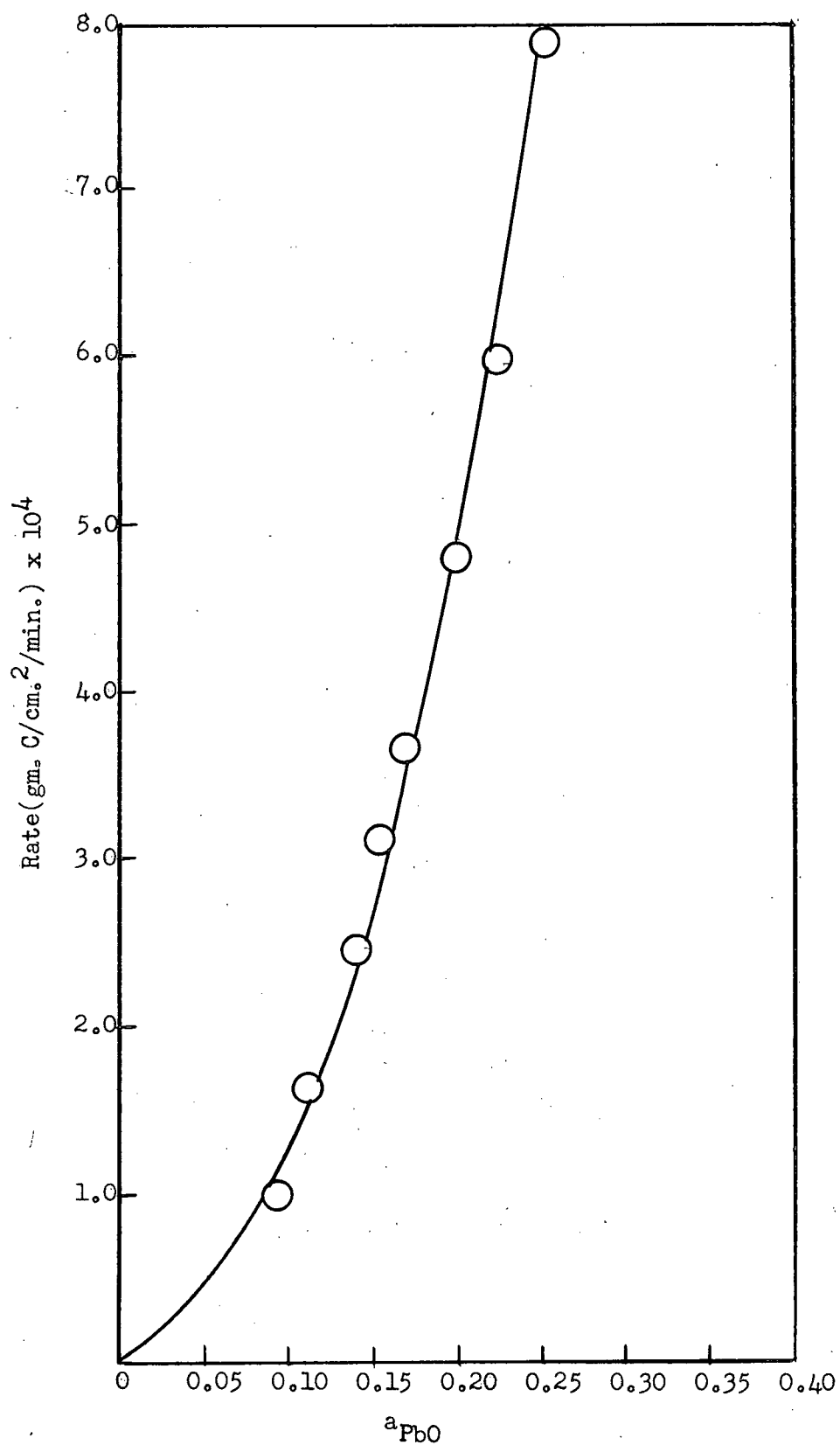


Fig. 7. Dependence of the rate of oxidation of graphite on the activity of lead oxide.

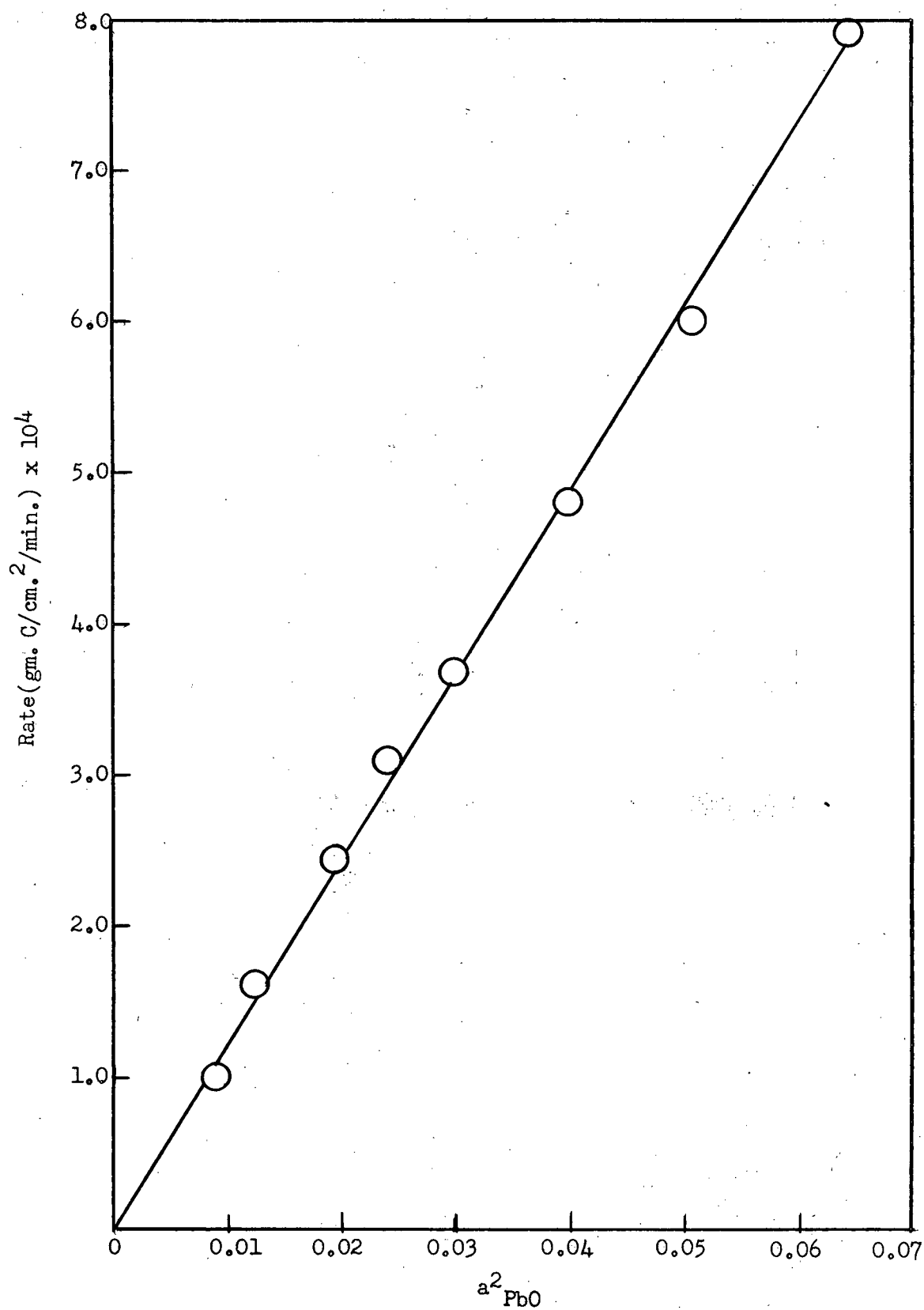


Fig. 8. Dependence of the rate of oxidation of graphite on the square of the activity of lead oxide.

TABLE II

Effect of activity of lead oxide in the melt
on the rate of oxidation of graphite.

Experimental temperature = 1000°C.

G.S.A. of graphite used in each experiment = 7.5 cm.²

| Percentage by wt. of PbO in the melt. | N _{PbO} | a _{PbO} | a _{PbO} ² | Rate (R) x 10 ⁴ (gm.C/cm ² /min.) |
|---|------------------|------------------|-------------------------------|--|
| 77.0 | 0.474 | 0.095 | 0.0090 | 1.00 |
| 78.8 | 0.499 | 0.110 | 0.0121 | 1.63 |
| 81.0 | 0.535 | 0.140 | 0.0196 | 2.45 |
| 82.0 | 0.551 | 0.155 | 0.0240 | 3.13 |
| 83.0 | 0.567 | 0.170 | 0.0289 | 3.67 |
| 84.0 | 0.586 | 0.200 | 0.0400 | 4.80 |
| 85.0 | 0.603 | 0.225 | 0.0506 | 6.00 |
| 86.0 | 0.624 | 0.255 | 0.0650 | 7.90 |

is very small. However, assuming a linear relationship between the activity of PbO and temperature, the temperature coefficient of activity was obtained directly from the above two values. The corresponding activities for different experimental temperatures (varying from 961°C to 1060°C) were obtained by interpolation (given in column 4, Table III). Knowing the experimental reaction rates and the activities, the values of k for different experimental temperatures were calculated from equation (3).

The value of the experimental activation energy was calculated by plotting the values of $\log_{10} k$ against the reciprocal of absolute temperature

TABLE III

Effect of temperature on the rate of
oxidation of graphite.

G.S.A. of graphite used in each experiment = 7.0 cm²
Percentage of PbO by weight in melt = 78.8.

| Experimental temperature in K° (T) | $\frac{1}{T^{\circ}K} \times 10^3$ | Rate (R) x 10 ⁴ (gm.C/cm ² /min.) | a _{PbO} | Experimental rate constant k x 10 ² (gm.C/cm ² /min) | -log ₁₀ k |
|---|------------------------------------|--|------------------|---|----------------------|
| 1234 | 0.810 | 0.95 | 0.106 | 0.85 | 2.070 |
| 1255 | 0.797 | 1.27 | 0.108 | 1.09 | 1.963 |
| 1273 | 0.785 | 1.63 | 0.110 | 1.35 | 1.870 |
| 1316 | 0.760 | 2.48 | 0.114 | 1.91 | 1.719 |
| 1333 | 0.750 | 2.90 | 0.116 | 2.16 | 1.666 |

(1/T°K) and was found to be 33 ± 2 kilocalories per mole. The results are summarised in Figs. 9 and 10 and Table III.

