THE ELECTROCHEMICAL DISSOLUTION OF GALENA

by

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ABSTRACT

The electrochemical oxidation and reduction of galena (PbS) was studied in aqueous solutions of perchloric acid between pH 0 and 4. The wide variation of rest potential as reported in the literature was explained on the basis of stoichiometric variations of this material as well as the activities of ionic and molecular species involved in the PbS equilibria. The stoichiometry of the anodic and cathodic reactions was determined to be primarily

$$PbS \rightarrow Pb^{++} + S^{o} + 2e^{-}$$

and

$$PbS + 2H^{+} + 2e^{-} \rightarrow Pb^{o} + H_2S$$

respectively. The irreversibility of anodic oxidation to lead sulphate was observed, with no sulphate produced below about 0.7 to 1.0 volt, depending on the pH. Polarization experiments revealed that ohmic, concentration, and activation polarization effects all contributed to the non-equilibrium behavior of PbS. Reaction of PbO_2 and MnO_2 with PbS was rapid and interpreted as a "galvanic" effect, relying on the conductivity of the reactants as a necessary condition for its success.

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INTRODUCTION

I GENERAL

Most of the world's supply of lead today is produced by a wholly pyrometallurgical treatment of lead concentrates containing galena (PbS), its chief mineral. The most common process involves a roasting operation to produce an oxide sinter of good physical properties, with subsequent reduction to metal in a blast furnace.

Three hydrometallurgical processes have been considered which involve leaching of an oxide or sulphate product and hence eliminate the smelting but not necessarily the roasting operation. The Tainton Process[1], developed between 1916 and 1925, is concerned with the leaching of a lead sulphate calcine with a brine solution and subsequent electrolytic reduction to metal. The Forward Process[2] is applicable to the leaching of lead sulphate which may be produced by either hydrometallurgical or conventional roasting techniques, utilizing aqueous solutions of linear organic amines such as DETA*, to form soluble Pb - amine complexes. Separation of lead is effected by precipitation with CO_2 and reduction of the resulting carbonate with C, CH_4 or CO at high temperatures, yielding lead of 99.99+ % purity. Very recently a process for leaching lead oxide or sulphate with strong NH_3 - $(NH_4)_2SO_4$ solutions has been patented.[3]

A process involving the direct attack of the mineral galena to yield a pregnant solution would eliminate pyrometallurgical steps with

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* Diethylenetriamine, $NH_2 - CH_2 - CH_2 - NH - CH_2 - CH_2\ NH_2$

their inherent gas and dust handling problems and might reduce the number of steps required to process lead concentrates. However, the chemistry of sulphide reactions in hydrometallurgical systems is not yet well understood and so such a process is difficult to design.

A primarily electrochemical study of galena has been undertaken because the nature of sulphides is such that electrochemical mechanisms have most successfully described their behavior in hydrometallurgical systems. This study has arisen from various related investigations of sulphide reactions as reported in the literature and as discussed under the following classifications:

(1) The relevance of electrochemical mechanisms to leaching reactions.
(2) The possibility of direct electrolytic treatment of sulphide electrodes.
(3) The role of galvanic action between minerals and its application to leaching.
(4) The conditions under which the pH-potential diagrams fail to be useful for kinetic reasons.
(5) The relationship of electrochemical measurements such as polarization and rest potential to the phenomenological and kinetic aspects of leaching and electrolysis.

II A REVIEW OF THE LITERATURE

(a) Electrochemical Mechanisms of Leaching Reactions

It has been determined that the acid leaching of PbS[4], CuS and $CuFeS_2$[5], ZnS[6], and other sulphides occurs principally by the overall reaction

$$MS + \tfrac{1}{2}O_2 + 2H^+ \rightarrow M^{++} + S^o + H_2O \qquad (1)$$

under oxygen pressure and below 120°C. The use of other oxidants such as Cl_2 and Fe^{+++} has been shown to yield a similar stoichiometry[7]. The fact that elemental sulphur and the metal ion are also products of electrochemical oxidation as well as the fact that most sulphides have a reatively high electronic conductivity suggest that electrochemical mechanisms may be useful in explaining leaching reactions.* The behavior of pyrite, according to Peters and Majima[8], is anomalous however, because the elemental sulphur yield in an oxygen pressure leach is always less than 50%. At low current densities the anodic electrochemical dissolution of pyrite was shown to yield no elemental sulphur, but only sulphate and ferric ions.

With the notable exception of pyrite, then, it has been suggested that under oxygen atmospheres and at temperatures below the melting point of sulphur, the acid leaching ofmost metallic sulphides occurs by an essentially electrochemical mechanism, with reduction of oxygen occurring at cathodic sites by the reaction

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (2)$$

and oxidation of the metal sulphide at anodic sites by the reaction:

$$MS \rightarrow M^{++} + S^o + 2e^- \qquad (3)$$

The summation of reactions (2) and (3) yields reaction (1).

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* A reaction is said to be electrochemical in nature if the anodic reaction is physically separated from the cathodic reaction, for which electron transfer occurs through a conducting path. This necessarily restricts the electrochemical mechanism to conductors or semiconductors. A purely chemical reaction is one in which the cathodic and anodic processes occur at the same site, and hence electron transfer does not occur over more than, say, one or two molecular distances.

(b) Electrolytic Treatment of Sulphides

A current commercial process[9] utilizes direct anodic dissolution of Ni_3S_2 matte anodes combined with solution purification and production of refined cathode nickel. The possibility of similar techniques for the processing of other sulphides has been investigated for Cu[10,11,12], Ni[11,13], Zn[14], and Pb[15,16,22]. Additional work of this nature has been done in the U.S.S.R. and is discussed in references (17) to (21).

Chizhikov and Kovylina[22], using cast and pressed galena anodes, concluded that $PbSO_4$ was formed in solutions of H_2SO_4 by the following reactions

$$PbS \rightarrow Pb^{++} + S^{o} + 2e^{-} \qquad (4)$$

and

$$Pb^{++} + SO_4^{=} \rightleftarrows PbSO_4 \qquad (5)$$

when the concentration of sulphate was high. In solutions of low sulphate concentration, $PbSO_4$ was thought to be formed through direct oxidation by evolved atomic oxygen according to the reaction

$$PbS + 4[O] \rightarrow PbSO_4 \qquad (6)$$

at sufficiently high potentials. Presumably, then, at low potentials, and in solutions containing no sulphate, the electrochemical oxidation of galena would occur by reaction (4) only.

Tsujikawa et al[23] reported that during the anodization of PbS at a constant potential of 400 mV (S.C.E.*), three products were formed in quantity which depended on Q/S, the number of coulombs passed per square centimeter. Figure (1) is a reproduction of their results, where X is the molar fraction of the anodic film formed by each reaction product. The three reactions said to be occurring were:

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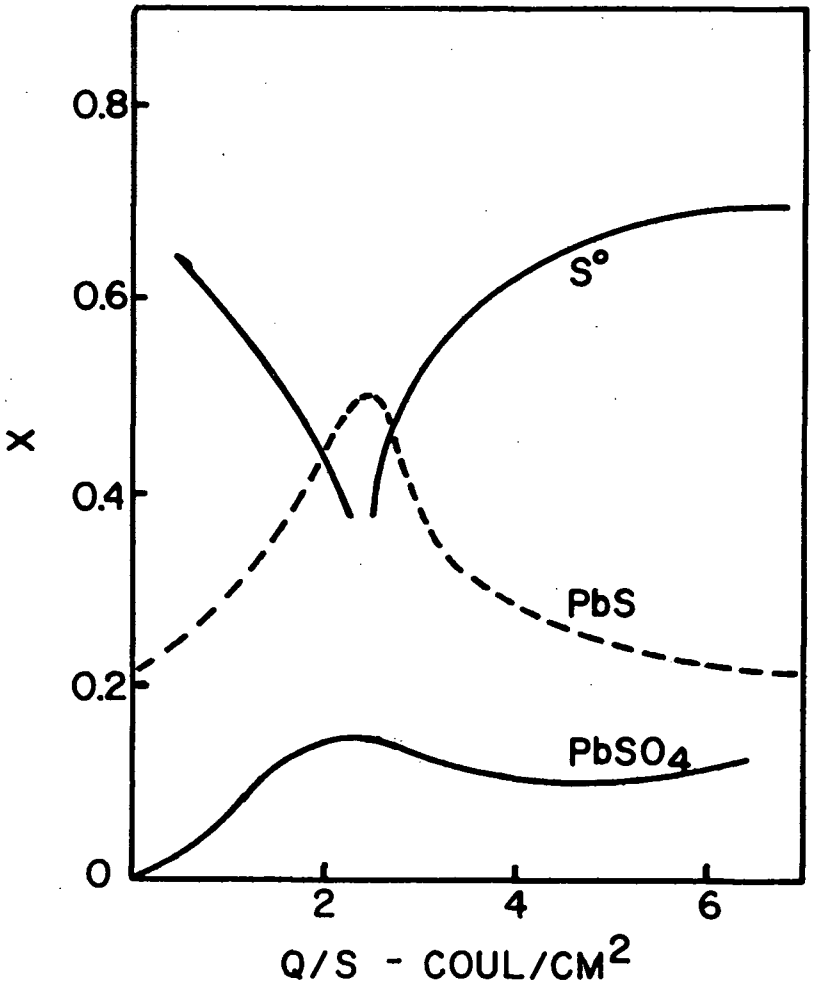
* vs. the saturated calomel electrode.



$$PbS\,(solid) \rightleftharpoons Pb^{++}(aq.) + S^{\circ}(film) + 2e^{-}$$

$$PbS(solid) + 4H_2O \rightleftharpoons PbSO_4(film) + 8H^{+} + 8e^{-}$$

$$PbS\,(solid) \rightleftharpoons PbS\,(film)$$

Figure (1) The molar fraction of oxidation product of PbS as a function of coulombs passed, and the proposed anodic reactions at 400 mv (vs. SCE) as determined by Tsujikawa et. al.

$$PbS(solid) \rightleftarrows Pb^{++}(aq.) + S^{o}(film) + 2e^{-} \quad (7)$$

$$PbS(solid) + 4H_2O \rightleftarrows PbSO_4(film) + 8H^{+} + 8e^{-} \quad (8)$$

$$PbS(solid) \rightleftarrows PbS(film) \quad (9)$$

As seen from the figure, for Q/S greater than about 6 coul/cm^2, the reaction film consisted of around 70% elemental sulphur.

Ito et al[16] found that the anodic dissolution of lead sulphide was most successful in lead perchlorate solutions but for various reasons was unsuccessful in lead fluosilicate, lead fluoborate, lead acetate, and lead nitrate.

A possibility other than anodic dissolution of sulphides is the electrolytic reduction to metal at a cathode. Electrochemical reduction of sulphides generally follows the reaction

$$MS + 2H^{+} + 2e^{-} \rightarrow M^{o} + H_2S \quad (10)$$

if overvoltages can prevent hydrogen discharge[24]. This alternative has not received much attention in the literature, probably because of the toxicity of H_2S and the difficulty in preventing reduction of impurity sulphides, as well as other reasons.

(c) Galvanic Effects Among Minerals

The fact that metal sulphides are relatively good electronic conductors suggests the possibility of galvanic action between sulphide particles in a slurry similar to galvanic corrosion between metals. It has been found experimentally by Gottschalk and Beuhler[25], Majima[26], and Peters and Majima[8], that the presence of pyrite increases the rate of dissolution of galena very significantly in an oxidizing leach. In the presence of oxygen pyrite has been observed to have the most noble rest potential of all sulphides[8] and is thought to act as a cathode where the

reduction of oxygen occurs; the anodic reaction is the oxidation of PbS to form elemental sulphur and lead ions by reaction (4). The same effect of pyrite on the minerals covellite (CuS), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS) was reported.

It has been shown by Peters[24], that a slurry of PbO_2 and PbS, neither of which dissolves appreciably by itself, will readily react to yield Pb^{++} and S^o in perchloric, acetic, and sulfamic acids. This is also thought to be a galvanic effect since both materials are electronic conductors; the reaction has been proposed as the basis for a possible commercial process.

Another consequence of the presence of pyrite in complex sulphide ores has been explained by Majima[26]. He suggests that the difficulty in flotation of such ores in acid solution is a result of the formation of a coating of elemental sulphur on the sulphide particles due to the oxidizing effect of pyrite. Thus galvanic effects are of importance in both leaching and flotation operations.

(d) Kinetics versus Thermodynamics

It is often found in hydrometallurgy that processes approach equilibrium rather slowly and therefore kinetic considerations are the primary concern of the investigator. However, the conditions of final equilibrium must be understood and the pH-potential diagrams have been found useful in summarizing these conditions in aqueous systems. pH-potential diagrams for lead sulphide have been prepared by McIntyre and are presented by Garrels and Christ[27]. The metal ion activities for which these diagrams were calculated are of more interest to a geochemist

than an extractive metallurgist. More useful diagrams have been prepared by Peters and Majima[8] and are discussed in a later section.

(e) Polarization and Rest Potential

In an attempt to more fully understand the non-equilibrium behavior of sulphides, electrochemists have begun to employ a favourite procedure of the corrosion scientists - the determination of polarization curves. These have been determined for PbS under various conditions by Tsujikawa et al[23] and by Chizhikov and Kovylina[22] but without much interpretation.

Intimately connected with polarization curves is the rest potential, which divides the anodic and cathodic domains of a material. A wide range of values for the rest potential of PbS has been reported; the values with their appropriate references are summarized in Table I.

(f) Lead Sulphide - a Description

Lead sulphide is a marginally covalent, non-stoichiometric compound with the NaCl structure. At about 400°K, the pure form undergoes a transition from extrinsic to intrinsic semiconductivity[30]. Its extrinsic semiconductivity arises from its non-stoichiometry as well as the presence of substitutional and interstitial impurity atoms. PbS can be made either n^- or p^- type by equilibrating the crystal under controlled atmospheres of sulphur and hence changing the stoichiometry. As the sulphur pressure, p_{S_2}, is increased, PbS undergoes a transition from n - to p- type semiconductivity. As the temperature of equilibration is lowered, the p - n equivalence point shifts to lower p_{S_2}. A description of PbS detailing its preparation, defect-structure, and semiconducting properties is given by Bloem, Kröger, and Vink.[31]

TABLE I

A SUMMARY OF REPORTED VALUES OF THE REST POTENTIAL OF GALENA

MATERIAL	SOLUTION	REST POTENTIAL (S.H.E.)	INVESTIGATORS	REF.
PbS (pressed)	100 g/l H_2SO_4	-.032	Chizhikov & Kov.	22
PbS (cast)	"	+.036	"	"
Galena	"	+.284	"	"
Galena	1 M $HClO_4$	+0.24	Majima	26
Galena	"	+0.23	Peters & Majima	8
Galena	1 M HCl	+0.29	Tsujikawa et al	23
Galena	"	+0.04	"	"
Galena	pH = 4	+0.40	Rachenberg	29
Galena	pH = 9	+0.33	"	"

Although PbS may be considered slightly ionic in character, it is useful to treat it as an alloy of elemental lead and sulphur. This simplification has been made in some of the arguments presented later.

III Scope of the Investigation

This investigation will have as its main objectives the determination of:

(1) The rest potential of galena and an explanation of the wide range of values as reported in the literature.

(2) The stoichiometry of electrochemical oxidation and reduction of galena in acid solutions.

