

THE OXIDATION OF CARBON BY  
CUPROUS OXIDE-LEAD OXIDE-SILICA MELTS

by

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Members of the Department of  
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THE UNIVERSITY OF BRITISH COLUMBIA

December. 1960

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# ABSTRACT

An investigation of the relationship between the kinetics of the oxidation of spectroscopic grade graphite with the oxidising potential of cuprous oxide-lead oxide-silica melts was undertaken. The kinetics of the reaction were studied at two temperatures over a wide range of oxidising potentials. In all cases it was observed that the rate of oxidation was proportional to the equilibrium oxygen pressure of the system and the square of the activity of the oxygen ions. The variation of the rate constant with temperature indicated that  $O^{--}$  are involved in the rate determining step. At a given temperature the rate constants for the simple  $PbO-SiO_2$  and the complex  $Cu_2O-PbO-SiO_2$  slags were found to be of the same order of magnitude, if  $O^{--}$  were considered. Hence the rate expression could be written as

$$k = A aO^{=2} e^{-E/RT}$$

The activation energy of oxidation of graphite was determined over a wide range of  $PbO-SiO_2$  composition, and found to have a value of  $22 \pm 2$  Kcal./mole. The activation energy for spectroscopic grade carbon was found to have a value of 22 Kcal./mole, indicating that the activation energy was independent of the nature of the carbon surface. The constant A was observed to have a value of 12 for the slags investigated.

The theory of the ionic equilibrium in silicate melts devised by Toop and Samis was extended to calculate  $aO^{--}$  and silica in multicomponent silicate slags. The present investigation appears to substantiate their theory.

The results obtained in this study indicate that  $a_{O^{--}}$  in an unknown silicate melt might be determined by oxidising carbon in the melt and measuring the rate of oxidation.

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## THE OXIDATION OF CARBON BY CUPROUS OXIDE-LEAD OXIDE-SILICA MELTS

### INTRODUCTION

The oxidation of carbon by oxygen and oxides is a reaction that has played a unique role in the history of mankind from time immemorial. Only recently, however, attention has been focussed on the kinetics and mechanism of the oxidation process. The kinetics of gaseous oxidation of carbon have been studied extensively during the past two or three decades. On the other hand the oxidation reaction with the oxidants in the molten state has not been thoroughly investigated, partly because very little is known about the structure of the liquid state. In view of this, the present investigation on the oxidation of carbon in cuprous oxide-lead oxide-silica melts has been undertaken to study the relationship between the rate of oxidation of carbon, and the nature of the reacting species of oxygen.

It is advantageous first to consider the present knowledge of the gaseous oxidation of carbon, so that the changes involved in replacing the gaseous oxygen by an oxidising liquid medium can be evaluated in the light of this data.

#### Kinetics of Gaseous Oxidation of Carbon:

The kinetics of reactions of carbon with oxidising gases such as oxygen, and carbondioxide have been studied by many including Langmuir, Sykes, Hinshelwood, Gulbransen and others <sup>1,2,3,4,5</sup>. The reaction can be looked upon as being made up of two basic processes, (A) Adsorption and (B) Chemical reaction and desorption. The rate controlling step is one

of these.

#### (A) Adsorption Process

Experimentally it has been found that the process is of the first order with respect to oxygen for pressures of 10 cms. of mercury of oxygen or higher, while a zero order reaction rate is found at low pressures. Also the concentration of sites does not influence the reaction order.

Gulbransen <sup>5</sup> has made a comparison of the experimental rates with those calculated from the absolute reaction rate theory, developed by Eyring <sup>6</sup>. He shows that either (i) mobile adsorption or (ii) immobile adsorption with dissociation is a possible rate controlling step. The equations for these cases have been worked out in appendix A.

It has been observed <sup>7</sup> that the heat treatment temperature affects reactivity of carbon in the oxidation process. The activation energy for the oxidation of carbon increases with the increase in heat treatment temperature. Sebastian and Mayers <sup>8</sup> have observed that the activation energy for the oxidation had a general relationship with the calcination temperature.

#### (B) Chemical Reaction and Desorption Process

Oxygen is adsorbed on to the carbon and it moves about in the graphite planes of the carbon to take up a position of bonding the carbon atoms in the periphery of the carbon crystallites. CO and CO<sub>2</sub> are desorbed by breaking the bonds between the peripheral carbon atom and the crystallite.

A large number of investigations in the field of carbon combustion have been carried out by Rhead, Sykes, Arthur, Gilliland, Bowring and others <sup>9,10,11,12,13,14,15</sup>. Their investigations indicate that:

- (1) Both CO and CO<sub>2</sub> are primary products of the combustion of carbon,
- (2) Two different mechanisms are operative in the desorption of CO and CO<sub>2</sub>. The apparent activation energy difference may be calculated from the CO/CO<sub>2</sub> rates at each temperature. It is found to be between 8 and 17 Kilo-calories,
- (3) At high temperatures the gas is predominantly CO,
- (4) Adsorbed hydrogen or water vapour accelerate the CO<sub>2</sub> desorption reaction while POCl<sub>3</sub>, PCl<sub>3</sub>, CCl<sub>4</sub>, NO, halogens, and Fe(CO)<sub>5</sub>,
- (5) Transition metals in the lattice promote the desorption of CO.

The desorption process has a bearing on the electronic arrangement in the carbon. <sup>16,17,18</sup> Long and Sykes <sup>19</sup> explain the mechanism of the desorption of CO and CO<sub>2</sub> on this basis.

#### Kinetics of the Oxidation of Carbon by Oxidising Melts

The kinetics of the oxidation of carbon by oxidising melts like alumina in cryolite, and slags have been studied by Rempel, Kodak, Haupin, Turnbull, Jena and others <sup>20,21,22,23,24</sup>. The electrochemical oxidation in cryolite melts has been extensively studied due to its importance in the aluminium industry. Here the anodic overvoltage involved influences the electronic structure of the carbon by increasing the proportion of CO<sub>2</sub> in the product gas <sup>23</sup>. The CO/CO<sub>2</sub> ratio of the product gas is also a function of the temperature of calcination of the carbon.

Oxidising slag melts have been employed to investigate the oxidation kinetics. Turnbull <sup>23</sup> investigated the oxidation of commercial graphite by employing lead borosilicate melts, with and without the application of electric potential. His studies were mainly concerned with the CO/CO<sub>2</sub> ratio. He obtained a rough value of  $2 \times 10^{18}$  atoms oxygen/cm<sup>2</sup>/sec at 1000°C for the rate of oxidation of commercial graphite in the above melt.

Jena <sup>24</sup> investigated oxidation of various forms of carbon in lead oxide - silica slags around 1000°C. He observed that:

- (1) The rate of oxidation of carbon is proportional to the geometric surface area of the specimen.
- (2) As in the gaseous and certain electrochemical oxidations the activation energy depended upon the nature of the carbon surface which is mainly determined by the calcination temperature. He obtained a value of  $33 \pm 2$  K.cal/mole for spectroscopic graphite,  $28 \pm 2$  K.cal/mole for petroleum coke, and  $22 \pm 2$  K.cal/mole for spectroscopic carbon.
- (3) The reaction rate was of the same order of magnitude for all types of carbon investigated.
- (4) At a given temperature the rate of oxidation was proportional to the square of the activity of lead oxide.
- (5) The product gas was predominantly CO<sub>2</sub> in all cases with 0.0 to 0.5% of CO.

#### Object and Scope of the Present Investigation

It appeared from Jena's work that the rate of oxidation of carbon had a distinct relationship with the oxidising potential of the slag. He had shown that the rate was proportional to the square of the

activity of lead oxide at  $1000^{\circ}\text{C}$  for all the types of carbon he had employed. It seemed that the relationship was of a more general nature in that the rate should be related to the oxygen pressure of the slag irrespective of the basic component. This could be verified by changing the oxygen pressure of the melt without substantially altering the lead oxide content of the slag, and measuring the change in the rate of carbon oxidation.

In the present investigation the lead oxide--silica slag was chosen as the oxidising agent for the following reasons:

- (1) The slag had already been studied by Jena and some details about its oxidising potential were known.
- (2) An examination of the phase diagram of lead oxide--silica system<sup>25</sup> (Fig. 1) shows that a large number of low melting slags can be obtained. Hence it was possible to cover a large range in oxidising potential at a single temperature. The temperature could also be varied over a wide range, from  $800^{\circ}\text{C}$  to about  $1100^{\circ}\text{C}$ , the maximum imposed by the experimental conditions.
- (3) The activities of lead oxide over a large range of composition of the lead oxide--silica system have been accurately determined by Richardson.
- (4) The rate of the oxidation of carbon in most of these melts was measurable at the present experimental temperatures.

The oxidising potential of the melt could be varied by adding small quantities of cuprous oxide to the lead oxide--silica melt. This oxide is much less stable than lead oxide at the experimental temperatures. Hence small quantities affect the oxygen pressure appreciably. The effect could be quantitatively evaluated since the necessary thermodynamic data was available.

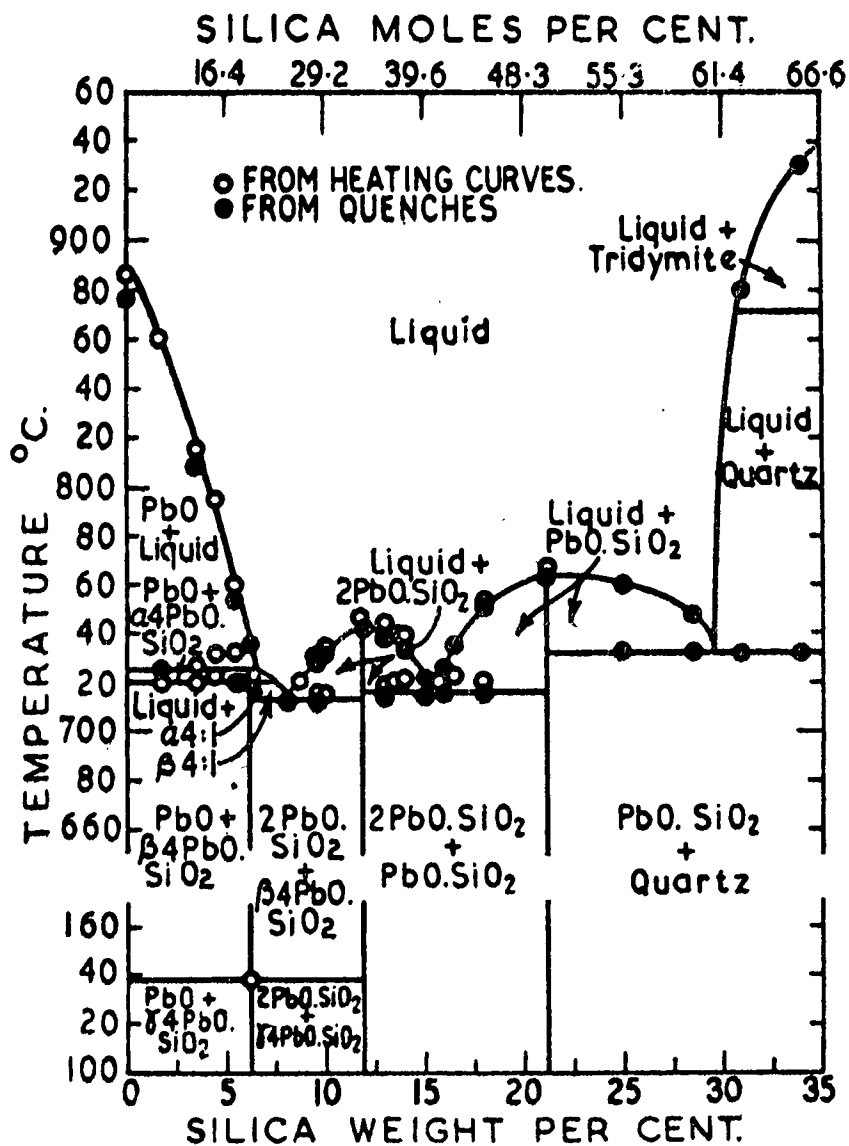


Fig. 1.

Lead Oxide - Silica Phase Diagram.



Another reacting oxygen species likely to be involved in the rate determining step was oxygen ions. When the investigation was commenced quantitative data was not available to evaluate its activity. Very recently Toop<sup>26</sup> has attempted to elucidate the structure of silicate slags on the basis of the ionic theory of slags and Temkin's rule<sup>27</sup>. He has developed a method for determining the most probable anions in any basic or acid slag in terms of an equilibrium constant involving singly bonded oxygen, doubly bonded oxygen and free oxygen ions in the melt. He has found that for an appropriate value of the equilibrium constant for these species, values of Temkin's ionic fraction of oxygen ions may be obtained that are close to, or equal to the experimental activities of various metal oxides in binary silicate melts. This observation has been verified mathematically by the application of Gibbs Duhem relationship to ionic silicate melts. Toop has also derived some ionic forms of the Gibbs Duhem equation for ternary systems and applied them to the  $\text{CaO-FeO-SiO}_2$  and  $\text{Cu}_2\text{O-PbO-SiO}_2$  systems. It was also the purpose of this investigation to verify his theory if oxygen ions were involved in the rate determining step.

Summarising, the object of the present investigation has been to identify the reacting state of oxygen. It appeared that the choice lay between (i) lead oxide expressed as  $a_{\text{PbO}}$ , (ii) molecular oxygen expressed in terms of oxygen pressure in atmospheres, (iii) oxygen ions expressed as  $a_{\text{O}^{2-}}$ .

If the reacting species were gaseous oxygen molecules or oxygen ions, the method could be used to evaluate them in unknown silicate melts.

Although Jena had found that at a particular temperature the rates of oxidation were of the same order of magnitude for the three

carbons investigated, the experimental activation energies varied widely. There appeared to be an inconsistency between these two observations. It was therefore thought that more investigations were necessary to resolve this.

## EXPERIMENTAL

### Apparatus

The experimental set up was the same as that used by Jena<sup>24</sup>, and is sketched in Fig. 2 where,

A = Globar Furnace

B = Chromel-Alumel Thermocouple to control the temperature of the furnace ( $+3^{\circ}\text{C}$ ) through a Leeds and Northrup Micromax controller.

C = Fireclay crucible containing the slag in contact with the metal phase.

D = Funnel. The stem of the funnel was a high temperature "Zirco-tube" (supplied by McDaniel Refractory Porcelain Co., Pennsylvania) and the cone portion was made of fired "synthetic lava". The cone was machined from grade "A" synthetic lava block (supplied by American Lava Corporation, Tennessee) and then fired slowly up to approximately  $1150^{\circ}\text{C}$ . The cone and the stem portion were joined by "Sairset" cement. In order to prevent the diffusion of the product gas through the refractory during a run, the cone portion of the funnel was coated completely with a paste of 78.8% PbO slag, and then fired slowly nearly up to  $1050^{\circ}\text{C}$  in order to coat the funnel uniformly. The thin coat did not cause a measurable change in the composition of the reacting melt.

E = Thin chromel rod holding in a loop a piece of carbon sample "F".

G = Glass tube. This was joined to the stem of the funnel, and carried

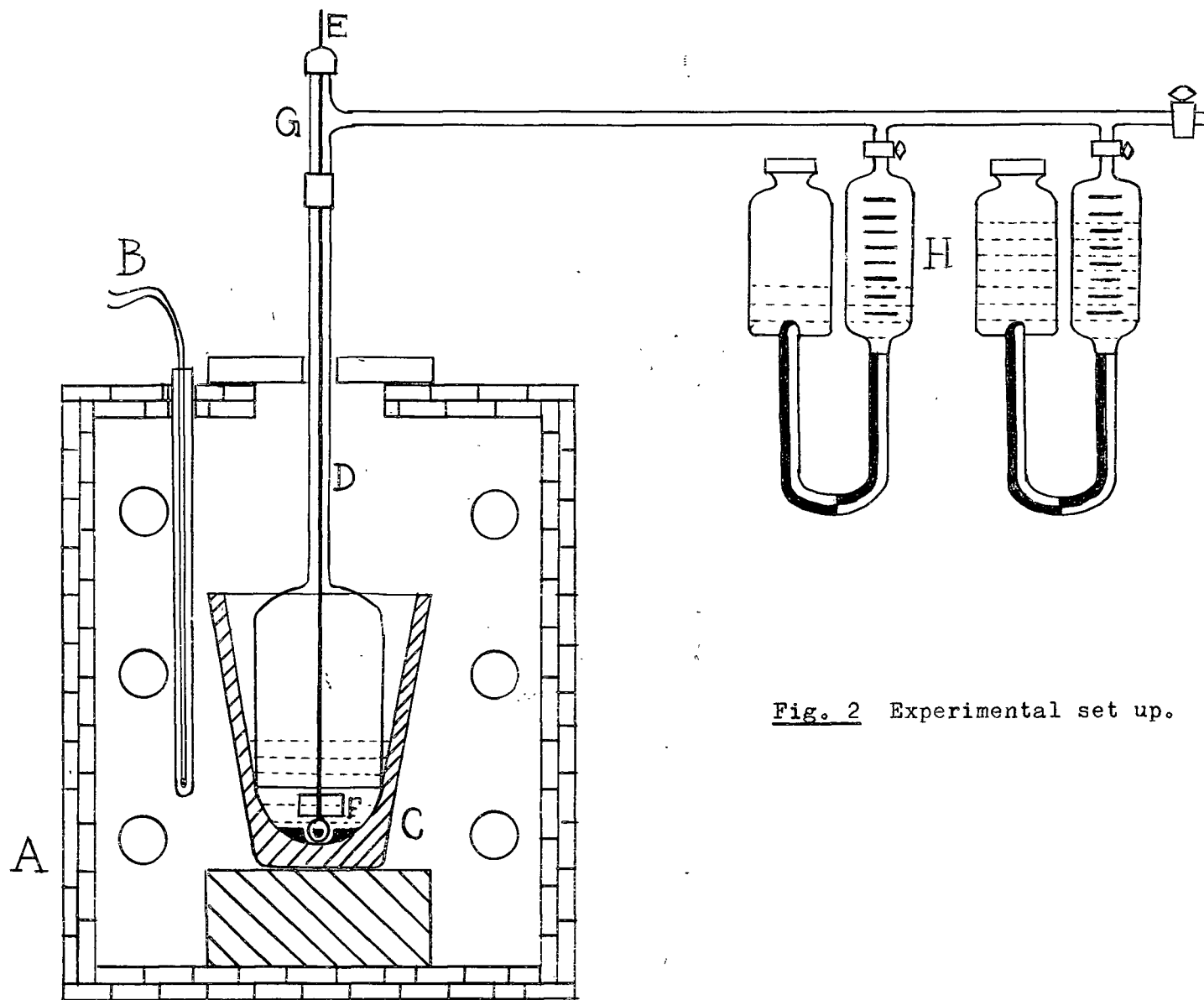


Fig. 2 Experimental set up.

a side tube which was joined to the glass collecting burettes "H".