(B) Oxidation of Carbon

(1) Oxidation rate as a function of G.S.A. of carbon.

Special carbon spectroscopic electrodes were machined to different sizes whose G.S.A. varied from 5.1 to 12.7 cm². Utilising these carbon specimens, the amounts of carbon oxidized per minute by a lead oxide-silica melt (containing 78.8% of PbO by weight) at 1000°C were determined and found to be directly proportional to the G.S.A. of carbon. The results are given in Figs. 11 and 12 and Table IV. The rate of oxidation of carbon in the above melt at 1000°C was found to be 1.17×10^{-4} gm.C/cm²/min..

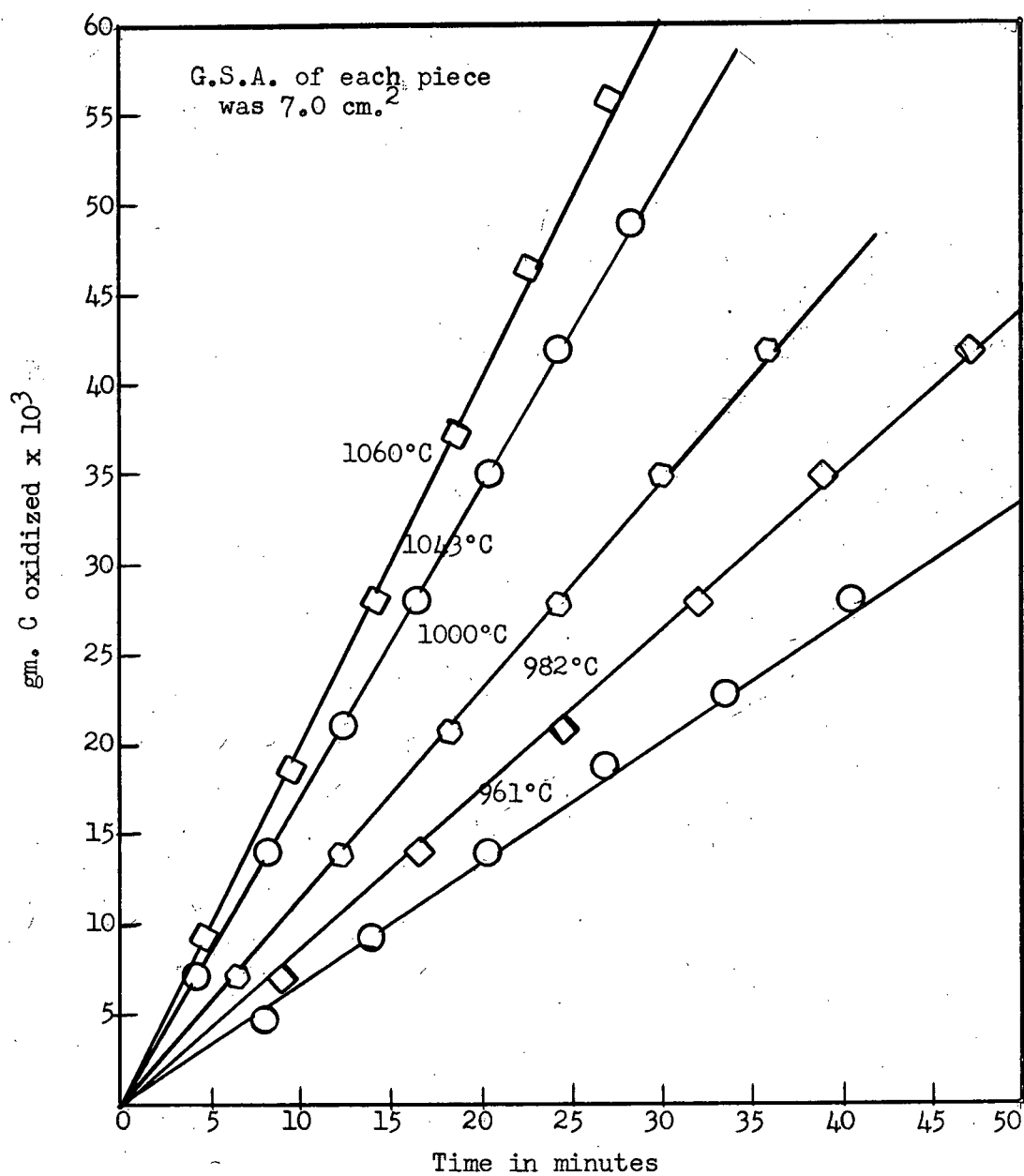


Fig. 9. Rate curves for oxidation of graphite at different experimental temperatures.

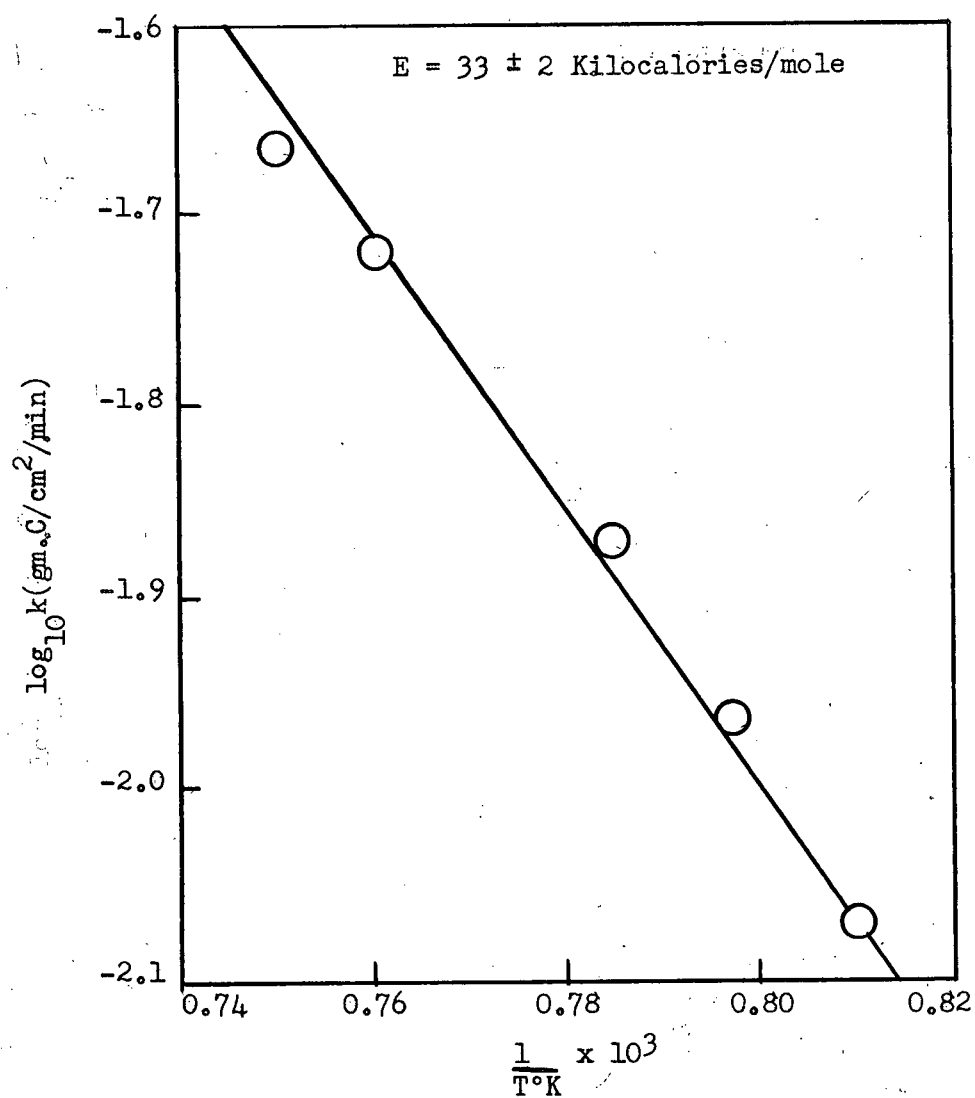


Fig. 10. $\log_{10} k$ vs $\frac{1}{T}$ for the oxidation of graphite.