(3) The polarization behavior of galena in acid solution.

(4) The rates of leaching of galena with "galvanic" oxidants such as PbO_2 and MnO_2 in perchloric acid slurries.

THERMODYNAMICS

A pH-potential diagram is a graphic representation of equilibria within an aqueous system under the rigorous conditions for which it is calculated. Peters and Majima[8] have prepared M-S-H_2O diagrams for several sulphides, including the Pb-S-H_2O diagram given in Figures (2(a) and (2(b). At lines on the diagram in which these species are involved, the total sulphate activity (as $SO_4^{=}$, HSO_4^{-}, or H_2SO_4) is unity for both diagrams, and the lead ion activity is 10^{o} and 10^{-3} in Figure (2(a) and (2(b) respectively. These values of $a_{Pb}{}^{++}$ have been chosen because they represent "ideal" pregnant and barren solutions of lead. The H_2S lines have been calculated for an activity of 10^{-1}, since its saturation molar solutility is 0.1 M at room temperature. The equation for each line on the diagram is given in Appendix A. Thermodynamic data for the calculations was taken from Garrels and Christ[27] as compiled from Latimer[28].

As mentioned previously, in hydrometallurgical systems it is often found that the reactions are dictated by kinetic rather than thermodynamic considerations. For example, sulphate ion is known to be stable far below the potential predicted for its reduction; the oxidation of elemental sulphur occurs very slowly in oxygen pressure-leaching systems; metastable species such as sulphite and thiosulphate are often found to persist for long periods of time. In fact, the pH-potential diagram as drawn has already incorporated some kinetic information: thermodynamically, the diagram should contain no information below the hydrogen line, since water is decomposed to form hydrogen gas and aqueous solutions thus become unstable. However, hydrogen

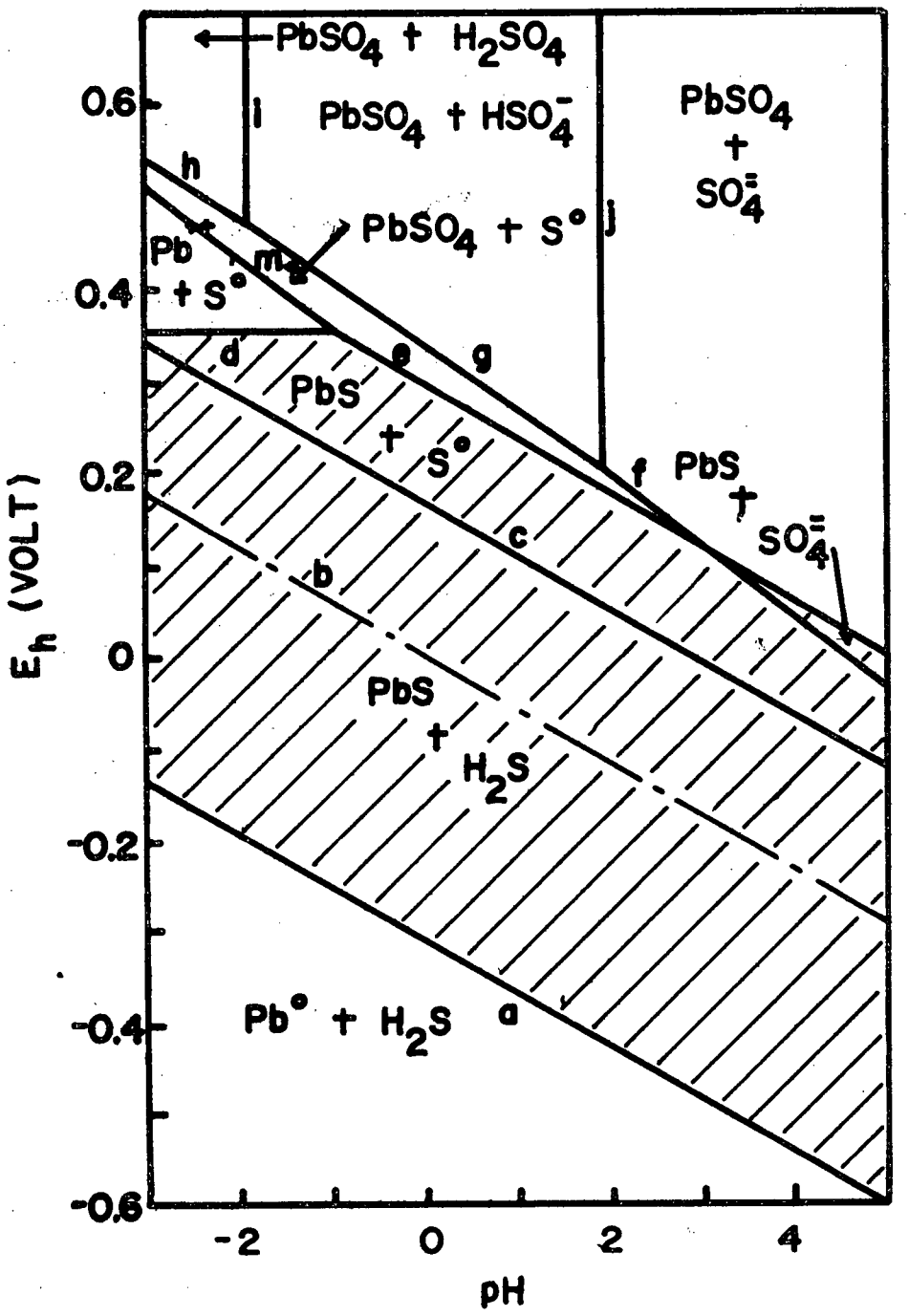


Figure (2(a)) pH-potential diagram for the system Pb-S-H_2O with total dissolved sulphate activity of unity, $a_{H_2S} = 10^{-1}$, and $a_{Pb^{++}} = 1$.

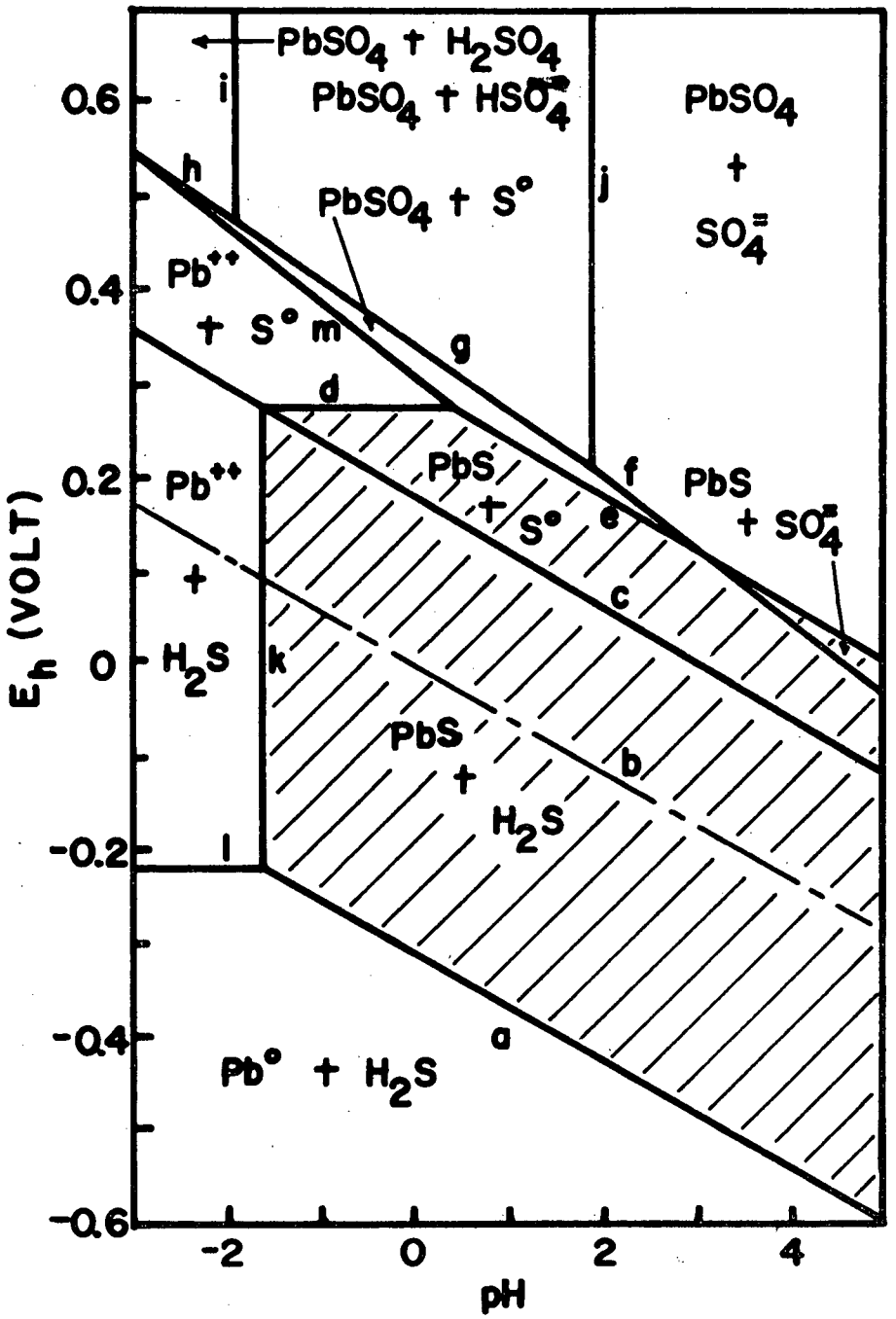


Figure 2(b)) pH-potential diagram for the system Pb-S-H_2O with total dissolved sulphate activity of unity, $a_{H_2S} = 10^{-1}$, and $a_{Pb^{++}} = 10^{-3}$.

overvoltage (a kinetic phenomenon) plays such an important role that often the decomposition of water does not occur to any measurable extent and hence can be ignored.

An examination of Figure (2(a) and (2(b) suggests that in order to move from the PbS-stable region, i.e. to decompose PbS, either an oxidation (upward on the diagram), a reduction (downward), or an acidification (leftward) must occur. The most obvious of these, acidification, requires the pH to be less than -1.5 when $a_{Pb^{++}} = 10^{-3}$ and $a_{H_2S} = 10^{-1}$. The use of hydrochloric and sulphuric acids to effect this produces insoluble $PbCl_2$ and $PbSO_4$, respectively, and hence would not be suitable. Nitric and perchloric acids, on the other hand, are so oxidizing at this concentration, that, again, $PbSO_4$ is formed. The pH at which acidification of PbS will yield Pb^{++} and H_2S can be raised by removal of H_2S or Pb^{++} from solution as it is formed. Even so, the kinetics as well as the toxicity of H_2S do not lend themselves to this technique.

The possibility of electrochemical oxidation and reduction of PbS is the main concern of the experimental investigation which has been undertaken.

EXPERIMENTAL

I Electronics

A Beckman "Electroscan 30", used for all the electrochemical experiments, was capable of performing the functions of pH-meter, high-impedance millivoltmeter, potentiostat (controlled-potential), and galvanostat (controlled-current). The potentiostat was capable of scanning over a given voltage range of from zero to 500 mv/sec.

In certain experiments where a knowledge was needed of the total coulombs passed, a Varitech "1187" Coulometer was connected between the platinum electrode and the "Aux. Electrode" terminal on the Electroscan.

II Preparation of the Galena Electrodes

The mineral (working) electrodes, whose analyses are given in Table II of Appendix B, were prepared from massive specimens of Kansas natural galena obtained from Ward's Natural Science Museum. Electrical contact was made through a wire soldered to a small strip of copper which was in turn cemented to the mineral surface with GC Electronics silver conductive paint. The mineral cube was mounted in "Koldmount" self-curing resin to insulate five of the six cube faces from the solution, as illustrated in Figure (3). The electrode face, parallel to the natural cleavage planes of the mineral, was polished down before each run to remove corrosion products from previous runs, with care taken to avoid work hardening due to excessive polishing.

III Components of the Electrolytic Cell

The electrolytic cell used for most of the experiments is

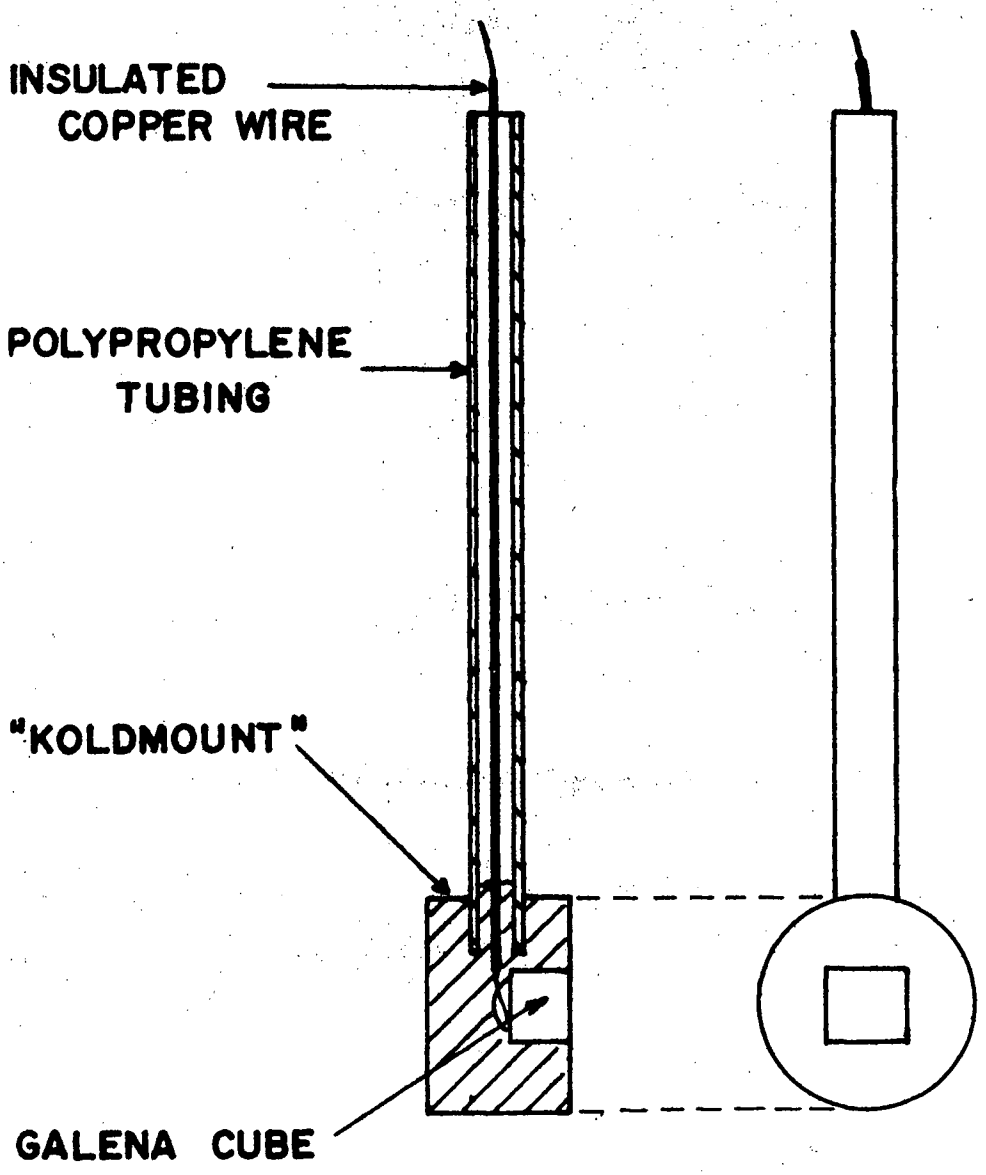


Figure 3 The galena (working) electrode.

illustrated in Figure (4).