### Materials

Special spectroscopic graphite and carbon electrodes were supplied by National Carbon Company in the form of rods of half-inch diameter. The chemicals used for the melt were of reagent grade.

### Procedure

A 1000-2000 gm. lot of the slag of the desired composition was prepared, and the mixture double sieved through a 35-mesh screen to ensure homogeneity. 100 gms. of the copper-lead alloy was prepared by mixing the metal powders in the required proportion. The alloy was equilibrated with 200 gms. of the slag at the desired temperature for three hours. About 200 gms. of the fresh slag mixture was then placed with about 40 gms. of this alloy in the crucible "C". The crucible and the funnel "D" (without the chromel rod holding the carbon) were then assembled in the furnace. The temperature of the furnace was raised at the rate of about  $200^{\circ}\text{C}/\text{hour}$  ( $100^{\circ}\text{C}/\text{hour}$  during the melting range of the slag). The slag was then maintained at the experimental temperature for  $2\frac{1}{2}$  to 3 hours to ensure equilibrium conditions. Then the funnel was taken out of the furnace and the cleaned chromel rod "E" holding a piece of carbon of known geometric surface area was rapidly introduced into the funnel. The funnel was dipped into the melt, so that the carbon piece was completely immersed into it, and the oxidation process began. The side tube of the glass tube "G" was next joined quickly to the burettes "H". The gases evolved due to the oxidation reaction were collected by displacement of an acidified 4N magnesium sulphate solution in the gas collecting graduated burettes "H"

under atmospheric pressure. The rate of gas collection was measured with a stop watch. The experiment was repeated (3-4 times) with the same alloy, using fresh slag each time, until concordant rates were obtained in two successive runs. This was done since the equilibrium distribution of copper between the slag and the metal phases was not accurately known. It was observed that the copper content of the alloy varied until the equilibrium distribution was attained.

The copper in the slag and the metal phases was determined electrolytically after the elimination of silica and lead as lead-sulphate. It was found from preliminary experiments that the lead content of the slags in contact with lead or lead-copper phase was not altered significantly during the course of an experimental run.

Jena's observation that the product gas consists of carbon-dioxide and 0.0 to 0.5 percent of carbon monoxide was confirmed by means of Orsat analysis. It was likely that some of the carbon-dioxide would dissolve in the magnesium sulfate solution during collection and hence there might be some error in the measurement of the volumes for different reaction times. To check this, known quantities of pure carbon-dioxide were collected in the burettes, at a rate less than the slowest observed reaction rate. It was found that less than 1.0 percent of total carbon-dioxide was dissolved in the solution under these conditions.

The chromel rod "E" carrying the carbon dipped into the metal phase during the run. To investigate whether this altered the reaction by introducing an unknown electrochemical factor a run was made in which the chromel rod was not in contact with the metal phase. It was found that the rate was not altered, ruling out this possibility.

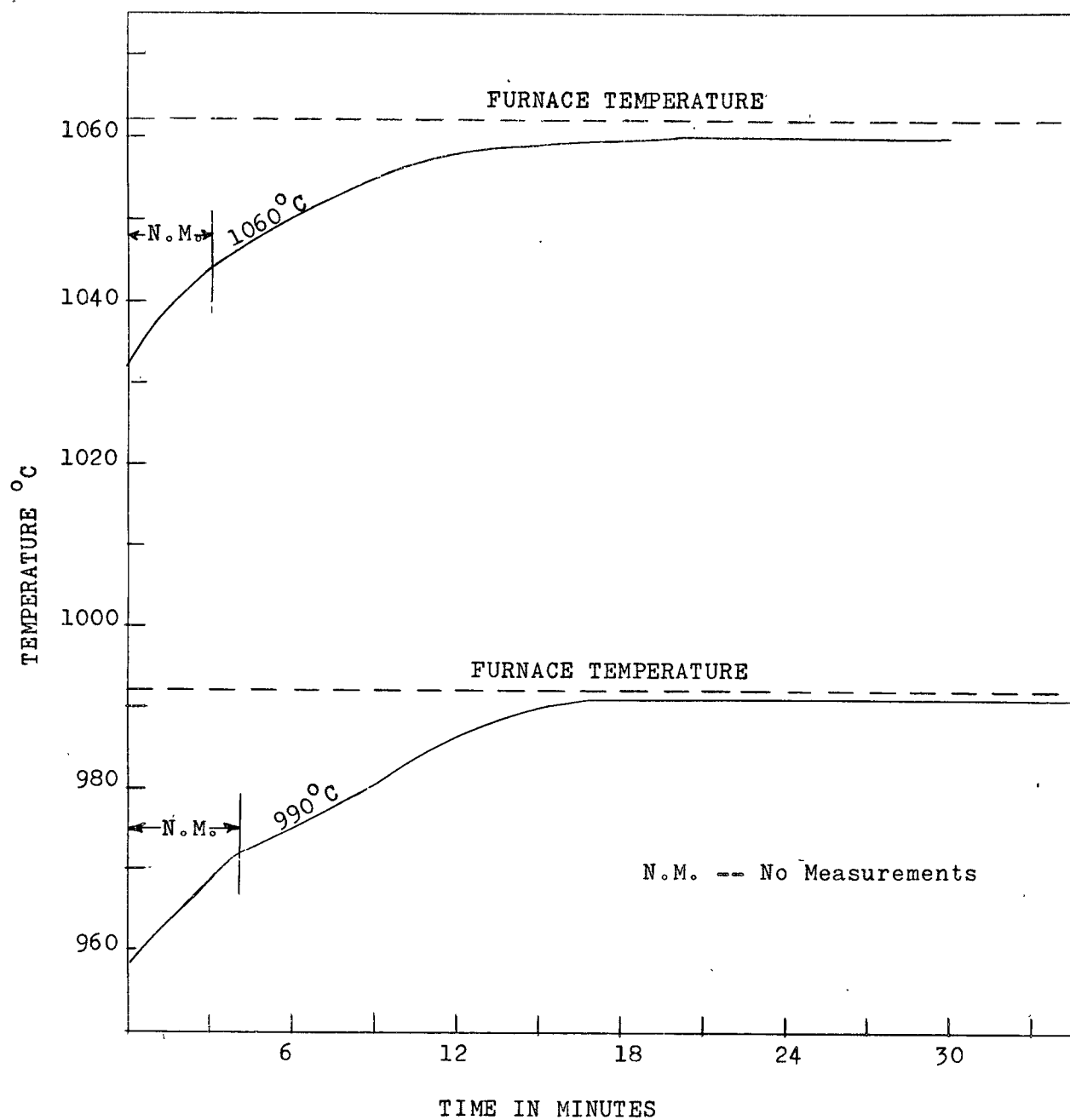


Fig. 3 Variation of slag temperature during an experimental run.

### Presence of Cupric Oxide

It was possible that the melt contained cupric oxide which would have altered the rate of oxidation. Calculations, based on free energy data revealed, however, that with the low oxygen potential of the system, the ratio of  $\text{CuO}/\text{Cu}_2\text{O}$  varied from  $0.5\text{--}3.0 \times 10^{-5}$  under the experimental conditions, rendering such a possibility unlikely.

### Temperature Control During the Run

The process of taking out the funnel "D" to insert the chromel rod "E", and introducing it immediately in the melt, cooled down the melt by  $30 - 40^\circ\text{C}$ . For this reason measurements were begun after 10 ccs. of the product gases were collected. In separate experiments, the chromel rod was substituted by a chromel-alumel thermocouple, permitting direct measurements of the slag temperatures. The temperature variation with time is shown in Fig. 3. It is seen that at the commencement of the run, the temperature of the slag is about  $15^\circ\text{C}$  below the furnace temperature, and that it rises to within  $2^\circ\text{C}$  of the furnace temperature in 10 - 15 minutes. Hence it might be expected that the rate of gas evolution is slower initially. However, since the observed rates were linear with time, it appears that factors like progressive decrease in oxygen activity of the melt, initial surface conditions of the carbon slug (unavoidable presence of fine carbon powder enhancing the rate), and progressive decrease of geometric surface area balance each other leading to overall linear rates.

### Reproducibility

For a particular set of experimental conditions, the amount of carbon oxidised was found to bear a linear relationship with the reaction

time. The rate of oxidation was obtained from the slope of the above line. It was found that the rates were reproducible to within  $\pm 5\%$ .

### Diffusion

Jena's observation that the rate of oxidation was independent of the stirring rates (1 - 3 revolutions per second) was confirmed. This indicated that under the present experimental conditions, diffusion of the reactants to the carbon surface was not rate controlling.

### CALCULATIONS

#### Oxidising Potential ~~Capacity~~ of the Slag

The oxidising potential of the slag can be evaluated in terms of the activity of lead oxide, oxygen pressure, or the activity of oxygen ions.

The activity of lead oxide in lead oxide-silica system has been accurately determined (estimated maximum error  $\pm 3.5\%$ ) by Richardson and Webb<sup>28</sup> at  $1000^\circ\text{C}$ ,  $1100^\circ\text{C}$  and  $1194^\circ\text{C}$ . His results for  $1000^\circ\text{C}$  have been reproduced in Fig. 4.

The oxygen pressure of the simple lead oxide silica slags can be calculated on the basis of the following reaction:



$$K = \frac{a_{\text{PbO}}}{a_{\text{Pb}} \cdot P_{\text{O}_2}^{1/2}} \quad P_{\text{O}_2} = \left( \frac{a_{\text{PbO}}}{a_{\text{Pb}} \cdot K} \right)^2$$

The necessary data has been included in the Appendix B. for the required temperatures.



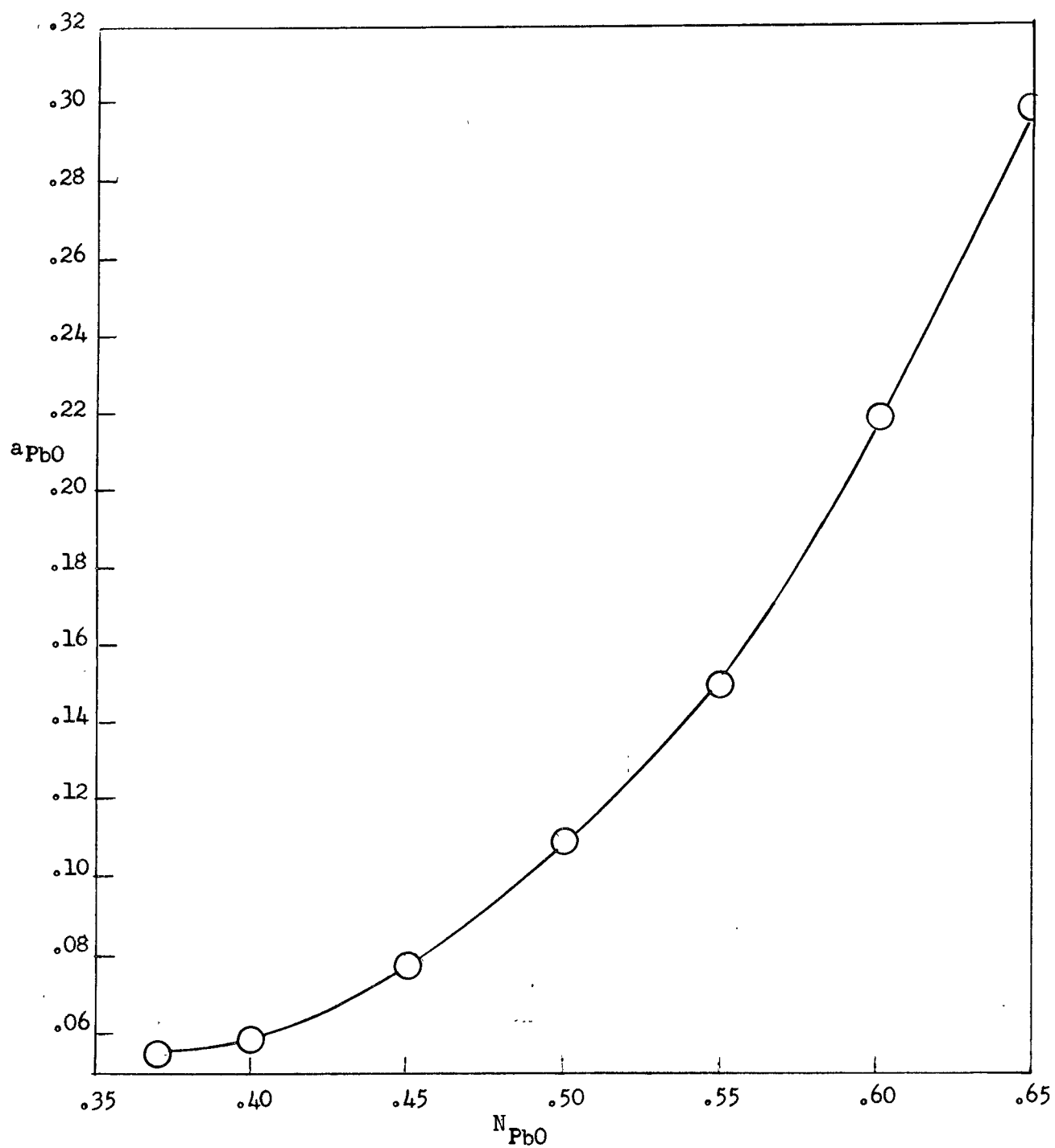
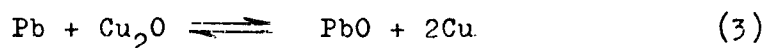
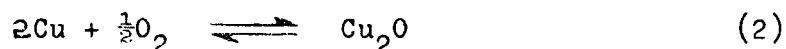


Fig. 4 Activity-mole fraction relationship of lead oxide.

For the complex cuprous oxide-lead oxide-silica slags the activities of the various components were calculated thermodynamically, on the basis of these additional equations:



The equilibrium constants were obtained from the free energy data as shown in the appendix. To calculate the activities for the metallic components the button in contact with the slag was analysed for copper and lead. The activity of the individual component was determined from the copper lead phase diagram using the relationship:

$$\text{Log } a. (\text{at } T^\circ\text{K}) = \frac{\Delta S_f}{4.575} \frac{T - T_m}{T} \quad (4)$$

where,  $\Delta S_f$  is the entropy of fusion of the constituent (2.29 eu).

$$T_m = \text{Melting point in } ^\circ\text{K}.$$

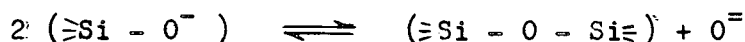
The liquidus curve of the leadrich side was taken from Klappa and Weil<sup>29</sup>.

From this data, for a given slag, the activity of cuprous oxide can be calculated if the activity of lead oxide in the slag is known. The maximum amount of cuprous oxide added is about 4 mole percent, with most of the slags containing less than 2 mole percent. Since such small quantities of cuprous oxide are involved, the activity of lead oxide in the lead oxide-silica slags may be assumed to be unchanged. Again, the variation of  $a_{\text{PbO}}$  is linear in this region<sup>26</sup>, and hence the general conclusions deduced later will not be altered in spite of this assumption. Knowing all the activities, the oxygen pressure of the system can be calculated from both copper and lead data. The values are given in Appendix B., Table I B. It will be observed that a close check is obtained.

The activities at one temperature are converted into activities

at another temperature using the relationship  $T_1 \log \gamma_1 = T_2 \log \gamma_2$ , or by plotting logarithm of activities against absolute reciprocal temperature, and extrapolating. Since the temperature range is small, errors in conversion are low. Again it is not the absolute values, but the relative variation over a small range, under the given conditions that is required.

The activity of oxygen ions in binary and ternary melts have been calculated on the basis of Toop's<sup>26</sup> theory. Fincham and Richardson<sup>30</sup>, recognizing that oxygen in silicate melts occurs in only three forms, singly bonded, doubly bonded and free oxygen ions, have suggested a very simple and probable equilibrium reaction:



or briefly



Toop proposed that under equilibrium conditions a quasi-chemical equilibrium constant may be written for this reaction,

$$k = \frac{(\text{O}^0)(\text{O}^-)}{(\text{O}^-)^2}$$

He assumes that  $k$  is a constant at a given temperature and is a characteristic of the cations present in binary or ternary silicate melts. By material balance considerations it may be shown that,

$$4k = \frac{\{4N - (\text{O}^-)\} \{2 - 2N - (\text{O}^-)\}}{(\text{O}^-)^2}$$

where  $N$  is the mole fraction of silica. This equation may be reduced to a series of quadratic equations of the standard form,

$$a (\text{O}^-)^2 + b (\text{O}^-) + c = 0 \quad (6)$$

so that,

$$(\text{O}^-) = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

Again, 
$$(O^{\equiv}) = (1 - N) - (O^{\equiv})/2$$

The concentration of silicate anions has been calculated by Toop for any value of  $N$  and  $k$ . Hence the mole fraction of oxygen ions can be calculated by the relationship

$$N_{O^{\equiv}} = \frac{(O^{\equiv})}{(O^{\equiv}) + (\text{Silicate anions})}$$

Toop has shown that at  $1100^{\circ}\text{C}$  for simple lead oxide-silica slags  $k = .01$ , and for simple cuprous oxide-silica slags  $k = 0.25$ . For these values of  $k$  the activities of oxygen ions is equal or nearly equal to the experimental activities of the basic oxide in the slag. Hence  $a_{O^{\equiv}}$  for simple lead oxide-silica slags may be readily determined from figure 4.