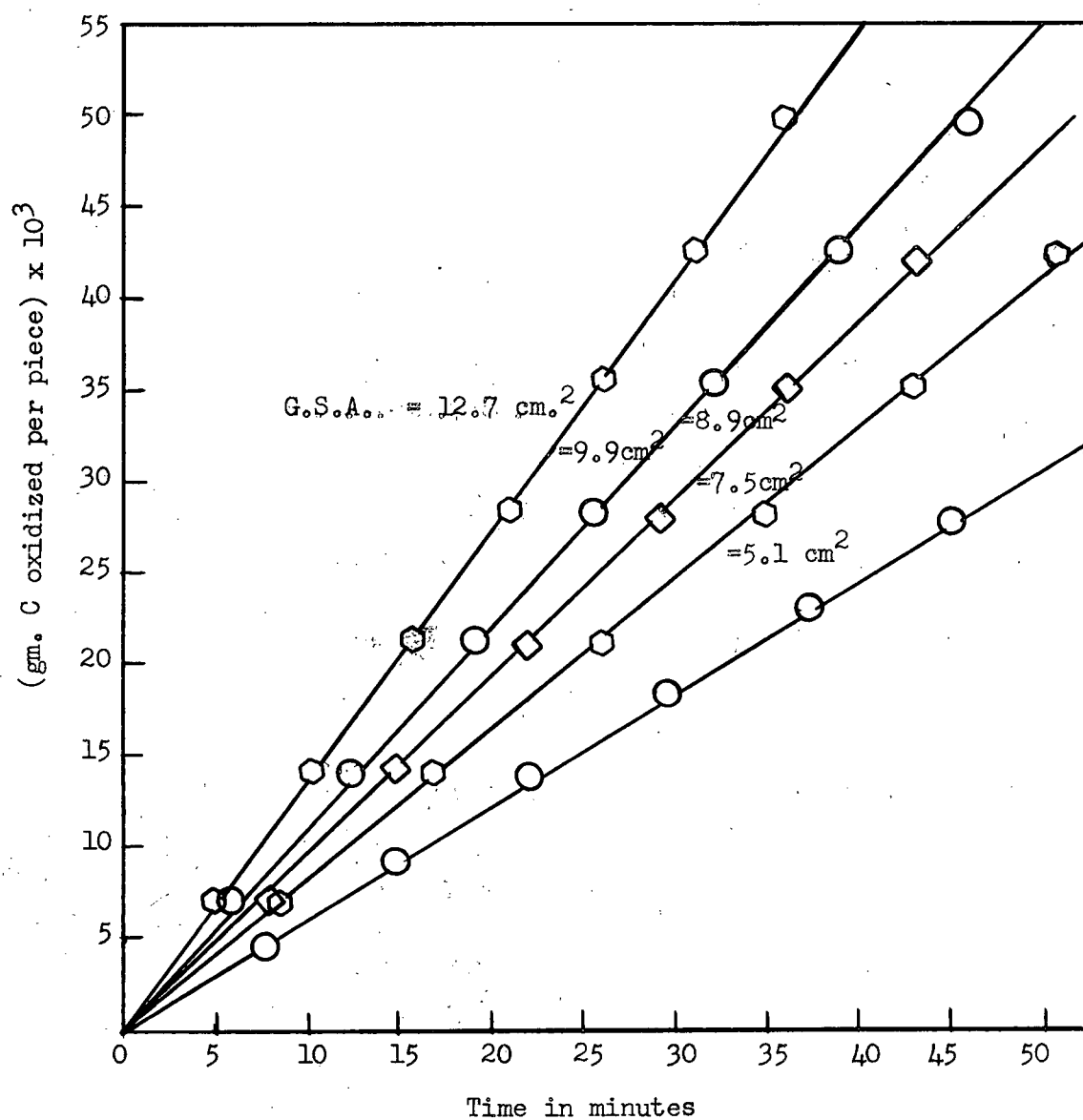


Fig. 11. Rate curves for oxidation of carbon having different geometric surface areas.

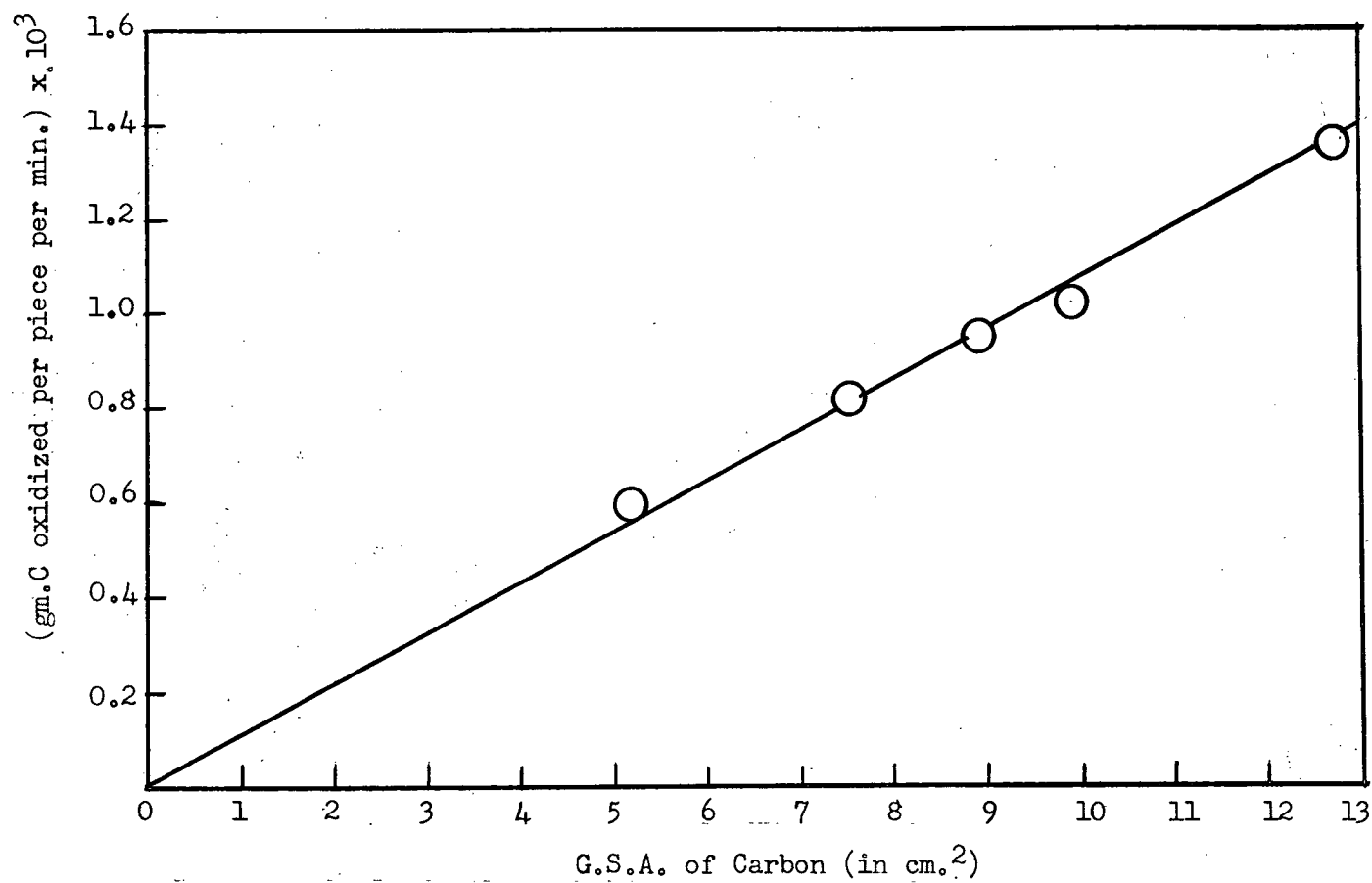


Fig. 12. Dependence of the reaction rate on the geometric surface area of carbon.

TABLE IV

Effect of geometric surface area of carbon on the rate of oxidation.

Experimental temperature = 1000°C

Percentage of PbO by weight in the melt = 78.8

| G.S.A. of carbon in cm^2 | (gram of C oxidized per piece per minute) $\times 10^3$ | Rate of oxidation (R) $\times 10^4$ ($\text{gm.C/cm}^2/\text{min.}$) |
|-----------------------------------|---|--|
| 5.1 | 0.60 | 1.17 |
| 7.5 | 0.82 | 1.10 |
| 8.9 | 0.95 | 1.07 |
| 9.9 | 1.18 | 1.19 |
| 12.7 | 1.36 | 1.07 |

(2) Effect of composition of lead oxide-silica melt on the rate of oxidation.

The rates of oxidation of carbon (using specimens of 7.0 cm^2 of G.S.A.) at 1000°C were determined for lead oxide-silica melts of different compositions. The composition of lead oxide in the melt varied from 77 to 86 percent by weight. The results of these experiments showed that the rate of oxidation was proportional to the square of the activity of lead oxide in the melt. The experimental results are summarised in Figs. 13 and 14 and Table V.

(3) Determination of the experimental activation energy of the oxidation of carbon.

The study of the oxidation of carbon in lead oxide-silica melt (containing 78.8% of PbO by weight) at different experimental temperatures

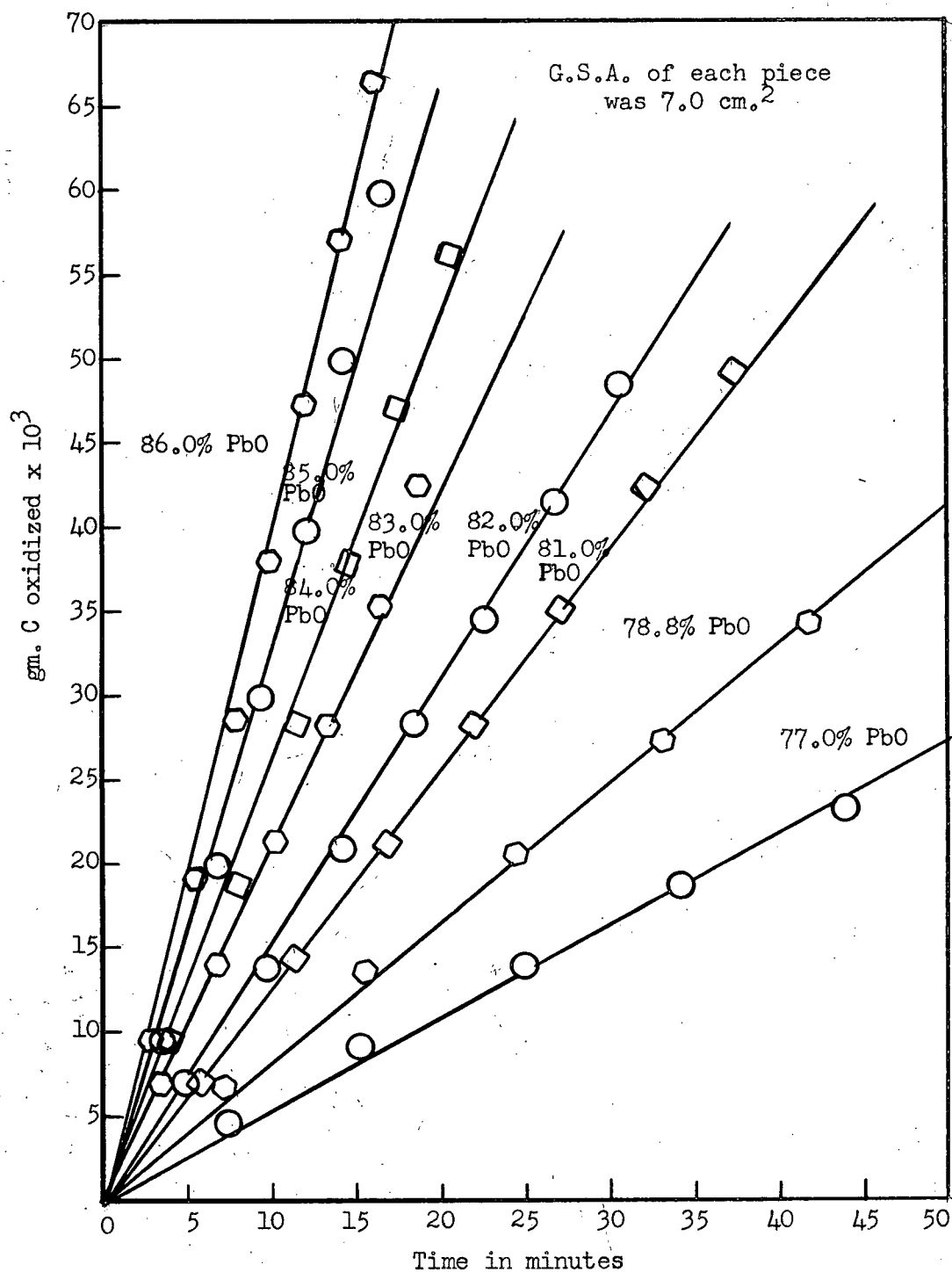


Fig. 13. Rate curves of oxidation of carbon by PbO-SiO₂ melts of different compositions.