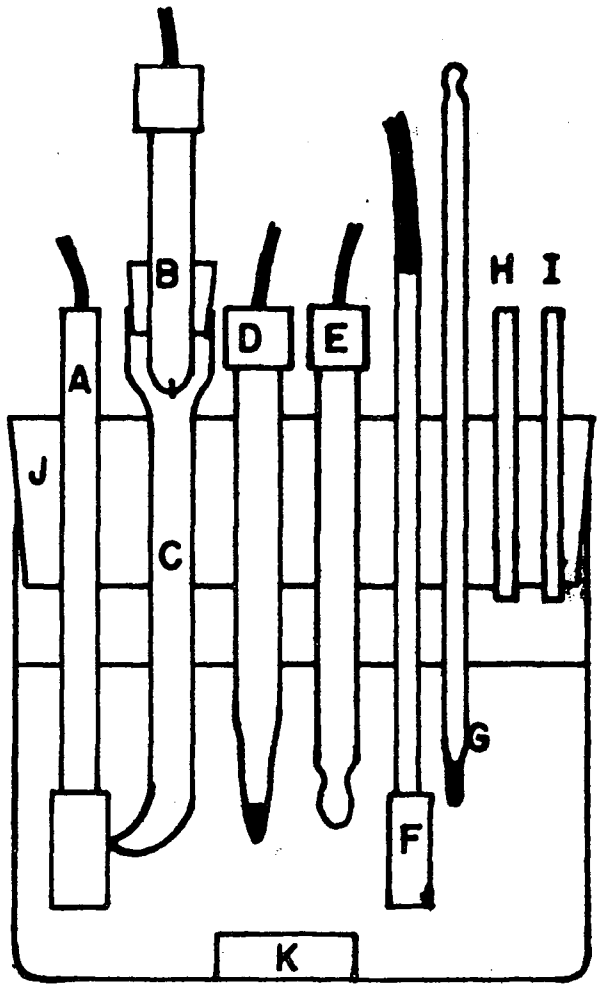
In all cases, the active electrodes were the galena (working) and platinum (auxiliary) electrodes, with finite currents passing between these two only. The other electrodes, present for measurement of pH and potential, drew essentially no current by virtue of the high impedance of the measuring circuit.

The Luggin capillary allowed measurement of the potential at the galena surface, minus a correction for iR drop originating either in the semiconducting mineral or in any films which may have been formed. All potential measurements were made relative to the saturated calomel electrode (S.C.E.), but reported relative to a standard hydrogen electrode (E_h, S.H.E.).

The Luggin capillary was prepared by drawing out pyrex tubing, breaking off the drawn-out portion, and successively fire-polishing the broken end until the liquid flowrate out of the capillary was less than 2 ml/day.

The calomel (reference) electrode was placed in a polyethylene cup fitted to the top of the Luggin capillary. The cup and capillary were filled with the same solution as used for the electrolyte of the cell. All attempts to use a KCl-agar bridge inside the capillary failed because of destruction of the gel by $HClO_4$, the main electrolyte used.

The platinum electrode was platinized in order to lower the hydrogen overvoltage and thus discourage plating of lead under cathodic conditions.



A. WORKING ELECTRODE

B. CALOMEL ELECTRODE

C. LUGGIN CAPILLARY

D. AUXILIARY (Pt) ELECTRODE

E. GLASS ELECTRODE

F. GAS DISPERSER

G. THERMOMETER

H. GAS OUTLET TUBE (a)

I. GAS OUTLET TUBE (b)

J. RUBBER BUNG

K. MAGNETIC STIRRING BAR

Figure (4) The electrolytic cell and auxiliary accessories.

A glass electrode was present to facilitate pH measurements with the calomel electrode as reference.

IV Reagents

Reagent grade perchloric acid was used for the experiments at low pH because of the solubility of lead perchlorate, the complete dissociation of the acid, and the lack of perchlorate complexing. For solutions of pH greater than 2, buffered solutions of sodium acetate and acetic acid were used.

RESULTS AND DISCUSSION

I The Effect of Perchloric Acid on the Saturated Calomel Electrode Potential

The potential of the reference electrode, the saturated calomel electrode, was taken to be +.244 volt relative to the standard hydrogen electrode at 21°C. A persistent problem in the accurate measurement of potentials is the presence of a liquid-junction potential, Ej, which arises across any liquid interface. The magnitude of this potential is dependent on the mobilities, concentrations, and valences of the ions on both sides of the boundary, and has been found to be both difficult to estimate and eliminate entirely. The problem is particularly acute in solutions of extreme pH because of the overwhelming presence of the highly mobile hydrogen or hydroxyl ions. Since the solution within the calomel electrode, KCl, is different from the solution which it meets, a liquid-junction potential is necessarily set up and hence would affect the potentials measured. However, there is no simple or unambiguous method of determining this quantity. Because of the difficulty in measurement of such a potential and the reported minimization of Ej in solutions joined by a saturated-KCl bridge[32], no estimation of its magnitude was attempted.

It is known, however, that the immersion of the calomel electrode in any solution which reacts with the components of the electrode may result in a departure of the potential from its normal value. For this reason, according to Mattock[33], the presence of dissolved oxygen, cyanides, sulphides, complexing agents, silver, and perchlorates are

to be avoided with use of the calomel electrode. The reaction of $HClO_4$ with KCl forms insoluble $KClO_4$ which would tend to plug the asbestos-fiber junction. To determine if the contact of the calomel electrode with $HClO_4$ had any effect on its potential, two calomel electrodes whose potentials were previously determined to agree within ±2mv, were placed in solutions of saturated KCl and 1 M $HClO_4$ respectively. The two solutions were joined by a filter-paper bridge and the difference in potential between the electrodes measured. A potential difference varying between 20 and 40 mv was obtained, with the electrode immersed in $HClO_4$ negative with respect to the other. The potential of the calomel electrode was therefore corrected by the average difference, 30 mv, and taken to be +0.214 volt. For solutions other than 1 M $HClO_4$, the corrected potential was determined in the same manner.

The correction of 30 mv was assigned to the calomel electrode immersed in 1M $HClO_4$ rather than the filter-paper bridge, because the physical nature of the asbestos-fiber junction is such that it is much more likely to be affected by $KClO_4$ precipitation.

II Rest Potential

Rest potential is defined as the potential between a given and reference electrode in a solution when the total external current is zero, i.e. as measured by a high-impedance voltmeter. The observed potential cannot always be related to a thermodynamic reversible potential since there may be small internal currents due to local cathodes and anodes on the electrode. The result of this is a non-equilibrium situation, polarization, and the observed potential is termed a "mixed" potential.

As mentioned previously, a wide variation in values of rest potential for galena has been reported. Values obtained in this laboratory, measured in deaerated 1M $HClO_4$ varied between 0.18 and 0.25 volts (vs. S.H.E.). The exact value seemed to be some capricious function of prior surface treatment, and reproducibility was poor.

In order to effectively explain the wide variation, the factors that determine a rest potential must be understood. If Figure (2(a) or (2(b) is examined, it will be seen that the PbS-stable (shaded) region is bounded by the horizontal and oblique lines representing the following equilibria:

$$Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS \qquad (11)$$

for which the equilibrium potential, E_h, is given by the equation

$$E_h = +.354 + .0295 \log a_{Pb^{++}} \qquad (12)$$

and

$$PbSO_4 + 8H^{+} + 8e^{-} \rightleftarrows PbS + 4H_2O \qquad (13)$$

for which,

$$E_h = +.298 - .0591\ pH \qquad (14)$$

and

$$PbS + 2H^{+} + 2e^{-} \rightleftarrows Pb^{o} + H_2S \qquad (15)$$

for which,

$$E_h = -.339 - .0295 \log a_{H_2S} - .0591\ pH \qquad (16)$$

if the activities of all solid species are unity.

If it is assumed for the moment that no mixed potentials are involved, i.e. only one of these equilibria is of importance at once, equation (12) will give the value of rest potential if the activities

of PbS and S^o at the electrode surface are unity. If $PbSO_4$ rather than S^o is present at unit activity, (14) will express the rest potential. Similarly, (16) may apply if both PbS and Pb^o are at unit activity. However, if the activities of S^o, $PbSO_4$, or Pb^o are not as stated, the lines may shift up or down and thus the rest potential can assume any value within the bounds of the calculated lines, viz, the shaded portion of the pH-potential diagram. It is even possible for the mineral to have a rest potential outside this area if the conditions for two processes seeking equilibrium simultaneously occur at the electrode surface, one of which involves the galena only as a catalyst or inhibitor. This must necessarily be a "mixed" and thus non-thermodynamic potential.*

These considerations suggest that it might be possible to adjust the composition of the galena such that the conditions are fulfilled for each of the boundaries of stability and therefore obtain a wide range of rest potentials.

A galena electrode was electrolyzed cathodically at a constant current density of 1 mA/cm^2 for about one hour in 1M $HClO_4$. This effectively formed elemental lead on the electrode surface by the reaction:

$$PbS + 2H^+ + 2e^- \rightarrow Pb^o + H_2S \qquad (17)$$

---

* An example of a "mixed" potential is pyrite in the presence of oxygen which exerts a rest potential of +0.63 volt, excessively more positive than expected from thermodynamic considerations.[8] This falls between the reversible oxygen potential of 1.23 volt at pH = 0 (p_{H_2} = 1 atm.) and the reversible pyrite potential of $+0.35 + .0295 \log a_{Fe^{++}}$.

The electrode was then placed in fresh deaerated molar perchloric acid and electrolyzed anodically at the same current density. At short intervals, 1.0 ml. samples of solution were taken for lead analysis by atomic absorption and the electrolysis interrupted to measure the rest potential. As the anodization proceeded, elemental lead was depleted according to the reaction:

$$Pb^{o} \rightarrow Pb^{++} + 2e^{-} \qquad (18)$$

After depletion of the lead film, the expected reaction was the formation of elemental sulphur by the reaction:

$$PbS \rightarrow Pb^{++} + S^{o} + 2e^{-} \qquad (4)$$

Hence, by these reactions, (Pb^{++}) was constantly increased throughout the anodization; at the instant of final depletion of the lead film, $a_{S}o$ would change abruptly from a low value up to unity, and $a_{Pb}o$ would decrease accordingly. By this technique it was hoped the values of rest potential obtained would fall between the theoretical boundary limits of PbS-stability, expressed by (12) and (16) at pH = 0.

The assumption of activity equal to concentration was made, which is valid at these concentrations, and as can be seen in Figure (5) the limits of the experimental curve corresponded very closely to the theoretical limits. Equation (16) was modified by substitution of a term for a_{H_2S}, calculated from the following equilibrium

$$Pb^{++} + H_2S \rightleftarrows PbS + 2H^{+} \qquad (19)$$

for which

$$K = \frac{1}{a_{Pb^{++}} \cdot a_{H_2S}} = 10^{7.22} \text{ at pH} = 0 \qquad (20)$$

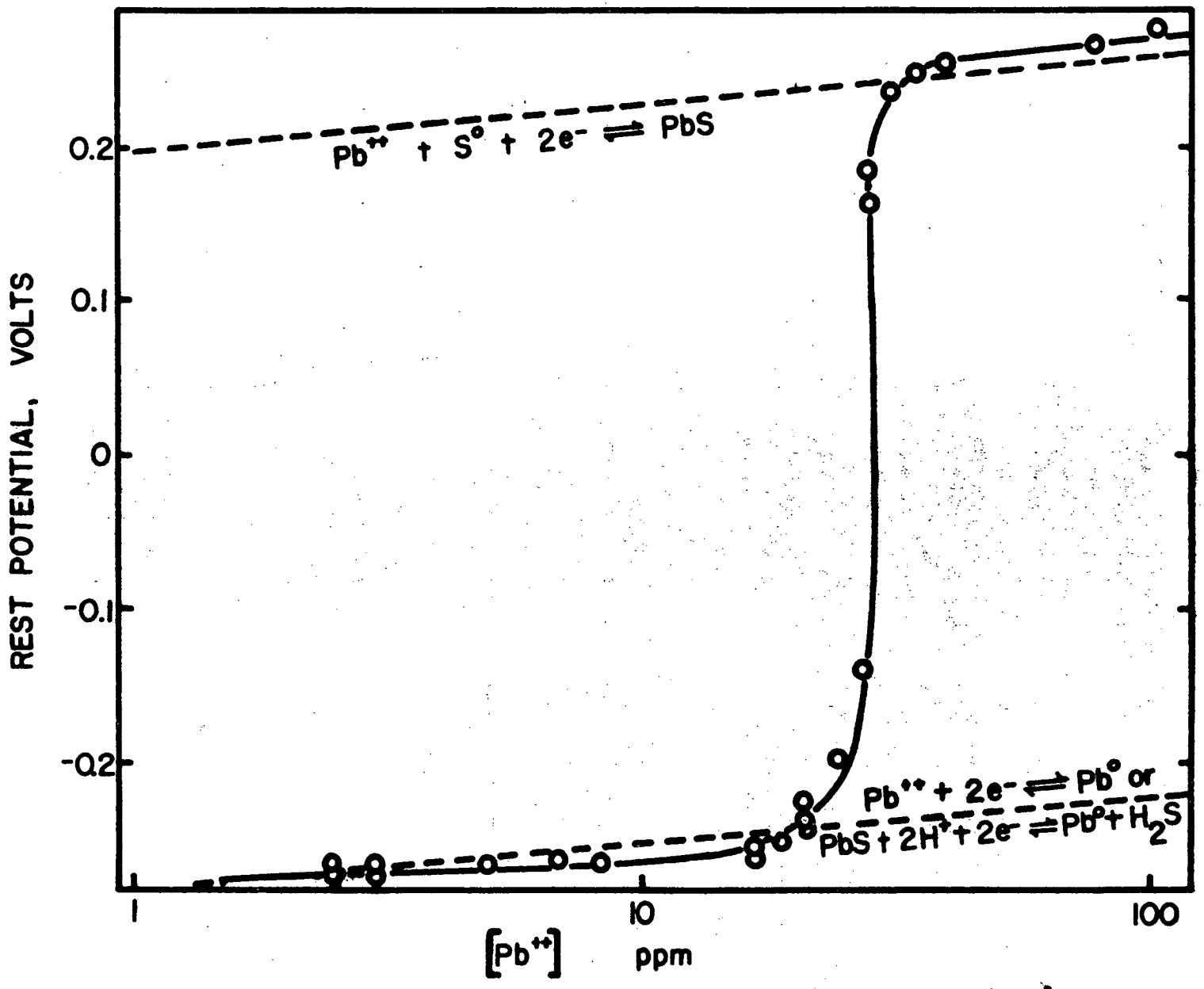


Figure (5) Experimental variation in the rest potential for low $[Pb^{++}]$ at pH = 0.