Each value of  $k$  has a corresponding free energy given by the relationship,

$$\Delta F = -RT \ln k \quad (7)$$

It is assumed that the free energies are additive, and knowing the mole fraction of lead oxide and cuprous oxide in the complex slag, the resultant free energy for the slag can be calculated as,

$$\Delta F_T = N'_{\text{PbO}} \Delta F_{\text{PbO}} + N'_{\text{Cu}_2\text{O}} \Delta F_{\text{Cu}_2\text{O}} \quad (8)$$

where  $N'_{\text{Cu}_2\text{O}} = \frac{N_{\text{Cu}_2\text{O}}}{N_{\text{PbO}} + N_{\text{Cu}_2\text{O}}}$  and  $N'_{\text{PbO}} = \frac{N_{\text{PbO}}}{N_{\text{PbO}} + N_{\text{Cu}_2\text{O}}}$

The corresponding value of  $k_T$  can be calculated for the complex slag, and used in the determination of  $N_{O^{\equiv}}$ .

For the simple lead oxide-silica slags  $N_{O^{\equiv}}$ , that is  $a_{O^{\equiv}}$  is known at  $1100^{\circ}\text{C}$ . At the experimental temperatures, sufficient data

does not exist for the calculation of  $N_{O=}$ , although  $a_{O=}$  can be suitably determined as mentioned earlier. Hence at this temperature the ratio between  $N_{O=}$  calculated at  $1100^{\circ}\text{C}$  and  $a_{O=}$  determined at this temperature is known. In absence of better data, it has been assumed that the same ratio holds for the complex slags, especially since only small quantities of cuprous oxide have been added. Hence  $a_{O=}$  for these slags may be determined from the  $N_{O=}$  values calculated at  $1100^{\circ}\text{C}$  as shown in the Appendix B, Table II B.

#### Weight of the Carbon Oxidised

It has been confirmed that  $\text{CO}_2$  is exclusively evolved as a product of oxidation, with a negligible proportion of CO (<0.5%). Hence from the volume of  $\text{CO}_2$  liberated, the amount of carbon oxidised can be calculated using ideal gas relationships.

### RESULTS

#### Oxidation of Graphite at $990^{\circ}\text{C}$ in $\text{PbO}\cdot\text{SiO}_2$ Slags

Special spectroscopic purity graphite electrodes of 0.5 inch diameter were machined so that their geometric surface area as measured by a micrometer was  $7.6\text{ cm}^2$ . With each slag the amount of carbon oxidised in unit time was determined. It was observed that a linear relationship was obtained in all cases as shown in Fig. 5. The oxidising potential of the slags were obtained from the data in Appendix B. The data is summarised in Table I. The rates of oxidation of graphite are plotted against the oxygen potential in Fig. 6 and against

the square of the activity of oxygen ions in Fig. 7. A linear relationship is obtained in both the cases indicating that the rate is a function of either of these. The rate constant  $k$  or the slope of the curve was found to be,

$$k = 4.4 \times 10^4 \text{ gmC/cm}^2/\text{sec/atm} \quad (\text{Fig. 6})$$

$$= 2.1 \times 10^{-3} \text{ gmC/cm}^2/\text{sec}/a_{\text{O}}^2 \quad (\text{Fig. 7})$$

TABLE I

Effect of oxidising potential of  $\text{PbO} \cdot \text{SiO}_2$  slags on the rate of oxidation of graphite at  $990^\circ\text{C}$

G.S.A. of graphite used in the experiment =  $7.6 \text{ cm}^2$

$\% \text{Cu}_2\text{O}$ in slag	$\% \text{Cu}$ in button	Oxygen Potential (atm) $\times 10^{10}$	$a_{\text{O}}^2$	Rate of carbon oxidation $\text{gmC/cm}^2/\text{sec}$ $\times 10^5$
0.0	0.0	1.10	.0121	2.77
0.50	1.3	1.18	.0135	3.07
0.68	1.8	1.21	.0143	3.20
0.80	2.2	1.23	.0150	3.38
1.02	4.2	1.32	.0168	3.70
1.10	6.4	1.41	.0176	4.01

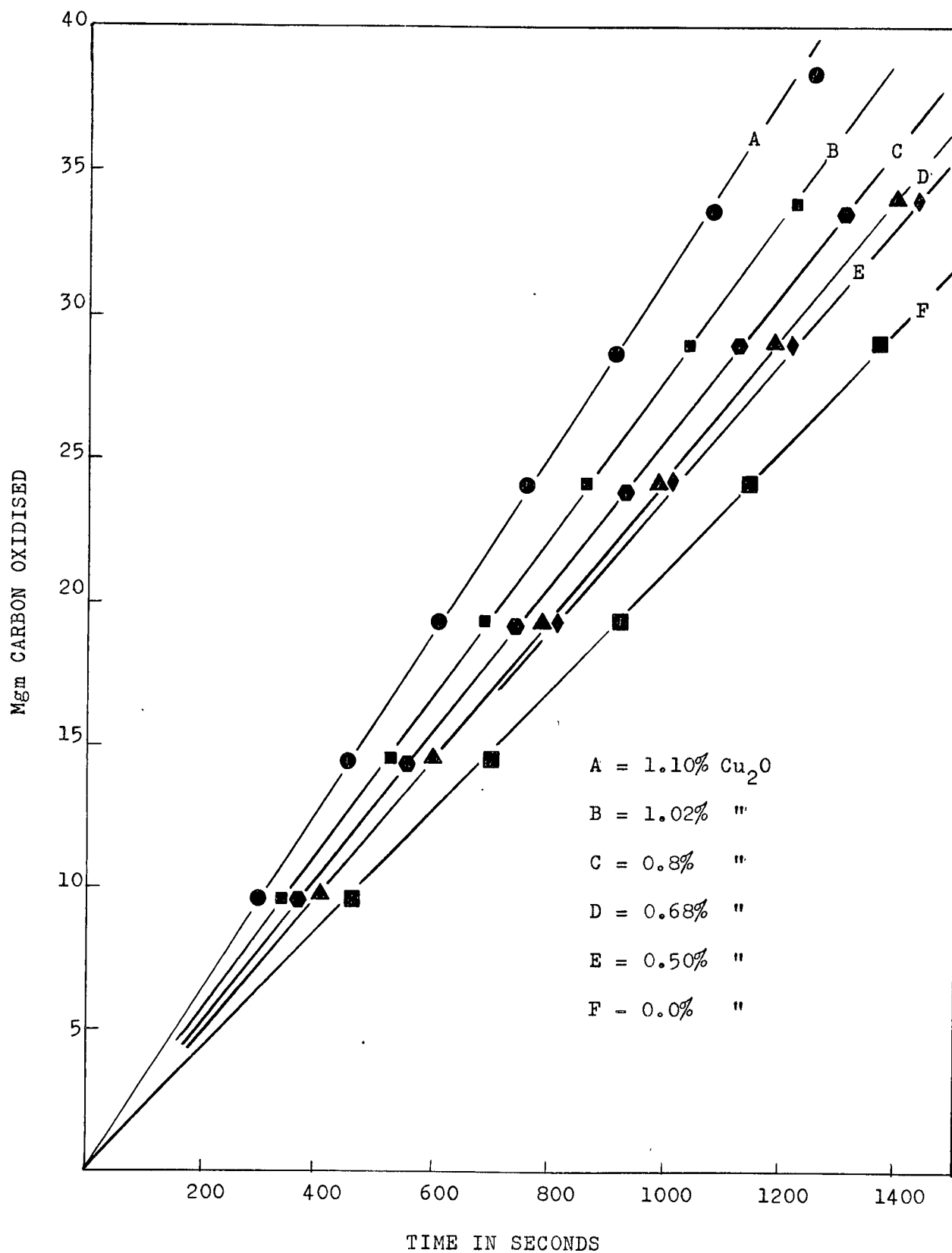


Fig. 5: Rate curves for the oxidation of graphite by  $\text{PbO} \cdot \text{SiO}_2$  melts at  $990^\circ\text{C}$ .

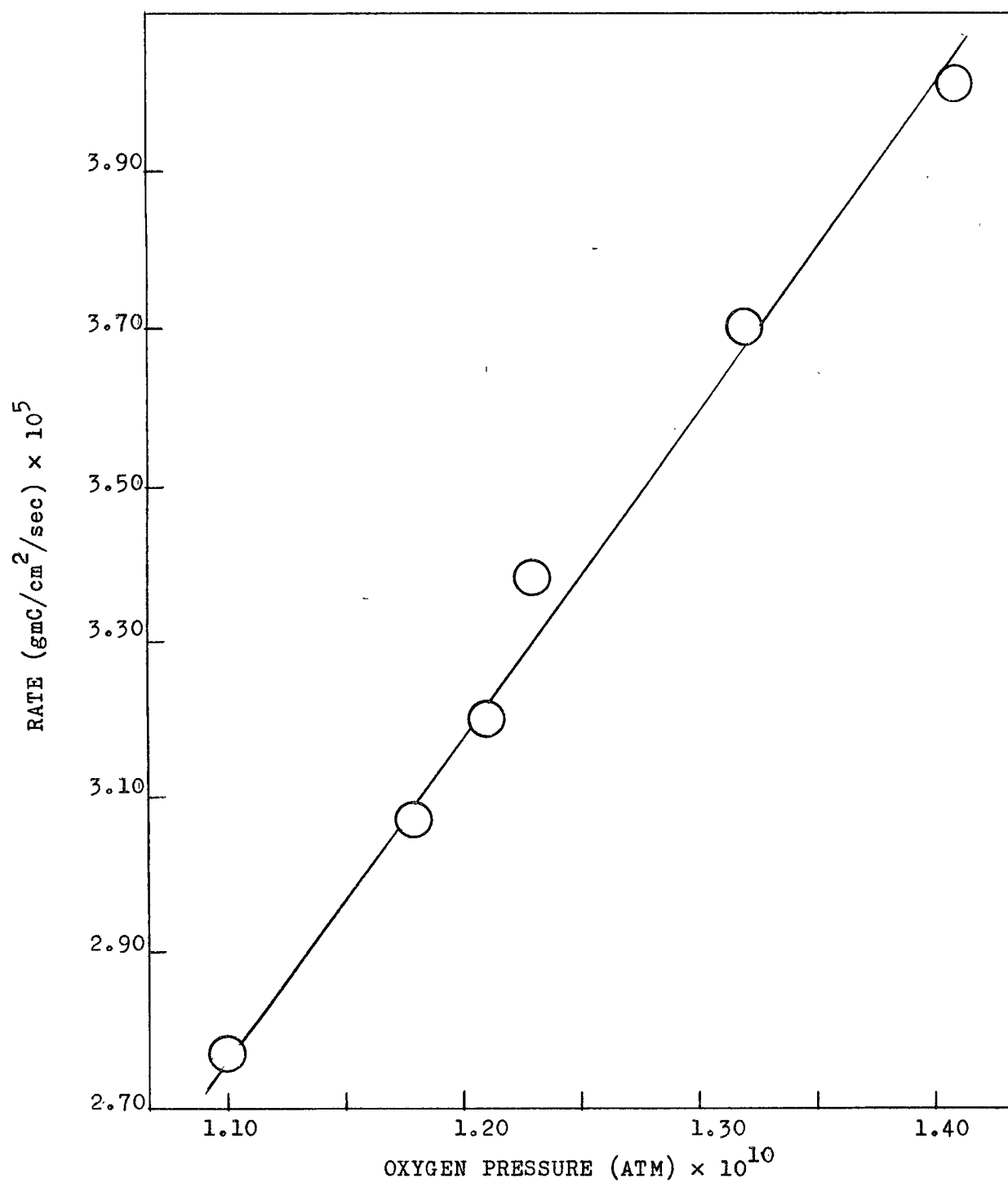


Fig. 6: Dependence of the rate of oxidation of graphite on the oxygen pressure of the  $\text{PbO} \cdot \text{SiO}_2$  with  $\text{Cu}_2\text{O}$  melts at  $990^\circ\text{C}$ .



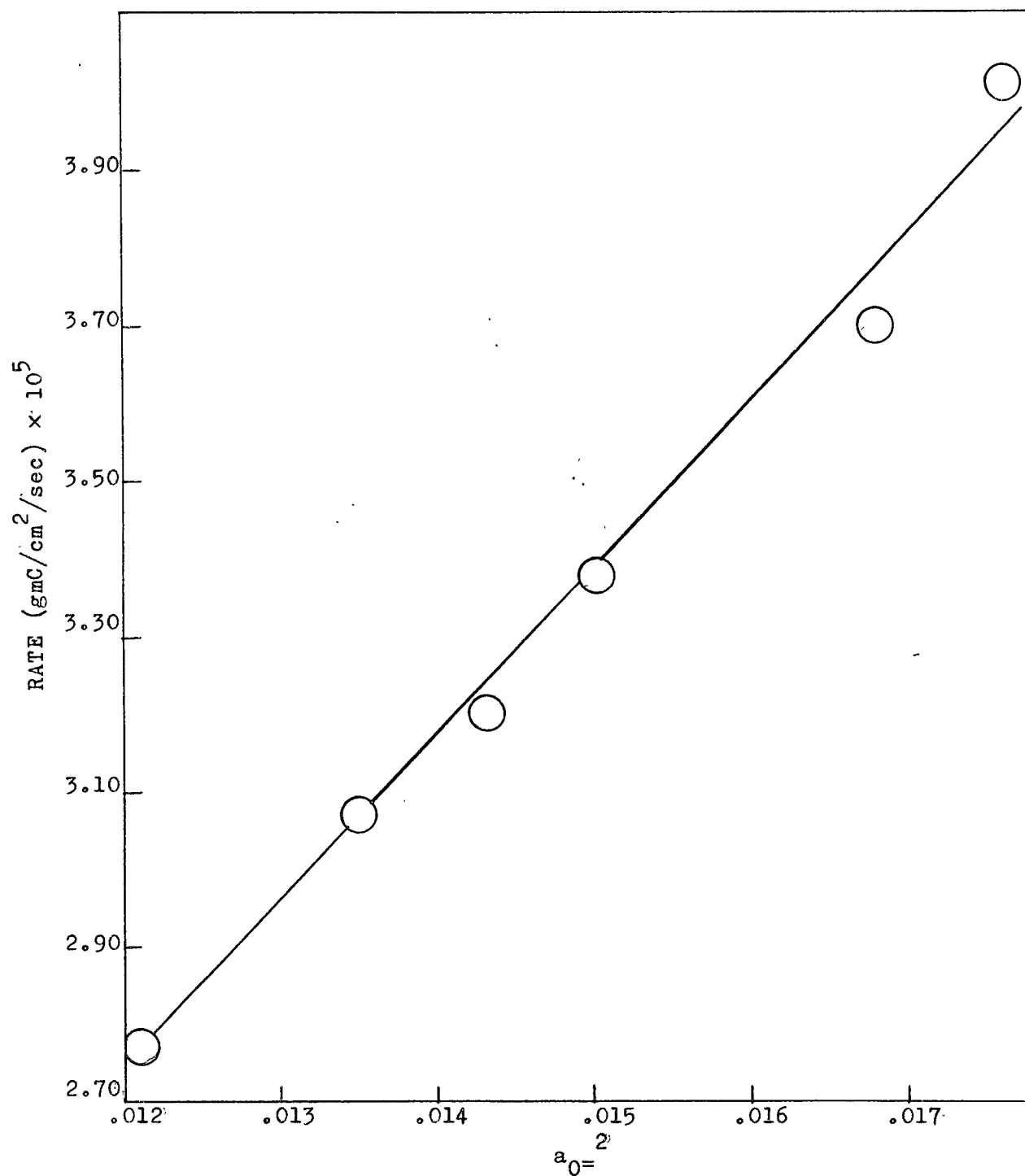


Fig. 7: Dependence of the rate of oxidation of graphite on  $a_0^2$  of the  $\text{PbO} \cdot \text{SiO}_2$  with  $\text{Cu}_2\text{O}$  melts at  $990^\circ\text{C}$ .

### Oxidation of Graphite at 850°C

The reaction was investigated at this temperature to determine the effect of temperature on the specific reaction rate constant, since it was believed that the rate constant associated with each oxygen species would vary uniquely with a change in this parameter. Again the two slags investigated at this temperature had markedly different rates of oxidation. This permitted the evaluation of the effect of oxidation rates on the rate constant at a given temperature.

