

A STUDY OF THE "ROAST-REACTION"
OF LEAD SULFIDE

by

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Members of the Department of Mining and Metallurgy

THE UNIVERSITY OF BRITISH COLUMBIA

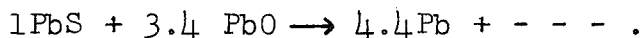
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ABSTRACT

The kinetics and mechanism of the "roast-reaction" of lead sulfide have been examined. The investigation, partitioned by the nature of the problem, included a study of (a) the "roast" which is the several reactions between galena (lead sulfide) and oxygen (or air) yielding oxides, sulfates and basic sulfates of lead, and (b) the reduction "reaction", between lead sulfide and the oxidation products of the roast leading to the production of lead metal.

The mechanism of the roasting of lead sulfide does not lead to the formation of distinct PbO and $PbSO_4$ phases. The products appear to be a mixture of basic sulfates throughout.

The rate of the reaction between PbS and PbO or $PbSO_4$ has been shown to be controlled by the transport of SO_2 from the reacting surface with gas velocities up to 5 cm./min. Under conditions of reduced pressure (< 5 mm. of Hg) the reduction reactions are shown to be heterogeneous and probably proceed by the adsorption of PbS vapor on the oxidized surface to form a $(PbS \cdot xPbO)^{\ddagger}$ basic sulfate type activated complex which subsequently decomposes to lead metal. The stoichiometry of this heterogeneous reaction has been checked for the PbS - PbO case with the use of a Pb^{212} tracer. The average value was measured to be



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A STUDY OF THE "ROAST-REACTION" OF LEAD SULFIDE

INTRODUCTION

The "Roast-Reaction", a High Temperature Oxidation-Reduction Process

The primary aims in the extraction of a metal from an ore are to obtain the maximum recovery of metal of suitable purity with the minimum number of separate processes, and to ensure that each process is carried out with the minimum of expenditure for process materials, energy and operational costs. Direct reduction processes for the recovery of metals are therefore to be desired but in the case of many ores, and in particular sulfides, direct reduction is not readily achieved. It is common practice then (14) to convert sulfides to some other compound more amenable to reduction. Often, sulfides are converted to oxides and occasionally, with careful control of roasting conditions, to sulfates. In a few cases they are converted to chlorides by chloridising roasting.

Having obtained the metal in the form of a more easily reducible compound, reduction is carried out. Carbon is the most common reducing agent used in high temperature process metallurgy; it also serves as a source of heat. In recent years hydrogen, iron, aluminum and ferrosilicon are being used in special processes. There are a few select metals whose extraction from their ores can be carried out by "mutual"

oxide-sulfide reduction; that is, the sulfide of the metal can be made to serve as the reducing agent for its own oxide. Mutual oxide-sulfide reduction can be predicted thermodynamically but only a few processes based on it have proven economical. Among these are the converting of copper matte and the air-reduction process for the recovery of lead from galena, the basis of which is the "roast-reaction".

The roast-reaction of lead sulfide was observed (6) as early as 1833 and was probably applied to lead metallurgy much earlier (31). The air-reduction process was first carried out in ore-hearth furnaces, later in reverberatory furnaces and even at present (8) some lead is being produced in ore hearths. It is highly probable that the chemical reactions which make up the "roast-reaction" play an important role in the blast-roasting and blast furnace smelting steps of modern lead metallurgy.

The term "roast-reaction" is used with reference to the sequence of reactions which take place when galena (lead sulfide) is heated in the presence of oxygen. Lead sulfide reacts with oxygen and, depending on the temperature, pressure, physical form and other characteristics of the sulfide, the products of reaction may be SO_2 , SO_3 , PbO , PbSO_4 , lead metal, basic lead sulfates and other oxides of lead.

Metallurgists of the last century noted that by careful control of the temperature the reactions could be separated into two more or less distinct steps. The first step, called the "roast", occurred at low temperatures with moderate or high oxygen pressures. Under these conditions lead sulfide could be roasted

and the products were found to be SO_2 , SO_3 , PbO , PbSO_4 and basic lead sulfates. Little or no lead metal was produced. In the second step, the "reaction", it was observed that at higher temperatures and with lower oxygen pressures the solid products of the "roast" could be made to react with excess PbS to form metallic lead and again SO_2 and SO_3 . The overall reaction became known as the "roast-reaction" and, if carried out with careful control of the temperature, could be made to yield chiefly liquid lead metal, SO_2 and SO_3 . Consequently it formed the basis of the air-reduction process of lead metallurgy.

Many chemical equations have been written to explain the steps of the "roast-reaction"; a limited few appear to describe the overall reaction adequately. The most significant of these are:

For the roast

1. $\text{PbS} + 3/2 \text{O}_2 = \text{PbO} + \text{SO}_2$
2. $\text{PbS} + 2\text{O}_2 = \text{PbSO}_4$
3. $2\text{PbS} + 7/2\text{O}_2 = \text{PbO} \cdot \text{PbSO}_4 + \text{SO}_2$
4. $\text{PbS} + \text{O}_2 = \text{Pb} + \text{SO}_2$
5. $\text{PbO} + \text{SO}_3 = \text{PbSO}_4$
6. $\text{SO}_2 + 1/2\text{O}_2 = \text{SO}_3$

For the reaction

1. $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$
2. $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$
3. $3\text{PbS} + 2\text{PbO} \cdot \text{PbSO}_4 = 7\text{Pb} + 5\text{SO}_2$
4. $\text{Pb} + \text{PbSO}_4 = 2\text{PbO} + \text{SO}_2$
5. $\text{SO}_2 + 1/2\text{O}_2 = \text{SO}_3$
6. $\text{SO}_2 = 1/2\text{S}_2 + \text{O}_2$

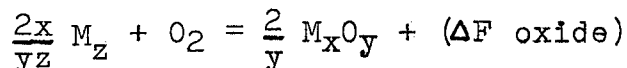
It has been noted (11) that at temperatures below 450°C the product of the roast is mainly PbSO_4 , particularly if slow oxidation is carried out in the presence of a catalyst. At temperatures greater than 450°C the product contains PbO , the amount of which increases with temperature. When the temperature reaches 750°C the "reaction" takes place and lead metal is set free. There is no evidence (17) of appreciable reaction between lead and its sulfide or oxide; nor is there between SO_2 and lead sulfide or sulfate, but at high temperatures lead metal reacts with excess PbSO_4 to yield PbO and SO_2 . The effects of materials such as silica, calcium sulfate, ferric oxide, lime and other basic oxides either added to or present as impurities in galena during roasting have been studied (18). It is not clear in what manner, if any, they act as catalysts.

Thermodynamics of the "Roast-Reaction"

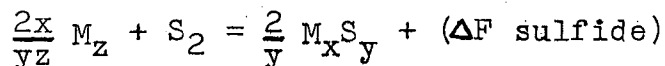
Probably the most useful method for assessing high temperature oxidation-reduction reactions in the thermodynamic sense is with the application of the Ellingham (9) type of free energy diagram.

As has been mentioned previously, lead sulfide is one of the group of sulfides from which metals can be extracted by "mutual" oxidation-reduction. The condition for this type of reaction is that the sum of the free energy of formation of the sulfide plus that of the oxide be less negative than the free energy of formation of sulfur dioxide from the elements at the

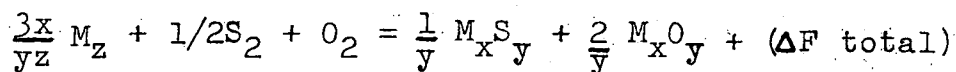
same conditions. The general equation for oxide formation can be written



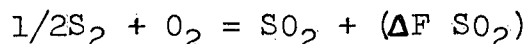
and that for sulfide formation



Dividing the sulfide equation in half and combining these one gets



The equation for sulfur dioxide formation is



and if "mutual" oxidation-reduction is to proceed, (ΔF total) must be less negative than ($\Delta F SO_2$). Figure I, which is a combined form of Ellingham diagram indicates the general possibilities for mutual oxidation-reduction. It is evident that metals less noble than lead are not obtained at readily accessible temperatures. The equation for the reaction between lead sulfide and lead sulfate is shown as an example of mutual sulfate-sulfide reduction.

The thermodynamics of the roast-reaction are usefully illustrated by Ellingham diagrams; for this purpose two diagrams have been prepared. Figure II shows the standard free energies of formation of the principal compounds which take part in the reactions. For purposes of clarity the free energy of formation lines for other metal oxides and sulfides are not included on the diagram but it is noteworthy that the oxide lines, all negative

in the temperature range 0°C to 1000°C (with minor exceptions) extend over a large region of stability; on the other hand the sulfide lines are mostly grouped in the region of the lead sulfide line. The positions of the free energy lines for CS_2 , H_2S , H_2O , CO_2 and 2CO confirm the relative merits of carbon and hydrogen as reducing agents for metal sulfides and oxides. The effectiveness of oxygen in displacing sulphur from sulfides is shown by the SO_2 line.

Figure III shows the standard free energies of reaction for those reactions which are thought to play the leading parts in the roasting and reduction of lead sulfide. It will be appreciated that values in Figure III are obtained by addition or subtraction of the requisite values shown in Figure II. Straight line plots have been used where deviations were small.

An examination of Figure III shows that most of the reactions are thermodynamically favorable between 700°C and 1000°C . However, in the roast-reaction, restrictions on the partial pressures of O_2 , SO_2 and SO_3 in the gas phase limit the number of compounds which can be present in appreciable quantities at equilibrium. This is of particular importance in the case of the basic lead sulfates.

The maximum partial pressure of oxygen which can be present in the ordinary lead roasting and smelting process is 0.21 atmospheres; this would be normal air. The maximum partial pressure of SO_2 can be 0.14 atmospheres; this would occur when the PbS was roasted with the theoretical amount of air to form PbO . Operating pressures will lie somewhere between these extremes.

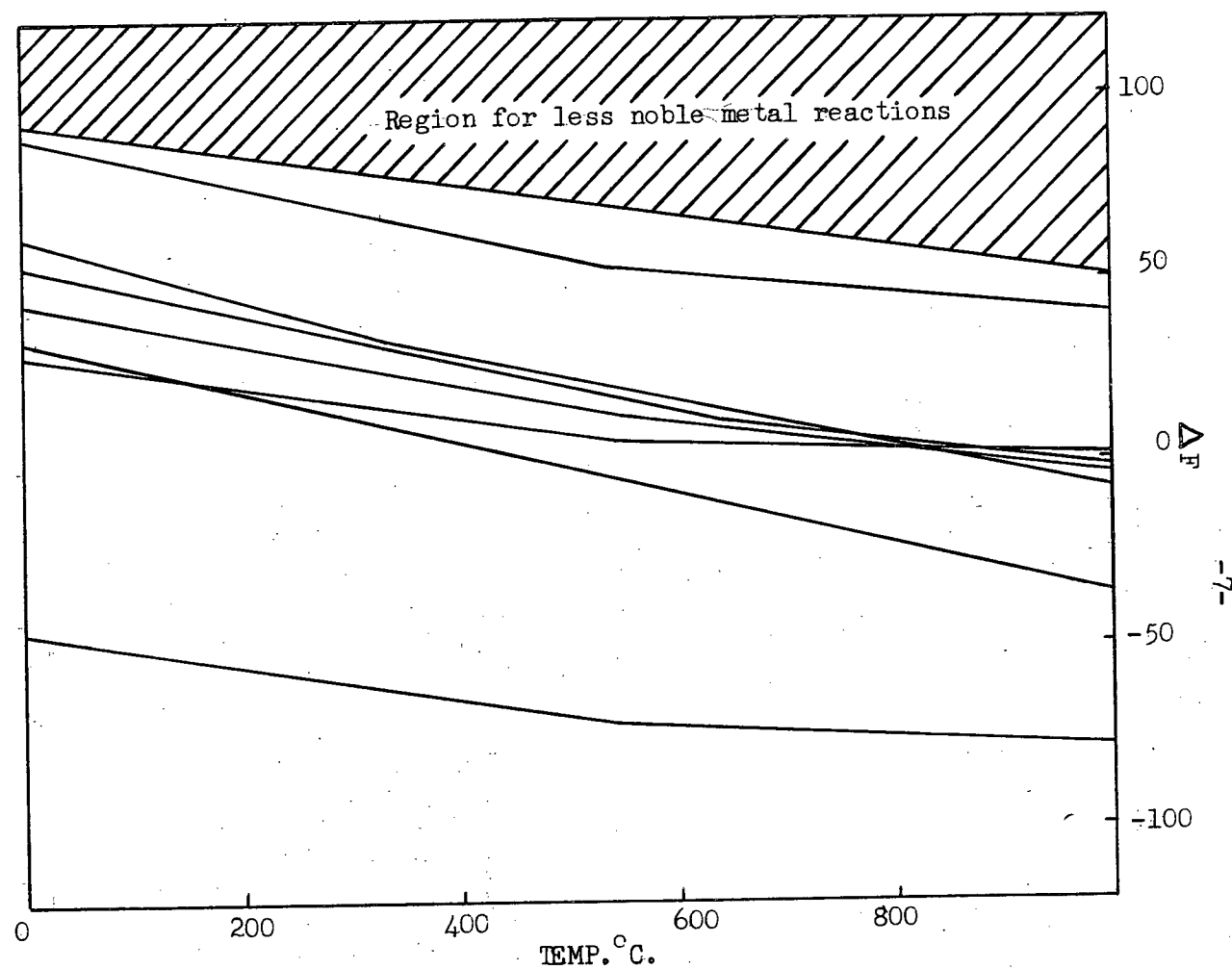
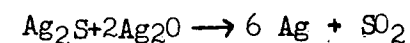
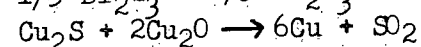
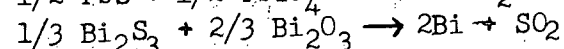
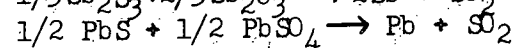
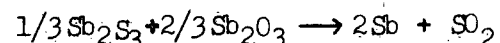
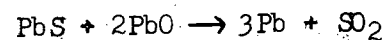
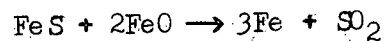


Fig. 1 Mutual oxide-sulfide reduction. ΔF in Kilocalories per mole of SO_2 gas.

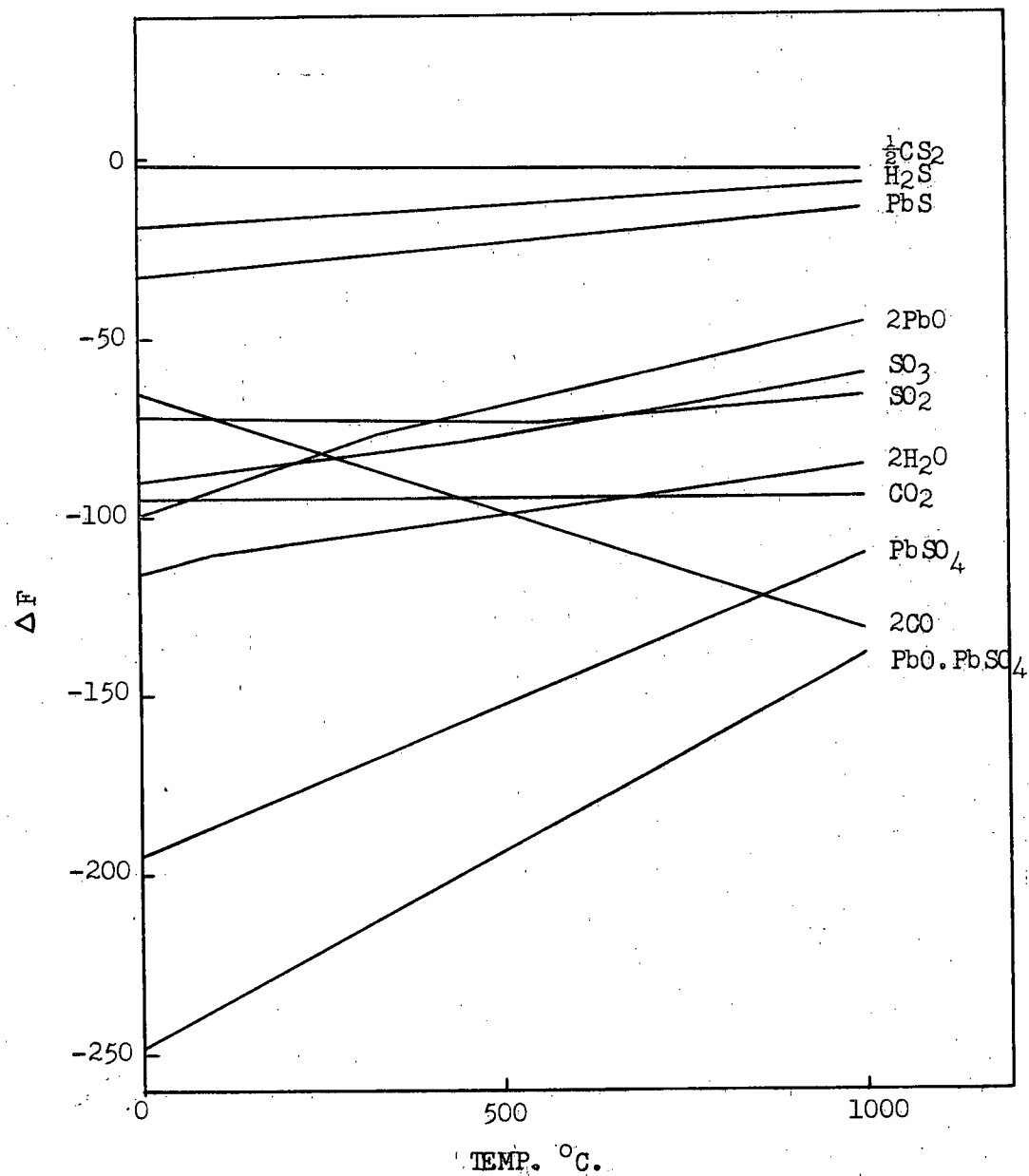


Fig. II Standard free energies of formation, ΔF in Kilocalories per mole of SO_2 .

The formation and decomposition of basic lead sulfates may be assumed to take place through the following series of reactions:

1. $\text{PbS} + 3/2\text{O}_2 = \text{PbO} + \text{SO}_2$
2. $\text{PbO} + \text{SO}_2 + 1/2\text{O}_2 = \text{PbSO}_4$
3. $2\text{PbSO}_4 = \text{PbO} \cdot \text{PbSO}_4 + \text{SO}_2 + 1/2\text{O}_2$
4. $3\text{PbO} \cdot \text{PbSO}_4 = 2(\text{PbO})_2\text{PbSO}_4 + \text{SO}_2 + 1/2\text{O}_2$
5. $4(\text{PbO})_2\text{PbSO}_4 = 3(\text{PbO})_3\text{PbSO}_4 + \text{SO}_2 + 1/2\text{O}_2$
6. $(\text{PbO})_3\text{PbSO}_4 = 4\text{PbO} + \text{SO}_2 + 1/2\text{O}_2$

Calculations (32) (12) of the equilibrium constants for the reactions indicate that the basic lead sulfates cannot exist under equilibrium conditions at roasting temperatures (700°C to 800°C) unless the atmosphere contacting them is almost pure air with no SO_2 or a SO_2 -nitrogen mixture with no oxygen. However, these conditions may be attained at points (13) within the solid bed.

The standard free energy of a reaction at a given temperature is a measure of its tendency to occur under those conditions when all the participating substances are at unit activity. Generally the consumption of reactants and formation of products of variable activity leads to a progressive decrease in free energy which will become zero at equilibrium, unless measures are taken to prevent this approach to equilibrium. The high temperatures of pyrometallurgical practice usually ensure that if a reaction has a positive tendency to occur, it will take place at a measurable rate. However, a positive driving force for a reaction under specified conditions is no guarantee that the reaction will take place with measureable velocity. Reaction velocities must be studied independently.