Upon substitution for a_{H_2S} at pH = 0, equation (16) becomes

$$E_h = -.126 + .0295 \log a_{Pb^{++}} \qquad (21)$$

which is the same equation as obtained for the equilibrium

$$Pb^{++} + 2e^- \rightleftarrows Pb^o \qquad (22)$$

It is known that a sulphur (or lead) variation of about 10^{-6} mole percent in the composition of galena represents the difference between lead saturation (where $a_{Pb}o = 1$) and sulphur saturation (where $a_S o = 1$). Therefore, minute composition changes can give rise to large variations in rest potential, as just observed by artificial imposition of conditions of lead and sulphur saturation. The reason for the large discrepancy in rest potentials as observed by other investigators is now obvious. These discrepancies merely represent stoichiometric variations in the galena sample under measurement, either inherent or imposed by prior treatment. The conditions of $a_{Pb^{++}}$ or a_{H_2S} may also affect the values to a lesser extent. Any operation which would produce heat and hence drive off sulphur such as casting, pressing, or polishing would tend to depress the rest potential. This is consistent with the values in Table I as well as the non-reproducibility of the values obtained in this laboratory.

III Stoichiometry of the Anodic Reaction at pH = 0

According to the pH-potential diagrams, the electrochemical oxidation of galena should proceed according to one or both of the following reactions at pH = 0, depending on E_h and the activities of ionic species:

$$PbS \rightarrow Pb^{++} + S^o + 2e^- \qquad (4)$$

$$PbS + 4H_2O \rightarrow PbSO_4 + 8H^+ + 8e^- \qquad (23)$$

The ratio of Faradays (electrical equivalents) of electricity passed to gm-ions of lead produced for each of these reactions is 2:1 and ∞:1 respectively. The formation of metastable sulphur species is also possible, but not likely at this low pH.

To determine the stoichiometry of the anodic reaction, a galena electrode was anodized at successively higher potentials between 0.50 volts and 1.20 volts in argon-purged molar perchloric acid. Below 0.50 volt, the currents were so small that impractical lengths of time were required to obtain sufficient lead in solution for analysis. Above 1.2 volt, the currents involved were greater than the capability of the current-measuring circuit, even for electrodes of very small apparent surface area. Two sets of runs were performed, with about 10 coulombs passed for the first set and about 30 for the second. The lead analysis was performed on a Unicam single-beam atomic-absorption spectrophotometer. The results are presented in Figure (6) and Table IV, Appendix C.

The approximately constant ratio of 2:1 at low potentials almost certainly confirms reaction (4) as the only anodic reaction of importance under these conditions. Above about 0.9 - 1.0 volt the ratio increased slightly and suggests a very minor contribution from reaction (23). No attempt was made to correct the potentials for the electrode resistance.

X-ray diffraction patterns were obtained from scrapings of the anodic film on the galena surface. The presence of only elemental

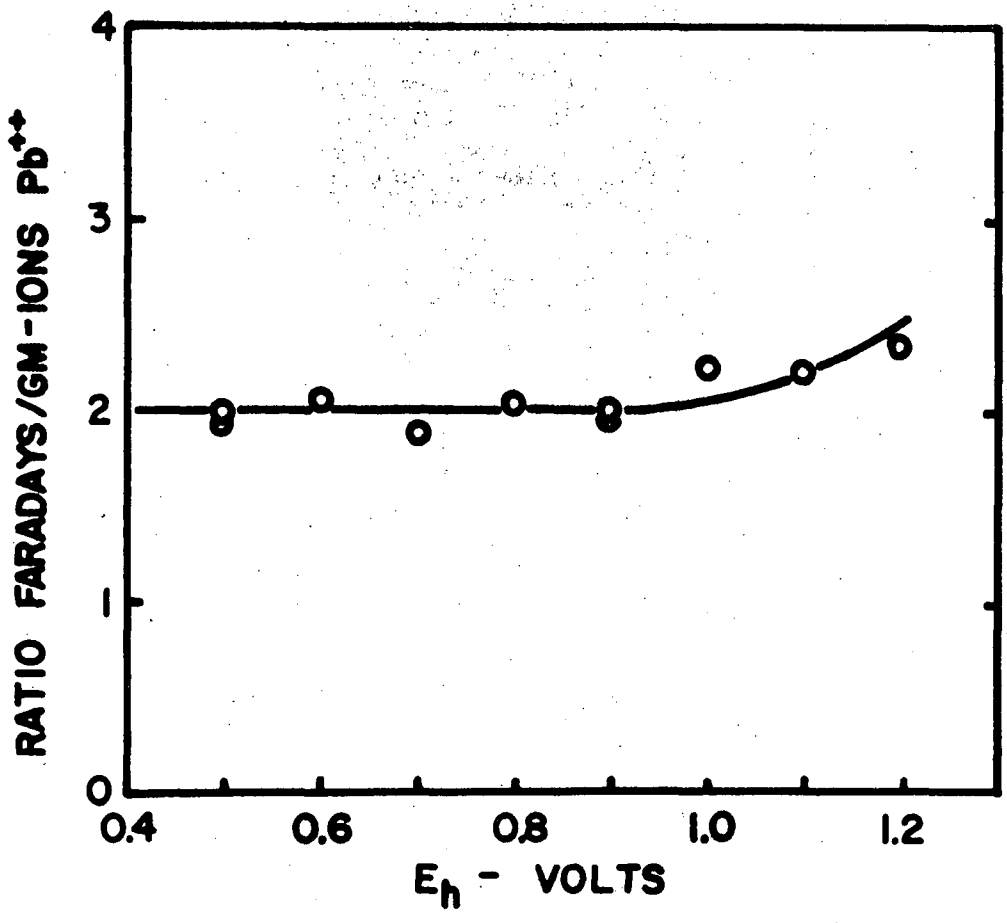


Figure (6) The stoichiometry of the anodic dissolution of galena as a function of E_h at pH = 0.

sulphur and lead sulphide was detected at all potentials. However, the highest F/gm-ion Pb^{++} ratio obtained, 2.33/1, represents a maximum of 4% of the PbS reacting to form $PbSO_4$ by reaction (23), which is too small an amount to be detected by common x-ray diffraction techniques.

These results indicate a departure from thermodynamic behavior since the pH-potential diagram predicts that at pH = 0, above about 0.3 volt, depending on $a_{Pb^{++}}$, sulphate should be formed.

IV The Nature of the Anodic Film

At potentials below about 0.6 volt, the anodic film was distinctly pale-yellow in color, indicating the presence of elemental sulphur. Above 0.6 volt, the film became dull-grey with no evidence of the sulphur, and strongly adherent. It was thought that this was due to the incomplete reaction of PbS.

To confirm that the PbS which showed up in the diffraction patterns was actually present in the surface film and not just removed from the unreacted mineral beneath the film, a galena electrode of very small surface area (.20 cm^2) was prepared; this was corroded at 1.2 volt for 12 hours to give a film about 3 mm. thick. Thus it was possible to remove the film without disturbing the unreacted PbS. The diffraction results confirmed that PbS was a primary constituent of the film.

From these results it was concluded that the anodic reaction proceeds according to reaction (4); below 0.6 volt, complete reaction takes place and the anodic film consists primarily of elemental sulphur;

above 0.6 volt, the reaction interface proceeds through the crystal, leaving an undetermined but considerable amount of unreacted PbS in the film.

V Stoichiometry of the Cathodic Reaction at pH = 0

The pH-potential diagram predicts that cathodization (reduction) of galena having a rest-potential on its upper boundary (as has been the case with the PbS used in this laboratory) should occur in a manner which first reduces the activity of sulphur, by the reaction

$$S^{o} + 2H^{+} + 2e^{-} \rightarrow H_2S \qquad (24)$$

until the lower boundary of PbS-stability is reached. At this point, further reduction according to the reaction

$$PbS + 2H^{+} + 2e^{-} \rightarrow Pb^{o} + H_2S \qquad (17)$$

should proceed. Below 0 volt, there is also the possibility of reduction of water to hydrogen, and if oxygen is present, it is thermodynamically reducible below 1.23 volt at pH=0. Since the effect of reaction (24) is to increase the activity of lead in PbS, and the hydrogen overvoltage on lead is very high, no hydrogen evolution would be expected. In addition, no oxygen reduction should occur since the solutions were purged with argon. Under these circumstances, it was expected that a high current efficiency for reaction (17) should be obtained at potentials for which practical current densities were possible.

To experimentally determine the current efficiency of reaction (17), a galena electrode was corroded at potentials from -0.3 to -1.0 volt in increments of 0.1 volt. The argon purge-gas containing evolved H_2S was passed through a 1M NaOH solution to absorb and permit analysis of H_2S.

The analytical procedure is given in Appendix D. An aspirator was used to draw the purge-gas through the caustic solution and to balance the pressure inside the electrolytic vessel since the system was prone to leakage. The vessel was sealed with tape and the aspirator adjusted until the pressure differential as determined by a mercury manometer became nil.

As can be seen from Figure (7) and Table V, Appendix C, the current efficiency of reaction (17) was over 95% except at potentials more positive than -0.5 volt. The current efficiency was observed to take a pronounced dip to about 80% at about -0.4 volt.

In Figure (8) are plotted the hydrogen overvoltage on lead as taken from Latimer[28], and the steady-state polarization curve for galena, as discussed later. At all potentials, the hydrogen overvoltage is higher than the polarized potential of the galena, except at about -.45 volt where the two curves come into coincidence. This coincidence explains the fall in current efficiency in the neighbourhood of -0.4 volt since it is only in this region that the conditions of current and polarized potential are favourable for hydrogen evolution.

As in the case of anodic reactions no attempt was made to correct for the potential drop across the galena electrode. However, in this case no insulating film was involved, and hence the resistance was more justifiably ignored.

VI The Polarization of Galena at pH = 0

A common technique in the study of metallic corrosion is the

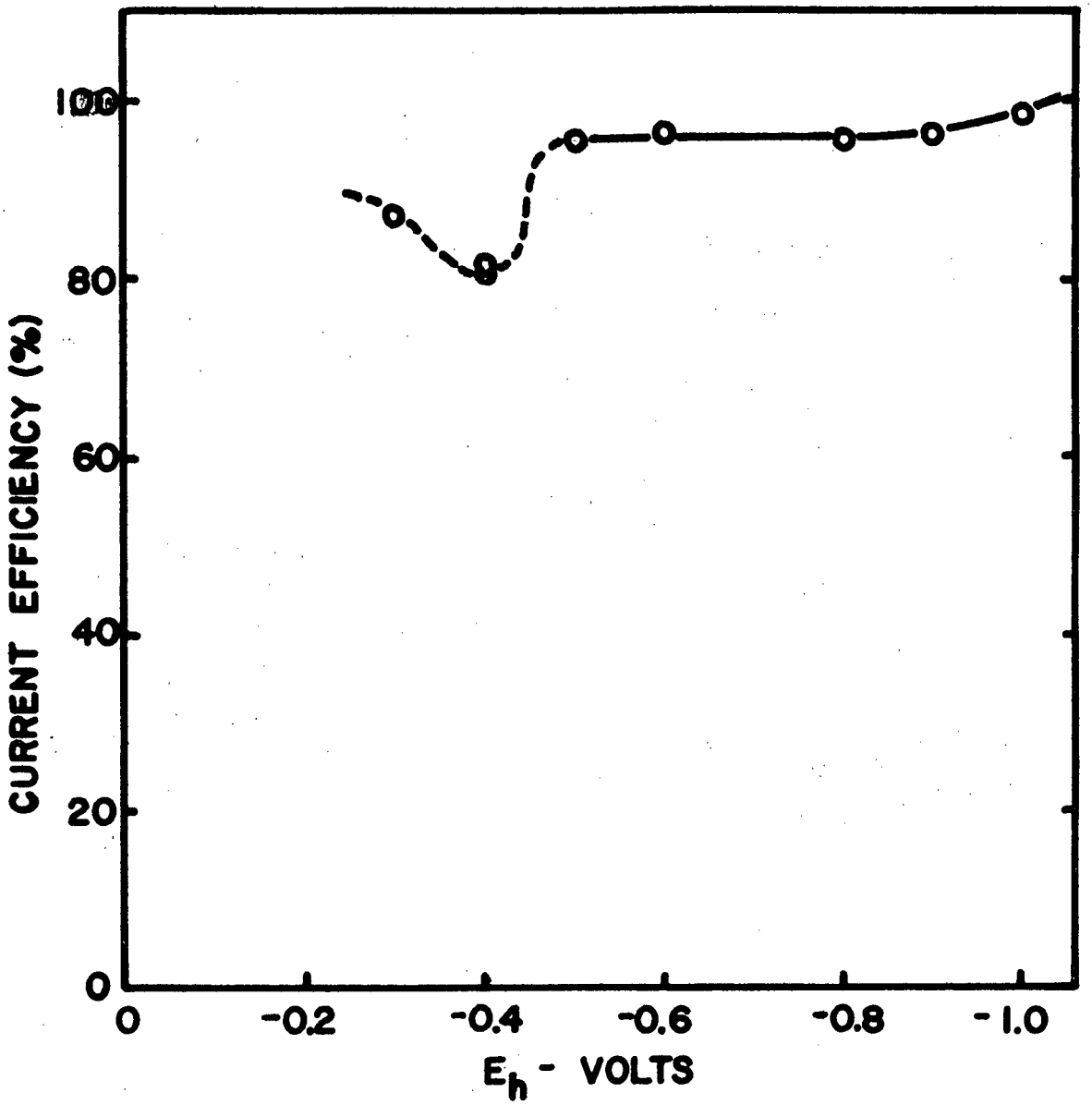


Figure (7) Current efficiency of the reaction $PbS + 2H^+ + 2e^- \rightarrow Pb^o + H_2S$.