#### (i) Oxidation of Graphite in 2PbO·SiO<sub>2</sub> Slags

The rates of oxidation of graphite (using specimens of 7.5 cm<sup>2</sup> of G.S.A.) were determined at 850°C for 2PbO·SiO<sub>2</sub> slags containing varying amounts of cuprous oxide (0.0 - 2.2%). The results of these experiments showed that the rate of oxidation is proportional to the oxygen potential or the square of the activity of oxygen ions. The experimental results are summarised in Table II and Fig. 8, 9, and 10. The rate constant in this case was found to be,

$$k = 1.1 \times 10^7 \text{ gmC/cm}^2/\text{sec/atm} \quad (\text{Fig. 9})$$

$$= 0.55 \times 10^{-3} \text{ gmC/cm}^2/\text{sec}/a_{\text{O}}^2 \quad (\text{Fig. 10})$$

TABLE II

Effect of oxidising potential of  $2\text{PbO} \cdot \text{SiO}_2$  slags on the rate of oxidation of graphite at  $850^\circ\text{C}$

G.S.A. of graphite used in the experiment =  $7.5 \text{ cm}^2$

$\% \text{Cu}_2\text{O}$ in slag	$\% \text{Cu}$ in button	Oxygen Pressure (atm) $\times 10^{12}$	$a_0 =$ <sup>2</sup>	Rate of Carbon oxidation $\text{gnC}/\text{cm}^2/\text{sec}$ $\times 10^5$
0.0	0.0	6.26	0.0784	4.98
1.25	3.2	7.25	0.097	5.93
1.90	5.4	7.72	0.112	6.75
2.25	8.3	8.15	0.120	7.27

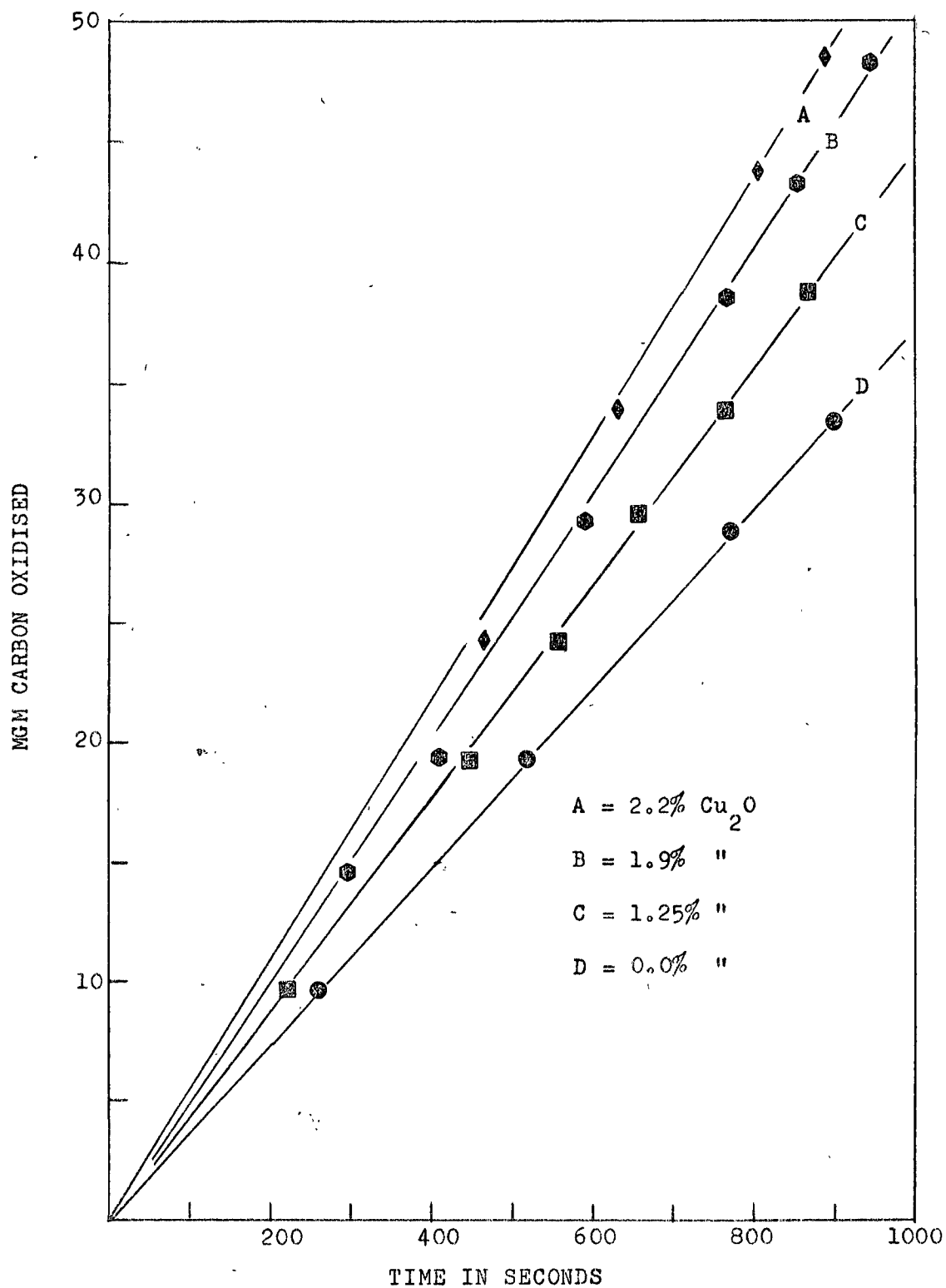


Fig. 8: Rate curves for the oxidation of graphite by  $2\text{PbO} \cdot \text{SiO}_2$  melts at  $850^\circ\text{C}$ .

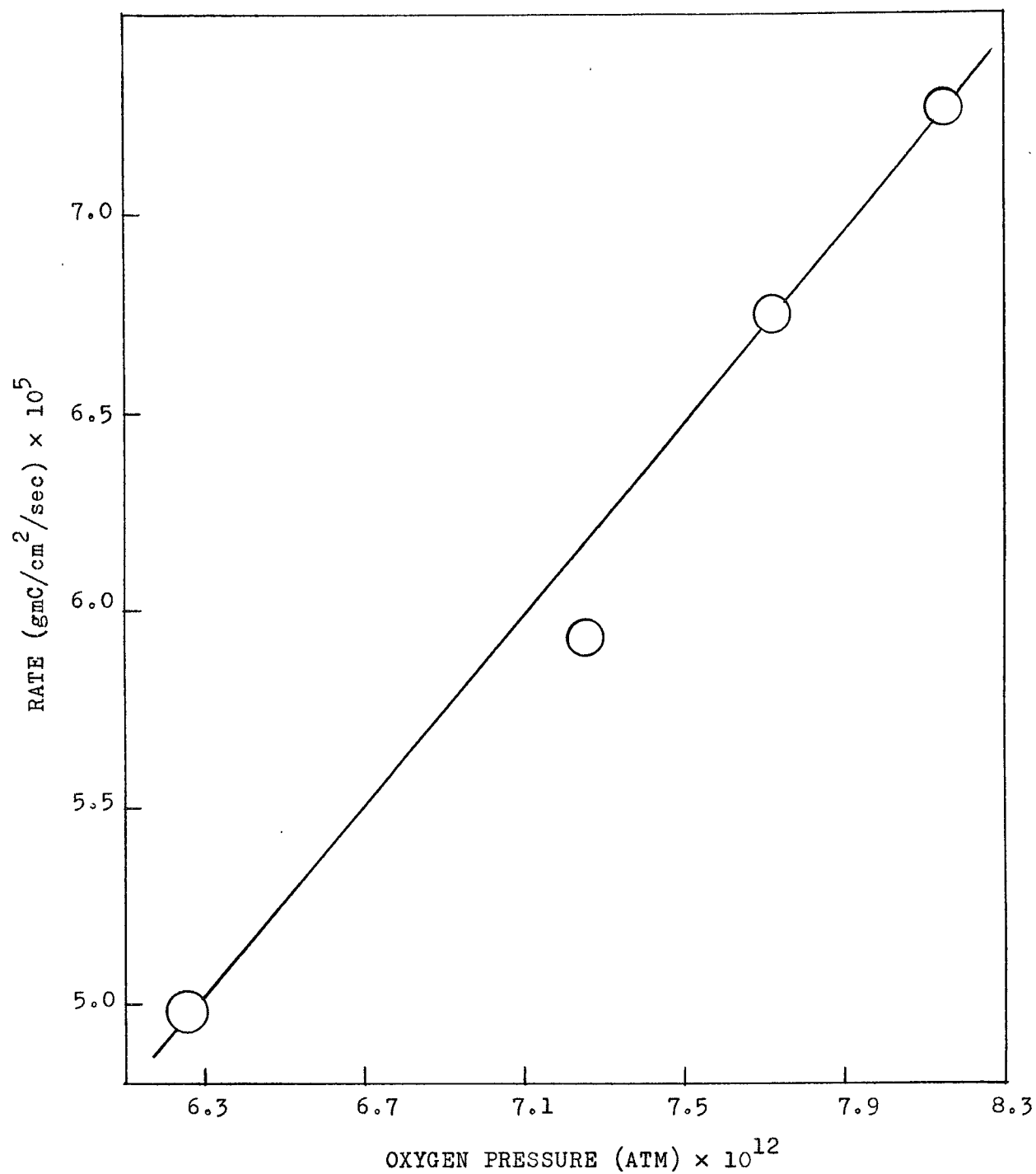


Fig. 9: Dependence of the rate of oxidation of graphite on the oxygen pressure of the  $2\text{PbO} \cdot \text{SiO}_2$  with  $\text{Cu}_2\text{O}$  melts at  $850^\circ\text{C}$ .

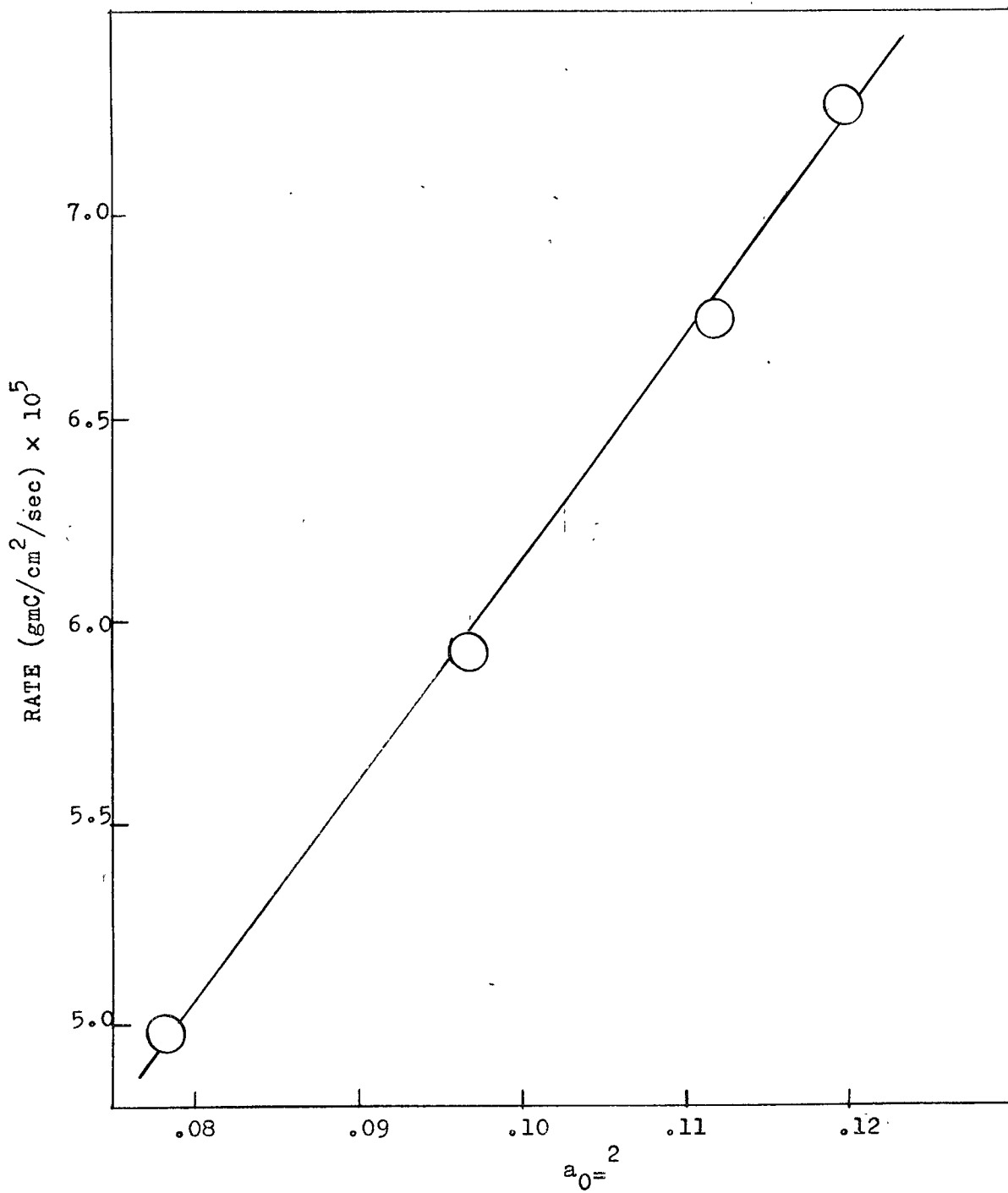


Fig. 10: Dependence of the rate of oxidation of graphite on  $a_0^2$  of the  $2\text{PbO} \cdot \text{SiO}_2$  with  $\text{Cu}_2\text{O}$  melts at 850°C.

(ii) Oxidation of Graphite in 1.5 PbO.SiO<sub>2</sub> Slags

This slag was chosen since at 850°C, it had oxidation rates nearly equal to those of PbO.SiO<sub>2</sub> slag at 990°C. The G.S.A. of the graphite specimen was 7.5 cm<sup>2</sup> and the cuprous oxide content varied from 0.0 to 1.7%. The results of these experiments demonstrated that the rate of oxidation is proportional to the oxygen potential or the square of the activity of oxygen ions. The experimental results are summarised in Table III and Fig. 11, 12 and 13. The rate constant in this case was found to be,

$$k = 1.3 \times 10^7 \text{ gmC/cm}^2/\text{sec/atm} \quad (\text{Fig. 12})$$

$$= 0.71 \times 10^{-3} \text{ gmC/cm}^2/\text{sec}/a_0^2 \quad (\text{Fig. 13})$$

These values indicate that the rate constants for both the slags are nearly the same, in spite of the large variation in rates of oxidation.

TABLE III

Effect of oxidising potential of 1.5 PbO.SiO<sub>2</sub> slags on the rate of oxidation of graphite at 850°C.

G.S.A. of graphite used in the experiment = 7.5 cm<sup>2</sup>

%Cu <sub>2</sub> O in slag	%Cu in button	Oxygen Pressure (atm.) × 10 <sup>12</sup>	a <sub>O</sub> <sup>2</sup>	Rate of carbon oxidation gmC/cm <sup>2</sup> /sec × 10 <sup>5</sup>
0.0	0.0	2.88	0.0361	2.79
1.0	2.6	3.27	0.0448	3.27
1.5	6.0	3.67	0.0502	3.76
1.7	8.4	3.76	0.524	3.98

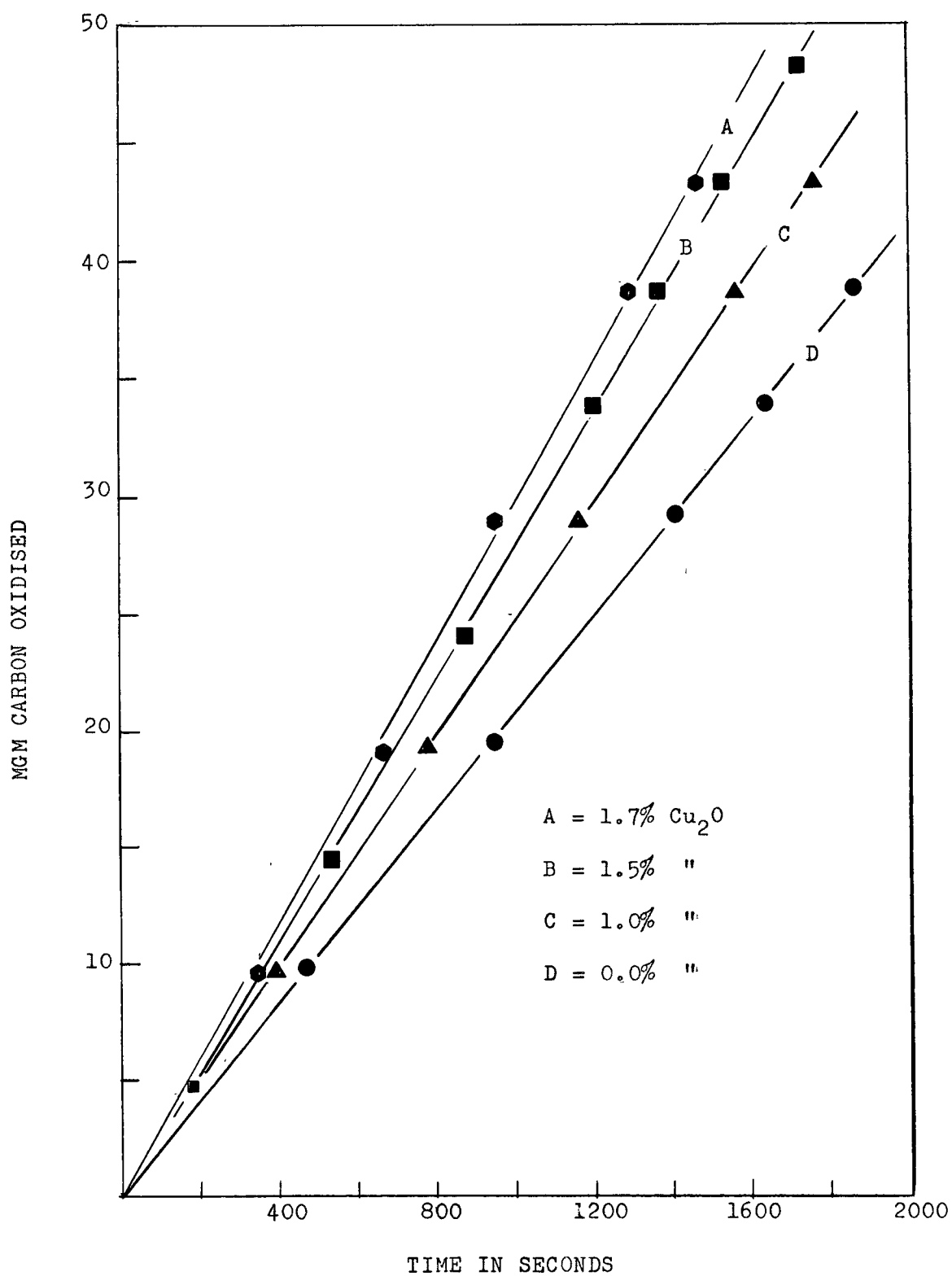


Fig. 11: Rate curves for the oxidation of graphite by 1.5 PbO·SiO<sub>2</sub> melts at 850°C.