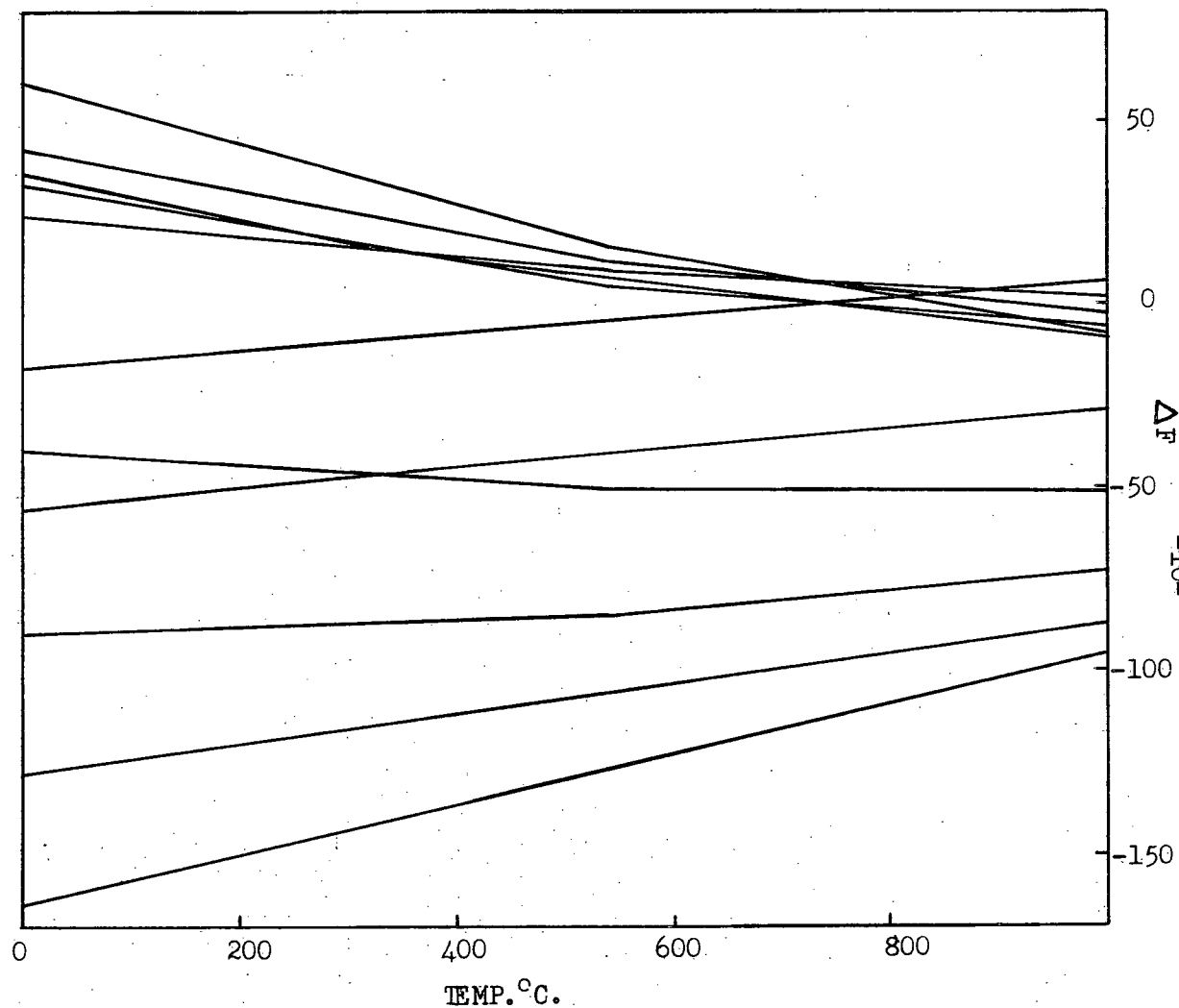
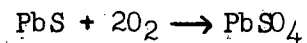
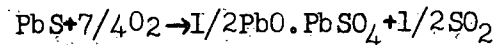
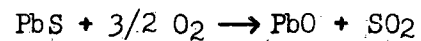
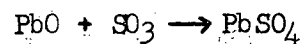
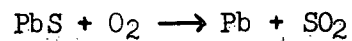
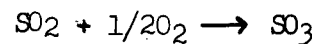
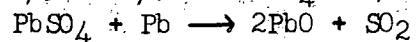
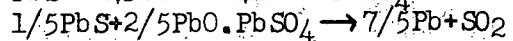
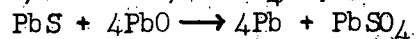
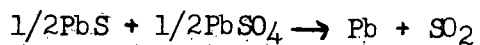
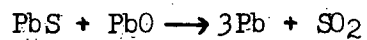


Fig. III Standard free energies of reaction.

Kinetics and Mechanism of the "Roast-Reaction"

In general, reactions involved in roasting and reduction processes are largely heterogeneous and occur at interfaces. Reactions between solids are likely to be very slow as in the absence of a gaseous or liquid phase, diffusion can only occur at the points of contact of the two solids. It has been suggested (7) that many reactions that appear to proceed via the solid state are in actual fact gas-solid reactions. However, Wenner (33) has assumed solid-solid reactions in a thermodynamic study of the roasting of galena.

The mechanism for a heterogeneous reaction such as the roast-reaction is comprised of several consecutive steps. For the "roast" they may be the following:

1. Transport of oxygen molecules from the bulk gas phase to the gas-solid interface.
2. Adsorption of oxygen on the solid surface, either as molecules or as atoms.
3. Diffusion of oxygen atoms or ions through the layer of oxides and sulfates to the reaction interface.
4. Chemical reaction between oxygen and lead sulfide, the oxygen replacing the sulphur in the lead sulfide lattice and combining with the sulphur ion to form SO_2 .
5. Diffusion of SO_2 from the zone of reaction through the product lattice to the surface and probable reaction enroute with oxygen ions to form SO_3 and subsequently PbSO_4 in the PbO lattice.

6. Dissociation of PbSO_4 and SO_3 at points of lower SO_2 concentration, "i.e.", points removed from the reaction interface, forming of basic sulfates and eventual reforming of SO_2 and PbO .
7. Desorption of SO_2 and SO_3 from the PbO surface layer at the solid-gas interface.
8. Transport of SO_2 and SO_3 from the interface into the bulk gas stream.

The mechanism of the "reaction" can be considered from two viewpoints: alternately, a solid-solid or a gas-solid reaction may be proposed. Choosing the reaction $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$ and assuming a solid-solid reaction the steps follow:

1. Diffusion of sulphur ions and (or) diffusion of oxygen ions through the product layer (liquid lead metal) to the zone of chemical reaction.
2. Chemical reaction between oxygen and sulphur ions to form SO_2 and SO_3 .
3. Diffusion of SO_2 and SO_3 through the product layer to the gas-liquid interface.
4. Desorption of SO_2 and SO_3 at the interface.
5. Transport of SO_2 and SO_3 from the interface into the bulk gas phase.

Assuming a gas-solid reaction, using the lead sulfide-lead oxide reaction again and letting lead oxide be the solid phase, there are the initial steps:

1. Sublimation of solid PbS .
2. Transport of gaseous PbS to the product interface.

3. Adsorption of gaseous PbS on the product interface. and again, the five steps for the solid-solid reaction. The lead sulfide-lead sulfate reaction is almost certainly more complex.

As has been pointed out previously, the magnitude of the free energy of a reaction is no measure of the velocity of the reaction. Reaction velocities must be independently examined and some knowledge of the mechanism must be at hand before measurements of reaction rates can be interpreted. In the case of a complex reaction consisting of several steps each step may be considered to have its own activation energy and to proceed at a rate common to all the steps. One step of the overall mechanism will be rate-controlling; of necessity it will be that step with the greatest activation energy. The observed activation energy then will be the net energy increase from the potential energy minimum of the separate reactants to the energy plateau of the activated complex of the rate controlling step. With gas-solid reactions in which there is a gaseous product and a gaseous reactant the rates at which reactants are brought to the surface and products removed from it may well control the overall velocity of the reaction (34). Reactions in the solid state are often controlled by interface diffusion processes which are slow, this in turn may result in lower activation energy values than expected for a given reaction at a specified temperature.

Fundamental Consideration of Structure and Chemical Reactivity*

The atoms: The electronic structures of oxygen ($1s^2, 2s^2, 2p^4$) and sulphur ($1s^2, 2s^2, 2p^6, 3s^2, 3p^4$) with two unpaired electrons in outer p orbitals result in bonding directions at right angles with the restrictions imposed by repulsion of neighboring like charges and hybridization. The expected valency of two is realized with both atoms in ionic bonding and in covalent bonding; sulphur also enters readily into covalent bonding with valencies of 3, 4 and 6 which is understandable as the number of valence electrons has increased from 4 to 6. Oxygen being strongly electronegative has the additional possibility of forming hydrogen bonds. Pauling's scale of electronegativities places oxygen at 3.5 and sulphur at 2.5. Radii of the atoms and divalent ions are 0.66 \AA and 1.32 \AA for oxygen and 1.04 \AA and 1.74 \AA for sulphur.

The lead atom has the electronic configuration of the xenon core followed by $5d^{10}, 5f^0, 6s^2, 6p^2$, thus the chemical properties will be inherent in the inert pair $6s^2$ and the two unpaired 6p electrons. The plumbous ion is more stable than the plumbic ion, hence true lead salts are divalent but in covalent bonding plumbic compounds are more stable which suggests the formation of four hybrid orbitals. Electronegativity

* The data in this section has been largely taken from L. Pauling's "Nature of the Chemical Bond", W. Huckel's "Structural Chemistry of Inorganic Compounds", N.V. Sidgwick's "Chemical Elements and their Compounds", and A.F. Well's "Structural Inorganic Chemistry".

values are given as 1.6 for Pb II and 2.4 for Pb IV. The atomic radius is 1.74 \AA , the ionic radii 1.21 \AA for Pb II and 0.84 \AA for Pb IV.

The molecules: The oxygen molecule O_2 is linked by four electrons which are accommodated in one sigma and one pi bond; each atom contains in addition two lone electron pairs. The structure of the molecule is somewhat unusual, it is paramagnetic due to parallel spins of the pi bond electrons and it demonstrates a kind of molecular unsaturation which results in great chemical activity, often allowing the whole molecule to combine with oxidizable substances. The O-O distance is given as 1.21 \AA and the bond energy 118.2 Kcal .

The sulphur dioxide molecule SO_2 has a bent structure, the O-S-O angle being 120° with the very short S-O distance of 1.45 \AA which suggests probable resonance between the two structures $\text{S} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$ and $\text{S} \begin{smallmatrix} \searrow \text{O} \\ \nearrow \text{O} \end{smallmatrix}$. The energy of the S-O bond from heat of dissociation values is 121 Kcal .

The sulphur trioxide molecule SO_3 is planar with an O-S-O angle of 120° and the S-O distance 1.43 \AA . The structure is probably a resonance hybrid of $\text{O}=\text{S} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$, $\text{O}=\text{S} \begin{smallmatrix} \searrow \text{O} \\ \nearrow \text{O} \end{smallmatrix}$, $\text{O}=\text{S} \begin{smallmatrix} \nearrow \text{O} \\ \nearrow \text{O} \end{smallmatrix}$ and the tendency to polymerize is a sign of the instability of the S-O bond. SO_3 begins to dissociate to SO_2 at 300°C , the bond energy being given as 108 Kcal .

The lead sulfide molecule PbS forms infinite 3 dimensional complexes of the rock salt structure with co-ordination numbers $\text{M:S} = 6:6$. The environment of the Pb atom then is 6 equidistant S atoms at 2.97 \AA but the Pb-S binding is not purely

ionic as solid PbS is opaque with a brilliant metallic lustre. The lattice is face centred cubic with a lattice constant of 5.9362, there being 4(PbS) per unit cell. The density of solid PbS is given as 7.596 at 26°C, the melting point as 1114°C and the vapor pressure at the melting point as 100 mm. of Hg. Lead sulfide is found in nature as the mineral galena which is believed to be formed by hydrochemical reactions. The disulfide does not exist.

Diffusion coefficients are available for PbS at temperatures from 700°C to 800°C. Anderson and Richards (1) observed diffusion coefficients of the order of 10^{-10} cm.²sec.⁻¹ for the self diffusion of lead in synthetic lead sulfide pellets. Scanlon and Brebrick (24) obtained a diffusion coefficient of 2×10^{-6} cm.²sec.⁻¹ for the diffusion of sulphur in natural galena crystals and Starkiewicz, Bate, Bennett and Hilsum (2) obtained diffusion coefficients of 10^{-6} cm.²sec.⁻¹ for the diffusion of sulphur in single crystals of synthetic galena.

Lead oxide exists in two polymorphic forms, tetragonal red and orthorhombic yellow. The orthorhombic form is stable at high temperatures, the transition occurring at 489°C. The tetragonal form has an extraordinary layer structure in which the metal atom is bonded to four oxygen atoms which are arranged in a square to one side of it. It is suggested that the inert pair of electrons of the metal atom occupy the apex of the tetragonal pyramid. There are 2(PbO) per unit cell, the lattice constants are given as $a=3.9759$ and $b=5.023$, the density of the solid is 9.355 at 27°C.

The self diffusion of lead in α PbO (tetragonal form) has been measured (15) and is expressed by the formula $D=D_0 \exp(-Q/RT)$ where $D_0=10^5 \text{ cm.}^2 \text{ sec.}^{-1}$ and $Q=66 \text{ Kcal./mole.}$ At 750°C this results in a diffusion coefficient of $9 \times 10^{-10} \text{ cm.}^2 \text{ sec.}^{-1}$.

In the orthorhombic yellow PbO the lead atoms are arranged in layers and between every layer of lead atoms there is a puckered layer of oxygen atoms. The Pb-O distances are 2.20 \AA , 2.18 \AA and 2.20 \AA with Pb bond angles of 93.0° , 89.6° and 73.6° . The nature of the bonds between adjacent lead layers is not clear. There are 4(PbO) per unit cell with lattice constants $a=5.489$, $b=4.755$ and $c=5.891$, the density of the solid being 9.642 at 27°C , the melting point 888°C with a vapor pressure of 0.35 mm. of Hg.

With both forms of the oxide the striking colors suggest that the bonds are not simple types. Lead oxide is found in nature as litharge, the red tetragonal form and massicot, the yellow orthorhombic form. They are rare minerals of secondary origin usually associated with galena. The suboxide Pb_2O does not exist.

The lead sulfate (PbSO_4) structure has an orthorhombic lattice with 4(PbSO_4) per unit cell. The lattice constants are given as $a=8.480$, $b=5.398$ and $c=6.958$. The density of the solid is 6.323 at 25°C . The color, transparent to white, suggests that the bonds may have considerable ionic character. Terem and Akalan (28) have studied the decomposition of PbSO_4 which they observed to start at 860°C . The activation energy of decomposition was measured to be 92 Kcal./mole in the

temperature range 860°C to 1300°C .

Lead sulfate is found in nature as the mineral anglesite, it is of secondary origin having been formed by the oxidation of lead sulfide and often occurs in concentric layers about a nucleus of unaltered galena.

Various forms of basic lead sulfate have been reported. Schenck (25) discusses the compounds $\text{PbO} \cdot \text{PbSO}_4$, $(\text{PbO})_2 \cdot \text{PbSO}_4$ and $(\text{PbO})_3 \cdot \text{PbSO}_4$ while Clark, Mrgudich and Schieltz (4) have found only the structures $(\text{PbO})_4 \cdot \text{PbSO}_4$, $(\text{PbO})_3 \cdot \text{PbSO}_4$ and $(\text{PbO})_2 \cdot \text{PbSO}_4$ in an extensive X-ray examination of basic sulfate preparations. All of the above compounds are listed in the A.S.T.M. card index of X-ray crystallographic data. Only the monobasic sulfate, $\text{PbO} \cdot \text{PbSO}_4$, is reported among minerals; the mineral, lanarkite, forms monoclinic crystals of density 6.29. The melting point is reported as 977°C .

Objects and Limitations of the Investigation

A limited amount of information (3) was found in the recent literature on the kinetics and mechanisms of the roasting and reaction of lead sulfide. The overall mechanism is without doubt complex and any simplification that could be invoked would be of assistance in a preliminary study. For this reason the "roast" was considered as distinct from the "reaction" although this division was arbitrary and probably could not be justified in a study of the combined roast-reaction.

Features of the separated mechanisms which were chosen for study initially were (a) the mechanism of sulfate formation in the roast (b) the kinetics of the reactions between lead sulfide and lead oxide and between lead sulfide and lead sulfate to form lead metal and (c) the stoichiometry of the reactions in (b). It was not planned to study the effects of structural alterations, defects or impurities or the thermodynamic equilibria of the Pb-O-S system in this research project.

EXPERIMENTAL PROCEDURE AND RESULTS

Materials

The materials used included reagent grades of lead sulfide, lead sulfate and lead oxide, Pueblo Brand test lead (C.P.) made by American Smelting and Refining Co. and sulphur flowers (technical grade), Baker and Adamson. Natural galena was obtained from the Department of Geology and Geography of the University of British Columbia. Synthetic galena was used in most of the tests, the preparation of this and of lead sulfate are described in Appendices A and B.

The Pb^{212} isotope used in the tracer study was extracted from a Th^{228} solution obtained from Atomic Energy of Canada Ltd., Chalk River, Ontario. The extraction procedure and the preparation of labelled lead sulfide are described in Appendix E.

The gases used were standard grades of cylinder nitrogen, oxygen, sulphur dioxide and hydrogen sulfide. The nitrogen was freed of water vapor and oxygen as described in Appendix C.

Apparatus

The reactions were carried out in alundum boats in conventional vitreosil tube furnaces. Temperature control was obtained with chromel-alumel thermocouples connected to Wheelco controllers giving an accuracy of $\pm 5^\circ\text{C}$ in the range 700°C - 800°C . Vacuum was obtained with a standard backing pump and checked with a mercury U-tube. Atmospheres were introduced by passing

the required gases through suitable purification trains and thence into the furnace. The apparatus used for briquetting samples consisted of a 100 ton hydraulic jenny, fitted with accessories for powder metallurgy work.

The X-ray diffraction patterns were obtained by standard powder methods using a Straumanis type camera on a Norelco diffraction unit. Radio-active counting was carried out in a Na(Tl)I "well" type scintillation crystal (National Radiac Inc.), mounted in a counter head manufactured by Philips Co. The pulses from the counter head were fed into an amplifier-scaler combination, also of Philips design. All counting was standardized with an Fe⁵⁵ solution giving an average counting rate of 29,500 counts per minute, the background throughout the experiments being about 1700 counts per minute.

Oxidation "Roast" Reactions

The mechanism of sulfate formation in the roast was examined by two methods. The first method consisted of roasting finely divided galena and analyzing the products chemically. In the second approach galena was briquetted, the briquets were roasted and subjected to microscopic and X-ray diffraction examination.

Experimental: In the initial study, two gram samples of synthetic galena, -50 mesh, were roasted in alundum boats for timed intervals in the temperature range 690°C-825°C. Gases were passed over the samples at rates up to two liters per

minute. In all cases samples were placed in the furnace at room temperature, the furnace then being brought to the desired temperature. The samples were removed from the furnace immediately after the roasting interval and blank roasts were run to correct for the heating up period.

The samples were analyzed for PbS and PbSO_4 , PbO^* being determined by difference; the analytical procedures are outlined in Appendix D, I. The weight change on roasting was obtained for each sample.

Results: A typical set of data obtained when galena was roasted in air is shown in Table I; as is indicated, slagging occurred at a temperature of about 825°C , the PbO attacking the alundum of the boat at this and higher temperatures. The weight changes of the total roast, PbS, PbSO_4 and PbO with temperature for two hour periods are shown in Figure IV.

The results of a large number of roasts carried out with various flow rates of oxygen and air are summarized in Figure V. The PbSO_4/PbO ratios are plotted against temperature. The scatter of the data did not allow the fitting of curves but some significance can be attached to the boundary conditions shown. Evidently, sulfate formation at constant temperature depends on (a) the partial pressure of oxygen and (b) the gas velocity over the roasting surface. Also, the starting temperature of the "reaction" is dependent on oxygen pressure. It was found that the "reaction" occurred at temperatures greater than 825°C for all oxygen roasts and for roasts in air flowing at two liters per minute. With lesser air flow

* Attempts to analyze for PbO directly were unsatisfactory.

TABLE I

Data obtained on roasting PbS in air at various temperatures. Two grams PbS, time 2 hours, rate of air flow 2 liters per minute.