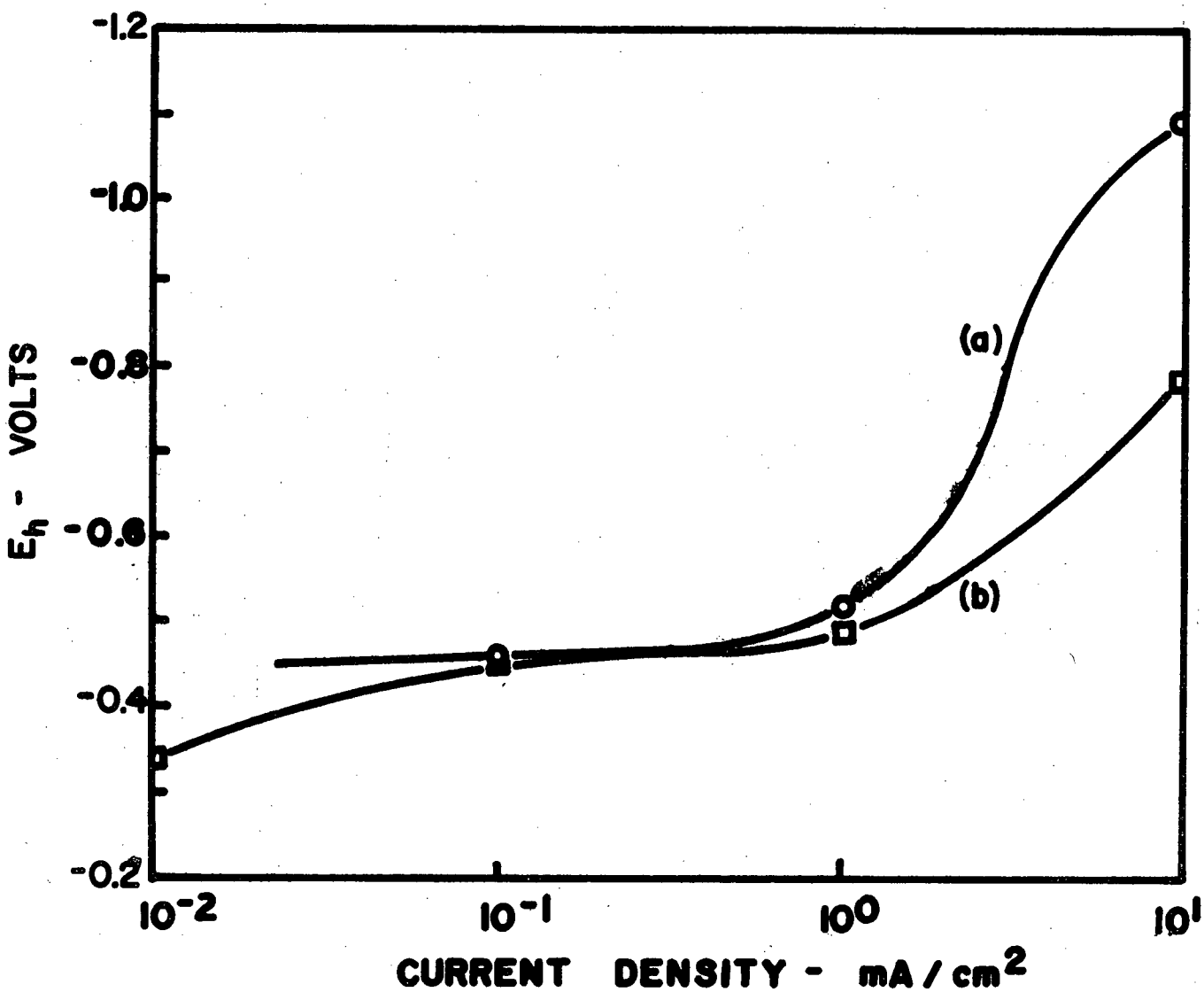


Figure (8) Coincidence of the hydrogen overvoltage curve (a) with the steady-state polarization curve (b) for galena.

determination of polarization curves. These express graphically the voltage-current relationships for a material when it is made either a cathode or anode in a corrosion cell. It was thought that this type of study could be performed on galena electrodes and would help in the understanding of how this mineral behaves under non-equilibrium, or current-carrying conditions.

Polarization is simply the change in potential of an electrode from its rest potential concomitant with a flow of current. The direction of potential change is always such as to oppose the shift from equilibrium. If the flow of current is controlled as the independent variable, the potential which the electrode assumes becomes the dependent, or measured variable. This is a "galvanostatic" technique for determining polarization curves, and is the more classical method. Conversely, if a potential is imposed on an electrode as the independent variable, a current will result and be measured as the dependent variable, a "potentiostatic" technique. Under certain conditions the curves determined by these two methods will be identical.

The results may vary depending on the method by which the potential is applied in the pototentiostatic case. If the potential is "scanned," the result is non-steady-state since current transients may be involved; in the case where the potential is applied in increments and the current allowed to reach a constant value for each value of potential, the result reflects steady-state conditions. In the figures mentioned below, polarization curves have been determined under several different conditions. However, for all runs the solution used was argon-purged 1M $HClO_4$ except where noted, and moderately stirred.

Two different galena electrodes, "X" and "Y", having cross-sectional areas of 1.79 and 2.47 cm^2 respectively, were used.

In Figure (9) are both anodic and cathodic steady-state polarization curves determined galvanostatically for electrode "X" in a solution containing 1M $Pb(ClO_4)_2$ as well as 1M $HClO_4$. The method of plotting, for consistency with later curves, is opposite to the normal convention, in that the independent variable, log current density, is the ordinate and the potential, E_h, is the abscissa.

Figures (10 and (11) show respectively, anodic and cathodic polarization curves determined potentiostatically for electrode "Y" in molar perchloric acid, for which the voltage scan rates were 4, 2, and 0 mv/sec. for curves (a), (b) and (c) respectively.

It is useful to discuss the behavior of galena according to the three types of polarization which can exist.

(a) Ohmic (iR) Polarization

The contribution from ohmic polarization, while normally negligible in metallic corrosion studies, is of greater consequence in studies involving galena because of its semiconductivity as well as its tendency to form insulating films. However, the critical variation of resistivity of this material around room temperature, the rectifying action of the PbS-Ag junction where electrical contact is made with the mineral*, and the presence of insulating anodic films all

* The effect of the rectifying junction is three-fold: the resistivity of the electrode can be expected to vary with current due to the typical non-linearity of rectifier voltage-current profiles; the overall resistivity will be remarkably different depending on the direction of current flow, i.e. for the anodic and cathodic directions; and the presence of current creep means that the resistance of the electrode for a particular current is not uniquely defined and hence will vary with scan rate.

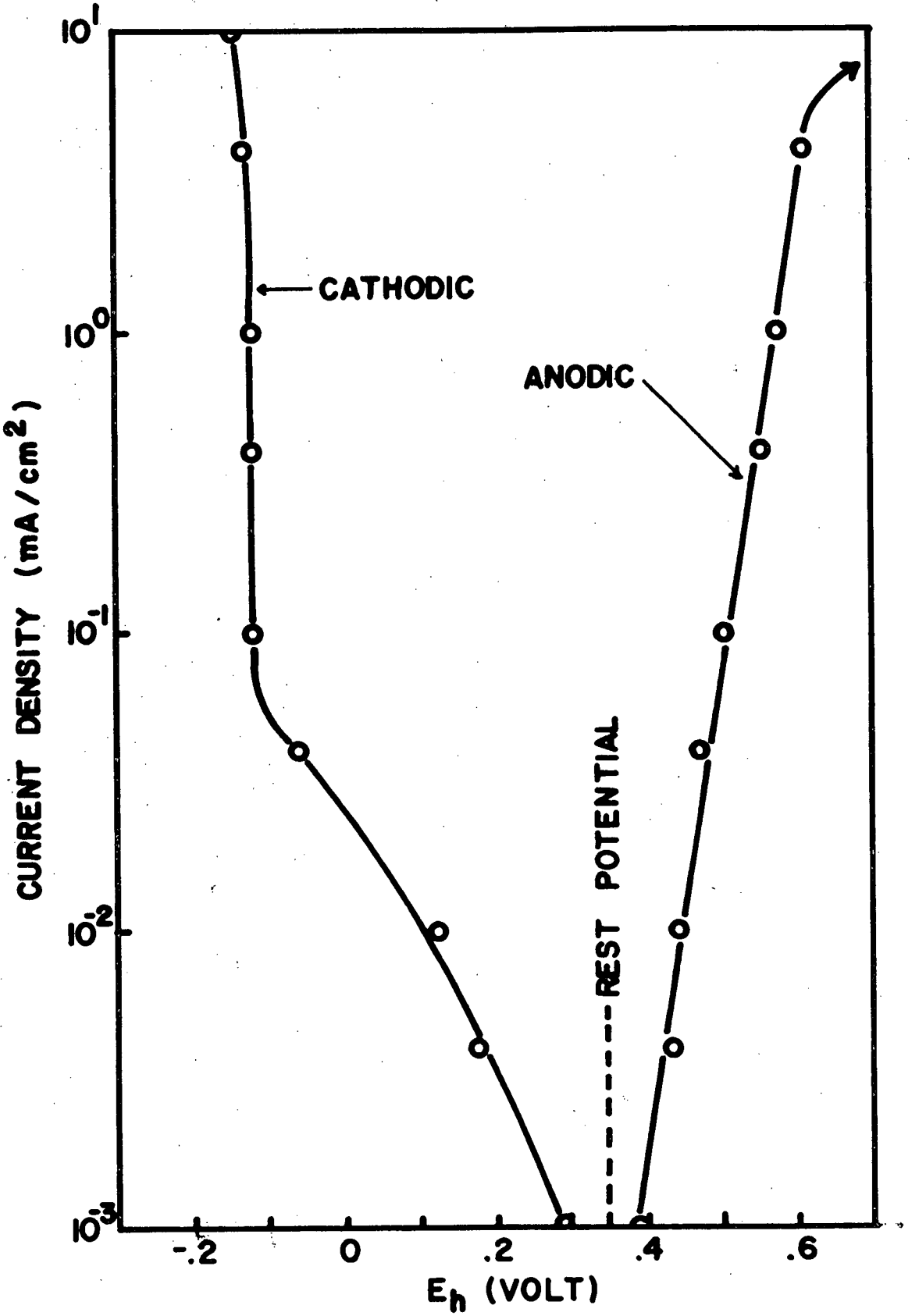


Figure (9) Galvanostatically - determined polarization curves (steady-state) in 1M $Pb(ClO_4)_2$ + 1M $HClO_4$ for electrode "X".

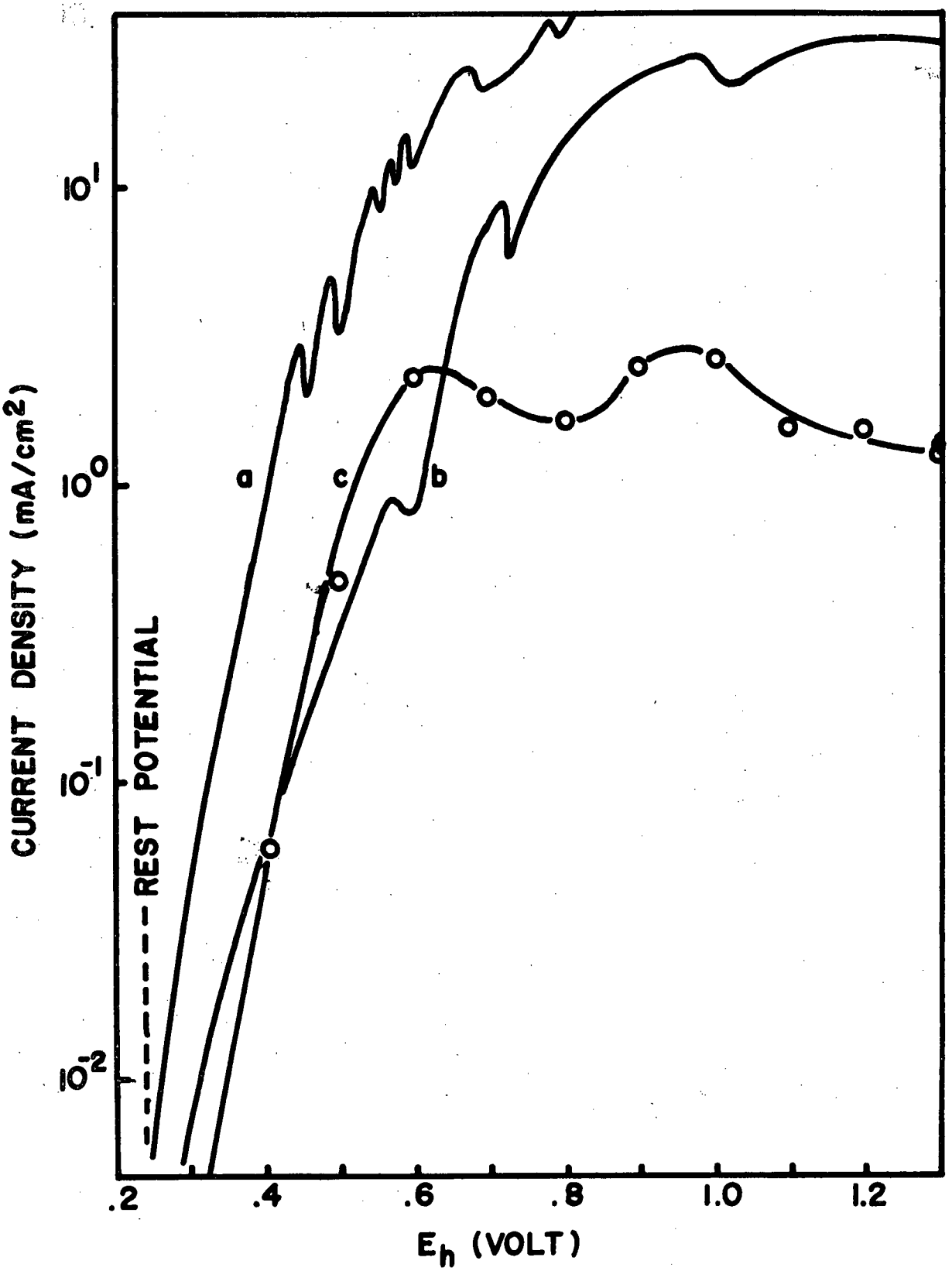


Figure (10) Anodic polarization curves in 1M $HClO_4$ for electrode "Y". Curve (a) 4 mv/sec. (b) 2mv/sec. (c) steady-state.

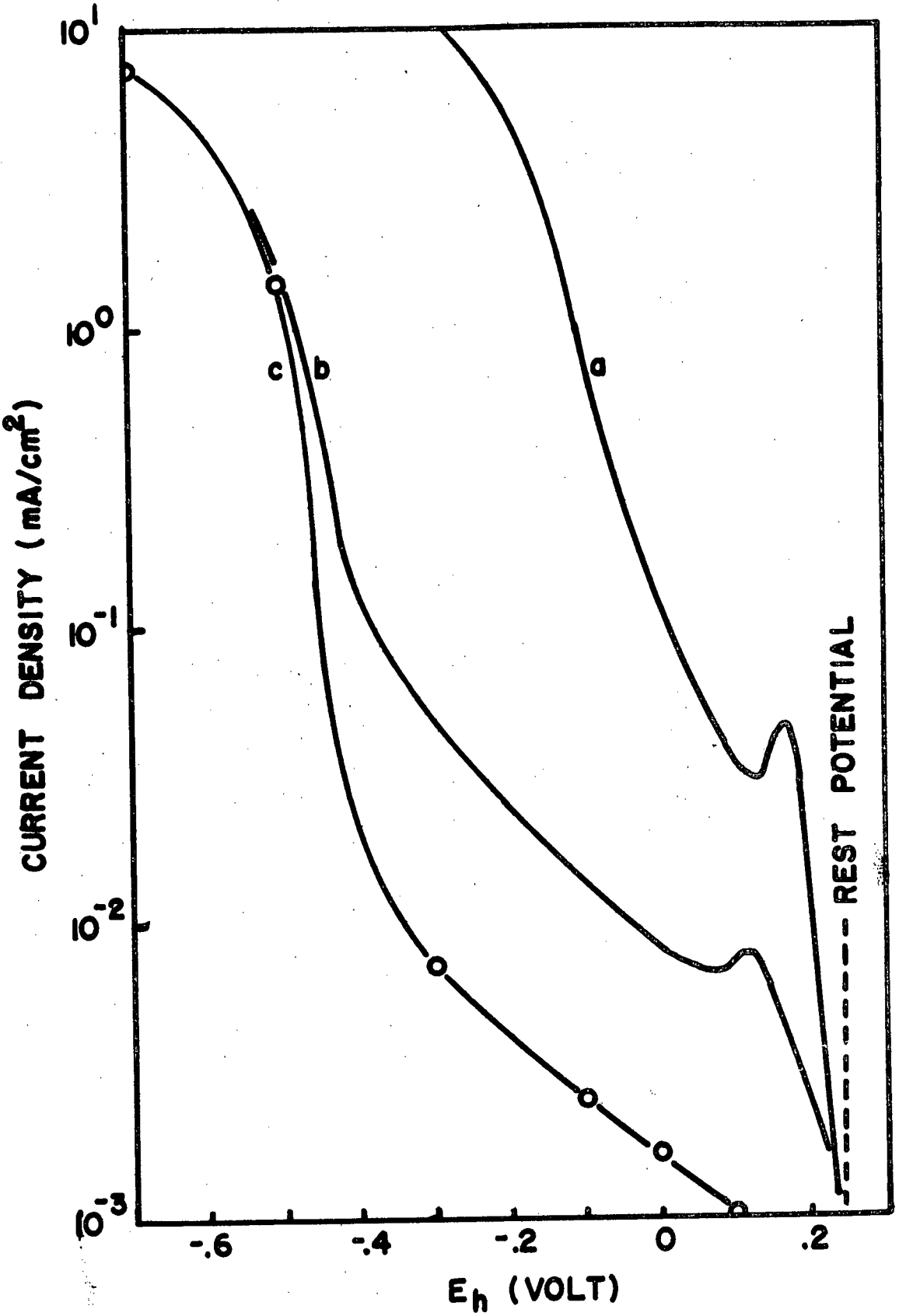


Figure (11) Cathodic polarization curves in 1M $HClO_4$ for electrode "Y". Curve (a) 4 mv/sec. (b) 2 mv/sec. (c) steady-state.

combine to present a formidable barrier to any quantitative evaluation of the ohmic contribution. A possible method of minimizing ohmic polarization has been proposed under CONCLUSIONS, Suggestions for Future Work.