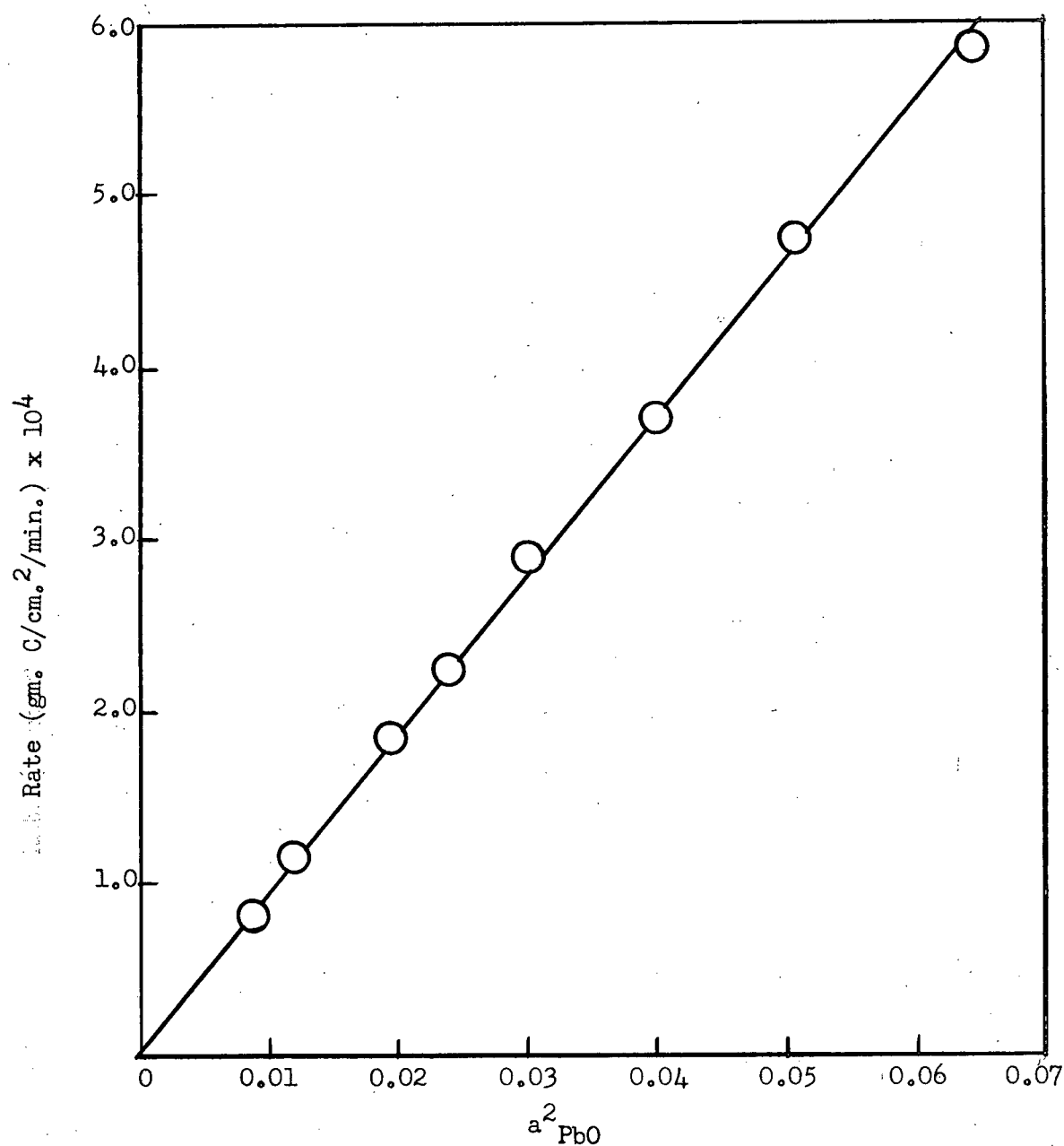


Fig. 14. Dependence of the rate of oxidation of carbon on the square of the activity of lead oxide in the melt.

TABLE V

Effect of activity of lead oxide in the melt on
the rate of oxidation of carbon.

Experimental temperature = 1000°C.

G.S.A. of carbon used for each experiment = 7.0 cm²

| Percentage of PbO (by weight) in the melt | N _{PbO} | a _{PbO} | a _{PbO} ² | Rate of oxidation (R) x 10 ⁴ (gm.C/cm ² /min.) |
|---|------------------|------------------|-------------------------------|--|
| 77.0 | 0.474 | 0.095 | 0.0090 | 0.79 |
| 78.8 | 0.499 | 0.110 | 0.0121 | 1.17 |
| 81.0 | 0.535 | 0.140 | 0.0196 | 1.84 |
| 82.0 | 0.551 | 0.155 | 0.0240 | 2.24 |
| 83.0 | 0.567 | 0.170 | 0.0289 | 2.90 |
| 84.0 | 0.586 | 0.200 | 0.0400 | 3.68 |
| 85.0 | 0.603 | 0.225 | 0.0506 | 4.76 |
| 86.0 | 0.624 | 0.255 | 0.0650 | 5.85 |

(varying from 958°C to 1063°C) by using carbon specimens of 7.0 cm² of G.S.A., was undertaken. From the reaction rate values of experimental rate constants 'k' were calculated as mentioned in the case of graphite. Then by plotting log₁₀k against 1/T°K, the experimental activation energy was determined as 22 ± 2 kilocalories per mole. The experimental results are summarised in Figs. 15 and 16 and Table VI.

(C) Oxidation of Petroleum Coke Mixture (Baked at 900°C)

Unlike the oxidation of graphite and carbon, the rate of oxidation of petroleum coke showed a gradual departure from the linear relationship with the reaction time after a few minutes. For example, the amount of carbon oxidized after 22 minutes of reaction from a piece of petroleum coke of 7.5 cm² of G.S.A. by a melt (containing 78.8% of PbO by weight) at 1000°C was

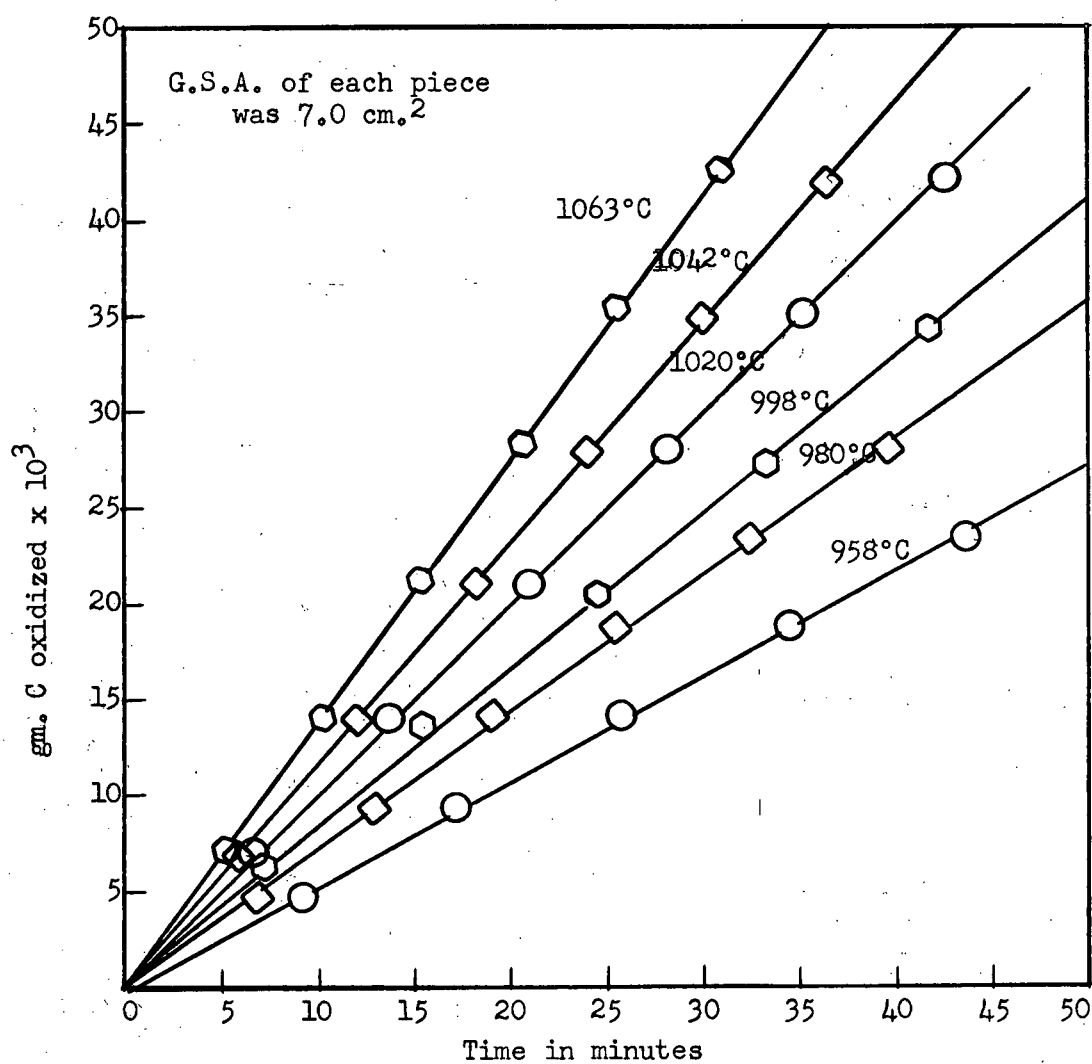


Fig. 15. Rate curves for the oxidation of carbon at different experimental temperatures.