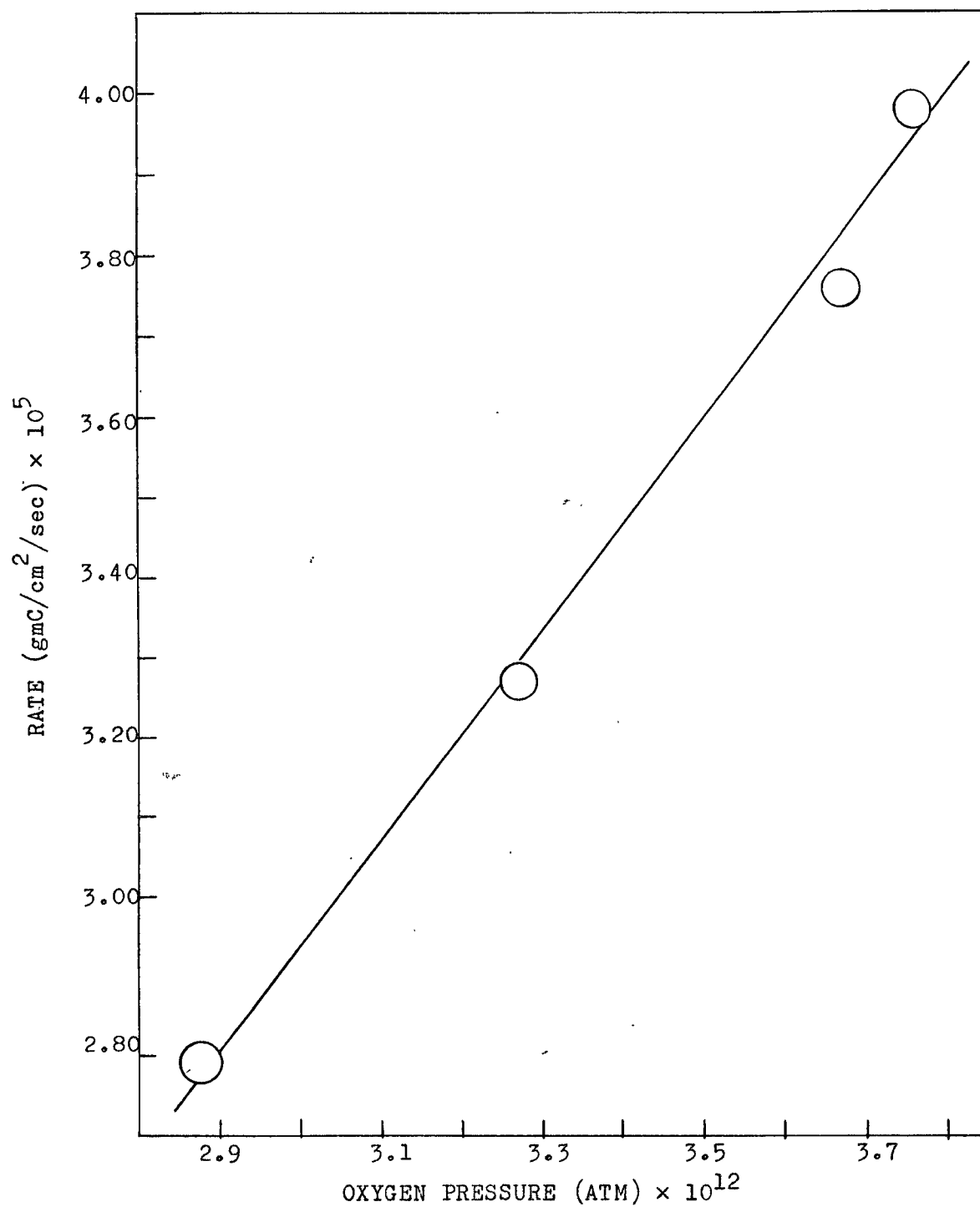


Fig. 12: Dependence of the rate of oxidation of graphite on the oxygen pressure of the 1.5 PbO·SiO<sub>2</sub> with Cu<sub>2</sub>O melts at 850°C.

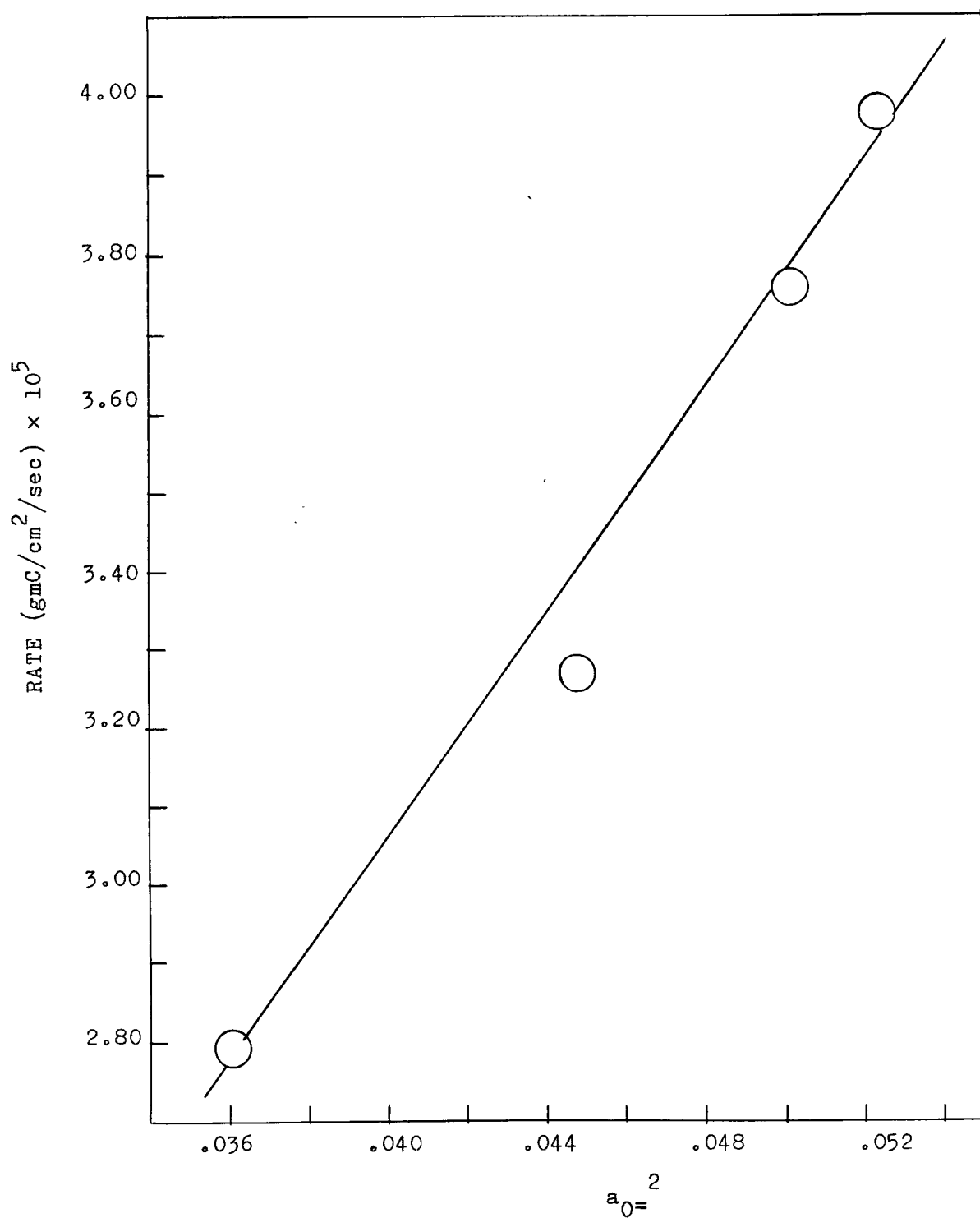


Fig. 13: Dependence of the rate of oxidation of graphite on  $a_0^2$  of the 1.5  $\text{PbO} \cdot \text{SiO}_2$  melts with  $\text{Cu}_2\text{O}$  melts at  $850^\circ\text{C}$ .

### Experimental Activation Energy

#### (A) Oxidation of spectroscopic grade graphite

The oxidation of spectroscopic grade graphite was investigated for four lead oxide-silica compositions over a wide range of temperatures. The G.S.A. of the graphite specimen employed in all the cases was  $7.5 \text{ cm}^2$ . The composition of the slags and the temperature range of each were

- (i)  $2\text{PbO} \cdot \text{SiO}_2$  ( $800 - 875^\circ\text{C}$ )
- (ii)  $1.5 \text{ PbO} \cdot \text{SiO}_2$  ( $842 - 939^\circ\text{C}$ )
- (iii)  $\text{PbO} \cdot \text{SiO}_2$  ( $961 - 1060^\circ\text{C}$ )
- (iv)  $0.85 \text{ PbO} \cdot \text{SiO}_2$  ( $998 - 1060^\circ\text{C}$ )

A linear relationship was obtained between the amount of carbon oxidised and time in all cases as shown in Fig. 14, 15, 16 and 17. The experimental rate constants were determined on the basis of the equation,

$$R = k a_0^2 \quad (9)$$

The logarithms of  $k$  are plotted against absolute reciprocal temperature in Fig. 18 (See Table IV). In all cases the activation energy determined by the product of the slope of the curve and  $2.303 R$  is found to be  $22 \pm 2 \text{ Kcal/mole}$ .

In Fig. 18 a line having an activation energy value of  $22 \text{ Kcal}$  is drawn through the point representing the value of  $k$  with  $\text{PbO} \cdot \text{SiO}_2$  slag at  $990^\circ\text{C}$ , since this value is most accurately known. It is seen that the data for  $\text{PbO} \cdot \text{SiO}_2$  and  $1.5 \text{ PbO} \cdot \text{SiO}_2$  slags falls on this line, whereas a deviation is observed for  $.85 \text{ PbO} \cdot \text{SiO}_2$  and  $2\text{PbO} \cdot \text{SiO}_2$  slags.

TABLE IV

Effect of temperature on the rate of oxidation of graphite

$$R = k a_0^2$$

G.S.A. of graphite used in the experiment =  $7.5 \text{ cm}^2$ 

	Temp- erature °C	$1/T^{\circ}\text{K}$ $\times 10^4$	$R$ $\text{gmC/cm}^2/\text{sec}$ $\times 10^5$	$a_0 =$	$a_0^2$	$k$ $\text{gmC/cm}^2/\text{sec}/2$ $\times 10^4$	$-\log k$
<u>2PbO·SiO<sub>2</sub></u>	800	9.318	3.00	0.262	0.0687	4.37	3.359
	825	9.106	3.83	0.272	0.073	5.25	3.280
	850	8.906	4.98	0.280	0.0785	6.34	3.198
	875	8.711	6.25	0.289	0.0835	7.5	3.125
<u>1.5PbO·SiO<sub>2</sub></u>	842	8.96	2.57	0.188	0.0353	7.3	3.137
	870	8.75	3.55	0.194	0.0376	9.45	3.025
	900	8.524	4.90	0.200	0.040	12.3	2.910
	939	8.253	6.64	0.208	0.043	15.45	2.811
<u>PbO·SiO<sub>2</sub></u>	961	8.10	2.28	0.106	0.0112	20.4	2.699
	990	7.92	2.87	0.110	0.0121	23.7	2.625
	1060	7.50	5.03	0.116	0.0135	37.2	2.429
<u>0.85PbO·SiO<sub>2</sub></u>	998	7.867	1.83	0.080	0.0064	28.5	2.545
	1033	7.659	2.60	0.0835	0.0070	37.2	2.429
	1060	7.502	3.38	0.0865	0.0075	45.0	2.347

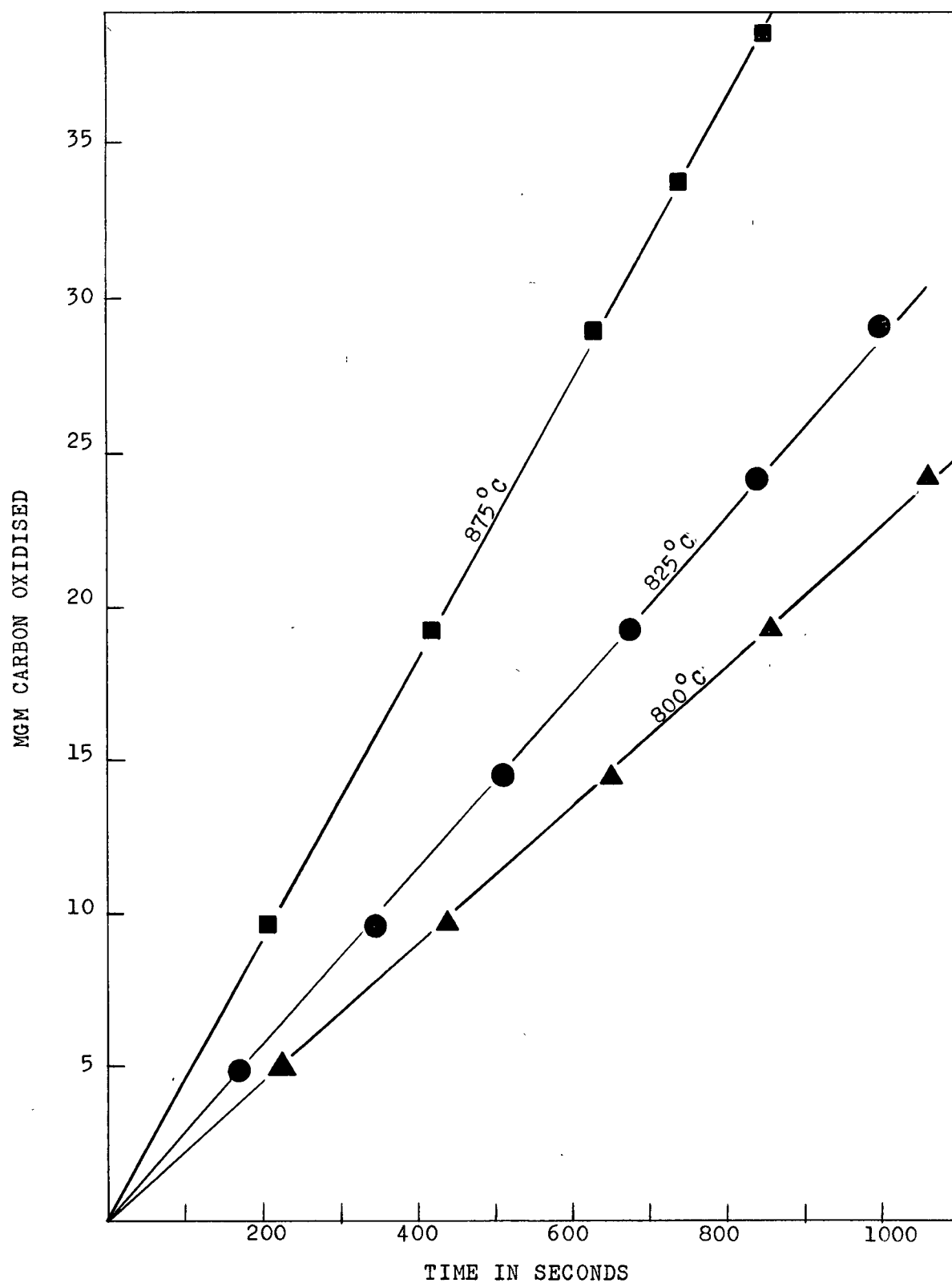


Fig. 14: Rate curves for the oxidation of graphite at different temperatures by  $2\text{PbO} \cdot \text{SiO}_2$  melts.