It is obvious that the ohmic contribution increases with the current drawn (E = iR) and at higher current densities is probably the main contribution to polarization. The tendency of individual curves to level off at high current densities is attributed to the inherent resistivity of the galena, whereas an actual drop of any individual curve is a result of an increase in resistance due to the formation of an insulating film. This is consistent with the observation that while both anodic and cathodic curves tend to level off, only the anodic curves actually drop. It is believed that the first peak in curve (c) of Figure (10) corresponds to the point at which the sulphur film resistance becomes appreciable with respect to the inherent electrode resistance, hence the curve begins to drop. The second peak at about .95 volt probably corresponds to the initiation of $PbSO_4$ formation in accordance with previous suggestions. The general trend toward lower currents with lower scanning rates (and hence longer reaction times) is consistent with an increasing film resistance. However, another factor, the rest potential shift, is also important, and discussed in the next section.

For the case of cathodic polarization, the determination of (17) as the dominant cathodic reaction obviates the consideration of film resistance. The polarization curves are still subject to the inherent semiconductor resistance and hence tend to level off but do not drop.

As mentioned previously, iR drop via the electrolyte between the calomel electrode and the mineral surface was minimized by use of a Luggin capillary.

(b) Concentration Effects

Concentration polarization is given by the expression

$$\Delta Ec = \frac{.0591}{n} \log \frac{(a_M^{+n})s}{a_M^{+n}} \qquad (25)$$

where $(a_M^{+n})s$ and a_M^{+n} are the metal ion activities next to the electrode surface and in the main body of solution respectively and n is the number of electrons involved in the oxidation or reduction reaction. At the anode, $(a_M^{+n})s > a_M^{+n}$ since metal ions are being discharged, and therefore $\Delta Ec > 0$; at the cathode $\Delta Ec < 0$.

In equation (25), the term a_M^{+n} is usually considered to be a constant and the concentration polarization is a result only of changes in the metal ion activity in the region of the anode or cathode per se. However, in the situation under study, a change in the value of a_M^{+n} has an effect also.

It was shown in a previous section that the rest potential varied with a_{Pb}^{++} according to the equation:

$$E_h = .354 + .0295 \log a_{Pb}^{++} \qquad (12)$$

An increase in a_{Pb}^{++} during anodization would increase the rest potential and thus decrease the driving force for the anodic reaction. Since the polarization experiments of Figure (10) were performed in solutions containing initially no lead ions, and a_{Pb}^{++} was continually increased by the anodic reaction (4), the lowering of the curves for lower scanning rates is consistent with an increased rest potential. This

effect is most pronounced at small deviations from the original rest potential because a_{Pb}^{++} would rapidly increase over several orders of magnitude. The lowering of the anodic curves is probably primarily a result of rest potential shift at low current densities and primarily increased film resistance at higher current densities.

The lowering of the rest potential in the cathodic case is a consequence of a reduction in a_S^o in the galena by reduction to H_2S or what is equivalent, an increase in a_{Pb}^o by reaction (17). A very small decrease in sulphur activity has been shown to rapidly drop the rest potential. The lowering of the curves for lower scanning rates and hence longer reaction times is consistent with a decreasing sulphur activity. In addition, the build up of H_2S will contribute to both rest potential shift and concentration polarization.

(c) Activation Polarization

Activation polarization, η, is given by the Tafel equation

$$\eta = \beta \log i/i_o \qquad (26)$$

where β and i_o are temperature-dependent constants for a given environment and electrode. If activation overvoltage was the only important form of polarization involved, a plot of log i versus potential should yield a straight line. Even below current densities at which ohmic polarization was likely to become important, the non-linearity of the curves of Figures (10) and (11) suggested that this was not the case, i.e. concentration polarization was of importance also.

The curves of Figure (9) were determined in a solution

containing 1M $Pb(ClO_4)_2$. It was thought that because of the high lead-ion activity, a_{Pb}^{++} in expression (12) would remain constant, and the ratio $(a_{Pb}^{++})_s/a_{Pb}^{++}$ in expression (25) would remain close to unity. Therefore, concentration effects could be ignored. As seen from the figure, above 0.4 volt and below -.12volt the Tafel equation was obeyed. The relationship of the polarization curves to the equilibria involving PbS may best be understood by inspection of Figure (12). The equations for the equilibria plotted on the pH - E_h portion were obtained by substitution of $a_{Pb}^{++} = (Pb^{++}) = 1$, assuming $\gamma_{Pb}^{++} = 1$, into equations (12) and (21), with inclusion of the pH term. From Figure (12) it can be seen that at pH = 0, the non-linear portion of the steady-state polarization curves falls between the two equilibria determined previously as representing the upper and lower boundary of rest potential. At potentials above and below these bounds, the Tafel equation is obeyed and therefore activation is the dominant form of polarization under these conditions.

The non-linear portion of the cathodic curve of Figure (9) when integrated, corresponds to a very small amount of reaction, and is probably a combination of the following reactions:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (27)$$

$$S^o + 2H^+ + 2e^- \rightarrow H_2S \qquad (24)$$

Although the solution was purged with argon, oxygen was evolved at the platinum anode and so would be present in low concentration. This as well as adsorbed oxygen on the mineral surface could conceivably be reduced. Reduction of water to hydrogen gas is a possibility also,

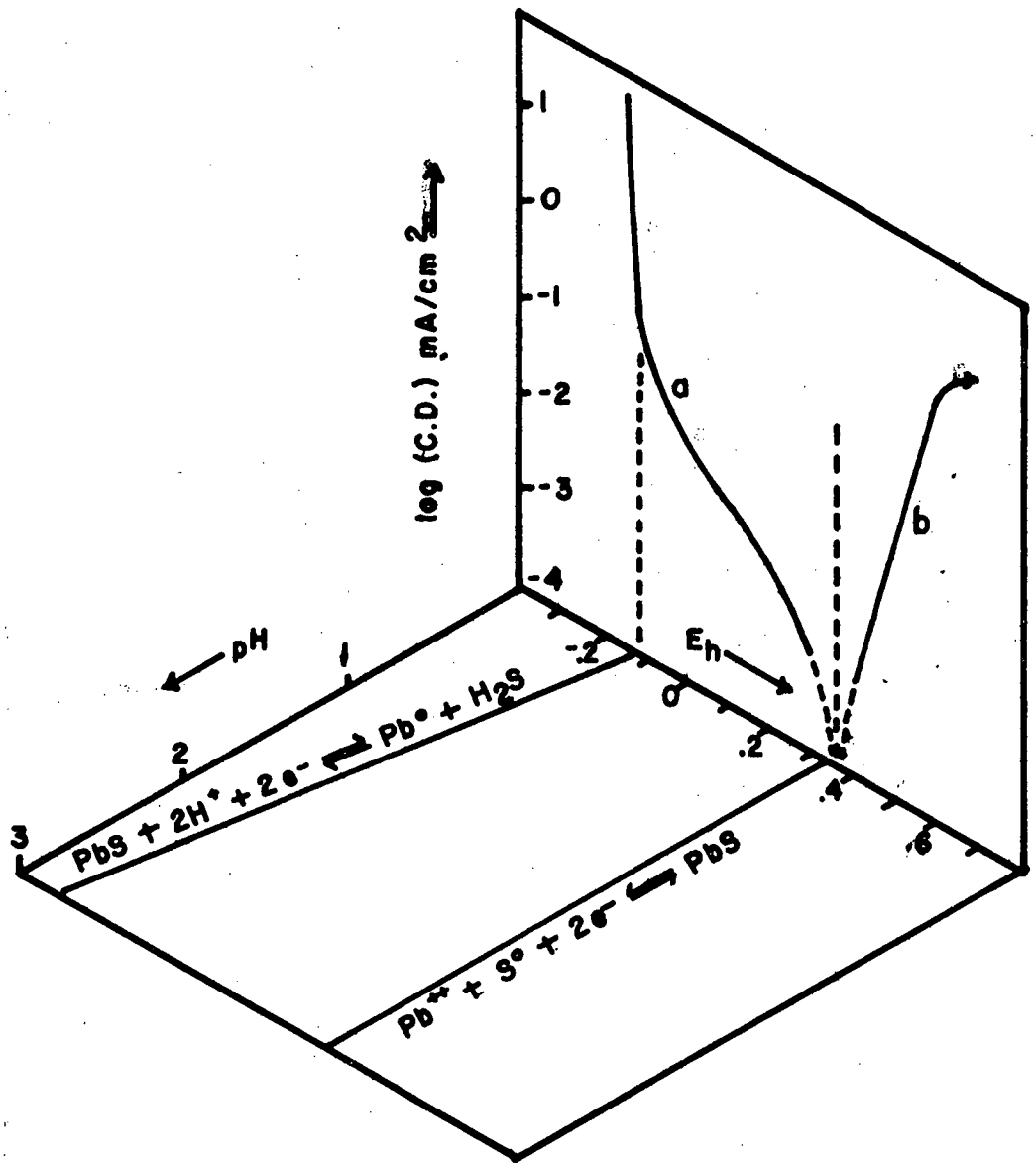


Figure (12) The relationship between polarization of PbS and equilibria at pH = 0.

(a) Cathodic Curve

(b) Anodic Curve

but due to the high hydrogen overvoltage on lead, is unlikely. Since the PbS electrode was initially saturated in sulphur as suggested by its high rest potential, reduction according to (24) is likely.

From these considerations, it appears that all three types of polarization mentioned contribute to the behavior of galena under current-carrying (non-equilibrium) conditions. The inherent resistivity of the galena as well as the formation of insulating films control its behavior at very high current densities, whereas at very low current densities the rest potential shift is significant. Under steady-state conditions, above the upper limit of rest potential, and below the lower limit, the Tafel equation was obeyed when concentration effects were minimized.

VII Anodization of Galena at pH > 0.

At pH = 0, it has been established that the equilibrium

$$Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS \qquad (11)$$

represents the upper boundary of PbS-stability. The oxidation to sulphate by the reaction

$$PbS + 4H_2O \rightarrow PbSO_4 + 8H^{+} + 8e^{-} \qquad (23)$$

has not been observed to occur below 0.9 to 1.0 volt, although it is favourable thermodynamically above about 0.3 volts. Since the irreversibility of the sulphate - producing reaction has been demonstrated at pH=0, it is also probable that irreversibility exists at higher pH.

Inspection of the pH - potential diagram reveals that for low $a_{Pb^{++}}$, above pH ≃ 0, the oxidation of PbS should yield sulphate directly, without the intermediate formation of elemental sulphur.

Although the method used in Section III could be used to determine the stoichiometry of the anodic reaction at pH other than zero, a less time-consuming but admittedly less rigorous method was adopted. A PbS electrode was submitted to oxidizing potentials in solutions of different pH and (Pb^{++}). The electrolysis was interrupted periodically to measure the rest potential assumed by the galena, and the value of this was taken to reflect the anodic reaction occurring. It was expected that the points, when plotted on the pH-potential diagram would fall along a line representing either the expected or a metastable equilibrium. One problem, of course, was the use of solutions of different composition and ionic strength which meant an estimation of activity coefficients would be required for accurate work. This was not done, and the assumption of activity equal to concentration was used.

The results are given in Table VI, Appendix C and in Figure (13). At pH = 0 and 2, the values of rest potential obtained for each anodizing potential were sufficiently close to permit the assumption that they represented the same value, and hence were averaged. At pH = 4 the rest potentials obtained for anodizing potentials of 0.4 and 0.7 volt were averaged, but at 1.0 volt the value showed a distinct tendency to drop; hence at 1.0 volt it was assumed that a different reaction was occurring.