Temp. °C.	Wt. of roast gm.	Wt. of insol. gm.	Insol. PbS found gm.	PbSO ₄ found gm.	PbO found gm.	Total roast found gm.	Total PbS found gm.
725	2.121	1.233	1.222	0.644	0.234	2.100	1.980
765	2.137	1.122	1.117	0.746	0.262	2.125	1.985
780	2.145	1.033	1.022	0.810	0.304	2.136	1.986
795	2.155	0.946	0.928	0.900	0.370	2.198	1.990
810	2.173	0.725	0.732	0.966	0.474	2.172	2.000
825	2.081	fused	0.598	1.006	0.548	2.152	1.990

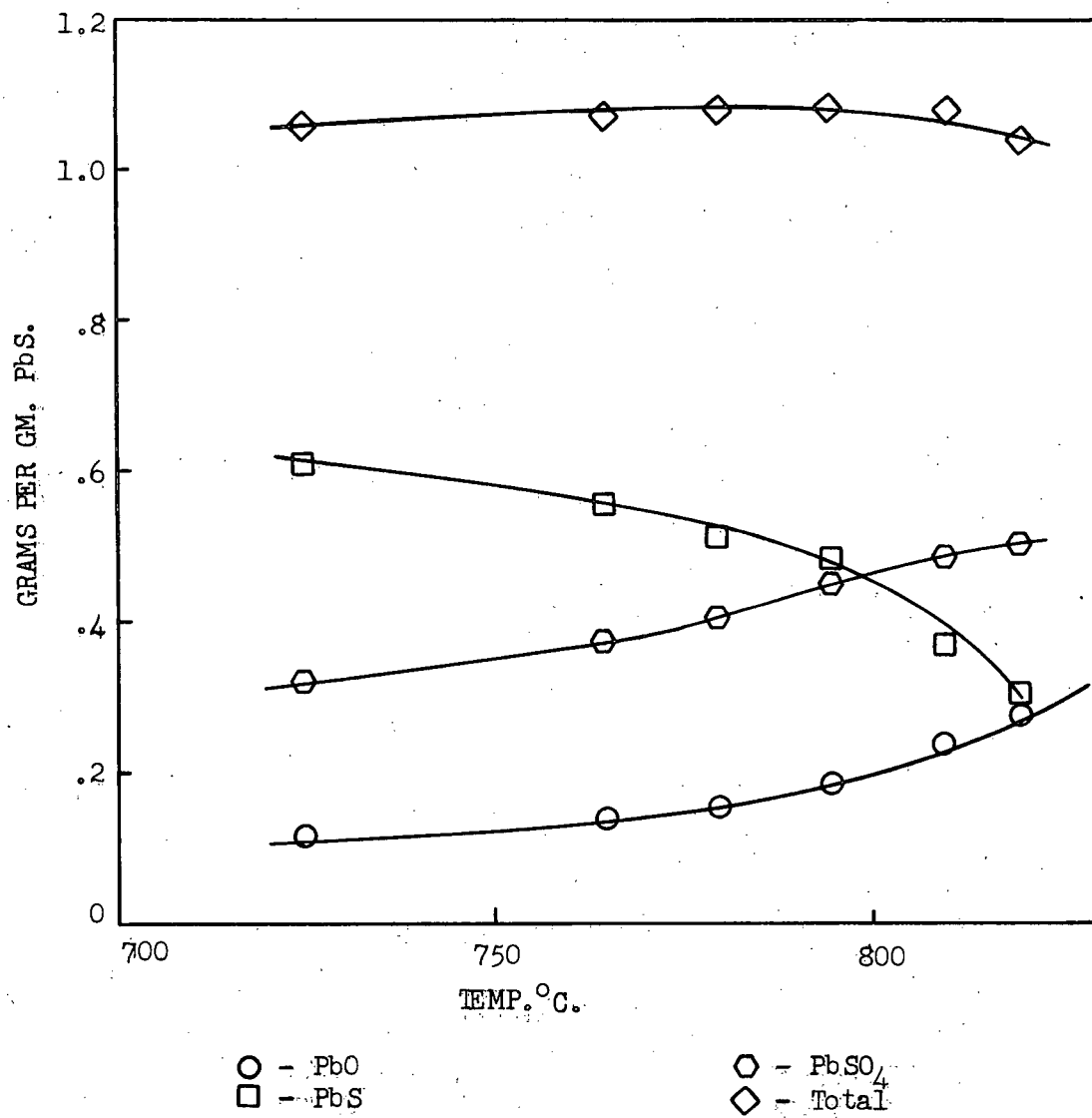


Fig. IV Weight changes on roasting PbS in air. Time of roasting 2 hours. Air flow 2 liters per minute.

rates the "reaction" started at lower temperatures, the minimum being 810°C at zero* air flow. The starting of the "reaction" was confirmed by the presence of lead metal detected with the stereoscopic microscope. The "reaction" invariably originated at depth in the sample, never on the surface.

In the initial roasts difficulty was experienced in obtaining a uniform temperature across the length of the sample. A zone of uniform temperature was realized by placing the roast in an inverted boat cover within an ordinary combustion boat and by preheating the gas entering the roasting zone, all as shown in Plate I.

Experimental: The samples used in the second mechanism study of the roast were prepared by briquetting the finely divided materials in a $1/2$ inch diameter cylindrical steel die; lead sulfide briquets were made by pressing 12 grams of PbS to 20 tons per square inch, this pressure giving a strong bond with a metallic surface. Synthetic galena or reagent grade lead sulfide could be briquetted with ease but a strong bond was not obtained with lead oxide or lead sulfate.

The briquets were placed in alundum boats, put into the furnace and roasted in a manner similar to that for powdered samples. Gradual heating up was found to minimize cracking of the specimens; the atmospheres included air, oxygen, and sulphur dioxide. After roasting and examination under a stereoscopic microscope the samples were mounted in bakelite.

* Zero flow rates were those in which a slight positive pressure of gas was maintained in the furnace.

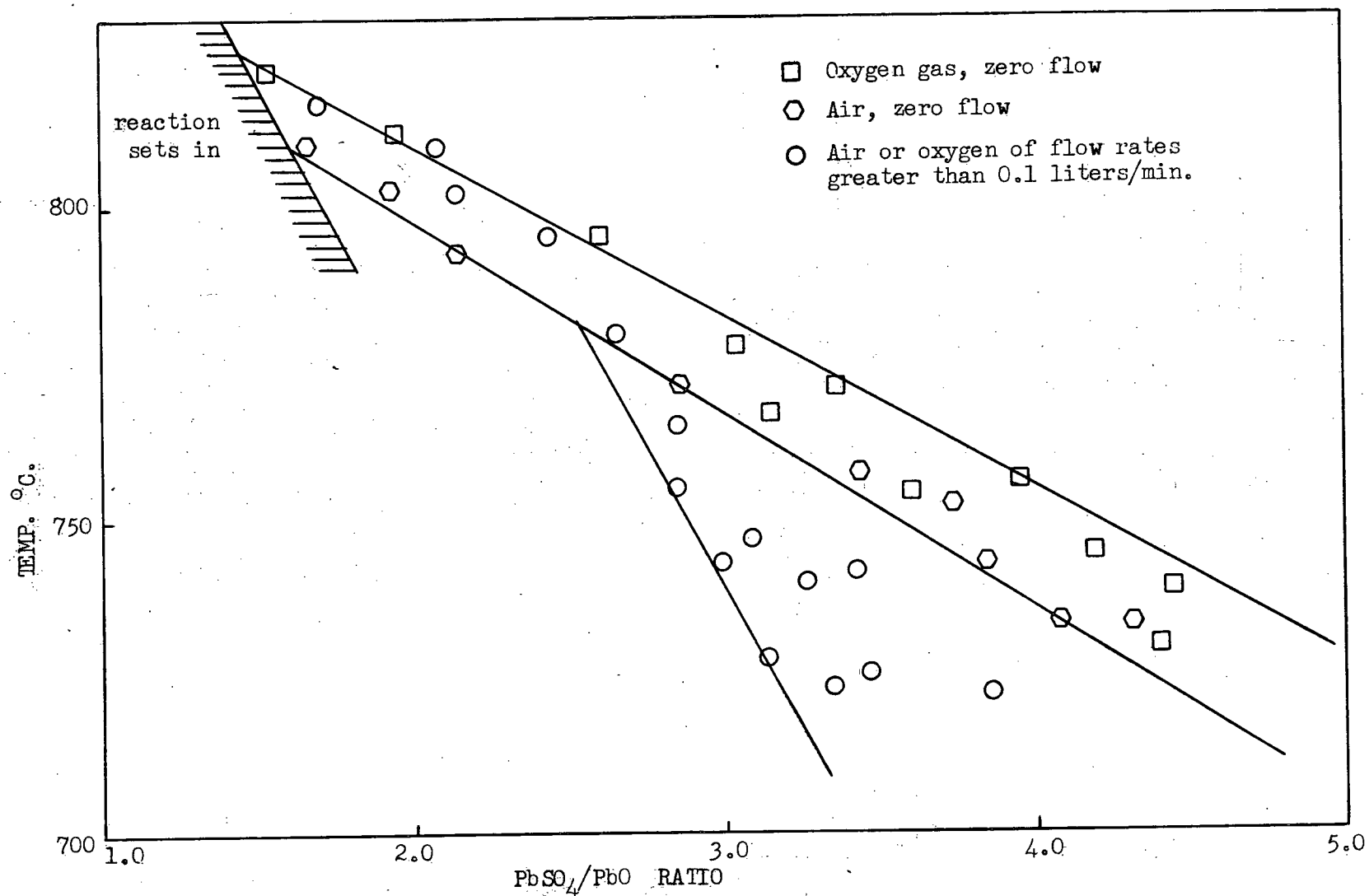


Fig. V Dependence of the $PbSO_4/PbO$ ratio on gas flow rate and oxygen pressure at various temperatures. 2 gm. sample of PbS powder, time of roasting two hours.

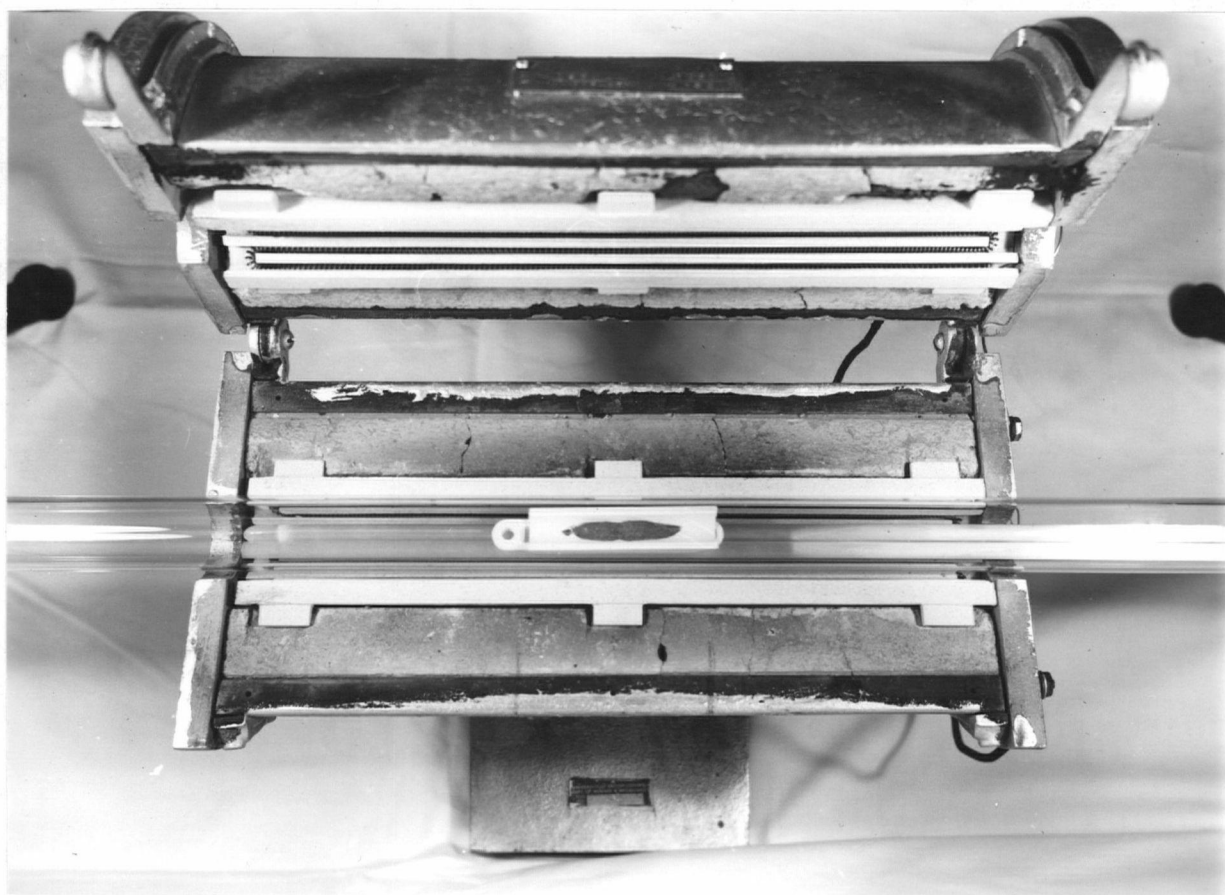


Plate I The apparatus used for the roasting. Air or oxygen was brought into the roasting zone from the right through the 6 mm. open ended vitreosil tube lying under the boat and withdrawn to the right. A vycor tube has been substituted for the vitreosil combustion tube for purposes of illustration.

Material for X-ray diffraction was removed in layers from the exposed face and Debye-Scherrer patterns of the layers were obtained using standard "powder" technique, all material being reduced to pass a 200 mesh screen. The mounted briquets were prepared for photomicrography. The average depth of the roasted material on the periphery of the PbS was measured with a micrometer eyepiece fitted on a Reichert Metallograph. The eyepiece was calibrated with a one millimeter standard scale consisting of 100 ten micron divisions ruled on an optical mirror.

Results: Plate II depicts a typical briquet before and after roasting in air. Roasting temperatures had to be kept below 810°C in air to prevent the "reaction" setting in. The rate of roasting was much slower in air than in oxygen and as a result attempts to obtain quantitative data on the rate of diffusion into the briquet were unsatisfactory. The rate of roasting in oxygen was measureable and the roast proceeded to a uniform depth over the entire briquet. The progress of the roast into the PbS briquet is illustrated in Plate III which contains photomicrographs of the PbS-bakelite interface after various roasting times. The rate of diffusion into the briquet was approximately linear as shown by Figure VI, the average rate being 7 microns (0.007 millimeters) per hour for a 96 hour period.

Standard X-ray diffraction patterns were obtained for reagent grade PbS , PbO and PbSO_4 chemicals; these are shown in Plate IV. Patterns of the synthetic galena, synthetic lead

sulfate and natural galena, in Plate V, demonstrate that the structures of these materials are in accord with the standard structures. All powder patterns of the roasted layers removed from PbS briquets were essentially the same regardless of the locality of the roasted material. Materials from (a) the surface of the roast, (b) the PbS-roast interface, (c) points between the surface and the interface and (d) material from deep cracks within the PbS surface gave the pattern shown in Plate VI. Attempts to index the lines in this pattern were not successful; probably the structure is a mixture of basic sulfates.

It is of interest to point out, also shown in Plate VI, that a very shallow bed of finely divided PbS tends to form a distinct PbSO_4 lattice on roasting in oxygen.

Reduction "Reaction" Reactions

The kinetics of the reaction were first examined in nitrogen atmosphere; the rate of the reaction was shown to be dependent on the rate of flow of nitrogen so the reaction was examined in vacuum. The study of the reaction as a gas-solid type resulted from observations made while running the "reaction" kinetics in vacuum; finally, the work on the stoichiometry of the "reaction" followed as a result of establishing that the gas-solid reaction did take place.

Experimental: The kinetics in nitrogen were studied using powdered samples. In the first instance one gram each of

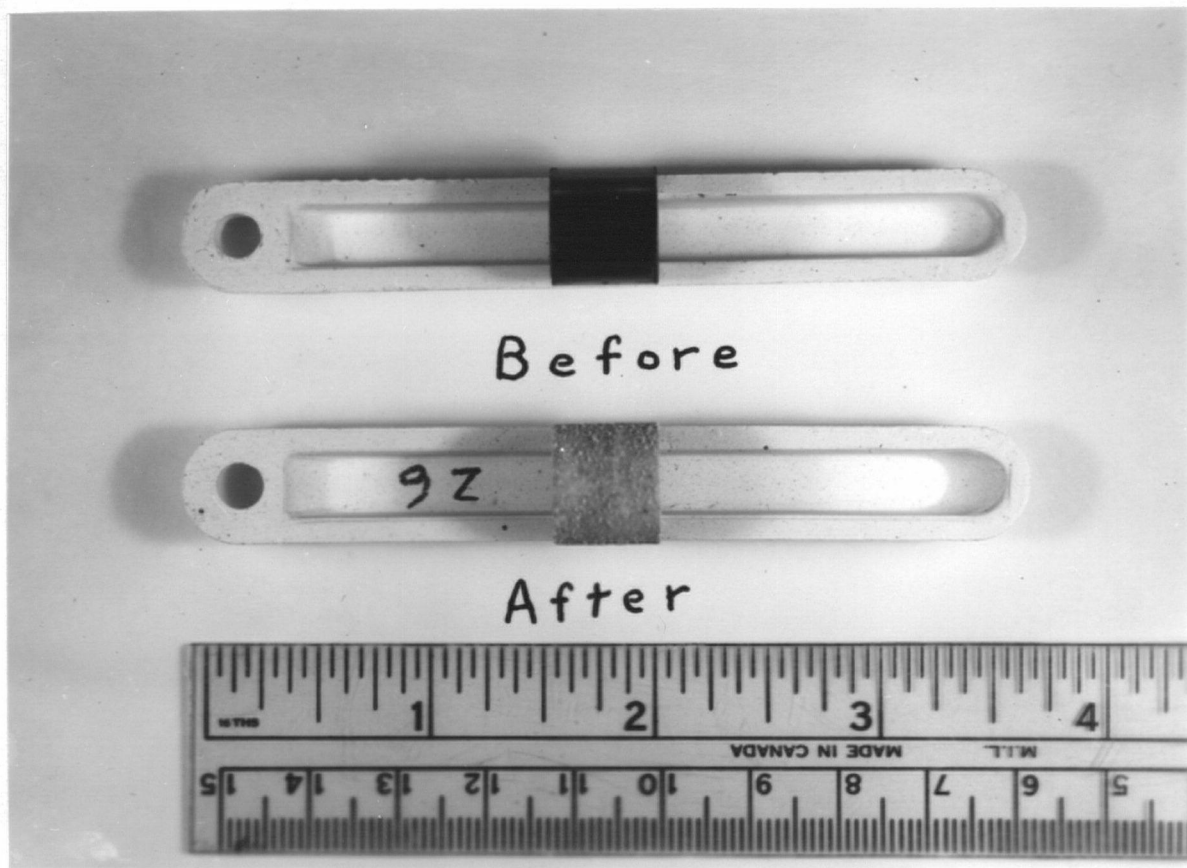


Plate II PbS briquets before and after roasting in air.
Temp. 800°C. Air passed at two liters per minute.

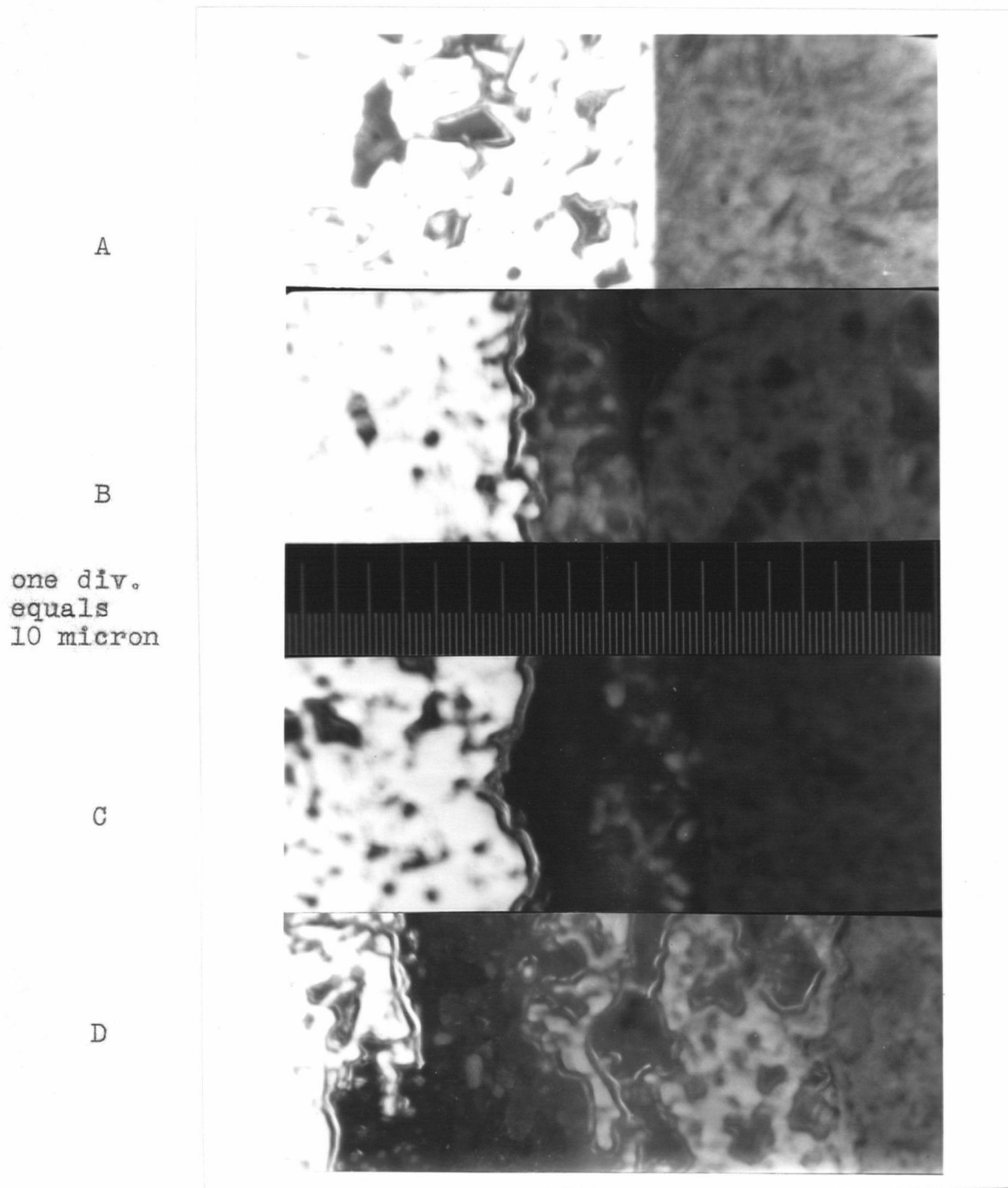


Plate III Photomicrographs of the lead sulfide-bakelite interface. A - unroasted PbS, B - roasted 24 hours, C - roasted 48 hours, D - roasted 96 hours. Temp. 810°C. Oxygen flow 0.1 liter per minute. 100x.