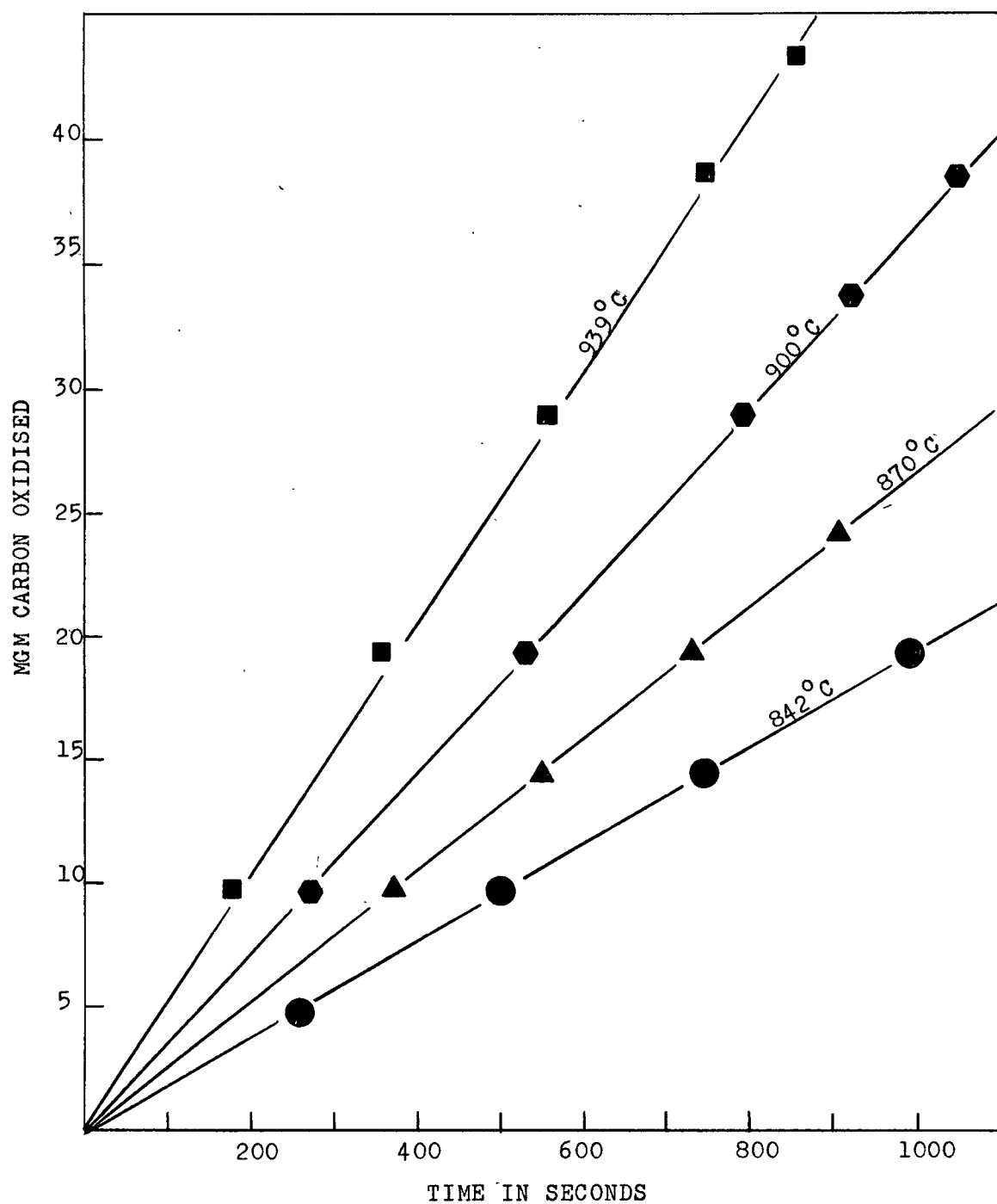
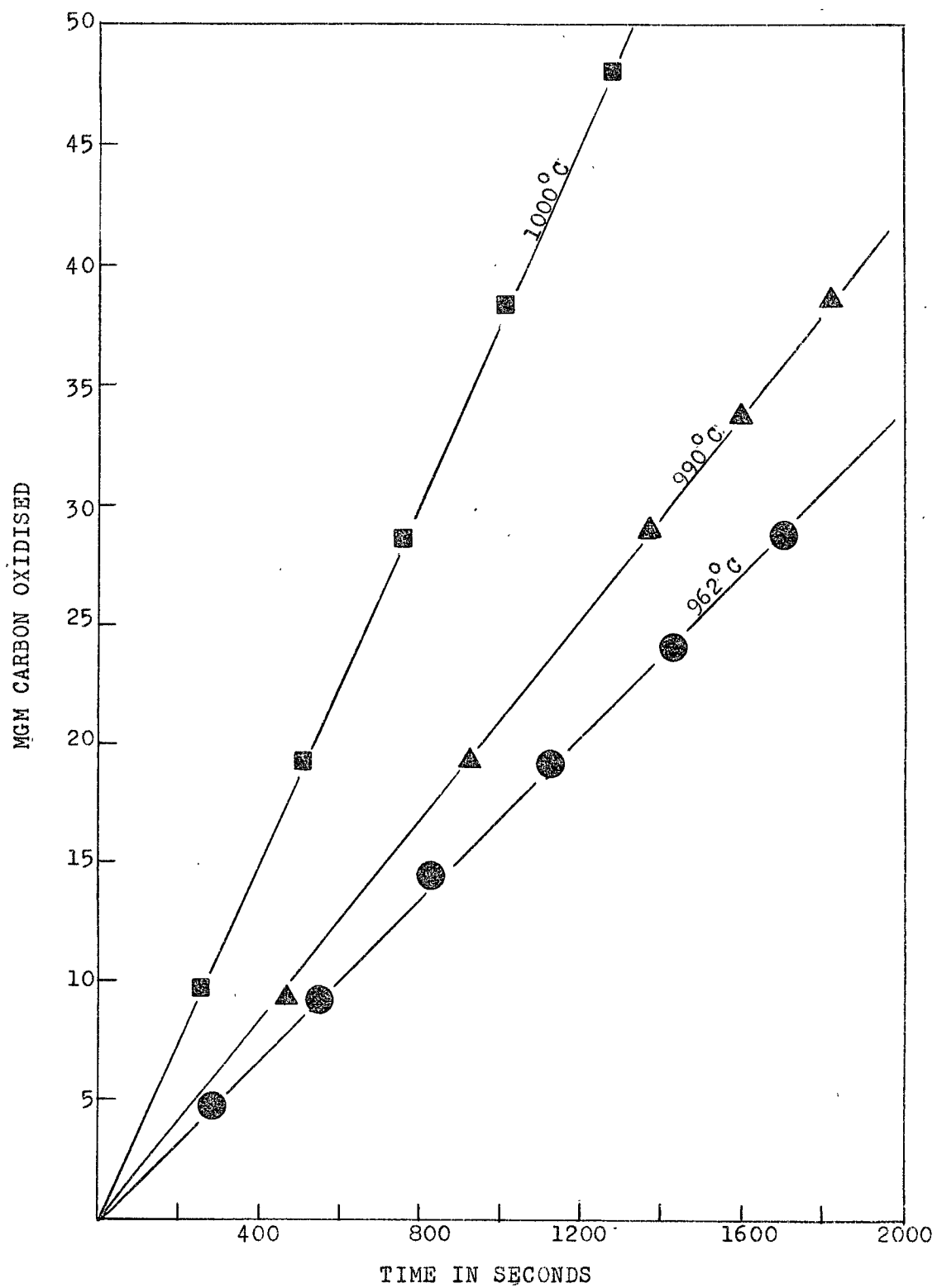


Fig. 15: Rate curves for the oxidation of graphite at different temperatures by  $1.5 \text{ PbO} \cdot \text{SiO}_2$  melts.



**Fig. 16:** Rate curves for the oxidation of graphite at different temperatures by  $\text{PbO} \cdot \text{SiO}_2$  melts.

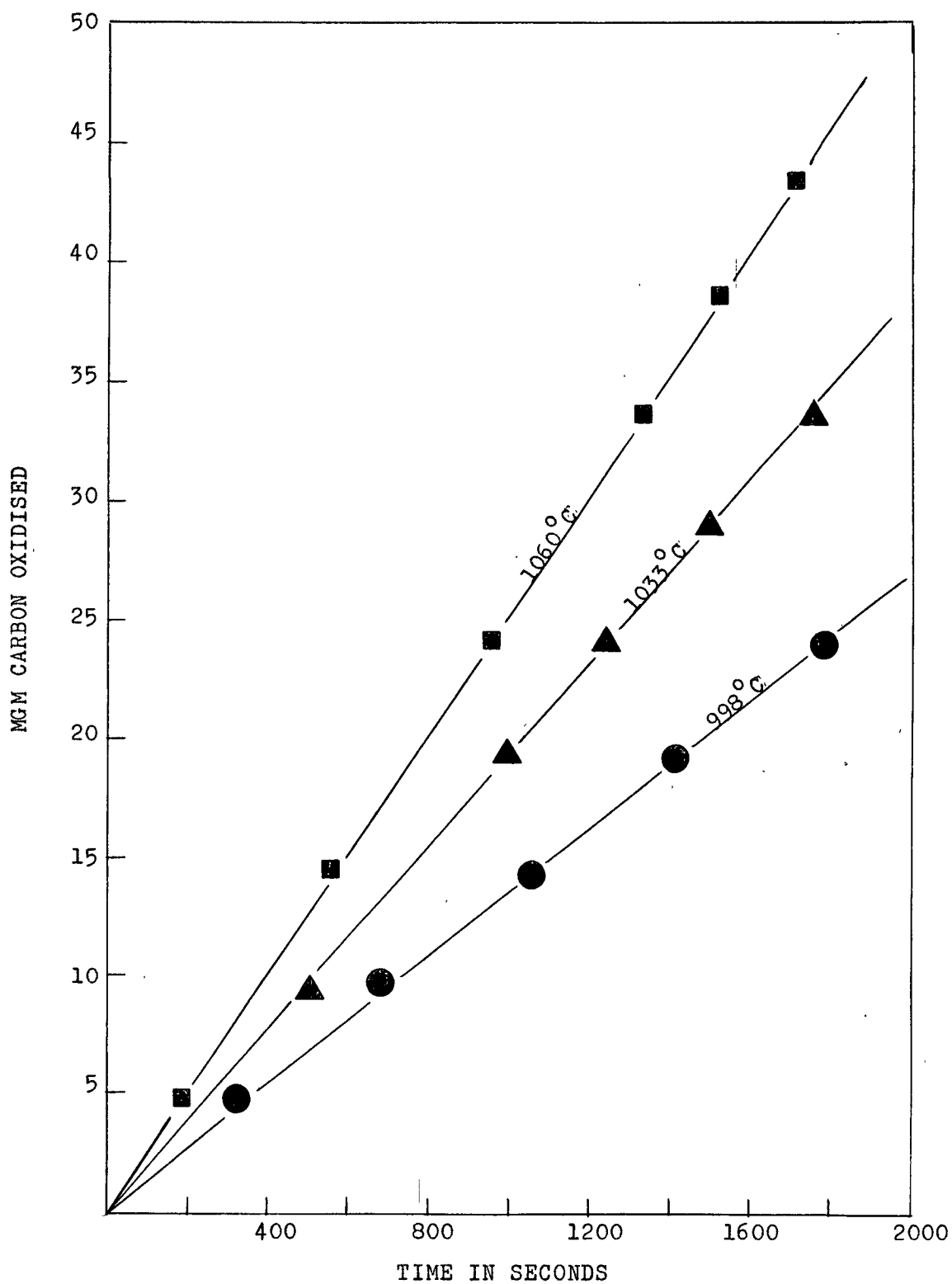


Fig. 17: Rate curves for the oxidation of graphite at different temperatures by  $0.85 \text{ PbO} \cdot \text{SiO}_2$  melts.



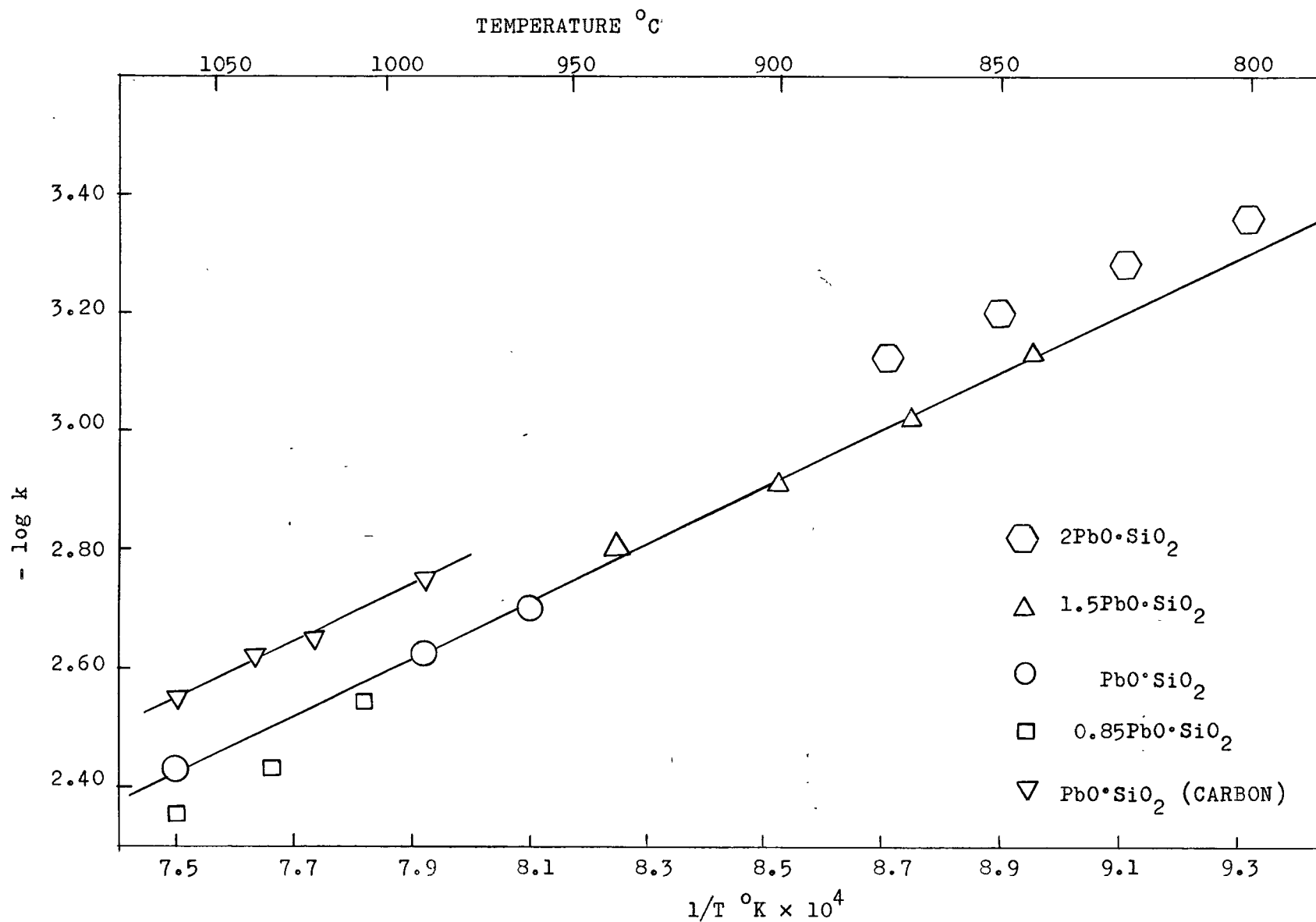


Fig. 18:  $\text{Log}_{10} k$  vs  $1/T \text{ } ^\circ\text{K}$  for the oxidation of carbons in various slags.

With  $0.85 \text{ PbO} \cdot \text{SiO}_2$  slag the rate of oxidation is very low, and the activity of oxygen ions is small, and hence probably not accurate. For  $2\text{PbO} \cdot \text{SiO}_2$  slag the discrepancy may be due to (a) experimental measurement of rates, (b) errors in conversion of oxygen ion activities from higher temperatures to the experimental temperatures, and (c) high rates at low temperatures likely to be affected by other processes as discharge of lead ions and diffusion of oxygen ions to the carbon surface. These causes will affect the rate constants. However, in all cases, the deviation from the mean line is less than 20%, which is considered to be satisfactory in view of so many sources of inaccuracies and complications involved.

Jena <sup>24</sup> obtained a value of  $33 \pm 2 \text{ K cal/mole}$  for the activation energy with  $\text{PbO} \cdot \text{SiO}_2$  slag. His values at higher temperatures tend to be the same as those obtained in the present case, whereas they are substantially lower at the lower temperatures.

#### (B) Oxidation of spectroscopic grade carbon

The oxidation of spectroscopic grade carbon was investigated with  $\text{PbO} \cdot \text{SiO}_2$  slag over a temperature range of  $990 - 1060^\circ\text{C}$ . The data is summarised in Fig. 19 and Table V. The results are incorporated in Fig. 18 in which the data for spectroscopic grade graphite is plotted. The activation energy in this case also lies in the range  $22 \pm 2 \text{ K cal/mole}$ . This value agrees with that observed by Jena.

The line for carbon is seen to be displaced from the mean line for graphite by a value of about 30%. It was experimentally observed that the slag wetted the graphite surface more effectively than the carbon surface. Hence this discrepancy may be attributed to such physical

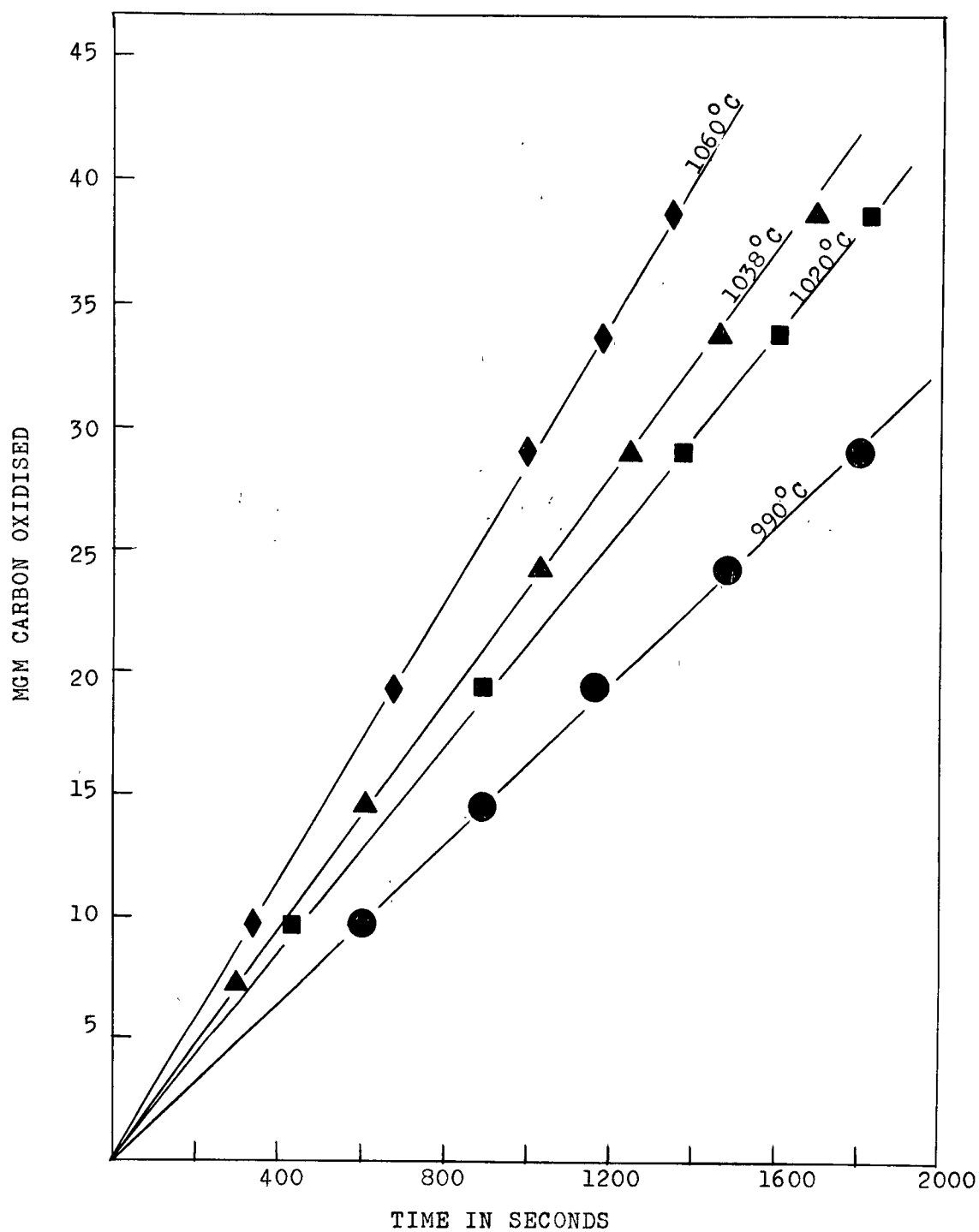


Fig. 19: Rate curves for the oxidation of spectroscopic grade carbon at different temperatures by  $\text{PbO} \cdot \text{SiO}_2$  slags.

factors as surface roughness, interfacial tension, etc.