A plot of these points (except the points just mentioned) on the pH-potential diagrams as in Figure (13) suggests that although the fit does not appear entirely satisfactory, the rest potential best fits the line representing the equilibrium

$$Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS \qquad (11)$$

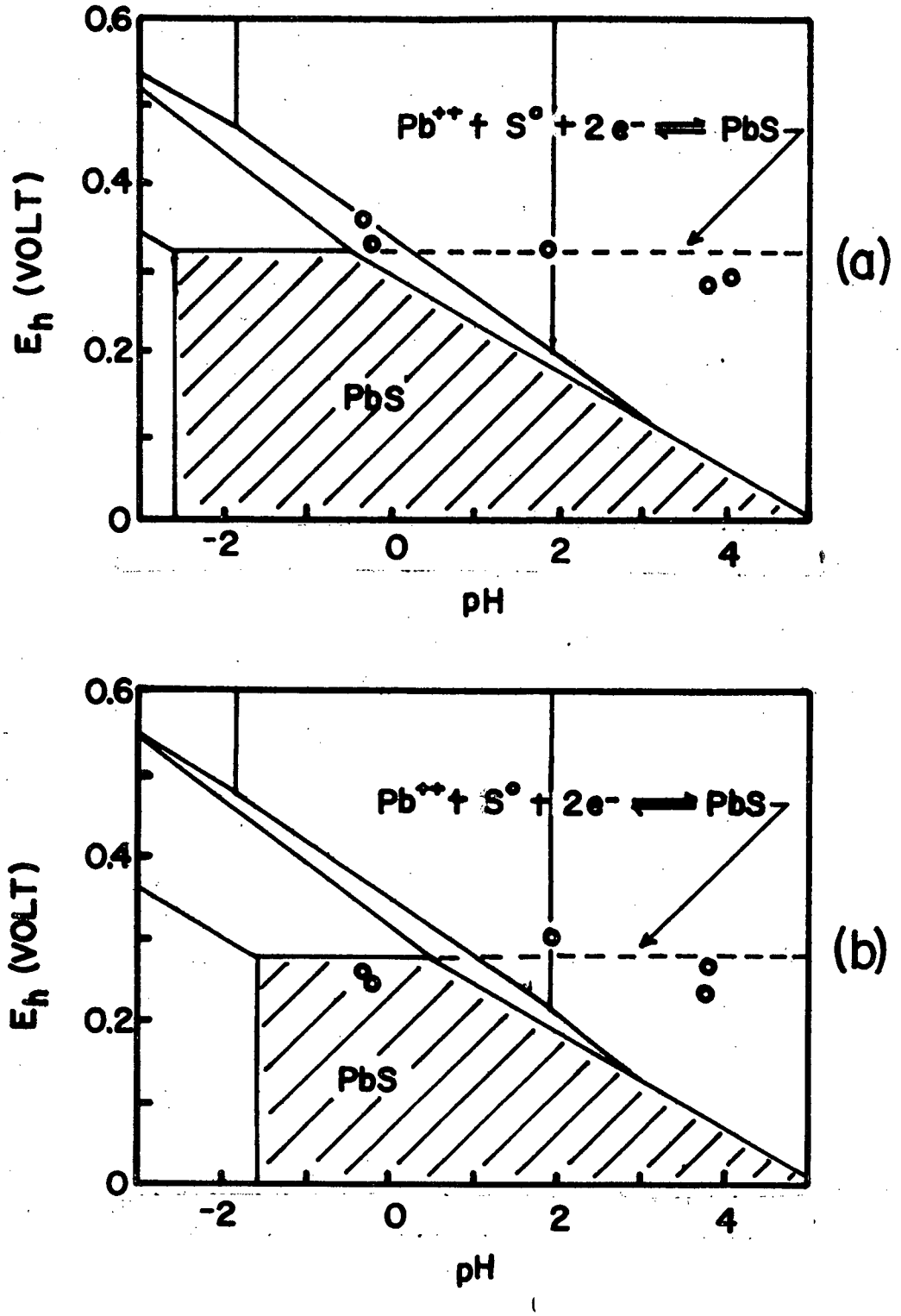


Figure (13) The values of rest potential as determined upon anodization of galena; (a) $[Pb^{++}] = 10^{-1}$M (b) $[Pb^{++}] = 10^{-3}$M.

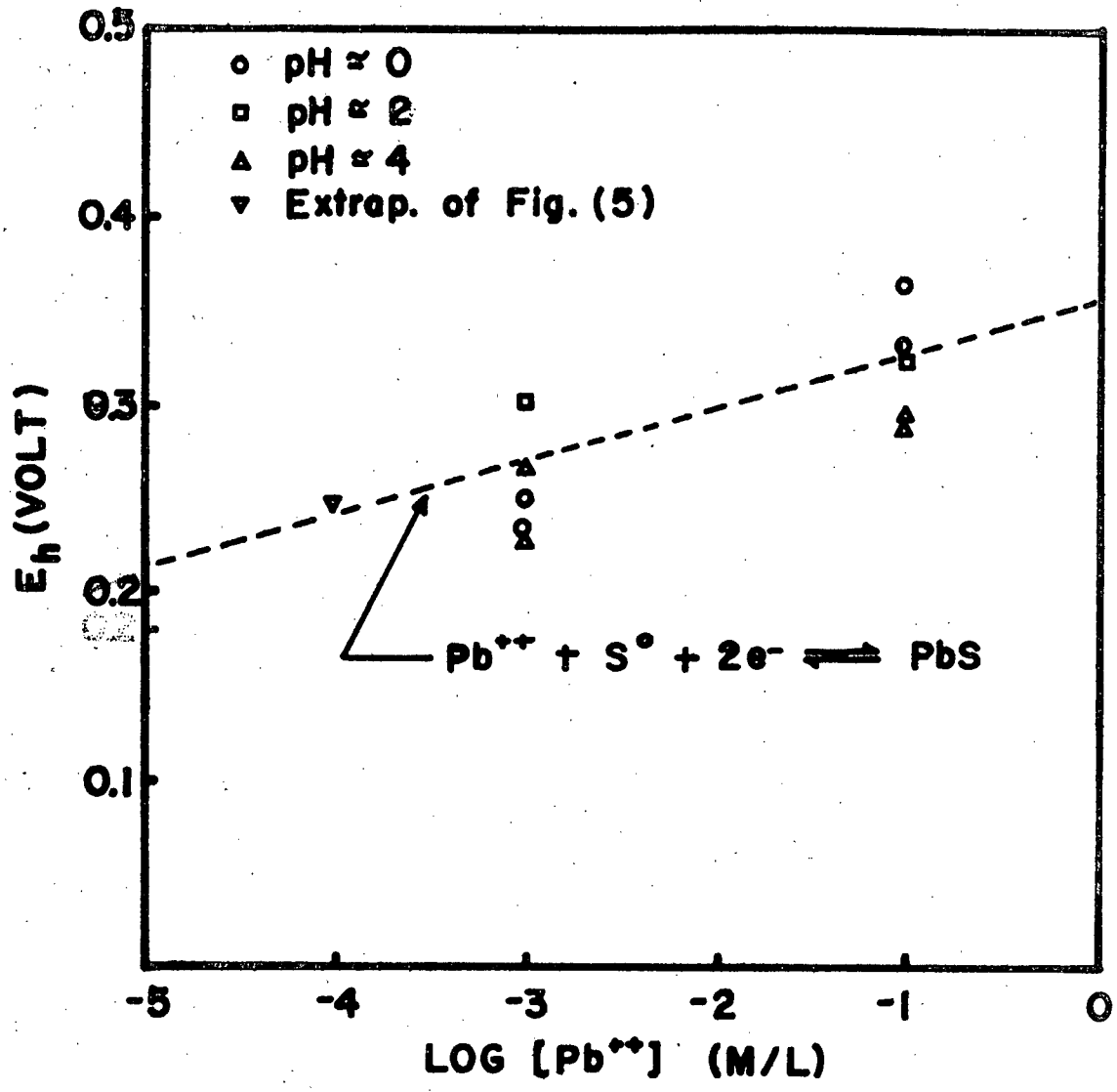


Figure (14) The values of rest potential, determined at various pH, as a function of $[Pb^{++}]$.

in spite of the thermodynamic prediction that it should fall along the line represented by the equilibrium:

$$PbSO_4 + 8H^+ + 8e^- \rightleftarrows PbS + 4H_2O \qquad (13)$$

In view of the simplification that activity equals concentration, and the likely existence of significant liquid-junction potentials, the fit is not unreasonable. However, if the points from both Figure (13(a)) and (13(b)) are plotted as a function of log $a_{Pb}{}^{++}$, Figure (14) results. The fit with equation (12) is considerably better. An additional point has been used from extrapolation of the curve of Figure (5).

The tendency of the rest potential to fall at pH = 4 after anodizing at 1.0 volt suggests that oxidation to sulphate is beginning under these conditions.

VIII The "Pseudo" pH-Potential Diagram

The results of previous sections suggest a modification of the thermodynamic pH-potential diagram to incorporate observed irreversible behavior as in Figure (15). The lower boundary of PbS-stability has been established at pH = 0, to be in accordance with the equilibrium

$$PbS + 2H^+ + 2e^- \rightleftarrows Pb^o + H_2S \qquad (15)$$

whose reversible potential is given by

$$E_h = -.339 - .0295 \log a_{H_2S} - .0591\ pH \qquad (16)$$

or when a_{H_2S} is not controlled by appropriate substitution:

$$E_h = - .126 + .0295 \log a_{Pb}{}^{++} \qquad (21)$$

This experimental lower boundary is in accordance with the thermodynamic boundary as predicted on the pH-potential diagram. There is adequate reason for belief that this equilibrium represents the lower boundary at pH > 0, although it has not been confirmed experimentally.

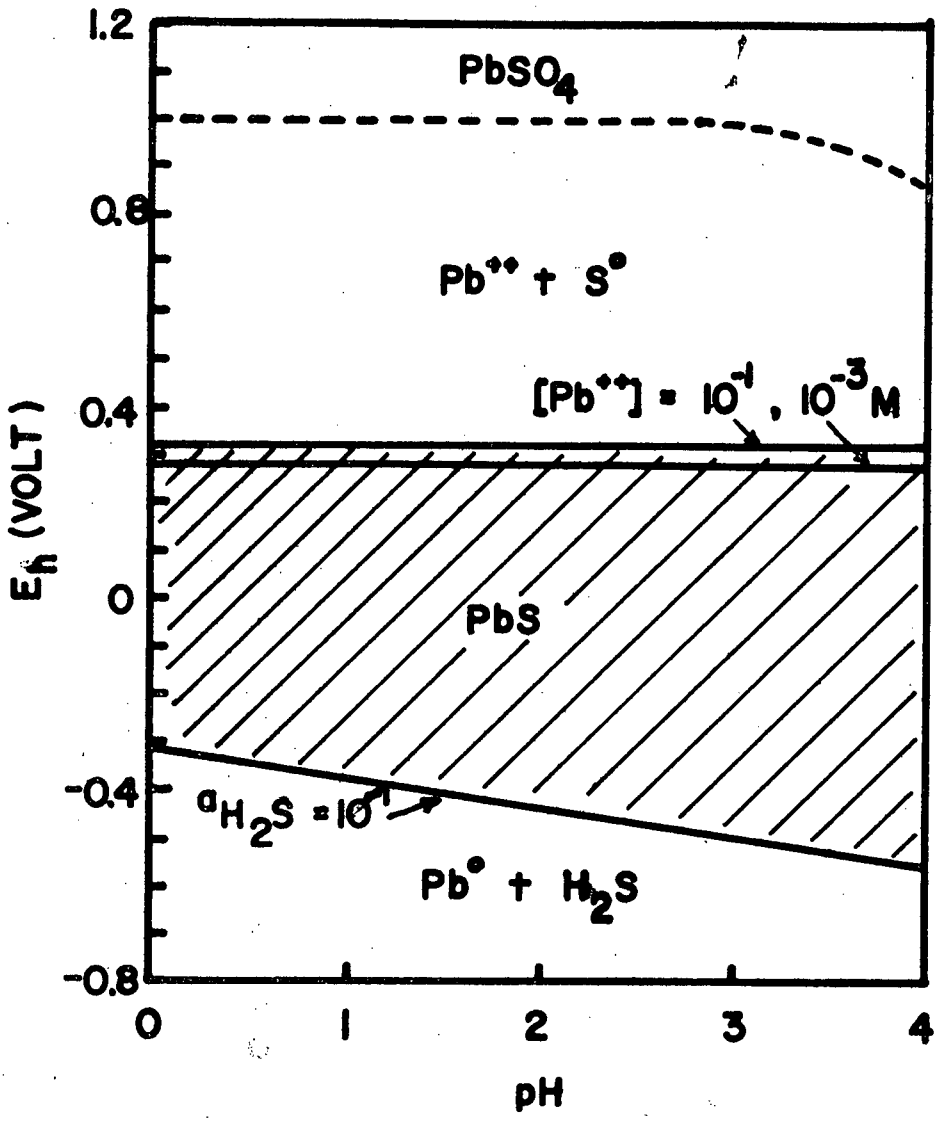


Figure (15) The "pseudo" pH-potential diagram for PbS as determined experimentally.

The upper boundary of PbS stability has been experimentally found to conform with the equilibrium

$$Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS \qquad (11)$$

whose potential is given by

$$E_h = + .354 + .0295 \log a_{Pb^{++}} \qquad (12)$$

between pH = 0 and 4. Above pH ≈ 0, this is not in agreement with the thermodynamic predictions of the pH-potential diagram.

The oxidation of PbS has been determined to occur according to the reaction

$$PbS \rightarrow Pb^{++} + S^{o} + 2e^{-} \qquad (4)$$

above the potential expressed by (12), and below 0.9 to 1.0 volt at pH = 0 and 0.7 to 1.0 volt at pH = 4. The elimination of ohmic polarization by methods outlined under CONCLUSIONS, suggestions for Future Work, would establish the actual potential at the electrode surface and allow a more accurate determination of the $(Pb^{++} + S^{o})/PbSO_4$ boundary.

VIX Galvanic Leaching of Galena

It has been shown that the electrochemical oxidation of galena in acid solution below about 1 volt generally yields lead ions and elemental sulphur, rather than the thermodynamically predicted product, lead sulphate. This immediately leads to the commercially interesting proposition of fabricating PbS into electrodes, electrolyzing, and recovering both lead and sulphur. This idea is not new, however. A possibility which has not received much previous attention is the imposition of potential through an electrically conducting oxidant such as PbO_2 or MnO_2. An intimate mixture of powdered PbS and either of these in a slurry

might be expected to react in a galvanic manner, with reduction of the oxidant and oxidation of the PbS occurring simultaneously.

In order to obtain a preliminary idea of the rates of such a reaction in this "galvanic" leach, 10.0 gm. of Pine Point Galena concentrate (-200 mesh) and 15.0 gm. of reagent grade PbO_2 (90%) or MnO_2 (99.5%) were made into a slurry with 250 ml. of 1M $HClO_4$. A typical assay of the Pine Point concentrate is given in Table III, Appendix B. Moderate stirring was employed and samples of solution were taken at frequent intervals to be analyzed for lead as described in Appendix E. The room temperature rate curves for both PbO_2 and MnO_2 are given in Figure (16). The solution potential was measured using a platinum and calomel electrode, and found to be between 0.9 and 1.0 volt for MnO_2 and 1.4 to 1.5 volt for PbO_2. The lower reaction rate for the MnO_2 leach is reflected by its lower potential. These potentials are not to be interpreted as standard electrode potentials since standard conditions were not employed and the measured potentials were undoubtedly polarized.

As can be seen from the curves of Figure (17), in which the percent PbS reacted was plotted as a function of time for the PbO_2 leach, the temperature dependence of the rate was fairly critical. The rate law of such a heterogenious reaction would undoubtedly be very complex as it involves the random contact between two solids of unknown surface area; no attempt was made in this direction.