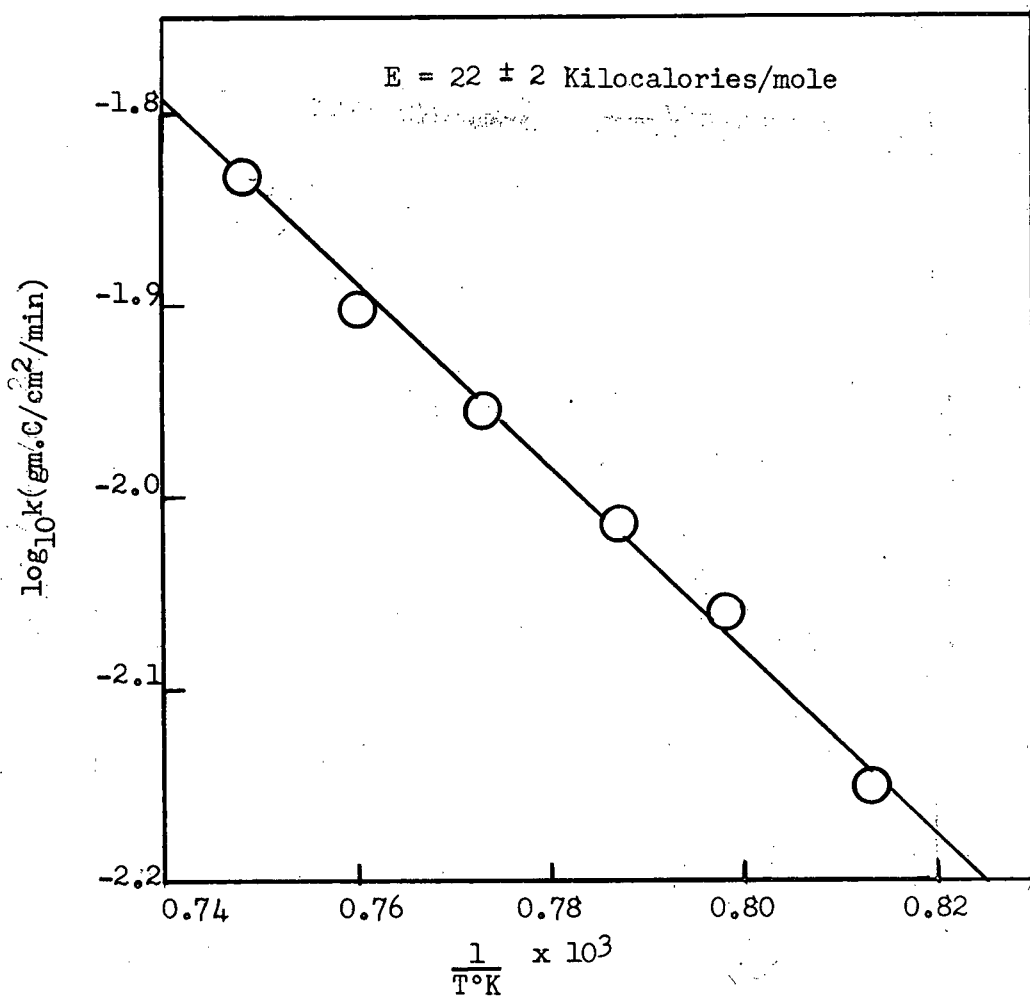


Fig. 16. $\log_{10} k$ vs $\frac{1}{T^{\circ}K}$ for the oxidation of carbon.

TABLE VI

Effect of temperature on the rate of oxidation of carbonG.S.A. of carbon used for each experiment = 7.0 cm^2

Percentage of PbO by weight in the melt = 78.8

| Expt'l temp. in K° (T) | $\frac{1}{T^\circ\text{K}} \times 10^3$ | Rate of reaction (R) $\times 10^4$ (gm.C/cm ² /min.) | a _{PbO} | Experimental rate constant (k) $\times 10^2$ (gm.C/cm ² /min.) | $-\log_{10} k$ |
|---------------------------------|---|---|------------------|--|----------------|
| 1231 | 0.813 | 0.79 | 0.106 | 0.71 | 2.152 |
| 1253 | 0.798 | 1.01 | 0.108 | 0.87 | 2.061 |
| 1271 | 0.787 | 1.17 | 0.110 | 0.97 | 2.014 |
| 1293 | 0.773 | 1.39 | 0.112 | 1.11 | 1.955 |
| 1315 | 0.760 | 1.63 | 0.114 | 1.25 | 1.903 |
| 1336 | 0.748 | 1.97 | 0.116 | 1.47 | 1.833 |

28.0×10^{-3} instead of 26.5×10^{-3} gram of carbon. This might be due to an increase in roughness of petroleum coke during the oxidation process. In order to avoid this error in the calculation of the rate of oxidation, only a few initial readings in an experimental run were considered.

(1) Relation of G.S.A. of petroleum coke with the rate of oxidation.

Samples of petroleum coke were machined to different diameters and different sizes. Each piece had a uniform diameter within $\pm 0.004\%$. The G.S.A. of specimens used in the experiments varied from 5.9 cm^2 to 12.7 cm^2 . The oxidation of these specimens by a lead oxide-silica melt (containing 78.8% of PbO by weight) at 1000°C showed that the amount of carbon oxidized per unit time was directly proportional to the geometric surface area. The results are summarised in Figs. 17 and 18 and in Table VII. The rate of oxidation at the above temperature and slag composition was found to be $1.6 \times 10^{-4} \text{ gm.C/cm}^2/\text{min.}$

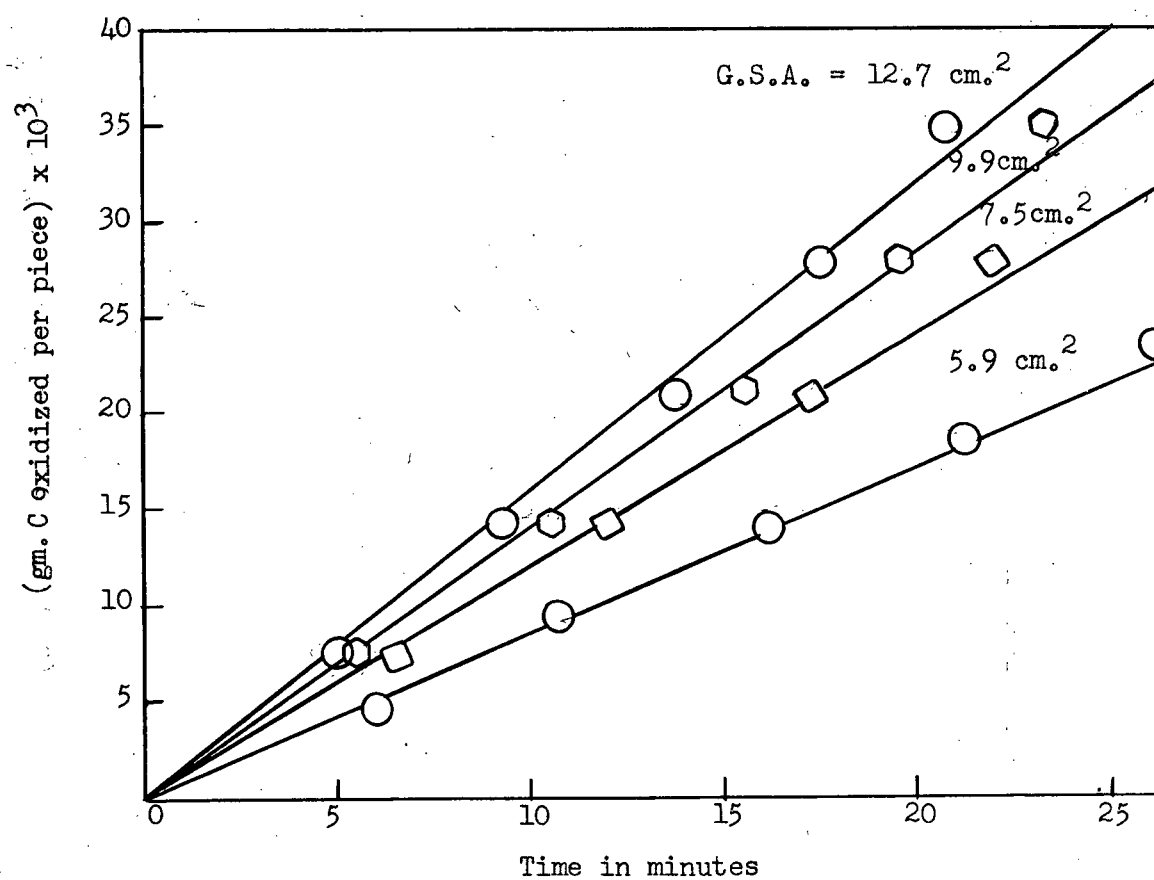


Fig. 17. Rate curves for oxidation of petroleum coke having different geometric surface areas.