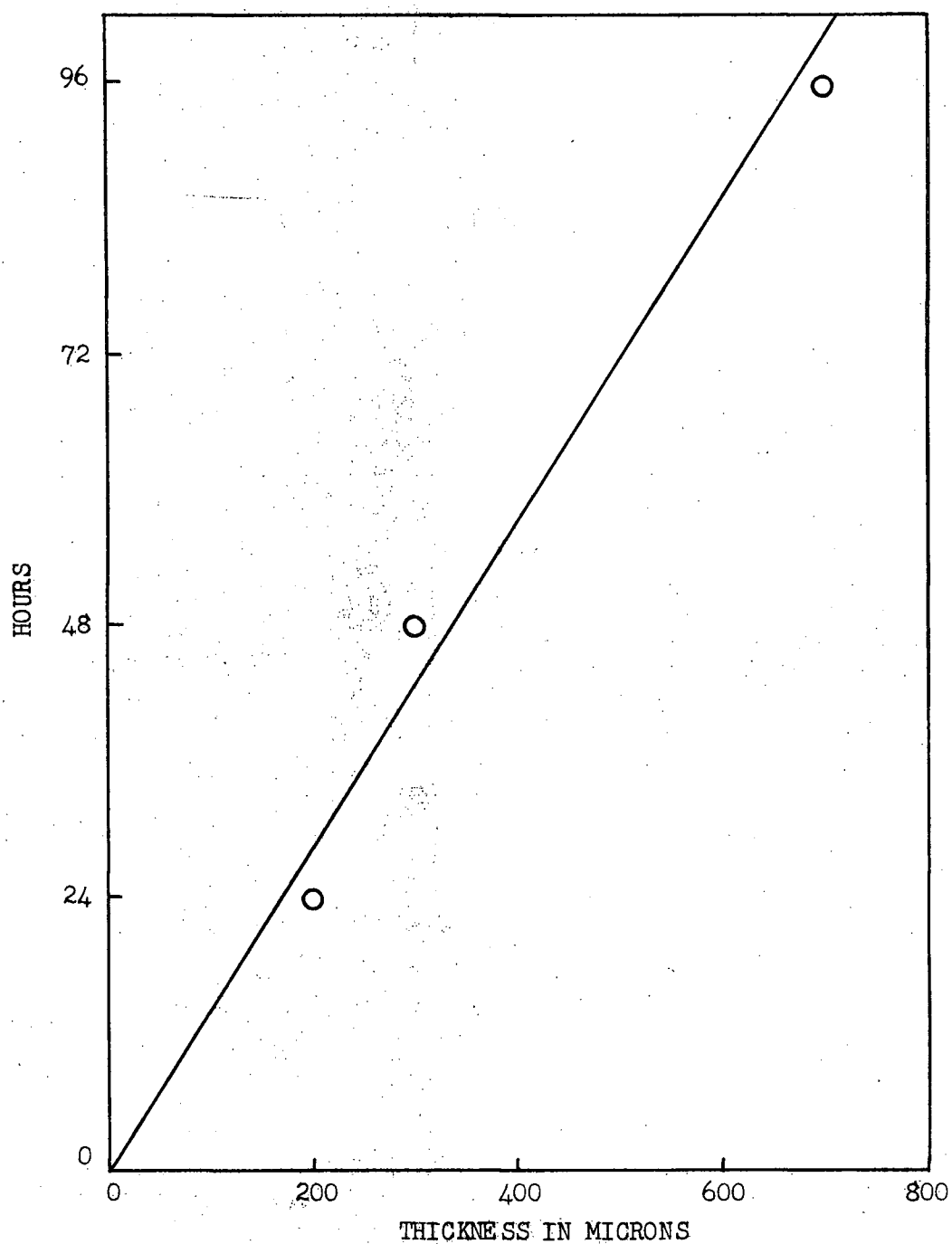


Fig. VI Rate of advance of roasted layer for PbS briquets. Temp. 810°C. Oxygen flow 0.1 liters per min.

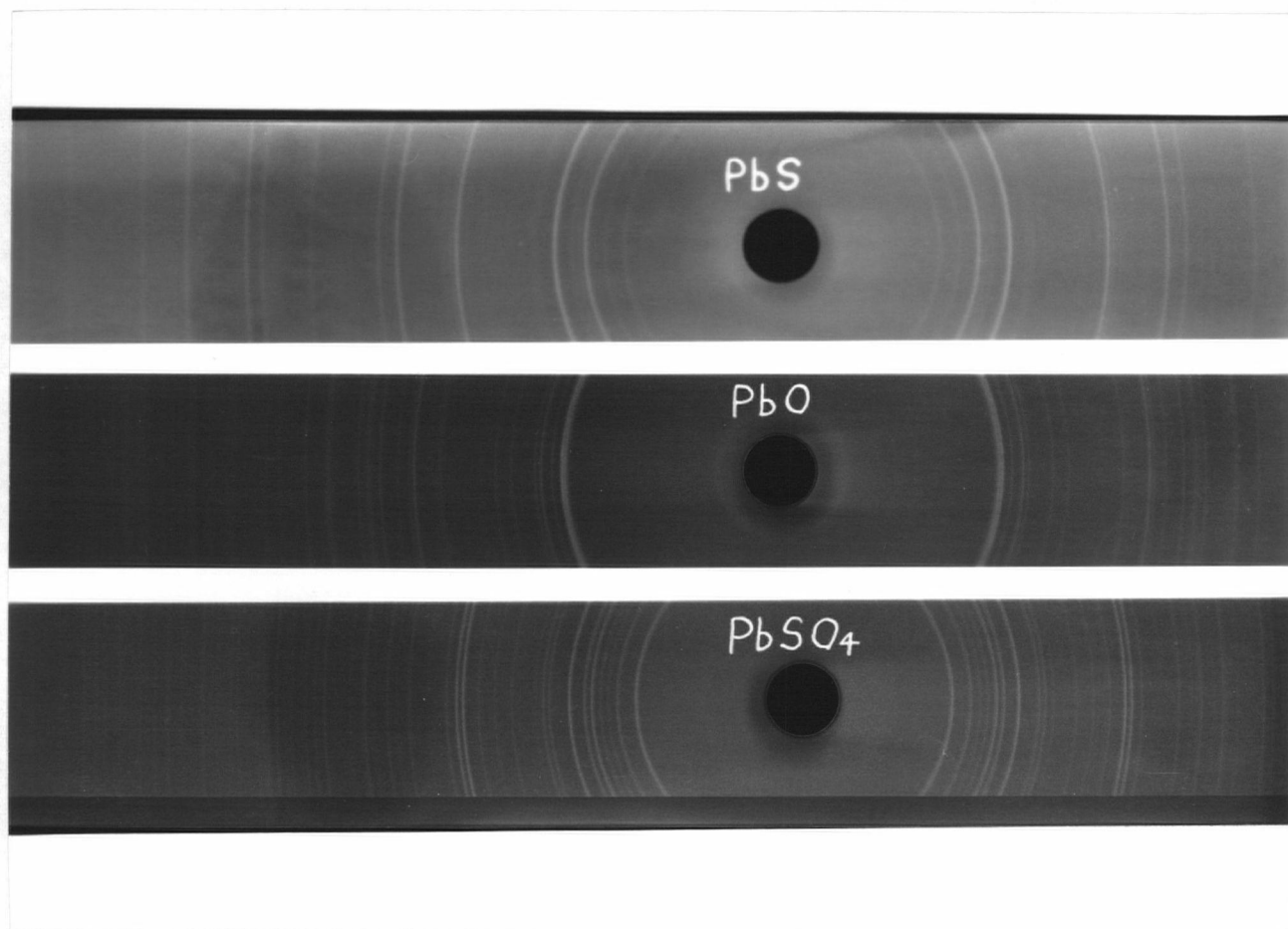


Plate IV Debye-Scherrer patterns of PbS, PbO and PbSO₄
reagent chemicals

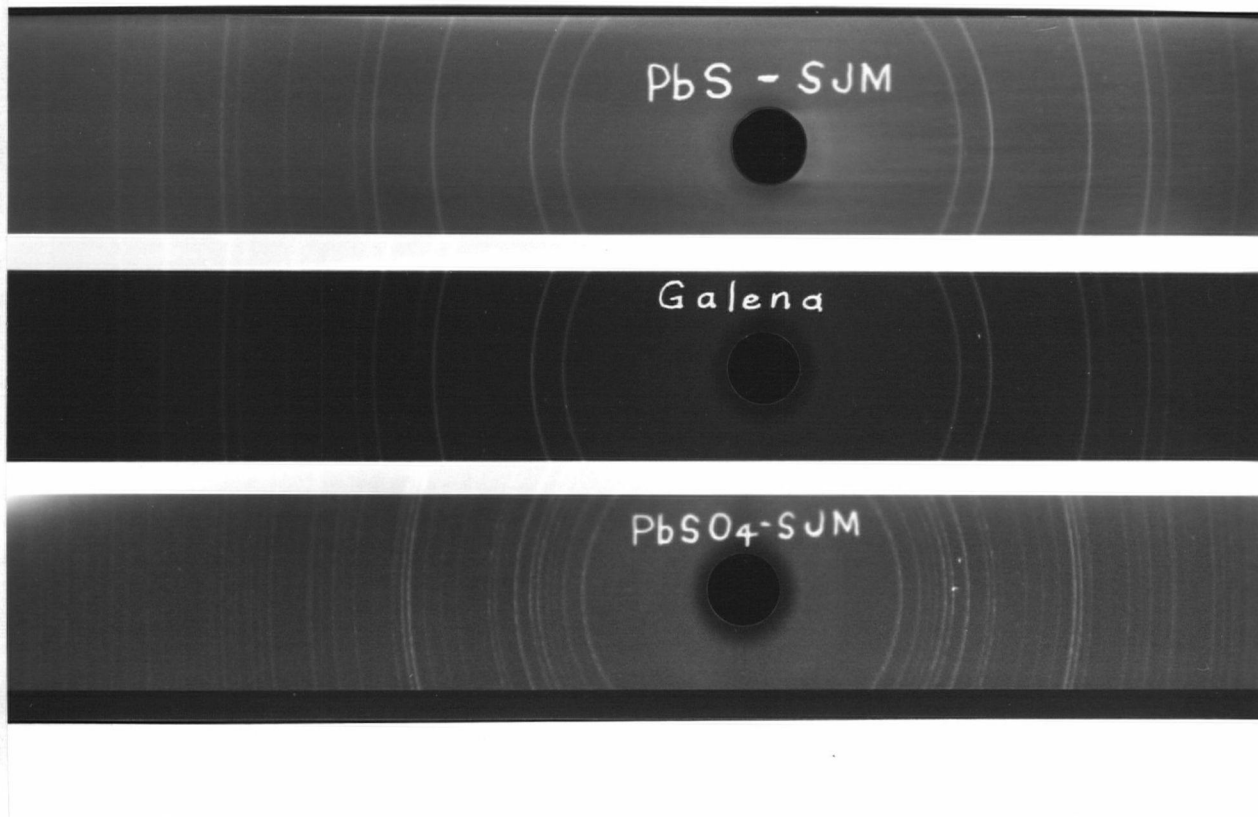


Plate V Debye-Scherrer patterns of synthetic galena,
natural galena and synthetic PbSO₄

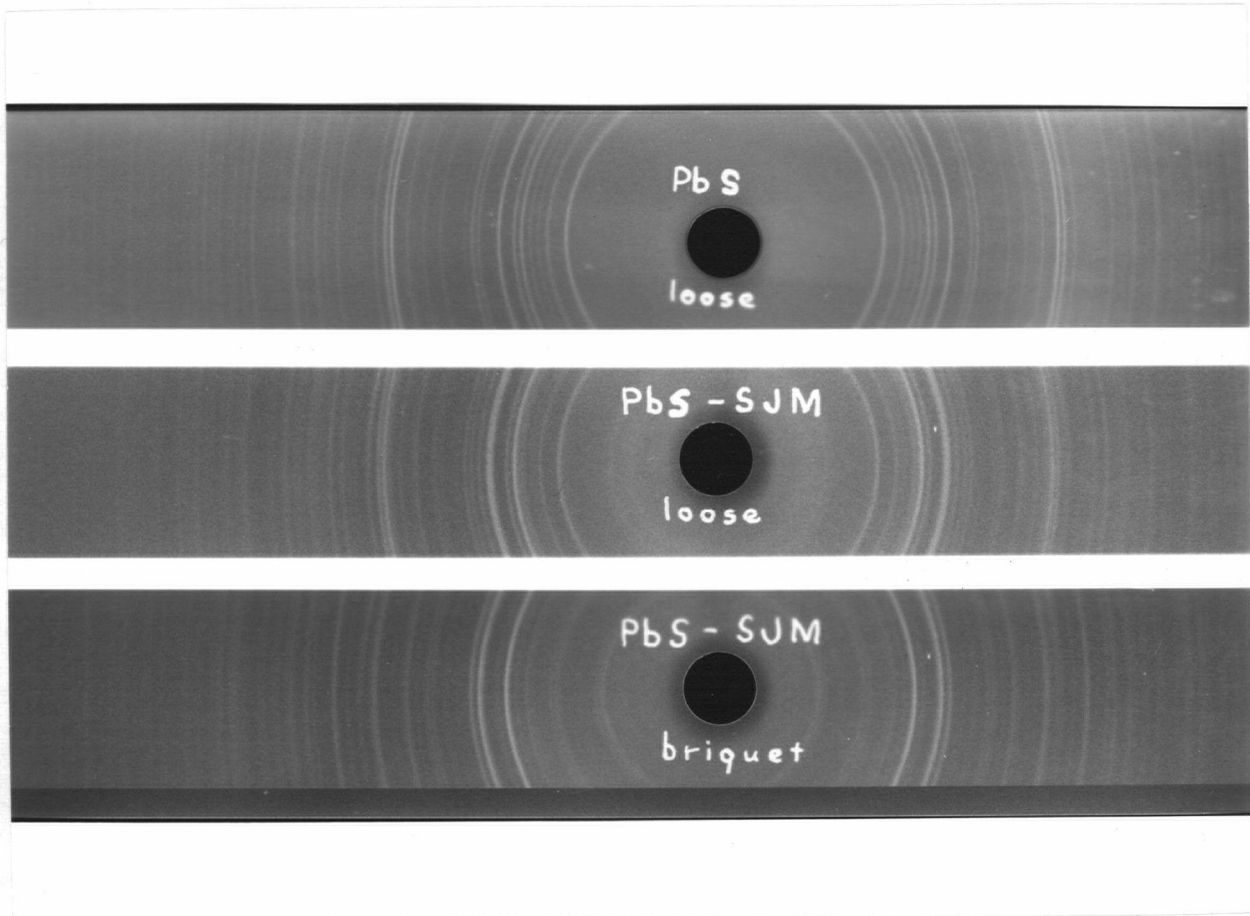


Plate VI Debye-Scherrer patterns for reagent PbS, synthetic galena (-50 mesh) and synthetic galena briquetted, roasted in oxygen. Temp. 800°C., time 24 hours, oxygen flow rate 0.1 liter per minute

lead sulfide and lead sulfate or alternately lead sulfide and lead oxide were intimately mixed, placed in an alundum boat and reacted in a conventional tube furnace in a purified nitrogen atmosphere. Reactions were carried out at 20° intervals in the temperature range 650°C to 850°C , a timed series at each temperature. The reacted samples were analyzed for lead metal only; a weight loss was also obtained.

Reactions with varying rates of flow of nitrogen were carried out next, using lead sulfide-lead sulfate mixtures. The samples were reacted for one hour at two temperatures, 700°C and 750°C , the rates of flow of nitrogen were varied from zero* to 0.3 liters per minute. The amount of lead metal formed was determined as in the previous runs.

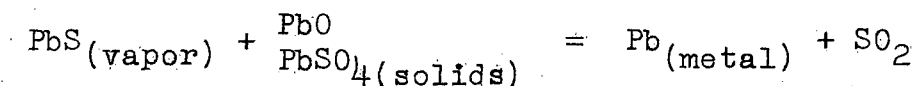
In the kinetic study in vacuum, lead sulfide-lead oxide mixtures were reacted in open alundum boats in the temperature range 700°C to 750°C . The furnace atmosphere was evacuated to a pressure of 0.1 cm. of mercury and reactions were carried out for periods up to two hours. Free lead metal was determined in the products.

Results: The "reaction" samples before and after reaction in nitrogen and vacuum are shown in Plate VII. It is apparent in the photograph that the reaction proceeds uniformly throughout the boat in vacuum whereas in nitrogen the reaction proceeds in the direction of gas flow. Data for the various runs are

* Zero rates of flow of nitrogen were those in which the apparatus was flushed as usual and the flow adjusted to a very slight positive pressure.

given in Tables II, III, IV, and V. The rate of formation of lead metal with time or with nitrogen flow was plotted linearly for the various temperature intervals. Examples of the plots are shown in Figures VII, VIII, IX, and X. Arrhenius plots were made for the time-temperature series in nitrogen and in vacuum, activation energies were calculated for these as shown on the plots Figures XI, XII, and XIII.

It was found during the first runs in vacuum that the results were not reproducible unless a clean furnace tube and thermocouple well were used for each reaction. This was originally attributed to reducing or oxidizing conditions in the fouled vitreosil tube, the walls of which contained condensed galena on the cooler portions. There was also evidence of slagging action such as from a PbO-SiO_2 reaction, this was most apparent on the thermocouple well. On running blank reactions with lead oxide, lead sulfate and lead sulfide it became evident that the magnitude of the reaction was quite large; further, lead sulfide showed no reaction to lead metal in a fouled tube whereas both the oxide and the sulfate were reduced to the metal. It was concluded that the PbS-PbO and PbS-PbSO_4 reactions in vacuum proceeded by the heterogeneous mechanism



and the research was then directed toward the examination of this mechanism. The absence of the lead sulfide phase in the "reaction" products suggested that a study of the stoichiometry of the gas-solid reaction would be possible and useful.