TABLE V

Effect of temperature on the rate of oxidation of spectroscopic grade carbon

Composition of the slag:  $\text{PbO} \cdot \text{SiO}_2$

G.S.A. of the carbon used in the experiment =  $7.5 \text{ cm}^2$

Temp. °C	$1/T^\circ\text{K}$	$R$ $\text{gmC}/\text{cm}^2/\text{sec}$	$a_0 =$	$a_0^2$	$k$ $\times 10^3$	$\log k$
990	7.92	2.16	0.110	0.0121	1.785	-2.748
1020	7173	2.83	0.112	0.0126	2.26	-2.646
1038	7.63	3.11	0.114	0.0130	2.39	-2.622
1060	7.50	3.81	0.116	0.0135	2.82	-2.550

### DISCUSSION

#### Experimental Activation Energy

In the present investigation at  $990^\circ\text{C}$  the rate of oxidation of graphite has been found to be  $2.77 \times 10^{-5} \text{ gmC}/\text{cm}^2/\text{sec}$  and for spectroscopic grade carbon it is  $2.16 \times 10^{-5} \text{ gmC}/\text{cm}^2/\text{sec}$ . Jena's <sup>24</sup> experimental rates at the same temperature are of the same order of magnitude, namely  $2.70 \times 10^{-5} \text{ gmC}/\text{cm}^2/\text{sec}$  for graphite,  $1.95 \times 10^{-5}$  for spectroscopic grade carbon and  $2.65 \times 10^{-5}$  for petroleum coke. In the present case the experimental value of activation energy is observed to be  $22 \pm 2$  Kcal/mole for both graphite and spectroscopic grade carbon. Jena, however, finds that the experimental activation energy

is  $33 \pm 2$  Kcal/mole for graphite,  $28 \pm 2$  Kcal/mole for petroleum coke and  $22 \pm 2$  Kcal/mole for spectroscopic grade carbon. He concludes from this that the activation energy is related to the nature of the carbon surface which is determined by the temperature of calcination of the carbon--in accordance with the observations made for gaseous and certain electrochemical oxidation processes. If the values of activation energy were to vary so widely as recorded by Jena, one would expect that the reaction rates at a given temperature for the various specimens would have been different.

In gaseous and electrochemical oxidation of carbon the  $\text{CO}/\text{CO}_2$  ratio of the product gases is determined by the desorption mechanism. The latter depends upon the nature of the carbon surface which in turn determines the activation energy. In the chemical oxidation of carbon by lead oxide-silica slags, only  $\text{CO}_2$  is found to be the oxidation product. In view of these observations, it is very likely that the nature of the carbon surface does not play an important role in the oxidation mechanism. Hence the observation in the present case that the experimental activation energy for the process has a value of  $22 \pm 2$  Kcal/mole irrespective of the nature of the carbon surface, appears to be reasonable.

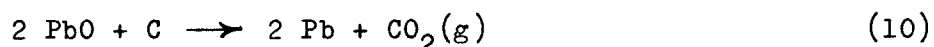
#### The Reactant State of Oxygen in the Rate Determining Step

It has been observed that the rates of oxidation of carbon bear a linear relationship with the following, (i) the square of the lead oxide activity for simple lead oxide-silica slags (ii) the oxygen pressure of the system (iii) the square of the activity of the oxygen ions (which is the same as the square of the lead oxide activity for simple lead oxide-silica slags<sup>26</sup>). Therefore it may be reasoned that one of these

three species, lead oxide molecules, gaseous oxygen molecules or oxygen ions participate on the reacting species in the rate determining step.

(i) Lead oxide molecules:

If the lead oxide molecules alone are involved in the rate determining step, the reaction can be written as

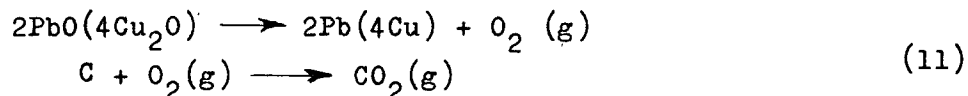


The rate of oxidation is then proportional to the square of the activity of lead oxide only as is found to be for simple lead oxide-silica slags. According to this proposal any other basic oxide in the slag should have no influence on the rate. It follows that if the activity of the lead oxide is changed by the addition of another basic oxide, the rate of oxidation should correspondingly change. When small quantities of cuprous oxide are added to the lead oxide-silica slags, the activity of lead oxide in the resulting ternary system is slightly diminished<sup>26</sup>. Hence a small decrease in the rate of oxidation should be anticipated. Actually it is seen that the addition of cuprous oxide increases the rate considerably. Hence the possibility that only the lead oxide molecules are involved in the rate determining step is eliminated.

(ii) Gaseous oxygen molecules:

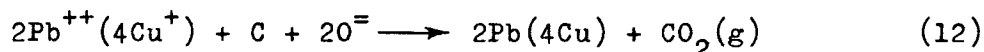
The reaction with the oxygen in the gaseous state will be considered next. Due to the dissociation of the basic oxides every slag has a definite equilibrium oxygen pressure determined by thermodynamic considerations. It may be imagined that the basic oxides near the carbon surface effectively dissociate under the experimental conditions, so that the carbon specimen is enveloped by a layer of gaseous

oxygen molecules. The rate controlling step then consists of the reaction of these molecules with the carbon surface, eg. adsorption on the surface. The concentration of the oxygen species can be expressed as pressure in atmospheres. The overall reaction can be written as



(iii) Oxygen ions:

If oxygen ions are involved in the rate determining step, it implies that gaseous oxygen molecules obtained by the dissociation of the basic oxides need not be considered as the reacting species. Instead, the oxygen ions present in the slag directly participate in the reaction which determines the overall rate. The concentration of the oxygen ions may be stated in terms of their activity which is determined by the ionic theory of slags. In this case the overall reaction can be written as



Application of the Experimental Data

The results obtained can now be utilised to examine the validities of the concepts (ii) and (iii).

(a) Gaseous oxygen molecules:

At a given temperature the velocity of the reaction can be expressed in terms of the Arrhenius equation

$$\text{Velocity} = \text{Oxygen Pressure} \times A \times e^{-E/RT} \quad (13)$$

where,

E = Activation energy per mole

A = Arrhenius constant

At 1163°K, for simple PbO.SiO<sub>2</sub> slag the observed rate is  $2.77 \times 10^{-5}$  gmC/cm<sup>2</sup>/sec for an oxygen pressure of  $1.10 \times 10^{-10}$  atm. At 1123°K, the corresponding values for 2PbO.SiO<sub>2</sub> slags are  $4.98 \times 10^{-5}$  and  $6.26 \times 10^{-11}$  respectively. Since A is essentially a constant, this implies that on this basis the activation energy has a negative value. This contradicts the observed value of  $+ 22 \pm 2$  Kcal/mole for the experimental activation energy.

TABLE VI

Summary of Rate Equation calculations for gaseous oxygen molecules

E = 22 Kcal/mole

Slag	Temperature °K	$\frac{k}{\text{gmC/cm}^2/\text{atm/sec}}$	Average k	A
Simple PbO-SiO <sub>2</sub>	1263	$2.3 \times 10^4$	$2.3 \times 10^4$	
PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	$4.4 \times 10^4$	$4.4 \times 10^4$	$2.6 \times 10^8$
Simple PbO-SiO <sub>2</sub>	1123	$0.85 \times 10^7$	$0.85 \times 10^7$	
2PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	$1.1 \times 10^7$	$1.2 \times 10^7$	$2.1 \times 10^{11}$
1.5PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	$1.3 \times 10^7$		

Again, at a given temperature, the rate constant k is equal to the slope of the rate vs. oxygen pressure curve. The pertinent data is incorporated in Table VI. From equation 13, k may be defined as

$$k = A e^{-E/RT} \quad (14)$$

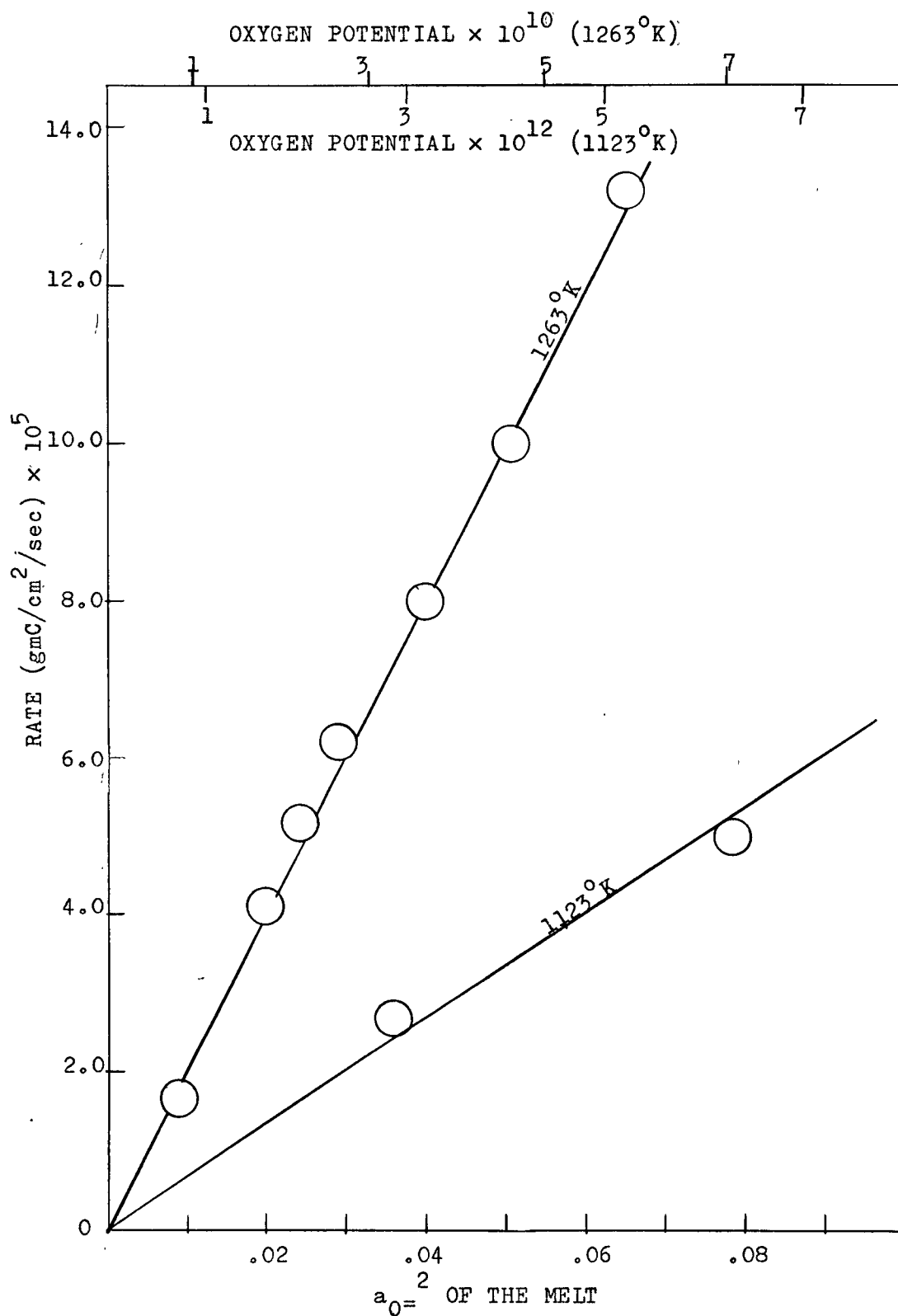
Hence A may be determined for both temperatures by substituting the values for k and E. Table VI reveals a large change in the values



of A with temperature.

The relationship between the rate of oxidation of graphite and lead oxide activity at  $1263^{\circ}\text{K}$  for simple  $\text{PbO}$  lead oxide-silica system was studied by Jena <sup>24</sup>. His results with appropriate modifications have been plotted in Fig. 20. In the same figure values for  $1.5 \text{ PbO} \cdot \text{SiO}_2$  and  $2\text{PbO} \cdot \text{SiO}_2$  at  $1123^{\circ}\text{K}$  have been incorporated. Table VI shows that the values of  $k$  at both the temperatures are higher for the complex slags by a factor of 1.5 - 2. This means that the curves for the complex slags do not pass through the origin of the graph.

Gulbransen <sup>5</sup> has shown that Eyring's rate equations are satisfied for mobile adsorption or immobile adsorption with dissociation in the case of gaseous oxidation of carbon by oxygen. If, in the oxidation by the slag, gaseous oxygen molecules are involved in the rate determining step, similar equations can be written, especially since the partition functions for the gaseous species are well known. The observed rate is about  $2 \times 10^{17}$  atoms  $\text{C}/\text{cm}^2/\text{sec}$  at  $1263^{\circ}\text{K}$ . Using these equations, rate values have been calculated in appendix A. It is shown that agreement between theoretical and experimental values is not obtained due to discrepancies in theoretical or numerical values. The situation arises mainly due to the large changes in entropy. In gaseous oxidation, gaseous oxygen molecules with three translational degrees of freedom become adsorbed on the carbon surface with two translational degrees of freedom in the case of mobile adsorption. Thus one translational degree of freedom equivalent to a factor of  $10^{-10}$  in the rate equation is lost, representing a large entropy change. A large concentration of oxygen molecules,  $10^{18}$  molecules/cc, however, <sup>a</sup> balances this effect. In the present case, the concentration of oxygen molecules is only about  $10^8$  molecules/cc; although



**Fig. 20:** Dependence of the rate of oxidation of graphite on the oxidising potential for the simple PbO-SiO<sub>2</sub> slags.

the adverse entropy change is the same. This leads to low theoretical values which are incompatible with the observed rates.

Again in gaseous oxidation both CO and CO<sub>2</sub> are evolved, whereas in the present case only CO<sub>2</sub> is liberated. Hence all the evidence so far leads to the conclusion that oxygen molecules are not involved in the rate determining step.

(b) Oxygen ions:

The summary of rate equation calculations for oxygen ions is given in Table VII. Here the variation in the values of k appears to be of the right order. Considering equation 14, we find that A has a value of 12 at 1263°K, and 11 at 1123°K, that is it is essentially constant within experimental errors. Calculation of the values of k for the simple lead oxide-silica slags from Fig. 20 reveals that they are in satisfactory agreement with the corresponding values of the complex slags. This again suggests that the oxygen ions are involved in the rate determining step.

In the case of ionic oxygen it is very difficult to write down suitable rate equations mainly because the partition functions of reactants in the liquid state are not known with certainty. It may be mentioned that the behaviour of oxygen ions in silicate slags might differ from oxygen ions in cryolite melts, due to the complex silicate anions in the former.

Determination of Oxygen Ion Activities in Unknown Silicate Melts

The results suggest that the activity of oxygen ions in an unknown silicate melt can be determined by measuring the rate of oxidation of carbon in it, provided that such measurements can be made. The rate

TABLE VIISummary of Rate Equation calculations for oxygen ions

$$E = 22 \text{ Kcal/mole}$$

Slag	Temperature °K	$\frac{k}{\text{gmC/cm}^2/\text{sec}/a_{\text{O}}^2} \times 10^{-3}$	Average $\frac{k}{\text{gmC/cm}^2/\text{sec}/a_{\text{O}}^2} \times 10^{-3}$	A
Simple PbO-SiO <sub>2</sub>	1263	2.1	2.1	-
PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	2.0	2.0	12
Simple PbO-SiO <sub>2</sub>	1123	0.7	0.7	-
2PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	0.55	0.63	11
1.5PbO.SiO <sub>2</sub> + Cu <sub>2</sub> O	"	0.71		

equation for the process may be written as

$$\text{Rate} = A a_{\text{O}}^2 e^{-22,000/RT}$$

As a consequence of the oxidation of carbon with oxygen ions, the basic ions in the slag are also reduced as indicated in equation 12. The change in free energy involved in this process will influence the kinetics of the oxidation process since if this change is unfavourable the oxidation can not proceed at all.

Hence, in order to investigate the oxygen ion activities, the rate equation will have to be modified by determining the rate of oxidation in this melt for a known value of the activity of the oxygen ions. The activation energy should remain unchanged (22 Kcal/mole).

Therefore A can be calculated for this reaction, and this value subsequently used to determine oxygen ion activities under other conditions.

### Calculation of Oxygen Ion Activities in Complex Silicate Slags

Through equations (7) and (8) an attempt has been made to extend Toop's analysis of silicate slag structure in the calculation of oxygen ion activities for silicate slags containing more than one basic component. It has been assumed that the free energies corresponding to the quasi-chemical equilibrium constants (equation 7) are additive. If  $N_1^i$ ,  $N_2^i$  etc. are the molefractions of the basic components defined as

$$N_i^i = \frac{N_i}{N_1 + N_2 + \dots + N_n}$$

where  $N_1$ ,  $N_2$  . . .  $N_n$  are molefractions of the basic oxides in the slag then the resultant free energy can be calculated as,

$$\Delta F = N_1^i \Delta F_1 + N_2^i \Delta F_2 + \dots + N_n^i \Delta F_n \quad (8a)$$

The corresponding value of k can be calculated for the complex slag and used in the determination of  $N_{O=}$ .

These assumptions may be considered to be valid if the behaviour of the oxidation of carbon is the same. It will be noted that the rate of oxidation is proportional to the square of the activity for both simple and complex slags. Also the rate constants for the oxidation of carbon are nearly the same at a given temperature for both simple and complex slags (Table VII). These two observations substantiate the assumptions made.