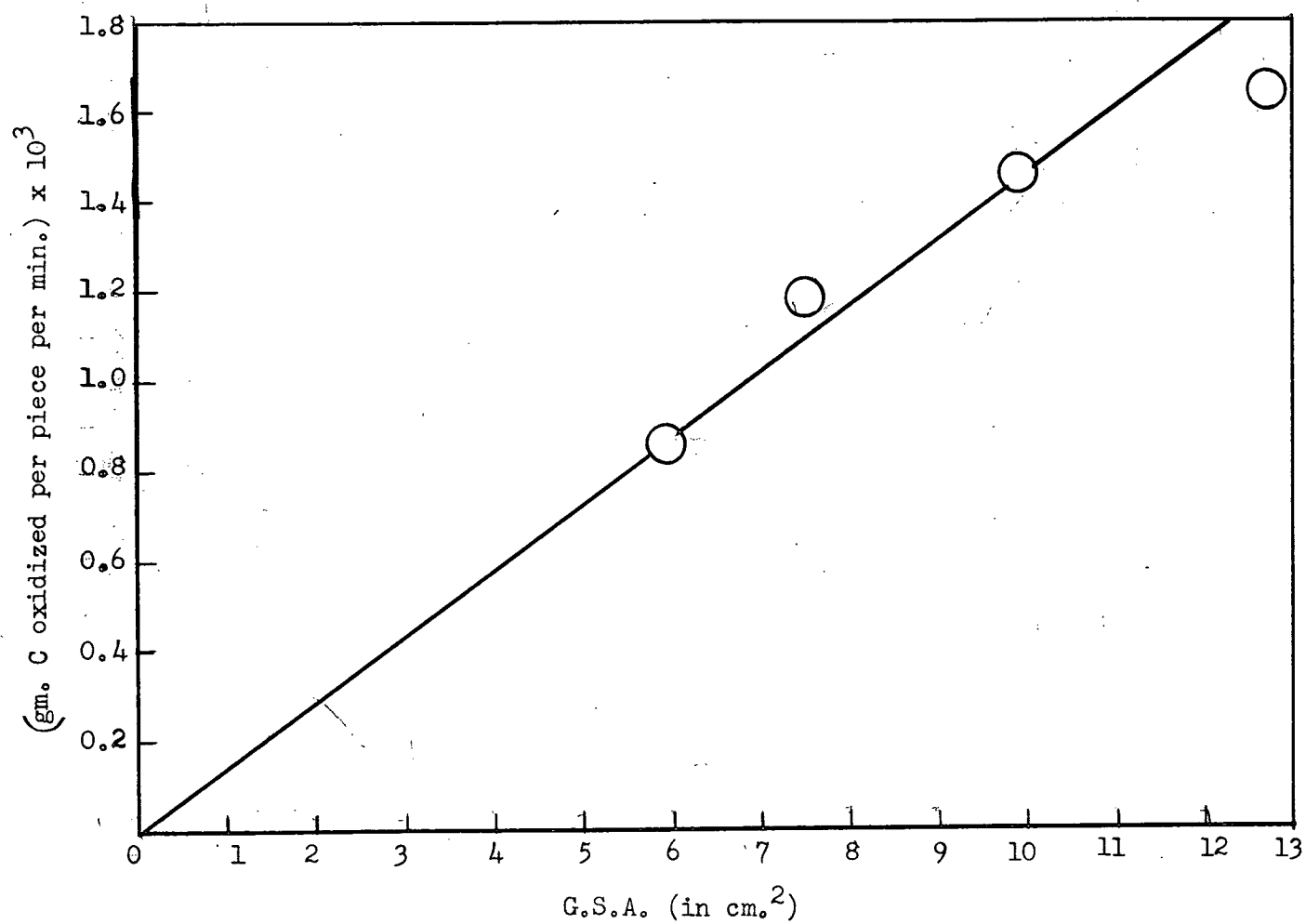


Fig. 18. Dependence of the reaction rate on the geometric surface area of petroleum coke.

TABLE VII

Effect of geometric surface area of petroleum coke on the rate of oxidation.

Experimental temperature = 1000°C.

Percentage of PbO by weight in the melt = 78.8

| G.S.A. of petroleum coke mixture (baked at 900°C) (in cm ²) | (gram of C oxidized per piece per min.) x 10 ³ | Rate of oxidation (R) x 10 ⁴ (gm.C/cm ² /min.) |
|---|---|--|
| 5.9 | 0.86 | 1.46 |
| 7.5 | 1.19 | 1.59 |
| 9.9 | 1.46 | 1.49 |
| 12.7 | 1.65 | 1.30 |

(2) Effect of the composition of lead oxide-silica melt on the rate of oxidation.

The study of the oxidation of petroleum coke at 1000°C using specimens of 7.5 cm² of G.S.A. by lead oxide-silica melts whose composition varied from 78.8 to 85.0% of PbO by weight, was undertaken. The experimental results showed that the rate of reaction was proportional to the square of the activity of lead oxide in the melt. The results are given in Figs. 19 and 20 and Table VIII.

(3) Determination of experimental activation energy of the oxidation of petroleum coke.

The rates of oxidation of petroleum coke by lead oxide-silica melt (containing 78.8% of PbO by weight) using specimens of 7.5 cm² of G.S.A., were measured for a number of temperatures varying from 980°C to 1065°C. The experimental rate constant k (gm.C/cm²/min.) at different experimental temperatures were calculated as before. Then by plotting log₁₀ k against 1/T°K,

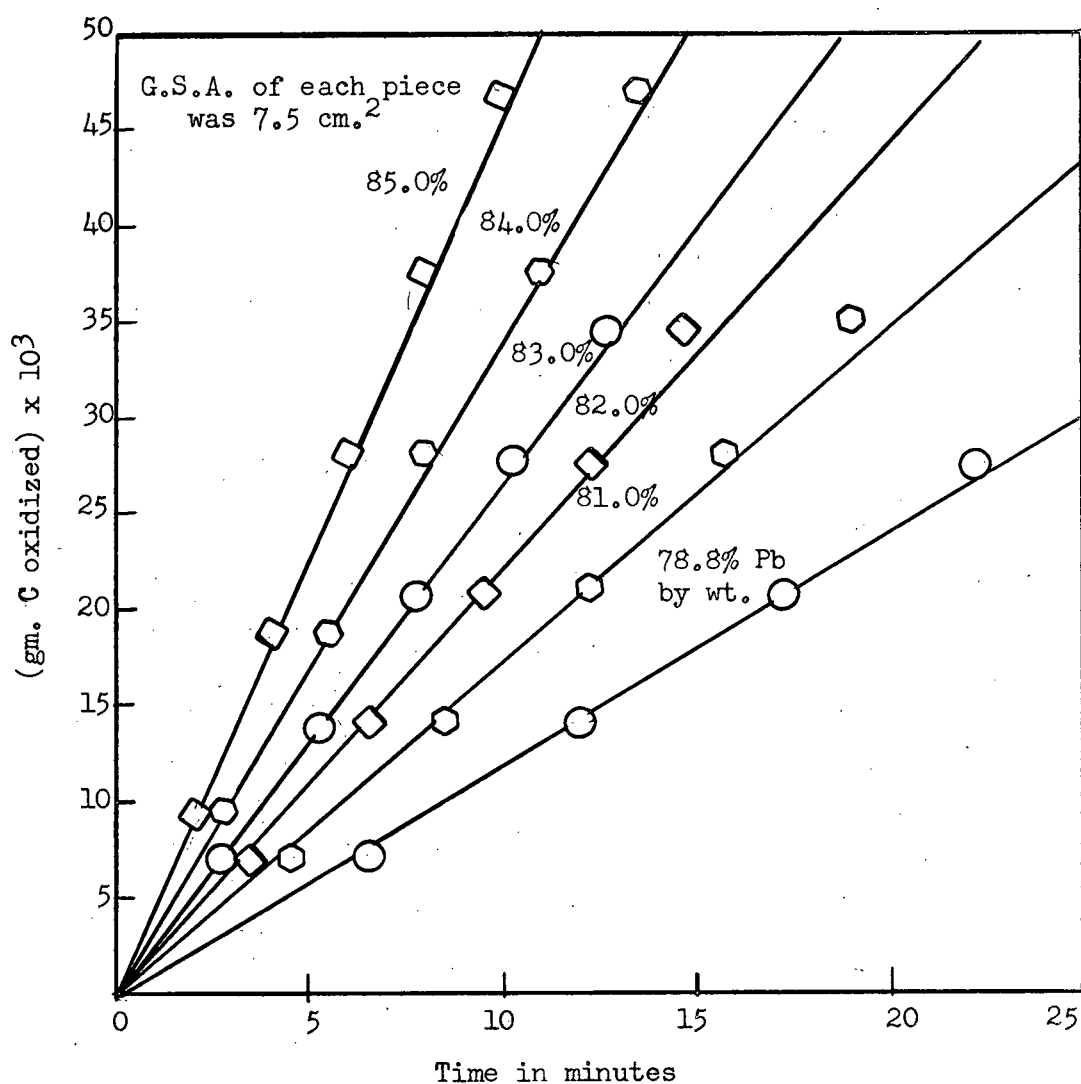


Fig. 19. Rate curves for oxidation of petroleum coke by PbO-SiO₂ melts of different compositions.