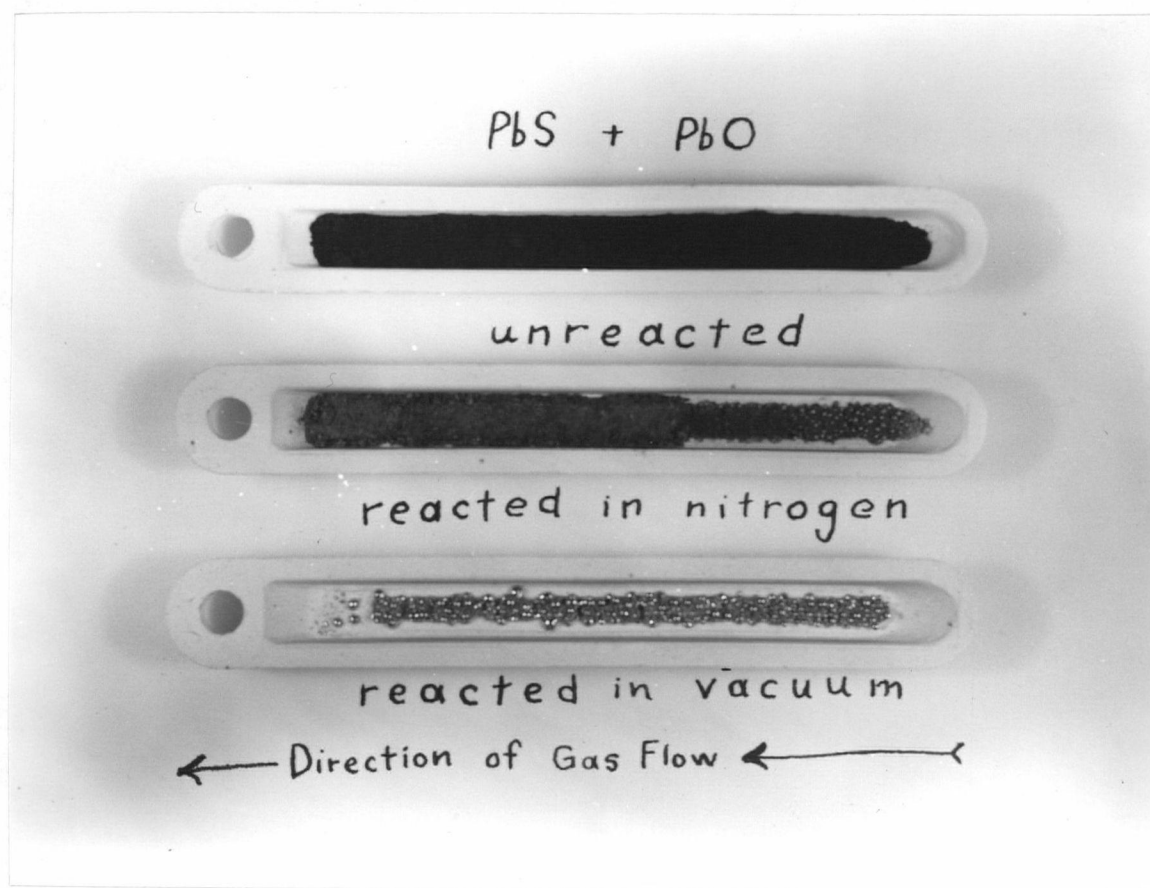


Plate VII The "reaction" between PbS and PbO in nitrogen atmosphere and in vacuum. Temp. 750°C., time 1 hour.

TABLE II

Data for PbS-PbSO_4 mixtures reacted in nitrogen. Two gram samples, basis for calculation one gram of reactant mixture.

Temp. °C.	Time min.	Pb metal gm.	Weight loss gm.
750	0	--	--
	60	.105	.079
	120	.434	.134
	180	.621	.166
770	0	--	--
	30	.264	.085
	45	.348	.093
	60	.401	.112
790	0	--	--
	30	.357	.084
	45	.620	.135
810	0	--	--
	15	.417	.083
	25	.690	lost
830	0	--	--
	10	.250	lost
	15	.425	.096
	20	.600	lost

TABLE III

Data for PbS-PbO mixtures reacted in nitrogen. Two gram samples, basis for calculation one gram of reactant mixture.

Temp. °C.	Time	Pb metal gm.	Weight loss gm.
650	0 hours	--	--
	12	.001	.008
	24	.026	.021
675	0	--	--
	12	.108	.071
	24	.175	.123
	32	.212	.123
700	0	--	--
	3	--	.048
	6	.111	.094
	9	.203	.108
	12	.298	.132
750	0	--	--
	1	.108	.048
	2	.211	.072
	3	.335	.094
	4	.510	.166
800	0 minutes	--	--
	15	.196	.031
	30	.326	.064
	45	.525	.138
	60	.685	.206
825	0	--	--
	15	.097	.066
	30	.273	.123
850	0	--	--
	15	.236	.071

TABLE IV

Data for PbS-PbSO₄ mixtures reacted in varying flow rates of nitrogen. Time of reaction one hour, basis for calculation one gram of reactant mixture.

Temp. °C.	Nitrogen Flow liters/minute	Pb Metal gm.
700	0.0	.002
	0.1	.095
	0.2	.126
	0.3	.140
750	0.0	.054
	0.1	.570
	0.2	.592
	0.3	.600

TABLE V

Data for PbS-PbO mixtures reacted in vacuum. Two gram samples, basis for calculation one gram of reactant mixture.

Temp. °C.	Time minutes	Pb metal gm.	Weight change gm.
720	0	--	--
	30	.063	.050
	60	.193	.080
	120	.365	.115
735	0	--	--
	7.5	.010	.064
	15	.403	.088
	30	.486	.102
750	0	--	--
	5	.619	.089
	10	.811	.111

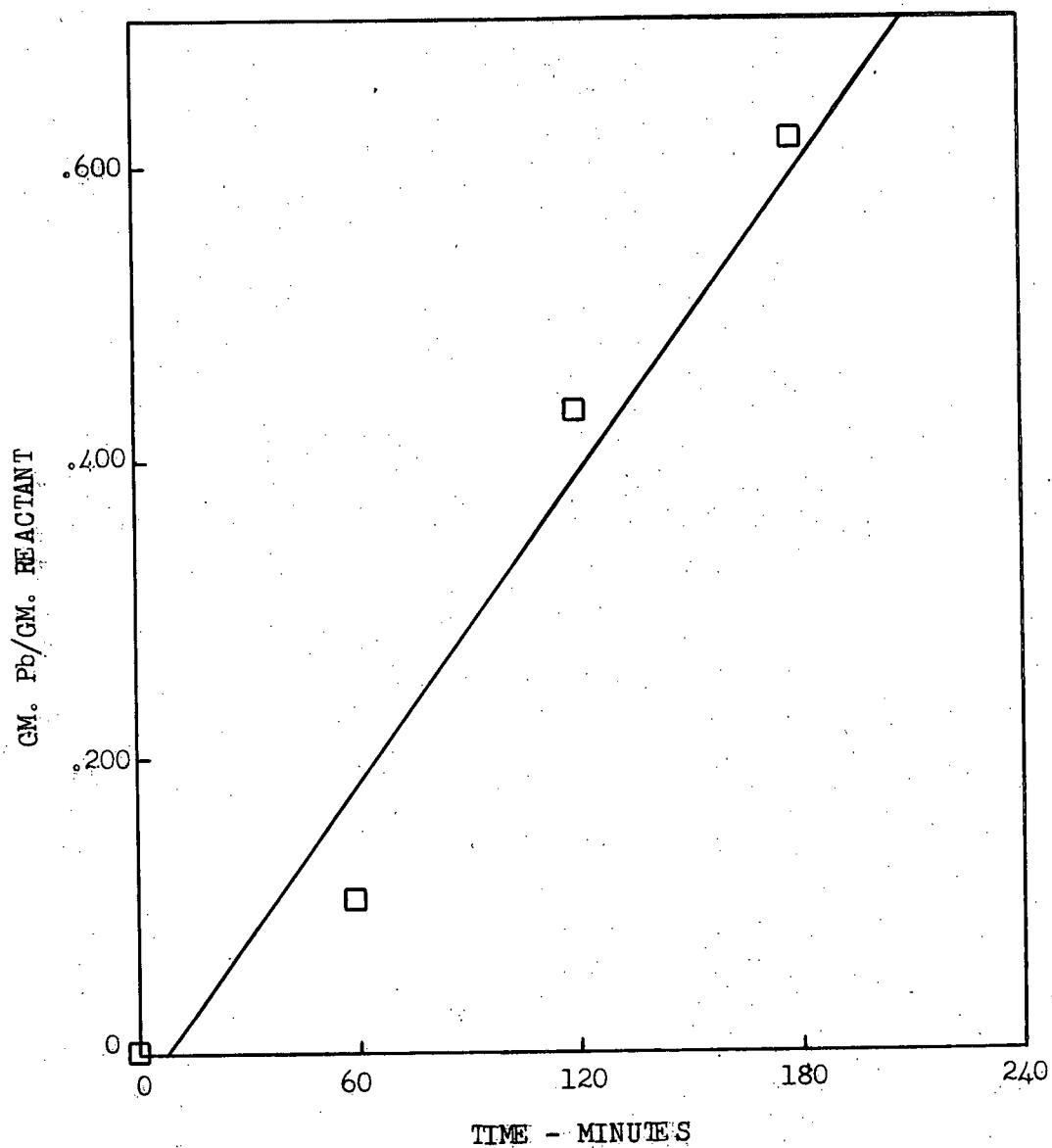


Fig. VII Rate of reaction of PbS-PbSO_4 mixtures in nitrogen. Temp. 750°C .

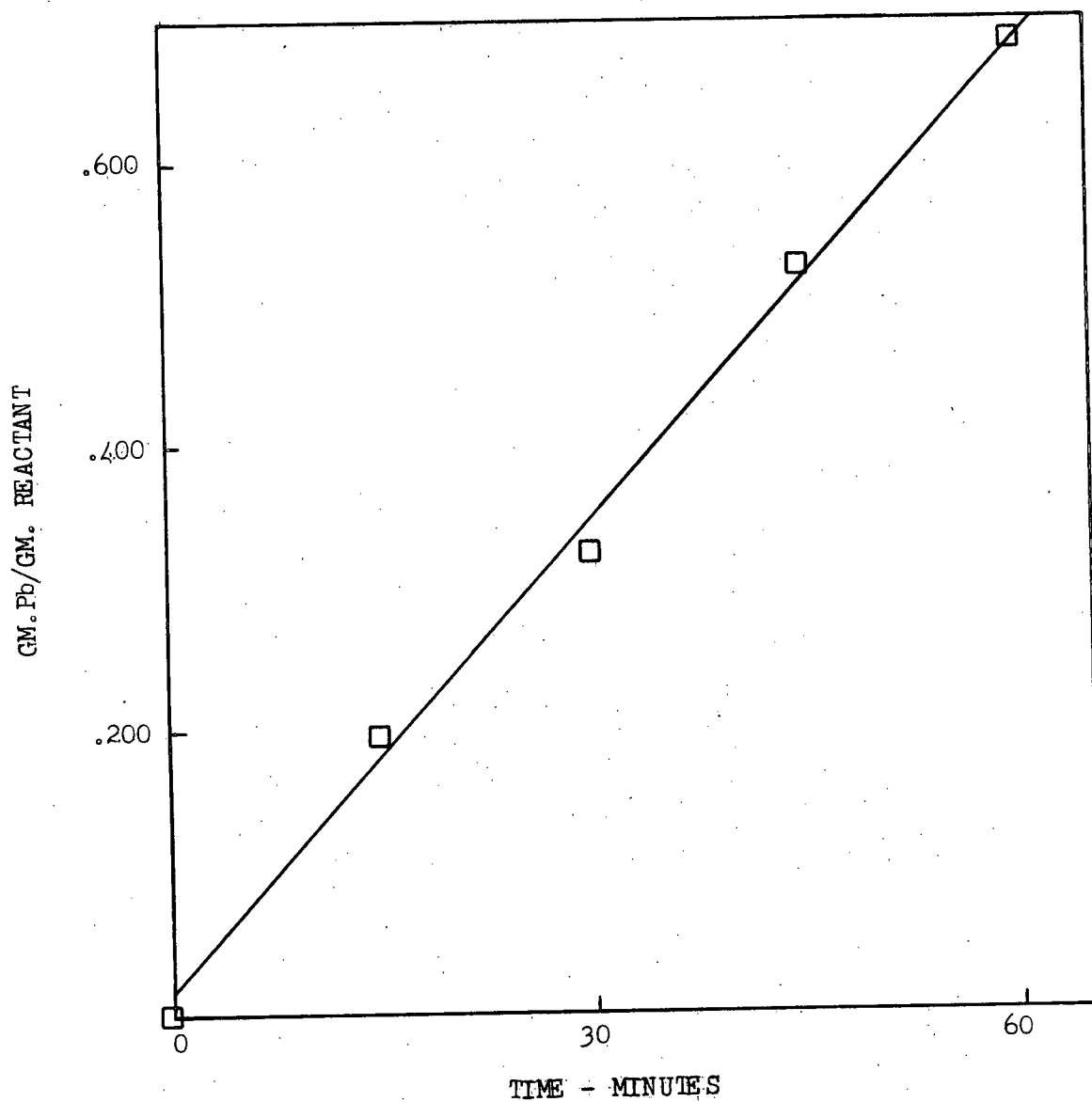


Fig. VIII Rate of reaction of PbS - PbO mixtures in nitrogen. Temp. 800°C.

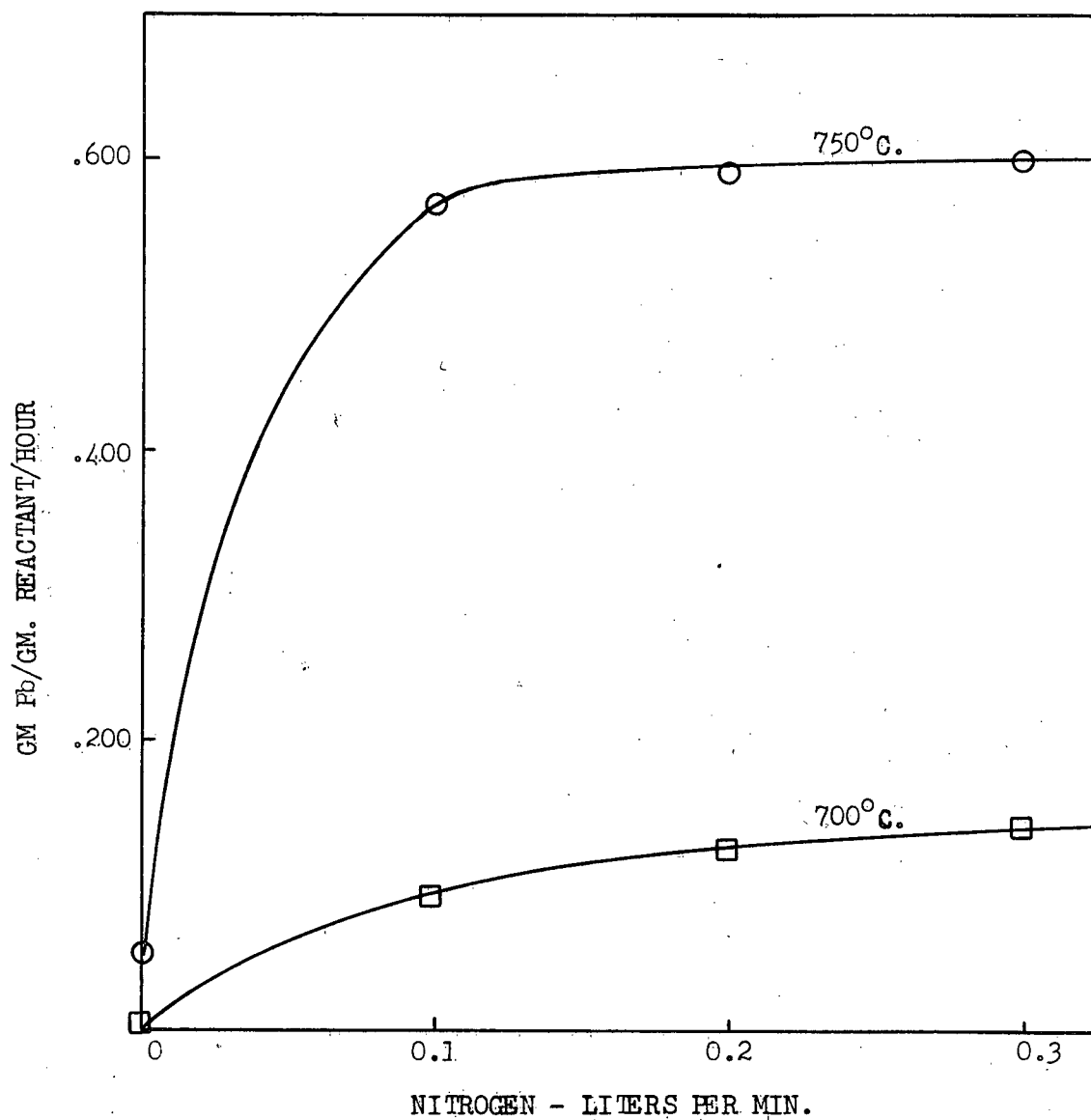


Fig. IX Dependence of the $\text{PbS} - \text{PbSO}_4$ reaction rate on nitrogen flow rates.

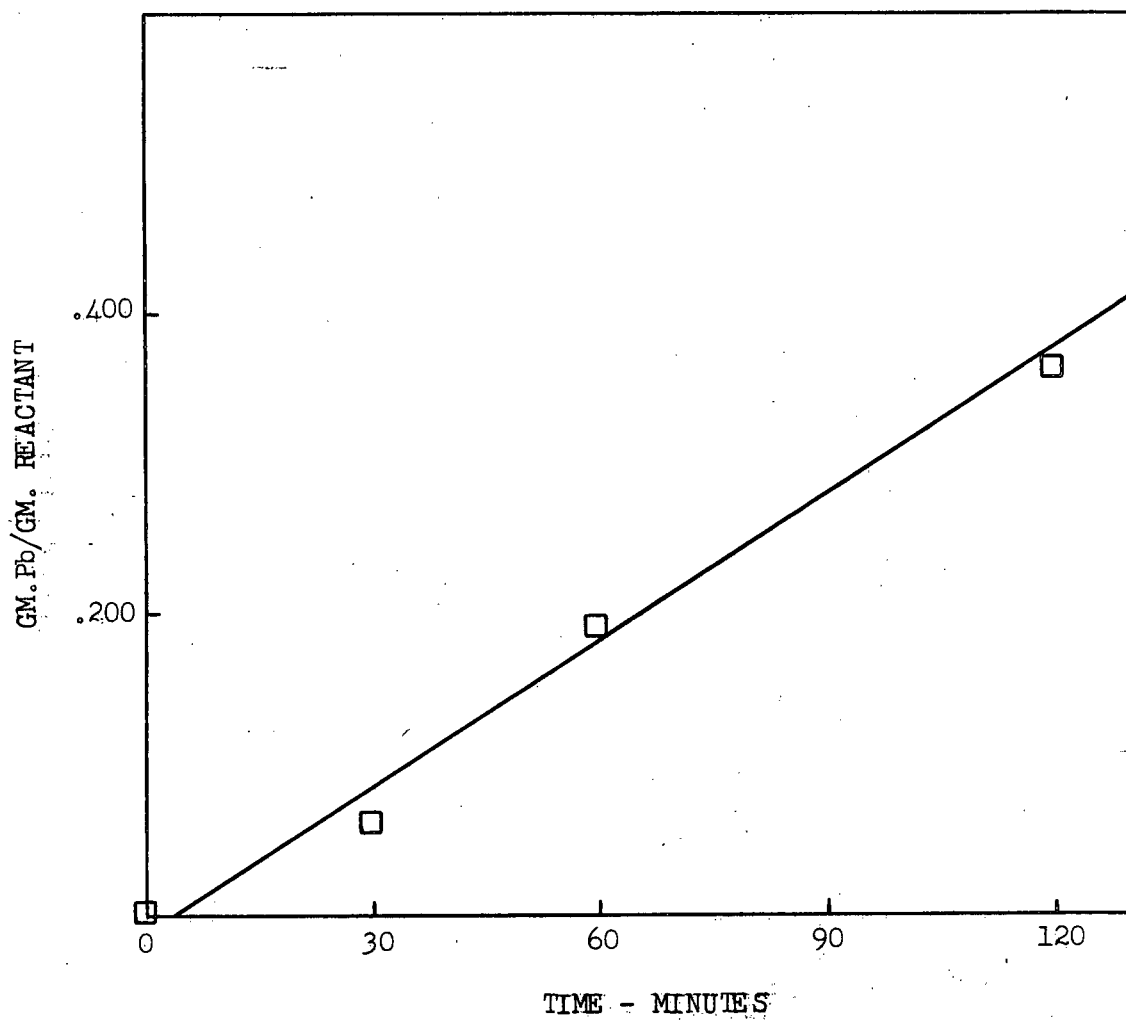


Fig. X Rate of reaction of PbS-PbO mixtures in vacuum.
Temp. 720°.