Toop in his thesis <sup>26</sup> has calculated the activities of silica and oxygen ions for the ternary system  $Cu_2O-PbO-SiO_2$ . He has experimentally determined the activity of silica with respect to liquid silica of the

silica saturation curve. Knowing the silica activities for the two binary systems, he has constructed the activity pattern for silica by drawing isoactivity lines which closely follow the shape of the saturation curves. On the basis of these lines he obtains the activity of oxygen ions by integrating the ionic form of Gibbs Duhem equation

$$d \log a_{O^2-} = - \frac{N_{SiO_2}}{1 - N_{SiO_2}} d \log a_{SiO_2} \quad (15)$$

Equations 7 and 8 may be utilised to calculate the activity of oxygen ions in this ternary system. It can be deduced from these equations that

$$\log k_T = N_{PbO} \log \frac{k_{PbO}}{k_{Cu_2O}} + \log k_{Cu_2O} \quad (16)$$

This equation indicates that the value of  $k_T$  is constant along straight lines joining the silica apex of the diagram with the  $Cu_2O$ - $PbO$  binary. Knowing  $k_T$ , the activity of oxygen ions can be calculated for any composition. This method has been used to calculate the isoactivity lines for oxygen ions<sup>33</sup> which are shown in Fig. 21. Toop's data is also shown in the figure for comparison. It is seen that the curvature of the isoactivity lines is smooth in the present case, whereas Toop's isoactivity lines show a pronounced 'kink' in the copper rich region.

The isoactivity pattern for oxygen ions may be utilised to calculate the isoactivity lines for silica by means of equation 15. This has been done along three composition paths. The integration constants for  $a_{SiO_2}$  were so chosen, that the integrated values of  $a_{SiO_2}$  approached the saturation activity values on the saturation curve. The isoactivity pattern for silica is given in Fig. 22, which also includes Toop's data.

Fig. 21: Iso-activity lines for oxygen ions in the  $\text{Cu}_2\text{O}$ - $\text{PbO}$ - $\text{SiO}_2$  system at  $1100^\circ\text{C}$

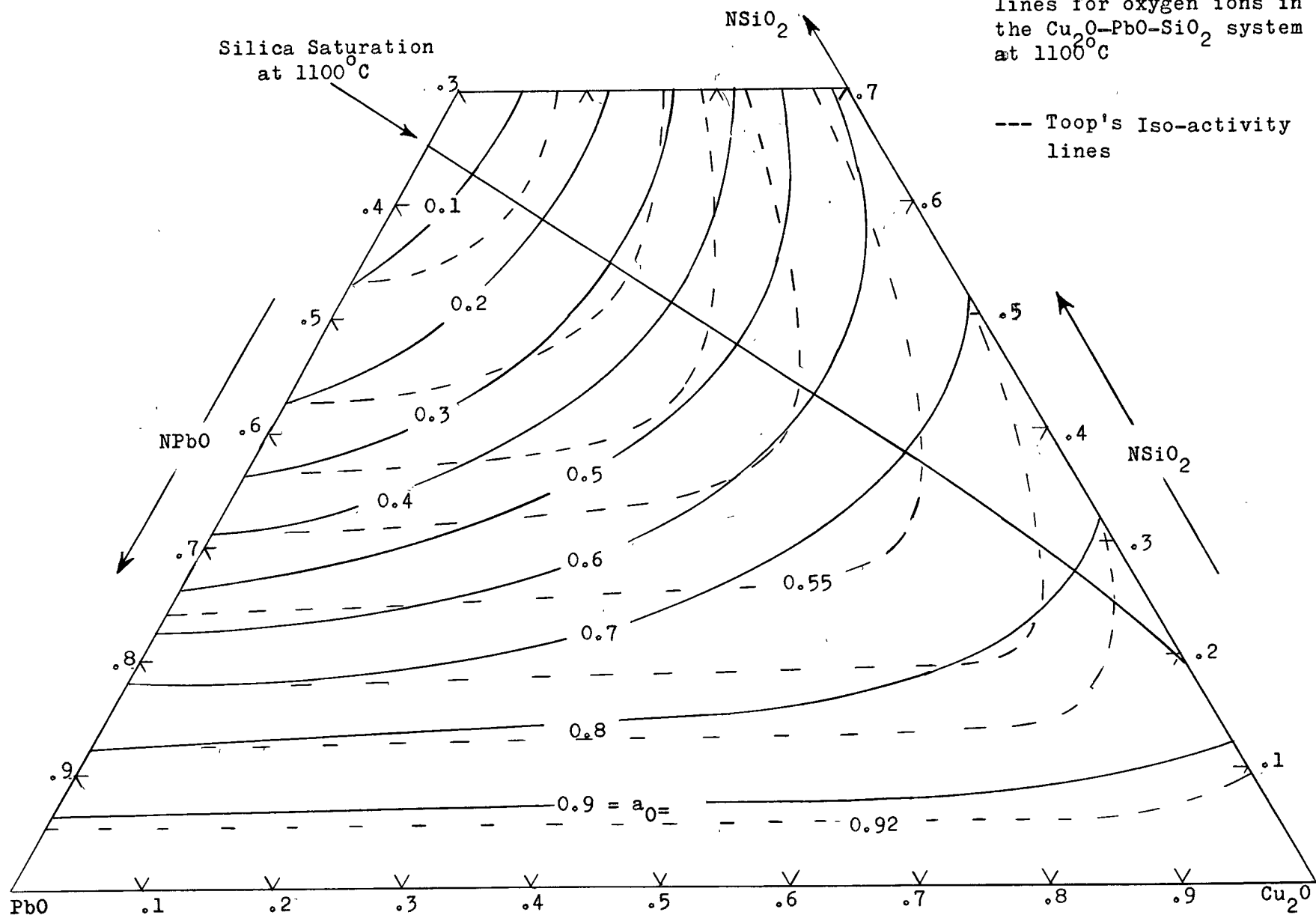
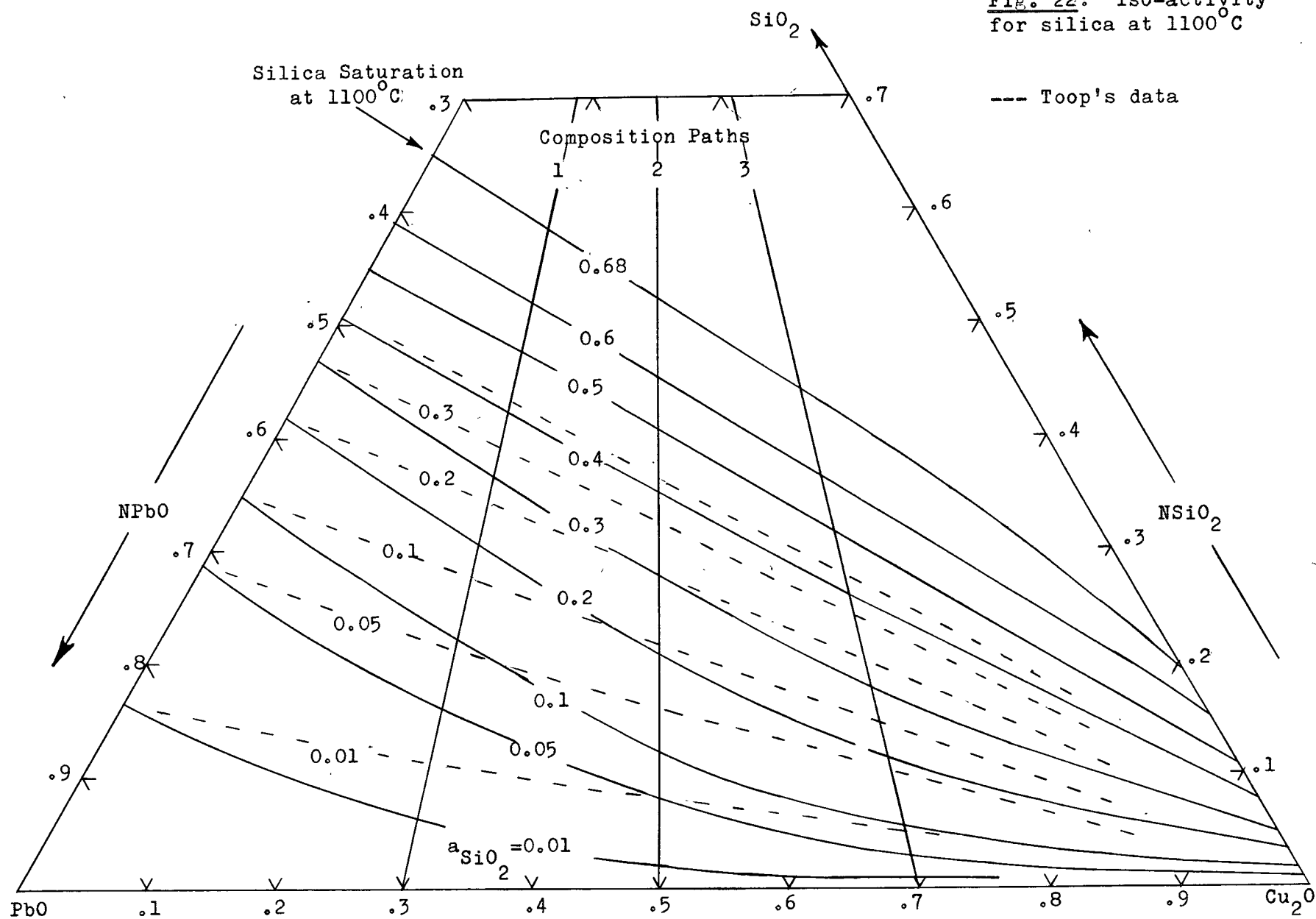


Fig. 22: Iso-activity  
for silica at 1100°C





Pronounced differences in activity values are observed towards the base of the diagram. The present data is believed to be more accurate, since it has been obtained from basic assumptions.

The same technique might be applied to evaluate the activities of oxygen ions, silica and the basic oxides in any multicomponent silicate system.

### CONCLUSIONS

(1) A study of the variation of the rate of oxidation of carbon with the oxidising potential of the cuprous oxide-lead oxide-silica slags was undertaken at different temperatures. The rate of oxidation was found to be proportional to the square of the activity of the oxygen ions.

(2) The experimental activation energy was found to have a value of  $22 \pm 2$  Kcal/gm. mole irrespective of the composition of the lead oxide-silica melt or the nature of the carbon specimen employed. Hence it appears that the nature of the carbon surface does not play an important role in the mechanism of oxidation.

(3) The results suggest that the activity of the oxygen ions in an unknown silicate melt may be determined by measuring the rate of oxidation of carbon in the melt.

(4) A method for the calculation of oxygen ion activities in multicomponent silicate slags has been devised.

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APPENDIX AAbsolute reaction rate calculations.Calculations for the gaseous oxidation of carbon.Mobile adsorption.

The rate equation for this case is<sup>5,6</sup>

$$\text{Rate} = \frac{kT}{h} C_g \frac{F^\ddagger}{F_g} e^{-\Delta E/RT} \quad (1)$$

Observed rate =  $7.2 \times 10^{11}$  molecules/cm<sup>2</sup>/sec.

$kT/h = 1.7 \times 10^{13}$  sec<sup>-1</sup> at 500°C.

$C_g = 2.5 \times 10^{18}$  molecules of oxygen/cc.

$e^{-E/RT} = 5 \times 10^{-11}$  at 500°C for  $E = 36.7$  Kcal

$F^\ddagger/F_g$  represents the entropy change in the process in terms of the partition functions. Gaseous oxygen molecules have three translational and one rotational degrees of freedom, whereas  $O^\ddagger$  as a mobile adsorbed layer has two translational and one rotational degree of freedom. Hence the net change in entropy for the reaction is  $f^\ddagger$  which has a value of  $3.3 \times 10^{-10}$  cm for oxygen.

$$\begin{aligned} \text{Rate} &= 1.7 \times 10^{13} \times 2.5 \times 10^{18} \times 3.3 \times 10^{-10} \times 5 \times 10^{-11} \\ &= 7.3 \times 10^{11} \text{ molecules/cm}^2/\text{sec} \end{aligned}$$

Immobile adsorption with dissociation

$$\text{Rate} = \frac{kT}{h} \sqrt{C_g} C_s \frac{F^\ddagger}{F} e^{-E/RT} \quad (2)$$

$$\frac{kT}{h} = 1.7 \times 10^{13} \text{ sec}^{-1}$$

$$C_s = 10^{15} \text{ cm}^{-2}$$

$$\sqrt{C_g} = 1.6 \times 10^9 \text{ cm}^{-3/2}$$

In this case the adsorbed  $O^{\ddagger}$  has no translational or rotational degree of freedom. Hence the entropy change is approximately given by

$$\frac{h^{3/2}}{(2\pi mkT)^{3/4} (8\pi^2 I kT)^{1/2}} \text{ cm}^{3/2} \text{ and is equal to } 10^{-16}.$$

$$\begin{aligned} \text{Rate} &= 1.7 \times 10^{13} \times 10^{15} \times 1.6 \times 10^9 \times 10^{-16} \times 5 \times 10^{-11} \\ &= 2 \times 10^{12} \text{ molecules/cm}^2/\text{sec.} \end{aligned}$$

#### Calculations for the oxidation of carbon in lead oxide silica slags

The observed rate for  $PbO.SiO_2$  slag at  $990^\circ C$  is of the order of  $10^{17}$  molecules/cm<sup>2</sup>/sec. The surface roughness factor for graphite is of the order of  $10^{2(31)}$ . Hence the experimental value is reduced to the order of  $10^{15}$  molecules/cm<sup>2</sup>/sec.

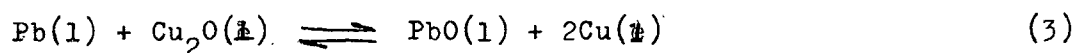
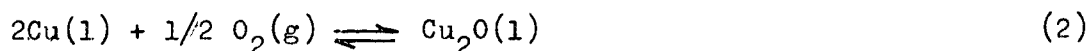
At  $990^\circ C$  the oxygen pressure for  $PbO.SiO_2$  slag is  $1.1 \times 10^{-10}$  atm. The corresponding concentration of oxygen is  $6 \times 10^8$  molecules/cc. Introducing this value in the equation 1 the rate is calculated to be of the order of  $10^6$  molecules/cm<sup>2</sup>/sec. for  $E = 22$  Kcal., which does not agree with the experimental value.

If it is assumed that the oxygen in the slag has somehow only two translational degrees of freedom in the melt, then in the process of adsorption there is no change in entropy. In this case the calculated rate is of the order of  $10^{17}$  molecules/sec/cm<sup>3</sup>. Hence there is agreement with the observed rate, but a discrepancy in the dimensions is obtained.

Similar results are obtained when immobile adsorption with dissociation is considered.

APPENDIX BFree energy and activity data for the calculation of oxygen pressure of the melts

The reactions utilised in the calculation of oxygen pressure of the melts are



The standard free energy changes <sup>32</sup> and the corresponding equilibrium constants at 1263°K are

$$\Delta F_1 = -23,437 \text{ calories} \quad K_1 = 1.05 \times 10^4$$

$$\Delta F_2 = -19,255 \text{ calories} \quad K_2 = 2.02 \times 10^3$$

$$\Delta F_3 = -4,182 \text{ calories} \quad K_3 = 5.225$$

At 1123°K these values are found to be

$$\Delta F_1 = -25,940 \quad K_1 = 1.12 \times 10^5$$

$$\Delta F_2 = -21,070 \quad K_2 = 1.26 \times 10^4$$

$$\Delta F_3 = -4,870 \quad K_3 = 8.87$$

The activity data for copper and lead at 1226°K is given in Table I B.

Data for the activity of oxygen ions

The data is summarised in Table II B.

TABLE I B

Oxygen potential data for the slags investigated

Wt % Copper in button	$N_{Cu}$	$N_{Pb}$	$a_{Cu}$ 1226°K	$a_{Pb}$ 1226°K	Oxygen pressure at 1263°K		Oxygen pressure at 1123°K		Oxygen pressure at 1123°K	
					For $PbO \cdot SiO_2$ slags		For $2PbO \cdot SiO_2$ slags		For $1.5PbO \cdot SiO_2$ slags	
					$\times 10^{10}$		$\times 10^{12}$		$\times 10^{12}$	
					Pb data	Cu data	Pb data	Cu data	Pb data	Cu data
0.0	-	1.000	-	1.000	1.10	-	6.26	-	2.88	-
0.5	0.0161	0.985	0.145	0.985	1.13	1.1	6.44	6.48	2.97	2.99
1.0	0.0318	0.968	0.252	0.972	1.16	1.15	6.62	6.64	3.05	3.06
2.0	0.0624	0.938	0.415	0.950	1.22	1.21	6.91	7.00	3.19	3.22
3.0	0.0915	0.909	0.536	0.930	1.27	1.25	7.19	7.20	3.33	3.33
4.0	0.120	0.880	0.623	0.914	1.32	1.28	7.40	7.48	3.44	3.46
5.0	0.146	0.854	0.683	0.902	1.36	1.34	7.65	7.73	3.52	3.56
6.0	0.172	0.828	0.739	0.889	1.40	1.38	7.83	7.83	3.61	3.61
7.0	0.197	0.803	0.777	0.879	1.43	1.42	8.01	8.01	3.69	3.69
8.0	0.220	0.780	0.802	0.873	1.45	1.43	8.10	8.11	3.73	3.74
9.0	0.244	0.756	0.825	0.865	1.48	1.47	8.20	8.20	3.77	3.78

TABLE II B

Activities of oxygen ions for the slags investigated

$N_{\text{Cu}_2\text{O}}$	$\% \text{Cu}_2\text{O}$	k	$2\text{PbO} \cdot \text{SiO}_2 (850^\circ\text{C})$		$1.5\text{PbO} \cdot \text{SiO}_2 (850^\circ\text{C})$		$\text{PbO} \cdot \text{SiO}_2 (990^\circ\text{C})$	
			$N_{\text{O}} =$	$a_{\text{O}} =$	$N_{\text{O}} =$	$a_{\text{O}} =$	$N_{\text{O}} =$	$a_{\text{O}} =$
0.000	0.00	.01000	0.326	0.280	0.212	0.190	0.130	0.110
0.008	0.41	.01026	0.330	0.285	0.224	0.201	0.136	0.115
0.016	0.82	.01053	0.350	0.301	0.232	0.208	0.146	0.1235
0.024	1.24	.01081	0.362	0.311	0.244	0.219	0.163	0.138
0.030	1.55	.01101	0.377	0.324	0.250	0.244		
0.035	1.80	.01119	0.383	0.329	0.258	0.231		
0.040	2.06	.01137	0.396	0.338	0.264	0.237		
0.045	2.32	.01156	0.404	0.347				
0.050	2.58	.01187	0.412	0.354				