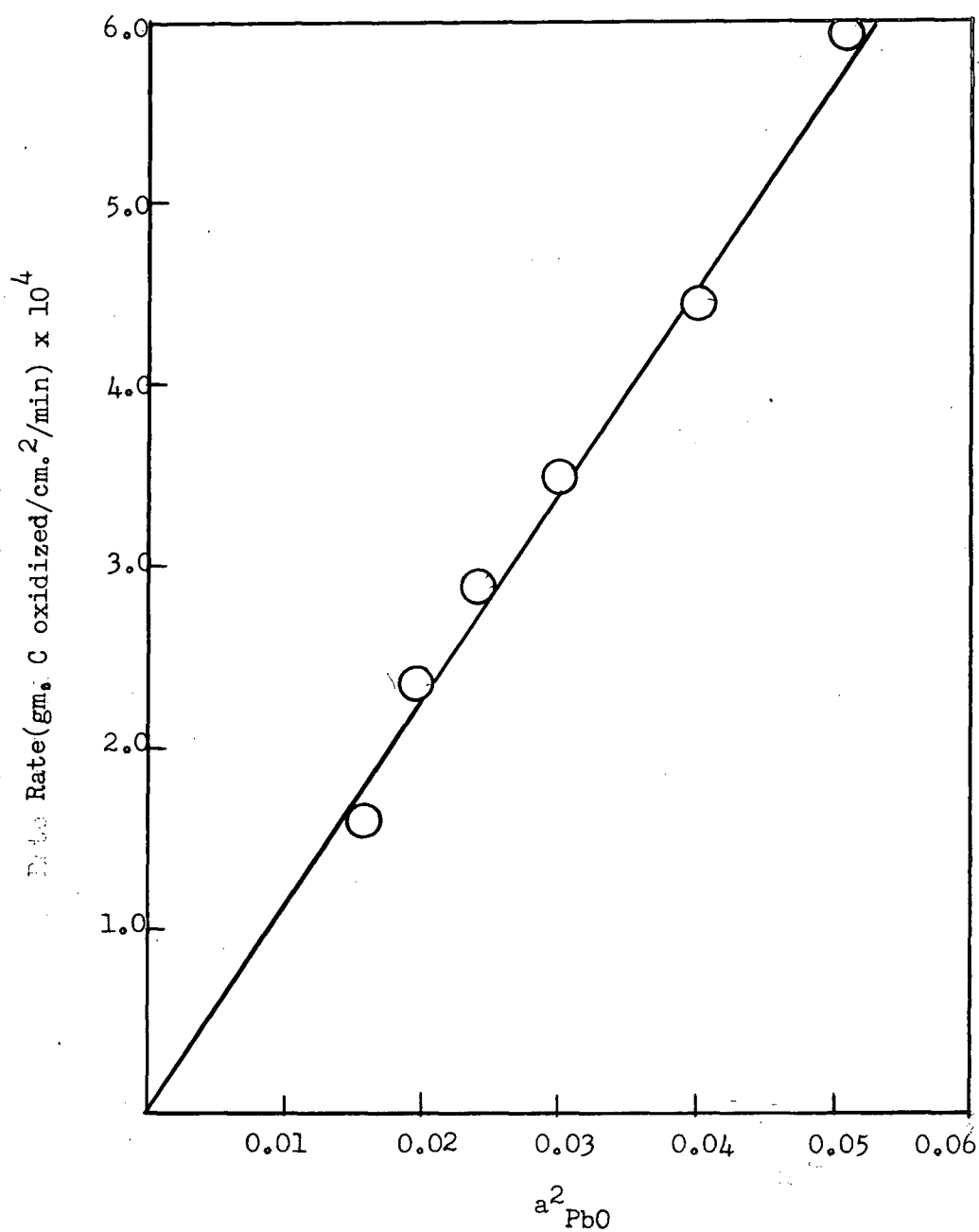


Fig. 20. Dependence of the rate of oxidation of petroleum coke on the square of the activity of lead oxide in the melt.

TABLE VIII

Effect of activity of lead oxide in the melt on the
rate of oxidation of petroleum coke.

Experimental temperature = 1000°C

G.S.A. of petroleum coke used in each experiment = 7.5 cm²

| Percentage of PbO by weight in the melt. | N_{PbO} | a_{PbO} | a_{PbO}^2 | Rate of oxidation (R) x 10 ⁴ (gm.C/cm ² /min.) |
|---|------------------|------------------|--------------------|--|
| 78.8 | 0.499 | 0.110 | 0.0121 | 1.59 |
| 81.0 | 0.535 | 0.140 | 0.0196 | 2.36 |
| 82.0 | 0.551 | 0.155 | 0.0240 | 2.91 |
| 83.0 | 0.567 | 0.170 | 0.0289 | 3.50 |
| 84.0 | 0.586 | 0.200 | 0.0400 | 4.45 |
| 85.0 | 0.603 | 0.225 | 0.0506 | 5.98 |

the value of experimental activation energy was determined and was found to be 28 ± 2 kilocalories per mole. The experimental results are summarised in Figs. 21 and 22 and Table IX.

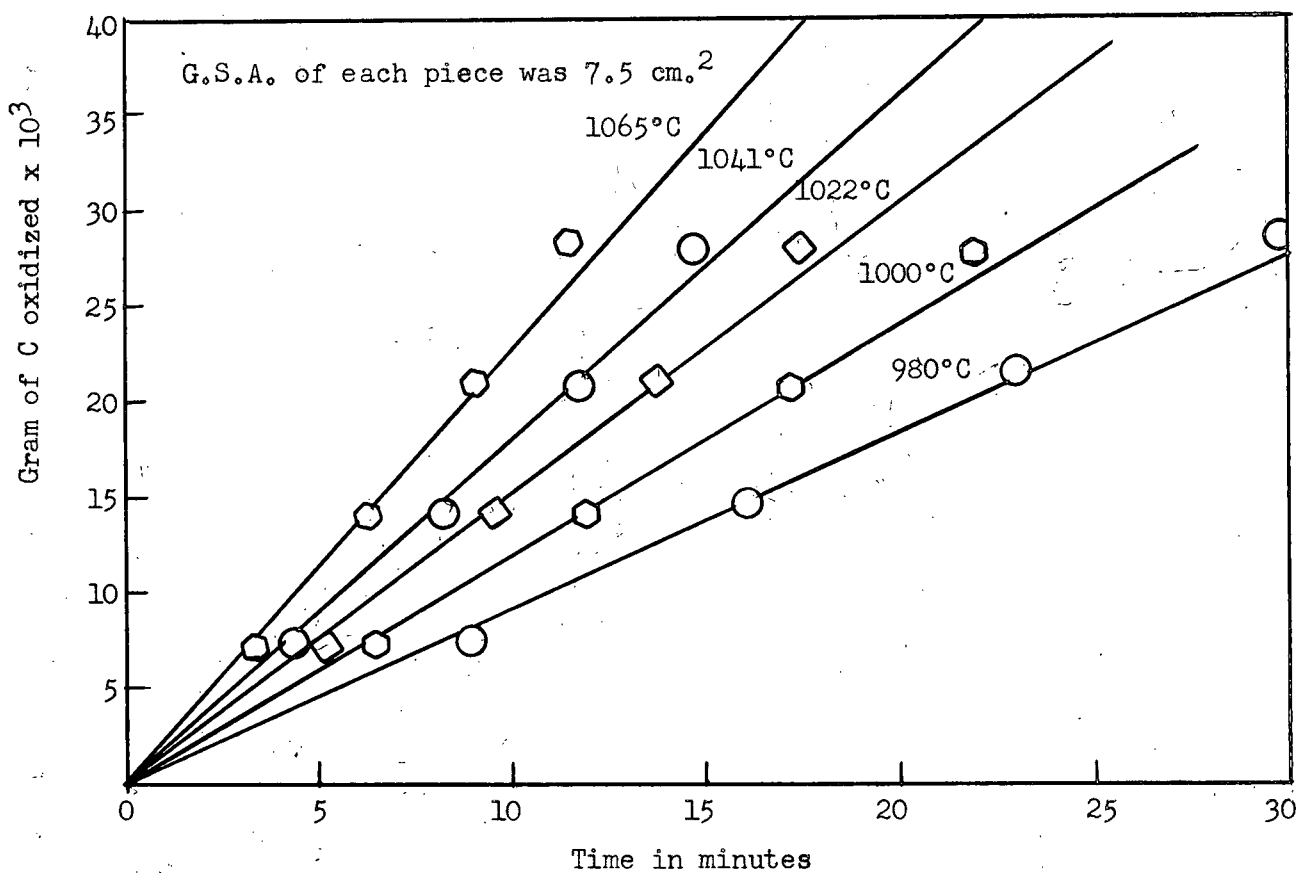


Fig. 21. Rate curves for the oxidation of petroleum coke at different experimental temperatures.

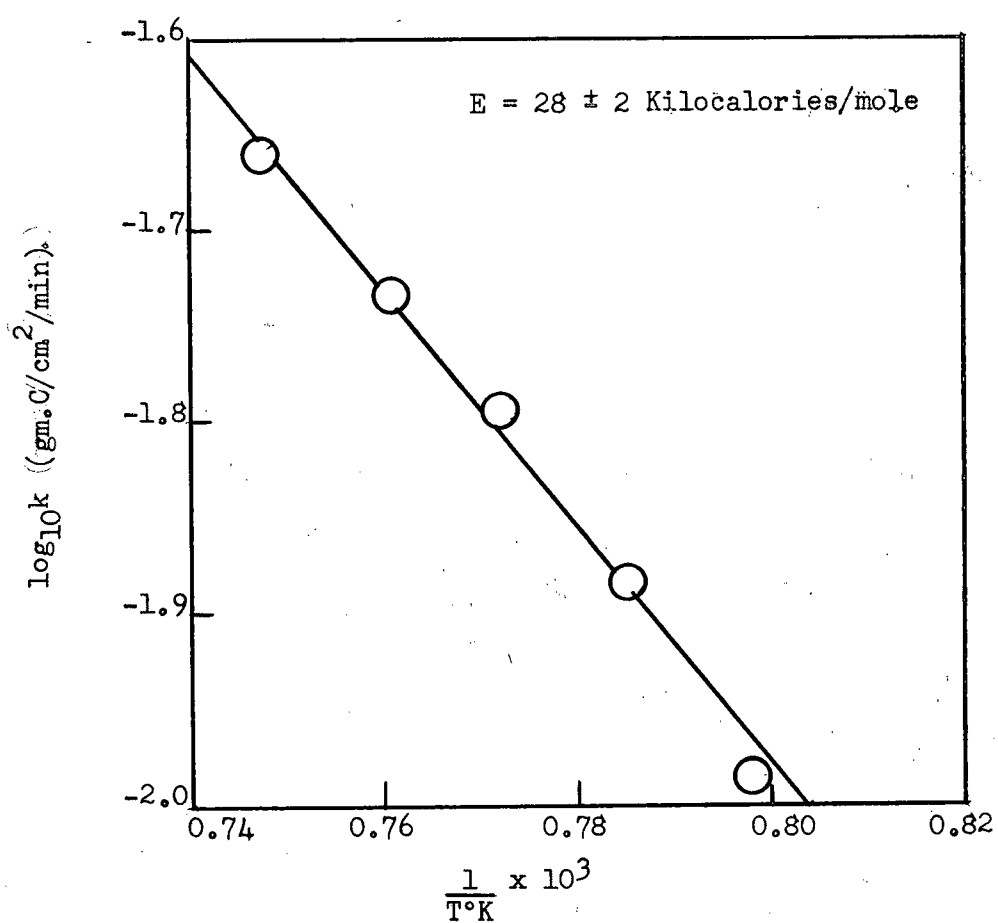


Fig. 22. $\log_{10}k$ vs $\frac{1}{T^{\circ}\text{K}}$ for the oxidation of petroleum coke.