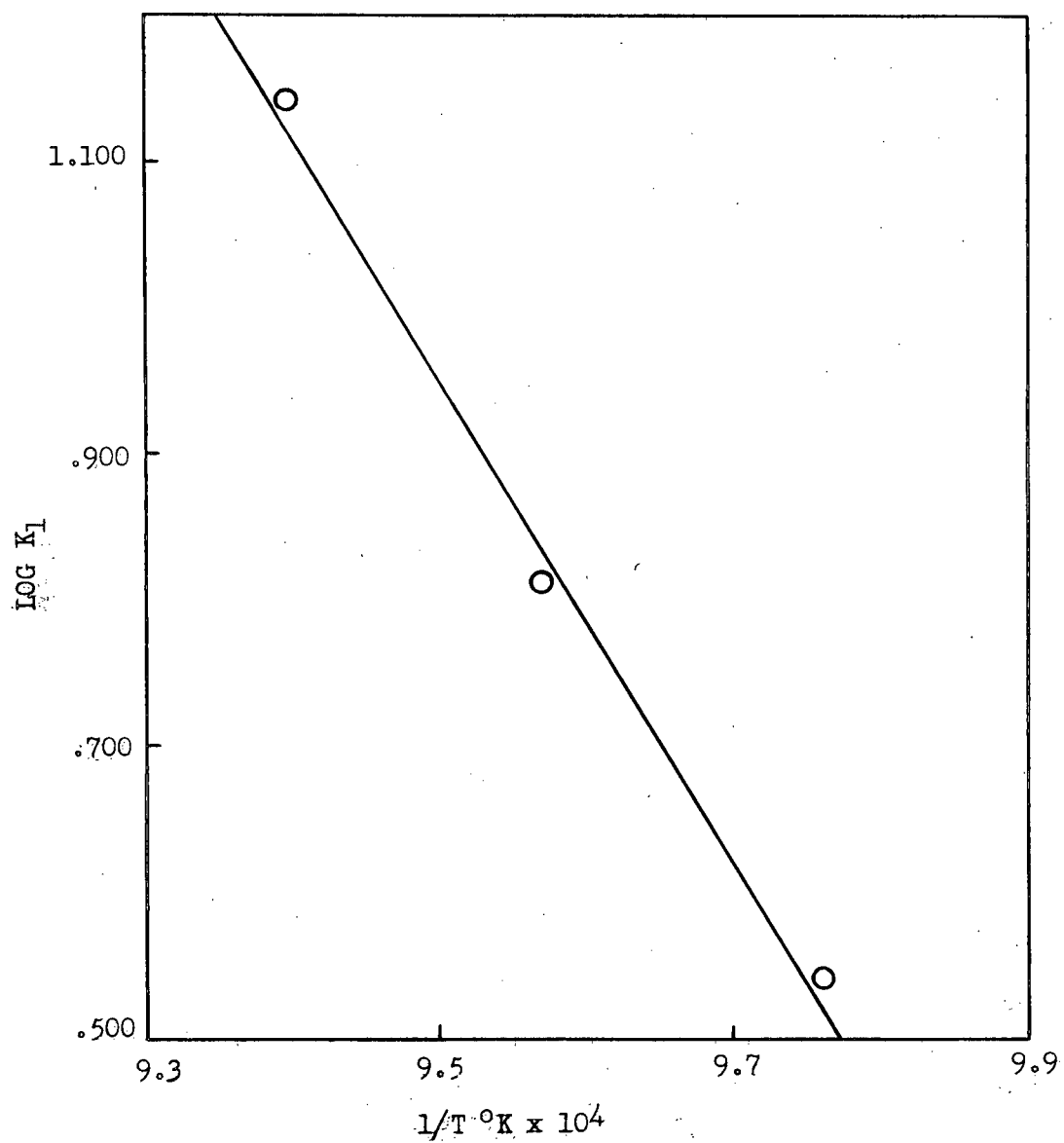


Fig. XI Arrhenius plot for PbS-PbSO₄ reactions in nitrogen.

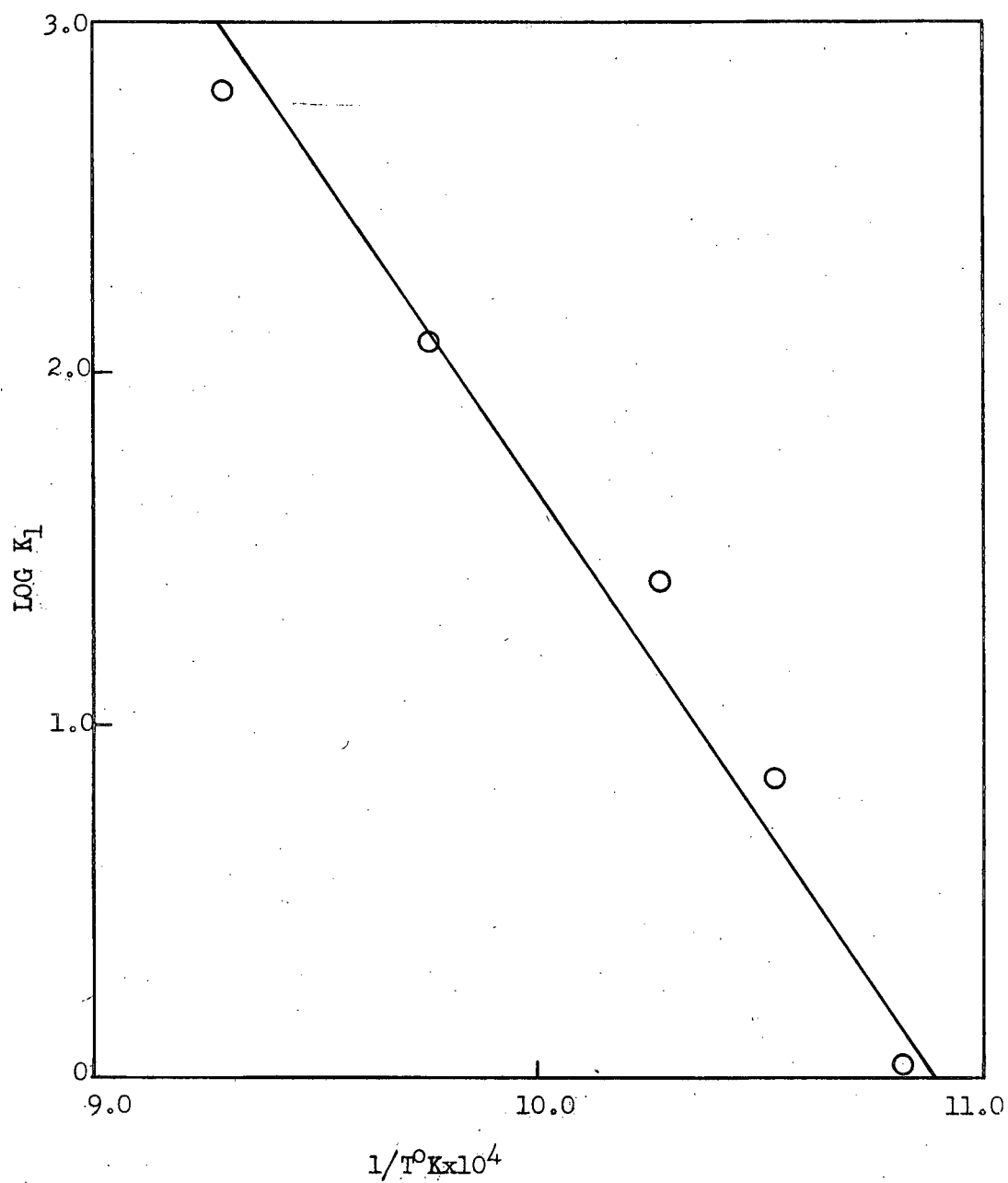


Fig. XII. Arrhenius plot for PbS-PbO reactions in nitrogen.

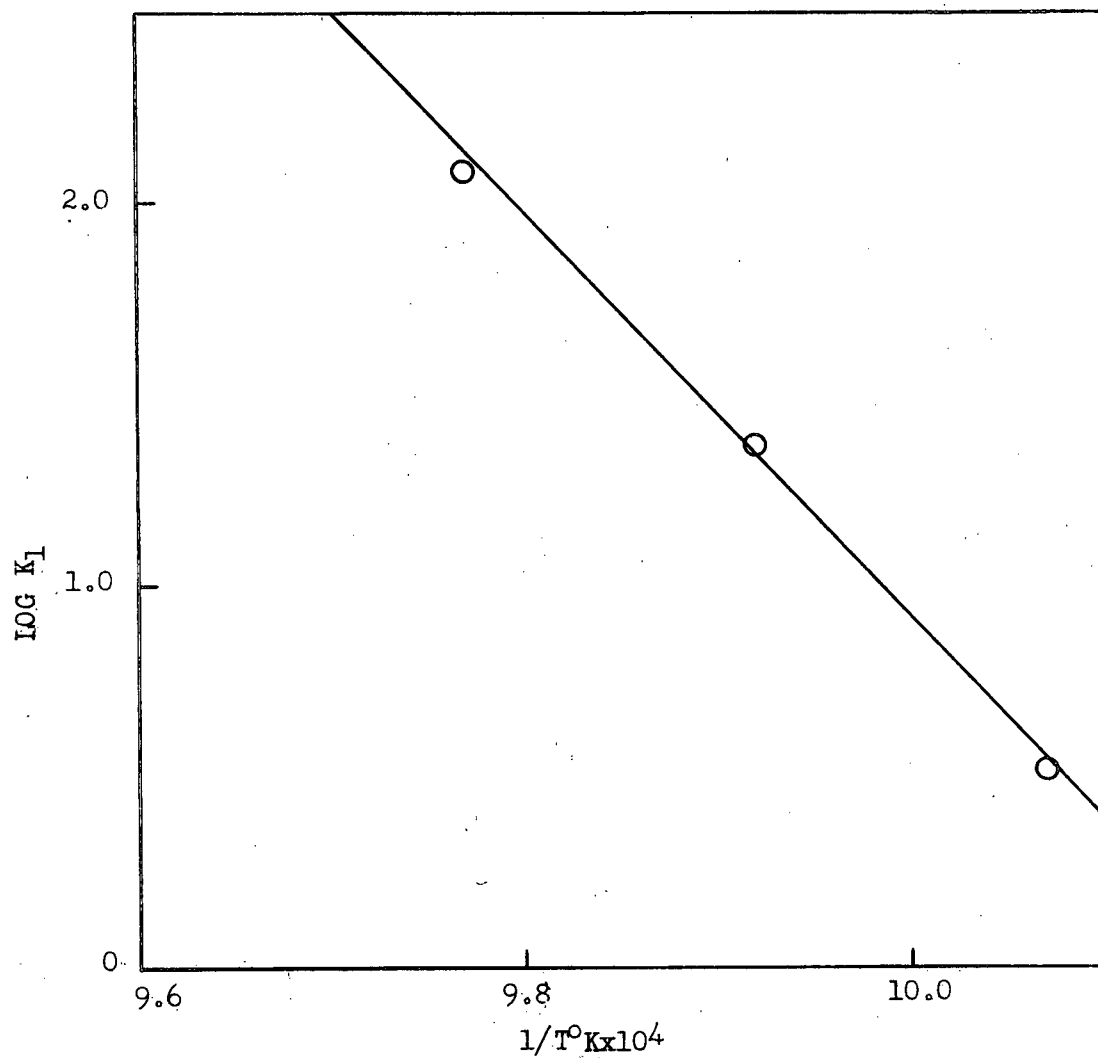


Fig. XIII Arrhenius plot for PbS-PbO reactions in vacuum.

Experimental: One gram samples of lead sulfide and lead oxide were placed in adjacent alundum boats, covered and reacted in vacuum as in the previous vacuum study. The temperature was maintained at 750°C and the time of reaction varied from zero to 90 minutes. Weight changes were determined on both boats, total lead was determined in the lead sulfide boat and metallic lead in the lead oxide boat.

Following the initial examination of the gas-solid reaction the study was extended using labelled lead sulfide in the distillation boat and lead oxide or lead sulfate in the reaction boat. The reaction apparatus and technique remained unchanged, the time of reaction was 30 minutes, the temperature 750°C for the oxide and 800°C for the sulfate. The specific activity (counts per minute per gram of lead metal) for the lead sulfide was obtained by counting the sulfide before reacting it in the furnace. The specific activity of the lead metal produced by the reaction was obtained by counting lead metal mechanically removed from the reaction boat. Removal of the lead metal was effected by placing the lead oxide boat containing the radioactive lead under a stereoscopic microscope and picking off the lead metal (present on the surface of the lead oxide in the form of small isolated spheres) with a pair of pointed tweezers. Usually the metal could be freed of oxide by dropping it in a small crucible a few times. The maximum amount of lead metal which could be obtained in a reasonable time by this method (100-200 mg. in 15 minutes) was placed in a tared counter vial, counted and weighed. The time of counting was noted and

the counting was continued to follow the decay curve. Calculations were made to relate the specific activity to a chemical equation for the reaction and thus obtain a figure for the stoichiometry.

Results: A reaction which was typical of all the vapor-solid phase runs is depicted in Plate VIII. There was no evidence of the formation of lead metal in any lead sulfide boat, nor was there any lead sulfide seen in the lead oxide boats; lead sulfate if present in the lead oxide boat was not observed under the microscope. Data for the nonradioactive lead sulfide-lead oxide reactions are given in Table VI and a plot of the weight changes with time is shown in Figure XIV. It is proposed that the weight loss of the lead sulfide corresponds approximately to that expected if the loss took place as result of the distillation of molecular PbS .

The data for the stoichiometry study with the use of the Pb^{212} tracer is summarized in Table VII. Three PbS-PbO reactions and one PbS-PbSO_4 reaction were carried out. The PbS-PbSO_4 reaction did not give reliable data, the amount of lead metal produced was very small (20 mg.) and the specific activity appeared to be equal to that of the labelled PbS . One of the difficulties encountered with the PbS-PbSO_4 reaction was that at temperatures less than 800°C the amount of Pb metal produced was small while at temperatures of 800°C or higher the finely divided PbS sublimed very rapidly. A typical decay curve for the PbS-PbO produced lead metal is shown in Figure XV; as is evident in the Figures XV and XVI the Bi^{212} was not in equilibrium with Pb^{212} in the lead metal although in all the

reactions examined it was in equilibrium in the PbS reactant.

The average stoichiometry of the PbS-PbO reaction (corrected for Bi²¹²) was given by $1\text{PbS} + 3.4\text{PbO} = 4.4\text{Pb} + \text{---}$.

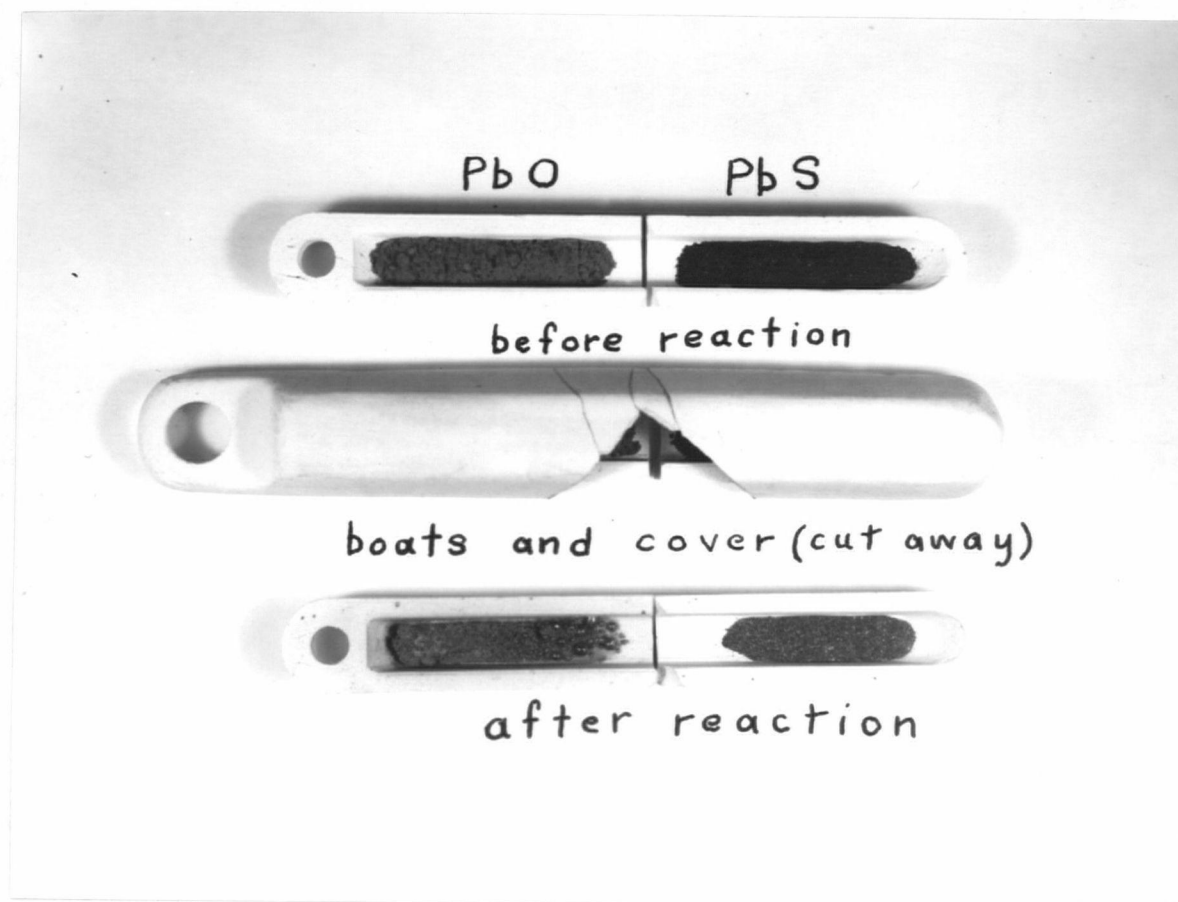


Plate VIII The gas-solid reaction between PbS and PbO in vacuum. One gram each of PbS and PbO. Temp. 750°C., time 30 min.

TABLE VI

Data for the stoichiometry study of the gas-solid PbS-PbO reaction in vacuum. Temp. 750°C.

Reaction No.	Time min.	PbO gain gm.	PbS loss gm.	Pb metal gm.	PbS found gm.
1	0	.004	.028	.055	.989
2	30	.029	.113	.197	.896
3	60	.029	.129	.226	.872
4	90	.037	.210	.347	.797
5	90	.063	.228	.385	.771

Reaction No.	Calculated Stoichiometry
1	$1\text{PbS} + 6\text{PbO} = 7\text{Pb} + \text{---}$
2	$1\text{PbS} + 3.8\text{PbO} = 4.8\text{Pb} + \text{---}$
3	$1\text{PbS} + 4.2\text{PbO} = 5.2\text{Pb} + \text{---}$
4	$1\text{PbS} + 4.9\text{PbO} = 5.9\text{Pb} + \text{---}$
5	$1\text{PbS} + 3.5\text{PbO} = 4.5\text{Pb} + \text{---}$
Average	$1\text{PbS} + 4.5\text{PbO} = 5.5\text{Pb} + \text{---}$

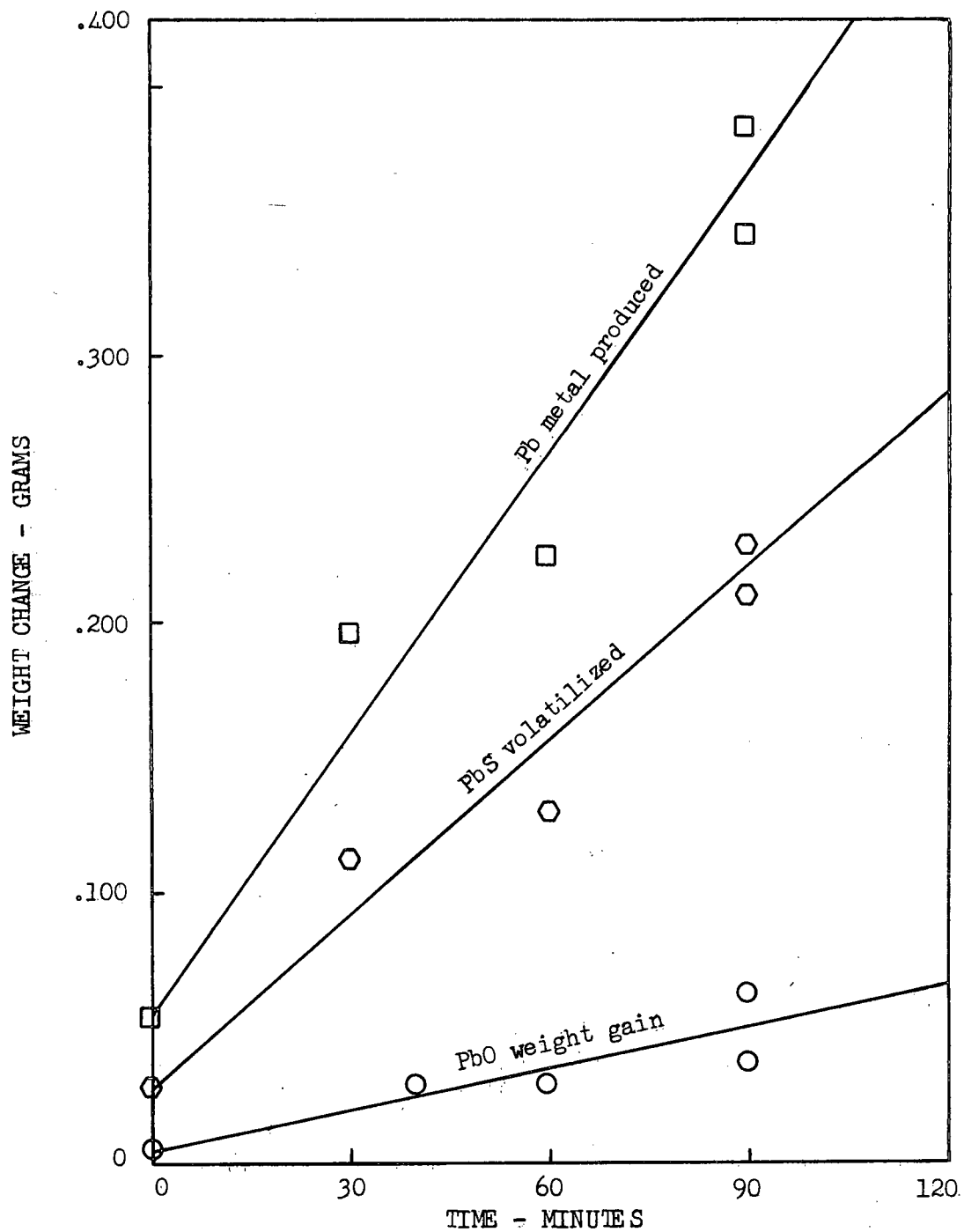


Fig XIV. Weight changes in PbS - PbO gas-solid reactions in vacuum. Temp. 750°C.

TABLE VII

Data for the stoichiometry study of the gas-solid PbS-PbO reaction in vacuum using the Pb²¹² tracer.

Reaction No.	PbS mg.	Specific Activity	Pb mg.	Specific Activity
1	273	774	209	182
2	274	822	142	185
3	264	723	154	165
Reaction No.	Calculated Stoichiometry			
1	1PbS + 3.25PbO = 4.25Pb + ---			
2	1PbS + 3.45PbO = 4.45Pb + ---			
3	1PbS + 3.38PbO = 4.38Pb + ---			
Average	1PbS + 3.4PbO = 4.4Pb + ---			

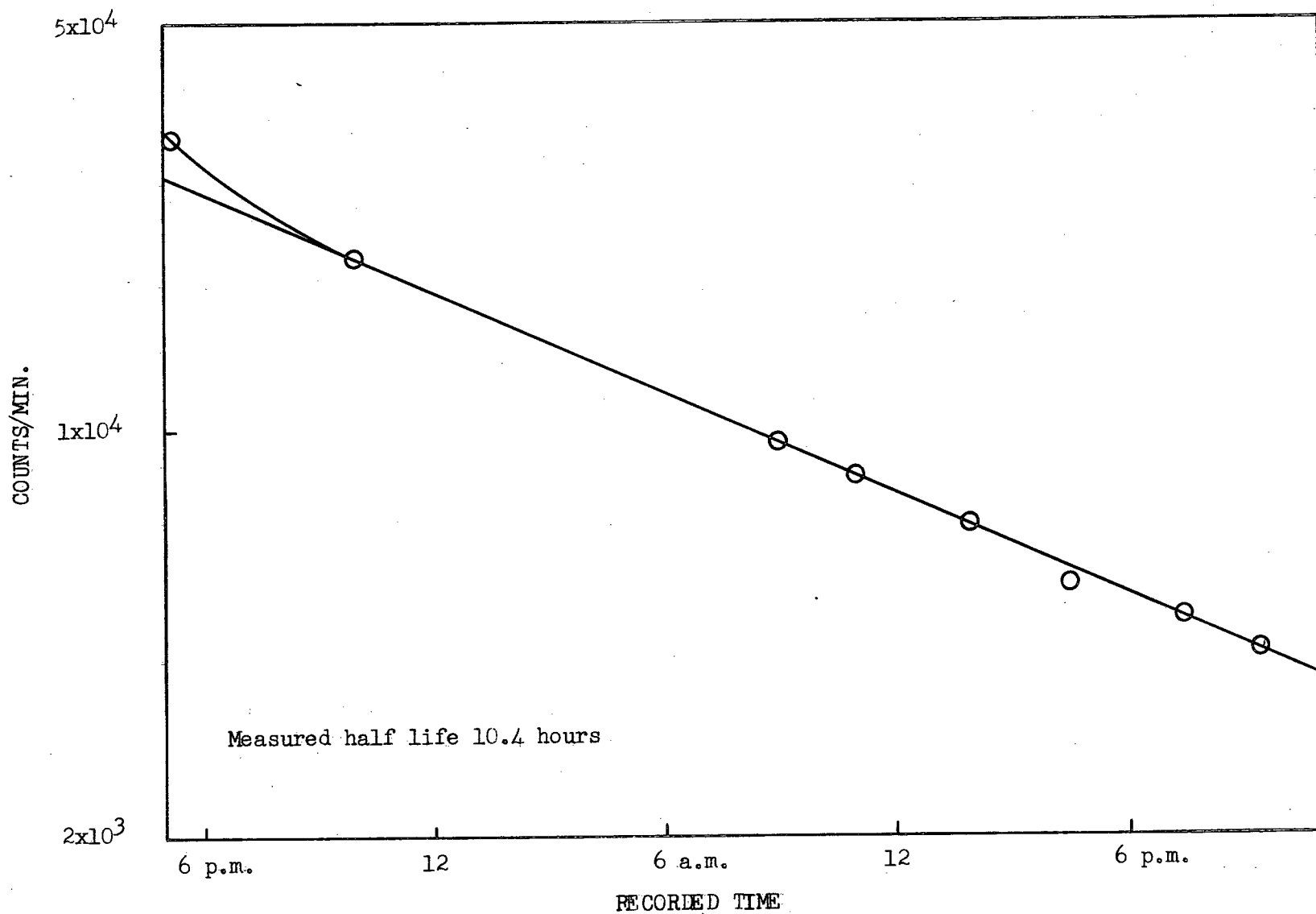


Fig. XV Decay curve for Pb^{212} produced by the gas-solid PbS-PbO reaction.

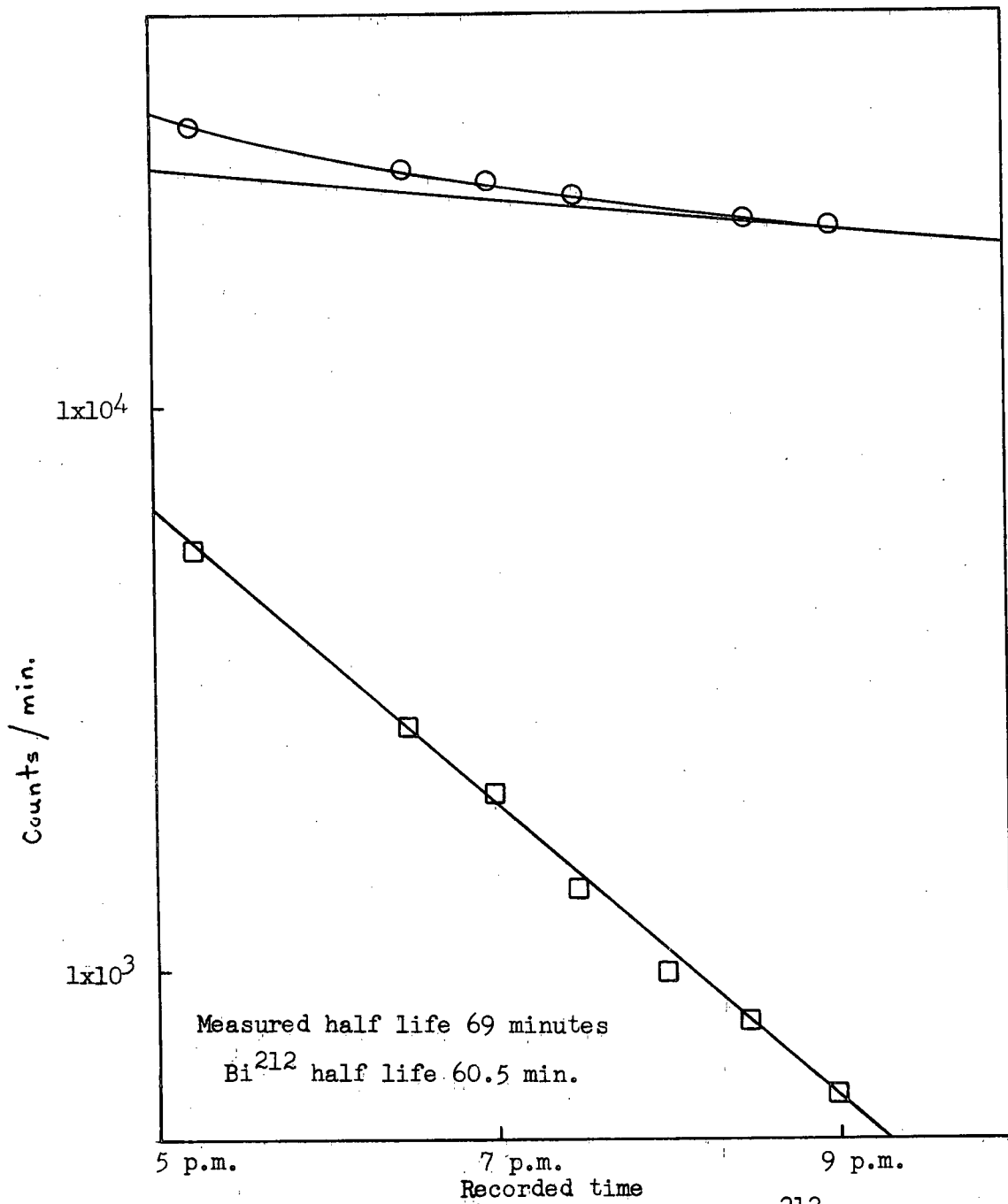


Fig. XVI. Decay curve for non-equilibrium Bi²¹² in the Pb metal.

DISCUSSION OF RESULTS AND CONCLUSIONS

The Roast

The data obtained from the roasting of finely divided PbS in air and in oxygen indicate the variables which influence lead sulfate formation. It is apparent (Figure V page 26) that lead sulfate formation is favored at low temperature and lead oxide formation at higher temperature. Superimposed on this fundamental characteristic of the roasting are the effects of the partial pressures of oxygen and SO_2 .

At constant temperature an oxygen rich atmosphere results in a higher degree of sulfation than does an oxygen lean atmosphere. The influence of the partial pressure of SO_2 upon sulfation only becomes apparent when the velocity of the gases passing over the solid surface of the roast is varied. As is well known a stagnant gas film resides at the surface of a solid when it is in a stream of flowing gas. The thickness of the film is a function of the velocity of the gas stream. The partial pressure of a gas such as SO_2 resident on the solid surface depends on both its partial pressure in the gas stream and the pressure gradient through the gas film. When the velocity of the gases passing over the solid surface is high the film is thin, the pressure gradient is steep and there is little resistance to the transport of SO_2 molecules from the surface. When the velocity

of the gas is low the stagnant film becomes thicker, the pressure gradient is gradual and the rate of transport of SO_2 molecules through the film controls the rate of sulfation. This follows in that a high partial pressure of SO_2 on and in the solid results in higher concentrations of lead sulfate.

As the temperature is increased the effect of the stagnant film lessens until the rate of sulfating becomes more or less independent of gas velocity; this can only mean that some other step in the sulfating mechanism has become slower than the transport step.

The equilibrium in the reaction $\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$ shifts to the left with increasing temperature and thus the rate of formation of SO_3 and hence that of PbSO_4 becomes less favorable thermodynamically. This step probably becomes rate controlling in the sulfate formation at higher temperatures.

The roasting of briquets of PbS was carried out with the object of locating and identifying the phases present in the roast. The mechanism of sulfate formation in the roasting of copper sulfide has been determined in this manner (20) (16).

The X-ray diffraction patterns show that if distinct PbO and PbSO_4 phases are formed when consolidated PbS is roasted they exist over limited distances, the bulk of roasted material being a mixture of basic sulfates.

The rate of advance of the roasted layer was observed to be linear when PbS was roasted in oxygen atmosphere; also, it was considerably faster than the rate when roasting in air. Peretti (22) has explained a similar linear roasting rate of

Cu_2S by suggesting that the slow step is the diffusion of reacting gases to the scene of the reaction through a film of counter-diffusing products. Diffusion control must then operate across a layer of constant thickness, a layer of Cu_2O for the case of Cu_2S roasting. Nonlinearity of roasting rates was coincident with the appearance of the CuSO_4 phase.

In the presence of a layer of basic sulfates of increasing thickness as observed in the roasting of PbS briquets the linear rate may result from the slowness of one of a number of steps which are not influenced by the depth of the roasted material. Such steps include:

- (a) The chemical reaction at the interface.
- (b) Adsorption and desorption of O_2 , SO_2 and (or) SO_3 gases.
- (c) A diffusion mechanism analagous to that observed in the roasting of Cu_2S , "i.e.", diffusion through a phase of constant thickness. Such a phase could be PbO or PbSO_4 .
- (d) Gas film transport at the surface of the roast.

Insufficient data have been obtained to assess the individual effects of these steps for the roasting of PbS briquets.

It is not immediately obvious why the rate of advance of the roast in briquetted PbS is so slow (0.007 mm./hr.) compared with the rate in briquetted Cu_2S (4.8 mm./hr.) at the same temperature (21). A possible explanation is that the Cu_2S was much more porous being formed by the diffusion of sulphur gas out of a CuS lattice (21).

Three observations were made, related to oxygen partial pressure, which may indicate the nature of the roasting mechanism.

1. The roasting of briquets proceeds more slowly in air than in oxygen. It is suggested that this is a structural phenomenon, "i.e.", the slowing of the rate with decrease in oxygen pressure is due to diffusion. At low oxygen concentrations the tendency is to form a nonpermeable structure; at higher oxygen concentrations the structure is permeable.

2. The roasting of consolidated PbS in oxygen or air leads to the formation of basic sulfates; the roasting of a very shallow bed of PbS powder in oxygen leads to the formation of normal PbSO_4 . The oxygen partial pressure at the reaction interface will certainly be lower in consolidated materials than in a thin layer of PbS powder: the SO_2 partial pressure, on the other hand, will not vary as much. The product of the partial pressures of O_2 and SO_2 at the reaction interface will then be considerably higher for shallow beds of powder. This leads to formation and stability of the normal sulfate; it also presents an explanation for the absence of normal sulfate in the roasted layer surrounding consolidated PbS.

3. The formation of a PbO phase has been observed only in the initial stages of roasting consolidated materials. When PbS briquets were put into a hot (750°C) oxygen atmosphere, distinct yellow-orange crystals form on the surface of the PbS. These crystals were not found at any later stage of roasting. It appears then that PbO may be the primary phase formed when PbS is roasted but its existence is confined to regions where O_2 is adsorbed directly on the reacting

surface and SO_2 desorbed directly from it. These are the regions of surface reactions only. It is perhaps of interest to note that similar PbO crystals appear during the "reaction" of PbS-PbSO_4 mixtures.

The Reaction

The study of the kinetics of the PbS-PbSO_4 and PbS-PbO reactions in nitrogen atmosphere indicate that the transport of SO_2 from the solid surface is rate-controlling even when the velocity of the gases over the surface is appreciable. This is evident in Figure IX (page 44) and in Plate VII (page 38).

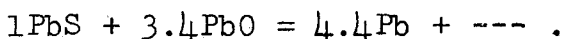
The appearance of a reaction interface in nitrogen atmosphere is related to the concentration gradient of SO_2 in the gas film which resides on the solid surface. The concentration gradient will decrease in the direction of gas flow, stifling the reaction at points beyond the interface.

The apparent activation energies for the reactions may be considered to be a measure of the height of the barrier for SO_2 transport from the solid surface into the bulk gas stream. The film thicknesses were not measured, hence the apparent activation energies are not of quantitative significance. Attempts to obtain reaction rates completely independent of gas flow were not successful although Figure IX (page 44) suggests the possibility.

The very high apparent activation energy (240 Kcal./mole) for the PbS-PbO reaction in vacuum is meaningless in that

the kinetic derivations used for isothermal systems are invalid in the system studied. In a system with pressures reduced to less than 5 mm. of mercury the rate of heat transfer is slow. With exothermic reactions temperatures at the reaction interface may go 100° to 200° higher than the measured furnace temperature. If the reaction is allowed to proceed nonisothermally the true temperatures must be measured before the reaction energetics can be evaluated. Cohn (5) has discussed this situation with reference to solid state reactions.

The stoichiometry of the PbS-PbO reaction is often written as $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$. The data of nonradioactive "reactions" suggested a stoichiometry greater than 1PbS:3PbO for the reaction in vacuum; the more accurate tracer study gave for the stoichiometry



The non-equilibrium amount of Bi^{212} which appeared in the lead metal product is not easily explained. It would seem that at some point in the reaction mechanism there exists a greater affinity for Bi^{212}S than for Pb^{212}S .

The Modified Mechanism

In view of the randomness of the observations resulting from the study of the "roast-reaction" it is perhaps worthwhile to recapitulate the entire model. The steps in the mechanism of the roasting of lead sulfide will be restated and examined, the steps in the "reaction" will be dealt with in like fashion.

The steps proposed for the roast are:

1. $O_2(\text{gas})$ transported through gas film to solid surface of the roast.
2. Diffusion of $O_2(\text{gas})$ through the roasted layer to the scene of the chemical reaction.
3. $O_2(\text{gas}) + \text{Pb-S}(\text{site}) \rightleftharpoons \text{Pb-S} \dots O_2(\text{equilibrium chemisorption})$
4. $\text{Pb-S} \dots O_2 = (\text{Pb-S-O}_2)^{\ddagger} \text{activated complex} \rightarrow \text{Pb-O}(\text{site}) + \text{SO}(\text{adsorbed})$
5. $\text{SO} + O_2 \rightleftharpoons \text{S-O}_3$
6. $\text{Pb-O}(\text{site}) + \text{S-O}_3 \rightleftharpoons (\text{PbSO}_4) \text{ structure}$
or with lower oxygen concentrations
 $\text{S-O}_3 \rightleftharpoons \text{SO}_2 + 1/2O_2$
and
 $2\text{Pb-O}(\text{sites}) + \text{S-O}_3 \rightleftharpoons (\text{PbO.PbSO}_4) \text{ structure}$
7. At points of lower SO_2 pressure
 $(\text{PbO.PbSO}_4) \text{ structure} \rightleftharpoons (x\text{PbO.PbSO}_4) \text{ structure} + \text{S-O}_3$
where $x > 1$ and integer.
8. $\text{S-O}_3 \rightleftharpoons \text{SO}_2 + 1/2O_2$
9. Diffusion of SO_2 to roasted surface.
10. Transport of SO_2 through gas film into roasting atmosphere.

It is suggested that the most critical feature of the roasting mechanism is the sensitivity of the lattice structure to oxygen and SO_2 pressure. This is illustrated by the absence of distinct PbO and PbSO_4 structures at depth.

Some modifications occur in the "reaction" mechanism as a result of the kinetic and stoichiometric studies of the PbS-PbO reaction in vacuum. The main PbS-PbO reaction is

assumed to take place between PbS vapor and a PbO solid surface.

The model is assumed to involve the following steps:

1. $\text{PbS}_{(\text{solid})} \rightleftharpoons \text{PbS}_{(\text{vapor})}$
2. $\text{PbS}_{(\text{vapor})}$ transported to PbO solid surface.
3. $\text{PbS}_{(\text{vapor})} + \text{Pb-O}(\text{site}) \rightleftharpoons \text{Pb-O} \dots \text{PbS} (\text{equilibrium chemisorption})$
4. $\text{Pb-O} \dots \text{PbS} = (\text{xPbO} \cdot \text{PbS})^{\ddagger} \text{activated complex} \rightarrow (\text{x+1}) \text{Pb} + \text{SO}_{\text{x}}(\text{adsorbed})$
5. $\text{SO}_{\text{x}}(\text{adsorbed}) \rightleftharpoons \text{SO}_3(\text{gas})$
or
 $\text{SO}_{\text{x}}(\text{adsorbed}) \rightleftharpoons \text{SO}_2 + 1/2\text{O}_2(\text{gas})$
6. $\text{SO}_3(\text{gas}) \rightleftharpoons \text{SO}_2 + 1/2\text{O}_2$
7. Transport of SO_3 , SO_2 and O_2 gases from solid surface.

Step 1.: The heat of sublimation of PbS is 56.7 Kcal./mole at 720°C and the vapor pressure is 3.1×10^{-2} mm. at the same temperature. The true reaction temperatures are unknown for the solid reactant mixture but if one assumes that the measured low temperature rate (0.003 gm./min. at 720°C) is correct then the reaction rate increases 40 times in the temperature interval. For the rate of sublimation of PbS to be the slow step the true final temperature must reach the vicinity of 865°C, the vapor pressure of PbS being 1.24 mm. here. This is not impossible for the case of the intimately mixed solids. However, for the vapor-solid reaction performed with isolated PbS and PbO phases Figure XIV (page 54) suggests that the rate of reaction is not linearly dependent on the sublimation

rate of PbS. If step 1. is assumed to be a fast step the activation energy will be of the order of 56 Kcal./mole, the heat of sublimation of solid PbS.

Step 2.: With intimately mixed solids such as in the reaction studied it is unlikely that transport of PbS vapor will control the reaction rate. This step is then assumed to be at equilibrium with a negligible activation energy.