TABLE IX

Effect of temperature on the rate of oxidation
of petroleum coke.

G.S.A. of petroleum coke used in each experiment = 7.5 cm²

Percentage of PbO by weight in the melt = 78.8.

| Experimental temperature in K° (T) | $\frac{1}{T^{\circ}K} \times 10^3$ | Reaction rate (R) x 10 ⁴ (gm.C/cm ² /min) | Activity of lead oxide (a _{PbO}) | Experimental rate constant: k x 10 ² (gm.C/cm ² /min) | -log ₁₀ k |
|---|------------------------------------|--|---|--|----------------------|
| 1253 | 0.798 | 1.22 | 0.108 | 1.04 | 1.983 |
| 1273 | 0.785 | 1.59 | 0.110 | 1.31 | 1.883 |
| 1295 | 0.772 | 2.01 | 0.112 | 1.61 | 1.793 |
| 1314 | 0.761 | 2.40 | 0.114 | 1.85 | 1.733 |
| 1338 | 0.747 | 3.00 | 0.117 | 2.19 | 1.660 |

DISCUSSION

From the study of the kinetics of the oxidation of graphite, carbon and petroleum coke by lead oxide-silica melts, it was found that the amount of carbon oxidized per unit time was proportional to the geometric surface area of the carbon sample and the rate of oxidation of lead oxide in the melt. The pressure of oxygen in the melt obtained from the dissociation of lead oxide was proportional to the square of the activity of lead oxide in the melt. Therefore, in every case the rate of oxidation was directly proportional to the oxygen pressure of the melt.

The rate equation for all cases investigated can be expressed by a general equation:

$$R(\text{gm.C/cm}^2/\text{min}) = k \cdot a_{\text{PbO}}^2 \quad \dots \dots \dots (3)$$

where a_{PbO} is the activity of lead oxide in the melt and k is the experimental rate constant. The values of $k(\text{gm.C/cm}^2/\text{min})$ for graphite, petroleum coke and carbon at 1000°C were found to be 1.35×10^{-2} , 1.31×10^{-2} and 0.97×10^{-2} respectively (given in column 5, Table X).

The experimental activation energy (E) values are given in column 6, Table X. This shows a range of values from graphite (33 ± 2 kilocalories per mole), petroleum coke (28 ± 2 kilocalories per mole) and carbon (22 ± 2 kilocalories per mole). As anticipated in the introduction, this characteristic gradation in the magnitude of E was expected because of the different heat treatment temperatures applied at the time of their manufacture.

From the above experimental rate constant values ' k ', it is observed

TABLE X

Summary of the results.

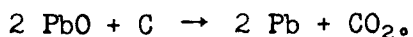
(Results at 1000°C)

| Percentage of PbO by weight in the melt. | Type of carbon used for oxidation | Reaction rate (R) x 10 ⁴ (gm.C/cm ² /min) | Activity of PbO in the melt. | Experimental rate constant k x 10 ² (gm.C/cm ² /min) | Experimental activation energy (kilocalories per mole) | Reaction rate (μ) x 10 ¹⁷ (atoms C/cm ² /sec) | After introducing S.R. factor, the value of μ x 10 ¹⁵ (atoms C/cm ² /sec). |
|--|-------------------------------------|---|------------------------------|--|--|---|--|
| 78.8 | graphite | 1.63 | 0.110 | 1.35 | 33 ± 2 | 1.4 | 1.4 |
| 78.8 | petroleum coke mix (baked at 900°C) | 1.59 | 0.110 | 1.31 | 28 ± 2 | 1.3 | - |
| 78.8 | Carbon | 1.17 | 0.110 | 0.97 | 22 ± 2 | 1.0 | - |

that the magnitude of k for graphite is nearly equal to that of petroleum coke and is higher by 0.4×10^{-2} than that of carbon. However, the experimental activation energy of the oxidation of graphite is greater than those of the other two. This might be due to one or both of the following factors: (i) the surface roughness factor (i.e., the ratio of the real surface area to the geometric surface area) was not the same in all three types of carbon; (ii) the activation entropy change involved in the oxidation process was not identical in all three cases.

Gulbransen and Andrew²⁷ determined the surface roughness of graphite using the adsorption of krypton vapour at liquid nitrogen temperature following the modified B.E.T. method. They found the surface roughness factor for graphite was of the order of 10^2 . In the present study the reactant is in the liquid state and because of the surface tension effects, the effective surface will probably be less than one hundred times the geometric surface area. Thus the true rate could be slower than the experimental value by less than 10^2 .

From the experimental results obtained in all cases, it appears that the reactant species in the melt contains oxygen atoms associated with two molecules of lead oxide. This may be inferred from the observation that in all cases the rate of oxidation was proportional to the square of the activity of lead oxide in the melt, i.e., was directly proportional to the equilibrium pressure of oxygen in the melt. In addition to this, it was also found that in all cases the product gas was carbon dioxide. Therefore the stoichiometry of the reaction for the oxidation of carbon in lead oxide-silica melt can be written as



If it was assumed that oxidation of graphite by the oxygen obtained from the dissociation of lead oxide in the melt and that by gaseous oxygen were identical, the mobile adsorption of the activated complex should be a possible rate determining step as observed by Gulbransen.⁵ In PbO-SiO₂ melt (containing 78.8 percent of PbO by weight) the reacting oxygen expressed as oxygen pressure was calculated from the dissociation of lead oxide (given in Appendix). Expressing this pressure in terms of concentration of oxygen, the value was found to be 5.4×10^8 molecules per cm³. Utilising this oxygen concentration and Gulbransen's experimental activation energy ($E = 36.7$ kilocalories per mole as compared to the value of 33 ± 2 obtained from the present study) for the oxidation of graphite in gaseous oxygen, the reaction rate was calculated in the same way as done by the above author. The rate value was found to be of the order of 10^6 atoms.C/cm²/sec at 1000°C where as the experimental rate in the above melt at 1000°C was found to be of the order of 10^{17} atoms.C/cm²/sec (given in column 7, Table X). Taking the highest surface roughness factor²⁷ value (10^2) possible for this case, the experimental value reduced to the order of 10^{15} atoms.C/cm²/sec. Therefore the mechanism for the oxidation of graphite in PbO-SiO₂ melt was not similar to that in the case of gaseous oxidation. The high difference in rate values of the oxidation of graphite in gaseous oxygen and in PbO-SiO₂ melt might be due to the difference in character of the reactants as well as the activated complexes in the above two mediums.

CONCLUSIONS

1. A study of the oxidation of graphite petroleum coke mixture (baked at 900°C) and carbon by lead oxide-silica melts was undertaken at different temperatures. Experimental results showed that the amount of carbon

oxidized per unit time was proportional to the geometric surface area of the graphite, carbon or petroleum coke investigated. The rate of oxidation was found to be proportional to the square of the activity of lead oxide in the melt, or in other words, the rate was directly proportional to the equilibrium pressure of oxygen obtained from the dissociation of PbO in the melt.

The general rate equation can be expressed as $R \text{ (gm.C/cm}^2\text{/min)} = k \cdot a_{\text{PbO}}^2$ where a_{PbO} is the activity of lead oxide in the melt and k is the experimental rate constant. The value of k is constant for a particular carbon. The values of k at 1000°C for graphite, petroleum coke and carbon were respectively 1.35×10^{-2} , 1.31×10^{-2} and 0.97×10^{-2} gm.C/cm²/min.

2. From the study of the rates of oxidation at different temperatures, it was found that the experimental activation energy of the oxidation process was in the order of

$$E_{\text{graphite}} > E_{\text{petroleum coke}} > E_{\text{carbon}}$$

The activation energy values for graphite, petroleum coke and carbon were respectively 33 ± 2 , 28 ± 2 and 22 ± 2 kilocalories per mole.

3. In all cases the product gas was carbon dioxide.

4. From the experimental results it appears that the stoichiometry of the reaction of oxidation of carbon by lead oxide-silica melts can be written as $2 \text{ PbO} + \text{C} \rightarrow 2 \text{ Pb} + \text{CO}_2$.

RECOMMENDATIONS

1. In order to determine the true values of the rate of oxidation of different types of carbon, it is necessary to correct the rate values expressed in terms of geometric surface area for the surface roughness of the

respective carbon. As mentioned before the effective surface roughness factors of different types of carbon in lead oxide-silica melt are not known. Thus methods for the measurement of the surface roughness factors of different types of carbon should be investigated.

2. From the present investigation it was found that the rate of oxidation was proportional to the square of the activity of lead oxide (or directly proportional to the pressure of oxygen obtained from the dissociation of lead oxide) in the melt. It would be very interesting to study the oxidation of carbon by mixtures of different metal oxides in silica melts. From this study it could be determined whether the reaction rate is proportional to the sum of the pressures of oxygen obtained from the dissociation of different oxides in the melt. This work may give an idea about the oxidizing power of an unknown melt from the magnitude of the rate of oxidation of carbon in that melt.

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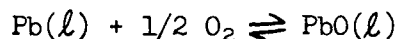
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APPENDIX

Calculation of Oxygen Pressure of Lead Oxide-Silica Melt.

The standard free energy²⁸ ΔF° of the reaction



is -22,900 calories at 1000°C. The equilibrium constant 'K' of this reaction is

$$K = \frac{a_{\text{PbO}}}{a_{\text{Pb}} \times p_{\text{O}_2}^{1/2}} = \frac{a_{\text{PbO}}}{p_{\text{O}_2}^{1/2}}$$

as the activity of lead is equal to 1. The value of K obtained from the value of ΔF° is 1.15×10^4 .

$$\text{or } K^2 = (1.15 \times 10^4)^2 = \frac{a_{\text{PbO}}^2}{p_{\text{O}_2}}$$

The activity of lead oxide in a lead oxide-silica melt (containing 78.8% of lead oxide by weight) is 0.110 at 1000°C.

Substituting the value of a_{PbO}^2 in the above equation, the value of p_{O_2} was found to be 9.3×10^{-11} atmosphere at 1000°C.

Converting this oxygen pressure to concentration units at this temperature, the concentration of oxygen (C_g) was found to be 5.4×10^8 molecules/cc.