Step 3.: Step 3. is concerned with the chemisorption of gaseous PbS molecules on the solid PbO surface sites. The PbS molecule may approach the surface and be chemisorbed on an active site, resulting in the formation of an activated complex on the surface and reaction to products or the molecule may be adsorbed on inactive sites and subsequently desorbed. Experimental data for heats or activation energies of adsorption for PbS have not been found. Further, it is not known what the nature of the active centers are on a PbO surface. It may be possible to adsorb gases on two different types of centers on a PbO surface; thus PbS vapor could feasibly be adsorbed in at least four ways (26). The velocity of gaseous adsorption on oxide surfaces varies considerably (27), slow adsorption usually being indicative of higher activation energies. This step will involve the large entropy decrease characteristic of gaseous-solid transitions.

Step 4.: Judging from the experimentally measured stoichiometry of $1\text{PbS}:3.4\text{PbO}$ the formation of the activated complex on the surface of the PbO must involve adsorbed PbS molecules and some $x(\text{Pb-O})$ groups where x is a multiple of

3.4. Such a formation may involve surface migration of oxygen atoms or ions; it could conceivably have a high activation energy and be the slow step in the process.

Step 5.: Depending on the partial pressure of oxygen in the region of the chemical reaction it is suggested that the desorption step may go either to SO_3 gas or to SO_2 gas and O_2 . Desorption data for such steps has not been found but again, the step may be slow, the minimum activation energy being the heat of desorption of the gas.

Step 6.: The dissociation of SO_3 to SO_2 is probably a fast step as the equilibrium in the reaction $\text{SO}_2 + 1/2\text{O}_2 \rightleftharpoons \text{SO}_3$ is well to the left at the temperatures encountered.

Step 7.: As has been experimentally confirmed the transport of SO_2 is rate-determining in nitrogen atmosphere at low gas velocity. Under conditions of reduced pressure this control is removed.

It will be observed that the possibility of diffusion of reactants and products through the liquid lead metal product has not been considered in the mechanism. The lead metal product in all reactions was observed to form in tiny spheres on the surface of the solid reactant leaving much of the surface exposed. This sphere formation is illustrated in Plate IX. The assumption has been made that PbS vapor is transported directly to the reactant PbO surface and gaseous products desorbed directly from the reacting surface.

The model for the PbS-PbSO_4 reaction and for the PbS -basic lead sulfate reaction is still in doubt. It is

probable that normal sulfate must undergo a transition to the basic structure before any reaction can proceed, this is suggested by the position of the "reaction" starting line on Figure V (page 26). The partial pressure of oxygen appears to be the critical factor in "reactions" then, as well as in the structure of the roast.

Conclusions

This research has been concerned with a general examination of the roasting and reduction of lead sulfide. The setting up of a model based on an assortment of information obtained by both early and recent workers has proven useful in that it shows clearly the many gaps in our knowledge of the kinetics and mechanism of the "roast-reaction". The arbitrary division of the process into the "roast" and the "reaction" is felt to be essential for a fundamental study; it is the first step toward simplification of a complex problem.

The results of experimentation have been valuable in two ways. Firstly they have supplied one or two of the missing steps in the mechanism and have indicated possible methods of filling other gaps. Secondly they have provided a guide for further theoretical and experimental study by uncovering pitfalls which must be avoided.

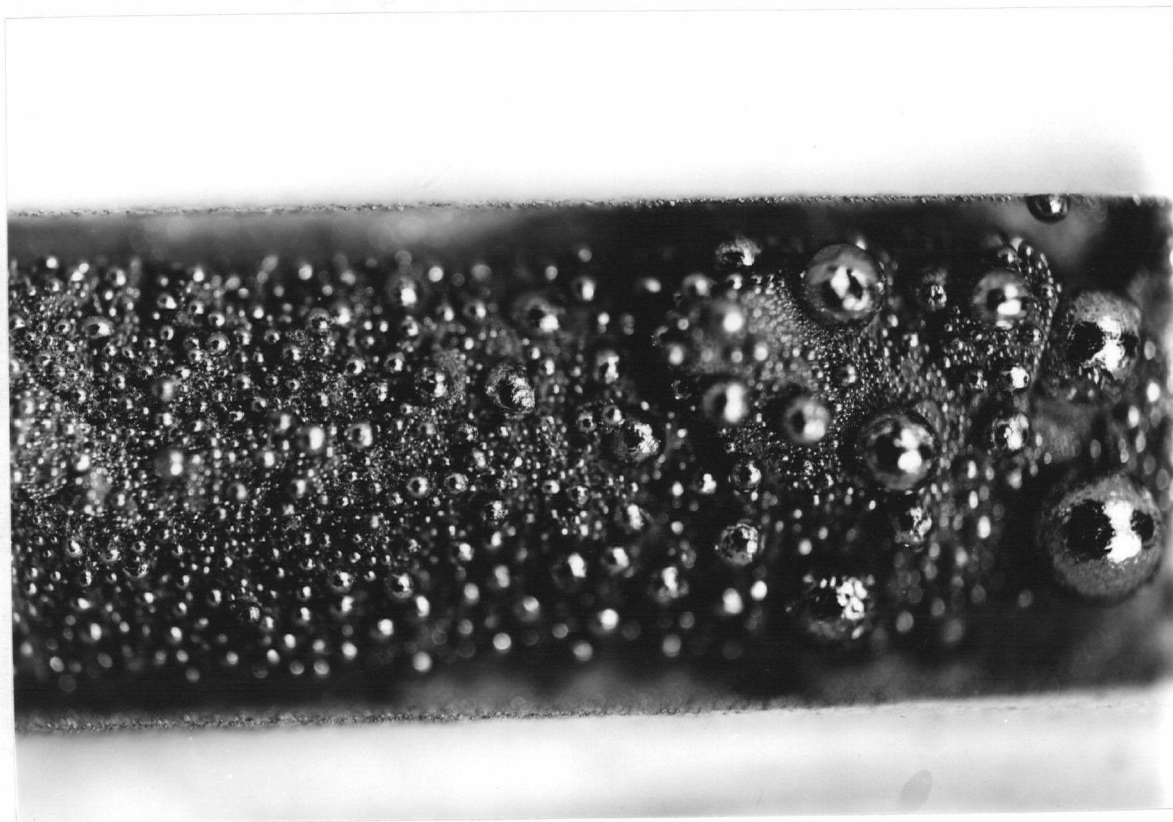


Plate IX The spherical formation of lead metal in the
PbS-PbO reaction. 10x.

RECOMMENDATIONS

It is recommended that the model proposed in this research project for the "roast-reaction" of lead sulfide be used as a starting point for further work. A few suggestions are listed which may prove helpful in experimental work.

1. The kinetics and mechanism of the roasting of lead sulfide should be examined using pure materials (synthetic galena) in the form of single crystals. Pure single crystals of galena of a size suitable for roasting (as large as two inches long and one half inch in diameter) have been prepared (²⁶~~24~~). Single crystal work is required to make available the surface area data for absolute reaction rate calculations (18) and to avoid the uncertainty inherent in proposing diffusion mechanisms for briquetted or polycrystalline materials. The methods of obtaining kinetic data should include weight change studies, preferably with the use of an autographic weighing system (17). It is suggested that the usual means of orienting and identifying phase boundaries in the roast (chemical analysis, petrography and X-ray diffraction) be supplemented by the use of the sulphur isotope S^{35} and the radioautographing of roasted cross-sections. This can be applied to single crystals or polycrystalline material alike. Roasting atmospheres may range from 100% oxygen through air to 100% nitrogen, pressures either reduced or greater than one atmosphere may be applied and gas flow rates varied from the

static conditions for equilibria studies to the conditions necessary to free chemical reaction rates from gas film transport control.

It is not recommended that the defect nature of the lead sulfide prepared or the effects of impurities (present in natural galena or added) be considered initially. Nor should SO_2 atmospheres (added SO_2) be used at first. Qualitative roasting tests carried out (not discussed in this project) with these variables were very confusing. It is felt that the consideration of such variables should be postponed until a clearer understanding of the roasting mechanism is at hand.

2. The stoichiometry of (a) the PbS-PbO solid-solid reaction and (b) the PbS-PbSO_4 solid-solid and gas-solid reactions should be examined. These reactions can be carried out in vacuum and in nitrogen, the Pb^{212} tracer technique is recommended for the examinations. The sulphur isotope S^{35} may have an application in some of the reactions.

The kinetics of (a) the PbS-PbO gas-solid and solid-solid reactions and (b) the PbS-PbSO_4 gas-solid and solid-solid reactions should be checked. It has been shown that some obstacles must be overcome in this. The rate-controlling SO_2 film must be removed for nitrogen atmosphere kinetic measurements. Increased flow rates, coarser particle size and solid reactant surfaces may all help. The heat transfer block in the vacuum study is analogous to film control. Intimately mixed solids can only be studied with the application of nonisothermal kinetic theory. The true reactant surface temperature must be

measured. It may be possible to approach isothermal conditions by obtaining crystals or fused lumps of PbSO_4 and PbO and allowing PbS films to evaporate and react on the surfaces. In all of the kinetic studies it is probable that the autographic weighing technique and the use of Pb^{212} and S^{35} tracers would be useful.

The dependence of the "reaction" starting temperature on oxygen pressure should be kept in mind and perhaps is worthy of closer examination in a future study of the "reaction" mechanism. It is suggested that this is closely related to the structural changes in the product with depth of the roasting layer over the PbS surface and with the degree of consolidation of reactants and products.

APPENDICES

Appendix A: The Preparation of Synthetic Galena

Synthetic galena was prepared by reacting test lead and excess sulphur together in a vented graphite crucible at a temperature of 500°C . Forty grams of sulphur were placed in the bottom of the crucible and covered with 80 grams of test lead, giving approximately 90 grams of galena in a batch. This galena was in the form of a blue-grey porous mass not unlike sinter, the individual particle size being about 14 mesh. This material was purified by fusion in a larger covered graphite crucible in the reducing flame of a gas muffle. Excess sulphur was added to the charge and it was taken to and held at 1200°C for fifteen minutes; then cooled slowly in the furnace. The product, which appeared identical to natural galena, was crushed to pea-size, blown free of carbon and reduced to -50 mesh in a mortar. The production of fines was minimized by repeated screening and a small amount of metallic lead was separated in this manner. Lead analyses of a carefully sampled portion of this galena gave an average purity of 99.2% PbS. The material was stored in a dessicator throughout the experiments.

Appendix B: The Preparation of Lead Sulfate

It was not originally intended to prepare lead sulfate, the reagent grade chemical being suitable for most purposes. However, in the course of mixing lead sulfide and dried reagent grade lead sulfate and on heating the mixtures, the evolution of H_2S was detected. Ignition of the lead sulfate at $600^{\circ}C$ with the intention of drying it and driving off any free sulfuric acid invariably resulted in decolorization of the sulfate to a grey shade similar to Portland cement. Minute quantities of carbon present in the ignited sulfate might cause the discoloration, consequently it was felt this lead sulfate might not give reliable results in the "reaction" study and other lead sulfate was prepared.

The lead sulfate used in the study was prepared by dissolving test lead in dilute nitric acid and precipitating the lead out with sulfuric acid. Repeated dryings with excess concentrated sulfuric acid and repeated washings with very dilute sulfuric acid were carried out until it was felt that the lead sulfate was free of nitrate.

Lead sulfate prepared in this manner remained pure white after ignition at $600^{\circ}C$ for one hour periods and gave no detectable odor of H_2S on thorough mixing with PbS . It was used in all subsequent experiments.

Appendix C: The Purification of Nitrogen

Cylinder nitrogen (Premium Grade) was found to contain too much oxygen to be used in the "reaction" studies. The nitrogen was freed of oxygen and water vapor by passing it through a train consisting of two gas washing bottles in series containing chromous chloride solution, two drying towers in series containing phosphorus pentoxide and a small vitreosil tube furnace charged with copper turnings and heated to 600°C . Lead sulfide heated in nitrogen which was passed through the train showed no signs of oxidation. The chromous chloride gas washers were operated such that the first one contained the solution of lesser activity and the second the fresh solution. Chromous chloride solution was prepared (27) in a Jones type reducer charged with amalgamated zinc. The solution was placed directly in a washing bottle and kept out of contact with air until used.

Appendix D: Analysis

I Analysis of the "roast" samples for PbS , PbO and PbSO_4 :

The combustion boats* containing the roasts were placed in one liter beakers and leached with a saturated solution of ammonium acetate for 6 hours. The temperature of leaching was kept just

* All alundum boats used in the project were leached in boiling 1:1 HNO_3 , leached in water, dried, fired at 900°C in a small pot furnace and stored in a dessicator until used. Boats were refired before reuse. Heavily slagged boats were discarded.

below the boiling point. The ammonium acetate solution, containing the dissolved lead oxide and lead sulfate was filtered off through a pyrex gooch filter of medium porosity. The filter, containing the boat and unreacted lead sulfide, was washed through with acetone and ether, placed in a vacuum desiccator and pumped off. A gross weight was taken and the filter and contents were placed in the original beaker, covered with concentrated nitric acid and boiled until clear. After reducing the volume of nitric acid and precipitated lead salts to 150 ml. the solution was made to 600 ml. with distilled water and heated to dissolve the lead salts. The filter was then removed and washed, 10ml. of H_2SO_4 were added to the solution and the lead contents were determined by the usual sulfate procedure.

Lead and sulfate were determined on the ammonium acetate filtrate as follows: the solution was made to 500 ml. and divided into two parts. Lead was determined on one part by precipitation as the oxalate and titration with standard permanganate. Sulfate was determined on the other part by first removing the lead by passage through an ion exchange column (Dowex 50-X12), then precipitating as barium sulfate in the usual way. Having the total ammonium acetate soluble lead, the total lead as sulfate and total lead as sulfide, the lead as oxide was calculated by difference. The analysis was subject to a check by means of the weight changes recorded; all combustion boats and filters being tared previous to use.

II The analysis of "reaction" samples for Pb, PbS, PbO and PbSO₄: The analytical procedure differed from that for "roast" samples in that the ammonium acetate insoluble portion consisted of a mixture of lead sulfide and lead metal. Two alternate procedures were used for the lead sulfide-lead determination. In the first procedure the boat plus lead metal-lead sulfide insoluble were weighed, the lead-lead sulfide was leached out with nitric acid and total lead was determined as the sulfate, the boat being tared within the pyrex filter. In the second procedure the lead was extracted by an ion exchange resin and determined as sulfate, the sulfide sulphur was determined as barium sulfate. When desired, lead oxide and lead sulfate were determined in the ammonium acetate soluble portion by the procedure used for "roast" samples.

Appendix E: The Preparation of Labelled Lead Sulfide

The Pb²¹² isotope was obtained by dithizone extraction of a solution of the Th²²⁸ parent isotope. A one millicurie solution of Th²²⁸Cl was obtained. This solution was diluted with 1:1 nitric acid and aliquoted to obtain an extraction solution with the desired Pb²¹² activity. The aliquot (two ml.), termed the parent solution, was placed in a 100 ml. pyrex separatory funnel and mixed with 5 ml. of a thorium nitrate solution (25 mg. Th in 1:100 nitric acid), 15 ml. of ammonium citrate solution (50 gm. in 100 ml. H₂O and basic with NH₄OH to pH 9) were added, the solution was mixed well and

made basic (pH 9) with NH_4OH .

Extraction of the Pb^{212} isotope was carried out as follows: 100 microliters of a lead solution (0.5 micrograms per microliter) were added to the parent solution with a micro-pipette. The solution was mixed well and the pH checked with thymol blue, NH_4OH being added if required. Three extractions with 5 ml. portions of dithizone solution (50 mg. dithizone per liter of chloroform) were carried out using standard technique (23). The third extraction invariably gave a clear green dithizone solution. The lead was back-extracted from the chloroform phase by shaking with 2 - 15 ml. portions of 1:100 HNO_3 . The aqueous phase was drawn off into a 400 ml. beaker, mixed with 10 ml. of a lead solution (25 mg. Pb per ml. in 1:100 HNO_3) and made to 200 ml. with water. This solution was mixed well, gassed with H_2S until clear (about one hour) and filtered onto a small disk of No. 42 Whatman filter paper in a stainless steel suction filter. The sulfide was washed with cold water, acetone and finally ether. The paper disk with precipitate was transferred to a small porcelain crucible, covered and placed in a vacuum dessicator. The dessicator was evacuated with a backing pump for one hour, after which the lead sulfide could usually be freed from the filter paper with a few taps. This lead sulfide was transferred to a tared glass (counter) vial, counted, weighed and then placed in an alundum boat and utilized in the "reaction" studies. The extraction procedure was repeated every 48 hours which maintained the

activity of the lead sulfide at a suitable level.

The Th^{228} solution was checked to determine whether it contained equilibrium amounts of lead and bismuth before any extractions were carried out. An aliquot of the solution was counted twice daily for a week and showed a constant level of activity after background correction. This was taken as satisfactory evidence of secular equilibrium, the half life of Th^{228} being 1.90 years (10).

The degree of separation of the lead isotope from the thorium parent isotope was checked by preparing a sample of the active lead sulfide, counting it to obtain a decay curve and measuring the half life as given by the curve. Separate samples gave measured half lives of 10.7 and 11.5 hours; the published value for the half life of the Pb^{212} isotope being given as 10.6 hours (10).

BIBLIOGRAPHY

1. Anderson, J.S. and Richards, J.R., J. Chem. Soc., London, 537 (1946).
2. Bate, G., personal communication, (Ref. ²⁶~~24~~).
3. Chizhikov, D.M., Frents, G.S., and Tratsevitskaya, B. Ya., Izvest. Akad. Nauk. S.S.S.R., Otdel. Tekh. Nauk., 1352 (1949).
4. Clark, G.L., Mrgudich, J.N. and Schieltz, N.C., Z. Anorg. Allgem. Chem. 229, 401-9 (1936).
5. Cohn, G., Chem. Revs., 42, 527 (1948).
6. Collet-Descotels, H.V., Ann. Chim. Phys., (2), 55, 441 (1833).
7. Dannatt, C.W., and Ellingham, H.J.T., Discussions Faraday Soc., 4, 131 (1948).
8. Dennis, W.H., "Metallurgy of the Non-Ferrous Metals", Sir Isaac Pitman and Sons, Ltd., London, 1954, p. 220.
9. Ellingham, H.J.T., J. Soc. Chem. Ind., 63, 125 (1944).
10. Friedlander, G., and Kennedy, J.W., "Nuclear and Radio-chemistry", John Wiley and Sons, Inc., New York, 1955, pp. 436, 439.
11. Hofman, E.M., "Metallurgy of Lead", McGraw-Hill Book Company Inc., New York, 1918, p. 42.
12. Kelley, K.K., Bull. U.S. Bur. Mines, 1937, No. 406, pp. 91, 98.
13. Kellogg, H.H., A.I.M.E. Trans., 8, 1105 (1956).
14. Liddell, D.M., "Handbook of Nonferrous Metallurgy", "Principles and Processes", McGraw-Hill Book Company Inc., 1945, pp. 276, 277.
15. Linder, R., Z. Naturforsch., 10a, 1027-8 (1955).
16. McCabe, C.L., and Morgan, J.A., A.I.M.E. Trans., 8, 800A (1956).
17. Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VII, Longmans, Green and Co. Ltd., London, 1927, p. 498.

18. Ibid., p. 500.
19. Ong Jr., J.N., Wadsworth, M.E., Fassell Jr., W.M., A.I.M.E. Trans., 8, 257 (1956).
20. Peretti, E.A., Discussions Faraday Soc., 4, 174 (1948).
21. Ibid., p.176.
22. Ibid., p.178.
23. Sandell, E.B., "Colorimetric Determination of Traces of Metals", 2nd. Ed. Interscience Publishers Inc., New York, 1950, pp. 388-396.
24. Scanlon, W.W., and Brebrick, R.F., Physica, 20, 1090 (1954).
25. Schenck, R., Z. Anorg. Chem., 142, 143 (1925).
26. Starkiewicz, J.S., Bate, G., Bennett, H., and Hilsum, C., Proceedings Phys. Soc., 70-B, 258 (1957).
27. Stone, H.W., Ind. Eng. Chem. (Anal. Ed.), 17, 495 (1945).
28. Terem, H.N. and Akalan, S., Compt. Rend. 232, 973-5 (1951).
29. Trapnell, B.M.W., "Chemisorption", Butterworths Scientific Publications, London, 1955, p. 73.
30. Ibid., p. 75.
31. Watson, R., Chemical Essays, London, 3, 273 (1782).
32. Wenner, R.R., "Thermochemical Calculations", McGraw-Hill Book Company Inc., New York, 1941, pp. 298-301.
33. Ibid., p. 301.
34. Woods, S.E., Discussions Faraday Soc., 4, 192 (1948).