It is expected that the results might depend quite heavily on the form of PbO_2 or MnO_2 used because of the relative oxidizing power as well as the ability of certain forms to undergo less polarization

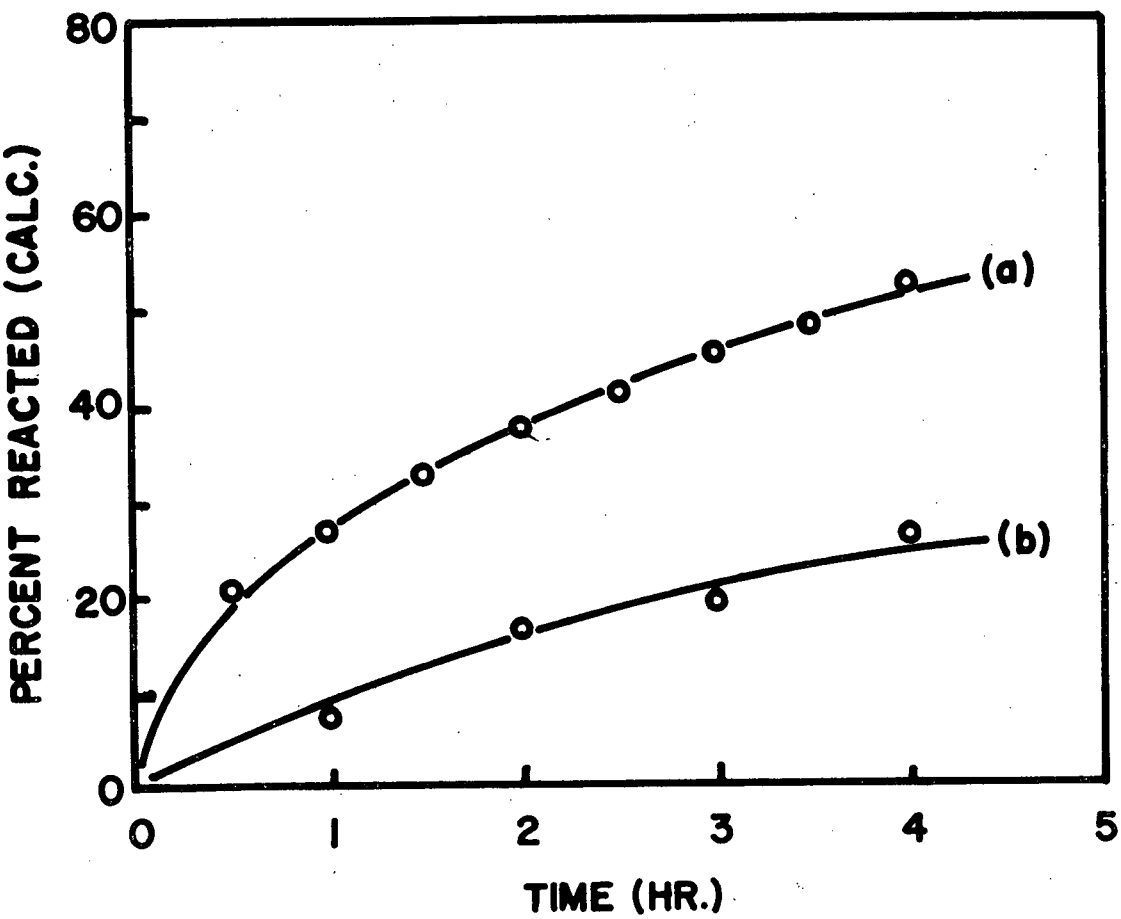


Figure (16) Rates of leaching at 25°C for
(a) $PbS + PbO_2$ and
(b) $PbS + MnO_2$

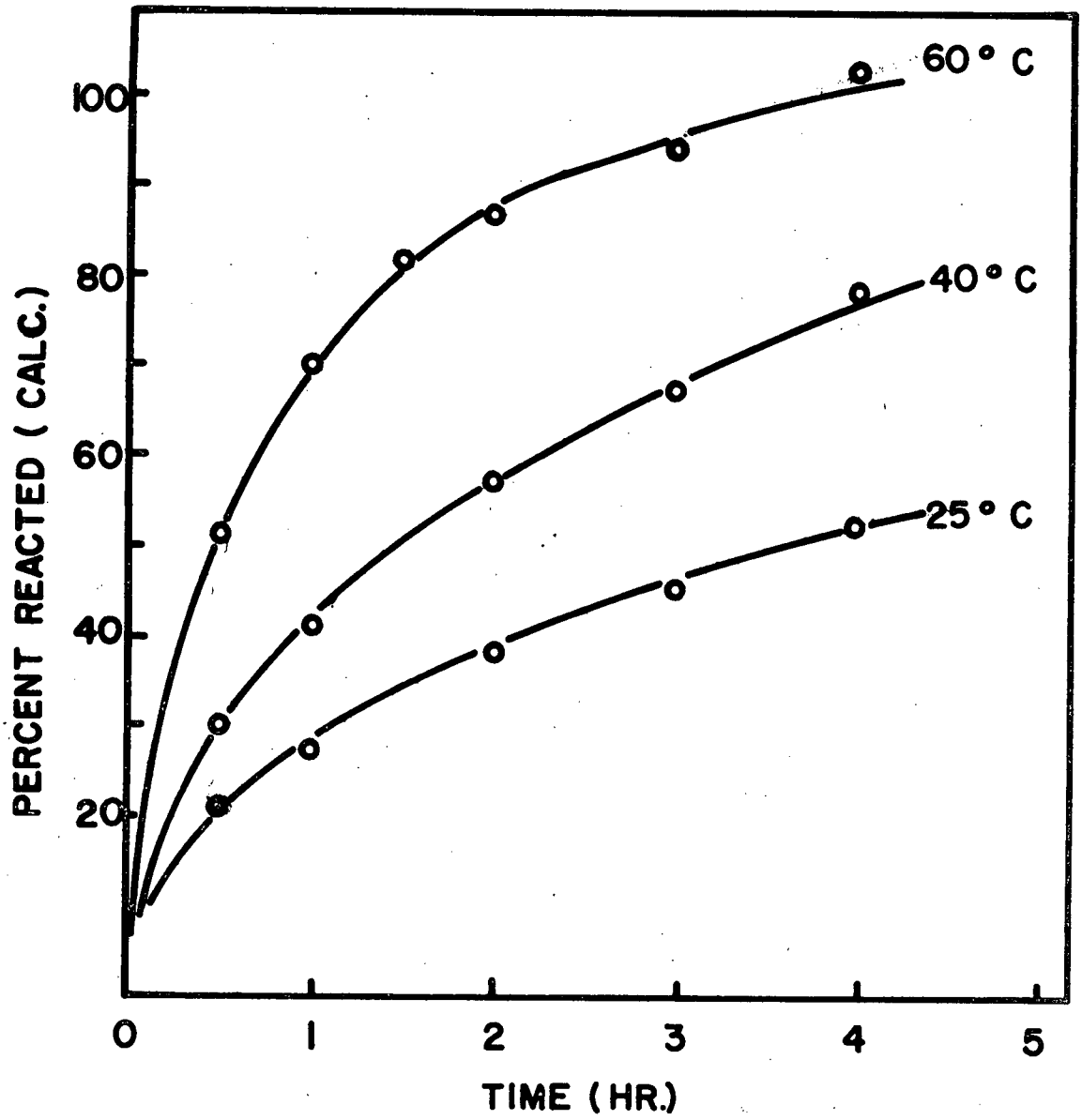


Figure (17) Rates of leaching of PbS + PbO_2 at different temperatures.

than others. The stoichiometry of PbO_2 is known to be variable[34] ($PbO_{\neq 1.95}$), and exists in two forms, α - and β - PbO_2. The β - form, whose preparation is discussed by Hamer,[35] is generally produced electrolytically at low pH. The potentials of the two forms are reported to be different but the magnitude of the difference is not generally agreed upon[36].

According to Maxwell and Thirsk[37], MnO_2 exists in four modifications, termed α-, β-, γ-, and δ-MnO_2. The standard electrode potential of each of these forms was measured (by Maxwell and Thirsk) under very closely controlled conditions and varied between 1.23 and 1.30 volts. This difference is not enough per se to suggest the use of one form over another. The important difference is the degree of polarization upon current flow and hence the ability to maintain a potential. In a galvanic leach as just described, the measured potential of the MnO_2 (pyrolusite, or β-MnO_2) was considerably lower than its standard electrode potential ($E^o \simeq 1.23$ volt), whereas the PbO_2 exerted a potential very close ($E^o \simeq 1.45$ volt). This is presumably a result of the rapid polarization of MnO_2 as compared to PbO_2. γ-MnO_2, the electrolytic form used in dry cell batteries, is reputed to undergo considerably less polarization and would therefore be a more desirable form[24].

In view of the previous conclusion that some oxidation to sulphate was suspected above about 1.0 volt, it is surprising that for the PbO_2 leach, almost 100% reaction to Pb^{++} was observed after four hours at 60°C. It is believed that if PbO_2 was present in great excess, further oxidation to sulphate and a resulting decrease in the

recoverable lead would result from precipitation of $PbSO_4$. However, because approximately stoichiometric amounts of PbS and PbO_2 were used for the reaction

$$PbS + PbO_2 + 4H^+ \rightarrow 2Pb^{++} + S^o + 2H_2O \qquad (28)$$

and because of the slowness of sulphur oxidation to sulphate, it was thought the reaction proceeded entirely according to (28). Once both the PbS and PbO_2 were consumed by the kinetically faster reaction, little PbO_2 was available for further oxidation. In the case of MnO_2, in spite of the fact that an excess was present, the polarized potential was not sufficient for oxidation to sulphate.

CONCLUSIONS

I General

(1) The reduction potential of the saturated calomel electrode containing an asbestos fibre liquid-liquid junction was found to be suppressed by strong perchloric acid solutions. The magnitude of the depression varied but was in the neighbourhood of 30 mv; it was not resolved whether this was a liquid-junction effect due to hydrogen ions or an attack on the KCl solution in the electrode by the perchlorate ion.

(2) The rest potential of galena was shown to be dependent on the activities of species involved in the equilibrium reactions of PbS. A range of rest potential between -0.27 volt and +0.27 volt was experimentally observed for galena in 1M $HClO_4$ containing from 3 to 100 ppm lead, by artificially causing the surface composition of a PbS electrode to vary between its stoichiometric limits. The upper limit was consistent with the equilibrium

$$Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS \qquad (11)$$

and the lower limit was consistent with

$$PbS + 2H^{+} + 2e^{-} \rightleftarrows Pb^{o} + H_2S \qquad (15)$$

The wide variation of rest potential of galena as reported in the literature was explained on this basis.

(3) The polarization curves determined under conditions in which concentration polarization was minimized, and at current densities for which ohmic polarization was negligible, obeyed the Tafel equation and hence were subject to activation polarization.

Under other conditions, all three types of polarization were important and the shape of the curves was particularly sensitive to film resistance, inherent resistiviy of the electrode, and the concentration of reaction products.

(4) At pH = 0, between 0.4 and 1.0 volt, PbS was determined to react at essentially 100% current efficiency by the anodic reaction:

$$PbS \rightarrow Pb^{++} + S^{o} + 2e^{-} \qquad (4)$$

Above 1.0 volt, the results strongly suggested but did not rigorously prove that oxidation to sulphate was beginning.

(5) At pH = 0, between - 0.3 and - 1.0 volt, PbS was observed to react at 80 to 100% current efficiency by the cathodic reaction:

$$PbS + 2H^{+} + 2e^{-} \rightarrow Pb^{o} + H_2S \qquad (17)$$

(6) From information gathered from stoichiometry determinations, polarization curves, and rest potential measurements, the behavior of PbS between pH = 0 and 4 was summarized on a "pseudo" pH-potential diagram which incorporated both thermodynamic and appropriate kinetic information. The upper and lower limits of rest potential were dictated by the equilibria (11) and (15) mentioned in (2) above. Above the upper limit of rest potential the anodic reaction was interpreted to be reaction (4), up to about 1.0 volt at pH = 0 and 0.7 to 1.0 volt at pH = 4. Above this poorly - defined limit, oxidation to sulphate was suspected but not rigorously proved.

(7) Above 0.6 volt, the anodic corrosion of single crystals of PbS was observed to proceed by movement of a reaction interface through the mineral but with much of the material left unreacted;

below 0.6 volt, the reaction film appeared to consist predominantly of elemental sulphur.

(8) An approximately stoichiometric slurry of PbS and PbO_2 in 1M $HClO_4$ was found to be about 50, 80, and 100% reacted after four hours at 25, 40, and 60°C respectively, to yield elemental sulphur and lead ions. The leaching with MnO_2 was considerably slower; only about 25% reacted after four hours at 25°C even with a large excess of MnO_2 present.

II Suggestions for Future Work

(1) A more accurate determination of the potential corresponding to the onset of sulphate formation is needed. In connection with this is a knowledge of the actual potential at the electrode surface, which would be known if the ohmic contribution to polarization were eliminated. This could be done by platinum "sputtering" on the six sides of the galena cube, and removal of the platinum from the exposed face of the electrode by polishing. This would cause electrical shorting of the mineral and eliminate the potential drop due to electrode resistance.

(2) Elimination of the reference electrode depression by strong perchloric acid is advisable if accurate potential measurements are to be made; the calomel reference electrode should be a "sleeve-type" rather than a "asbestos-fibre" type since the more rapid flowrate of the former will prevent diffusion of $HClO_4$ into the reference electrode; effects due to precipitation of $KClO_4$ at the junction also would be less serious.

(3) The oxidation of anodes made from pressed or cast PbS, or permeable bags containing powdered PbS should be investigated as a possible commercial process.

(4) Another possible application which should be investigated is the oxidation of an acid slurry of galena to Pb^{++} and S^{o} by contact with a conducting container such as graphite placed at an appropriate positive potential. Oxidation of powder is advantageous in that no fabrication of electrodes is necessary, and both inherent and film resistances are minimized. The cathode could be separated from the slurry by a semi-permeable membrane. Solution purification would be required and could be performed in a manner similar to that done at Inco for Ni_3S_2[9] with a head maintained on the cathode compartment to prevent diffusion of impurities inward.

(5) An investigation should be carried out to determine the rates of PbS leaching obtainable with each of the various forms of MnO_2, in particular, the electrolytic grade, as this is the form which would probably be produced in any recovery process for MnO_2.

(6) The deportment of impurities such as sulphides of Zn, Fe, Ag, As, Sb, Bi, In, and Sn during the anodic dissolution of galena needs to be investigated. This is of utmost importance with regard to commercial processing.

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APPENDIX A

THE EQUILIBRIA INVOLVED IN THE pH-POTENTIAL DIAGRAMS OF FIGURES (2(a) AND (2(b))

Equations have been calculated for a total sulphate activity (as $SO_4^{=}$, HSO_4^{-}, or H_2SO_4) of unity, $a_{H_2S} = 10^{-1}$, and $a_{Pb^{++}} = 10^{0}$ and 10^{-3}, using the I.U.P.A.C. convention for reduction potentials.

(a) $PbS + 2H^{+} + 2e^{-} \rightleftarrows Pb^{o} + H_2S$

$E_h = - .310 - .0591\ pH$

(b) $2H^{+} + 2e^{-} \rightleftarrows H_2$

$E_h = 0.00 - .0591\ pH$

(c) $S^{o} + 2H^{+} + 2e^{-} \rightleftarrows H_2S$

$E_h = .172 - .0591\ pH$

(d) $Pb^{++} + S^{o} + 2e^{-} \rightleftarrows PbS$

If $a_{Pb^{++}} = 10^{0}$, $E_h = .354$

If $a_{Pb^{++}} = 10^{-3}$, $Eh = .275$

(e) $PbSO_4 + 8H^{+} + 8e^{-} \rightleftarrows PbS + 4H_2O$

$E_h = .298 - .0591\ pH$

(f) $SO_4^{=} + 8H^{+} + 6e^{-} \rightleftarrows S^{o} + 4H_2O$

$E_h = .357 - .0788\ pH$

(g) $HSO_4^{-} + 7H^{+} + 6e^{-} \rightleftarrows S^{o} + 4H_2O$

$E_h = .339 - .0689\ pH$

(h) $H_2SO_4 + 6H^{+} + 6e^{-} \rightleftarrows S^{o} + 4H_2O$

$E_h = .357 - .0591\ pH$

(i) $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$

$pH = -1.9$

(j) $HSO_4^- \rightleftarrows H^+ + SO_4^=$

$pH = +1.9$

(k) $Pb^{++} + H_2S \rightleftarrows PbS + 2H^+$

If $a_{Pb^{++}} = 10^0$, $pH = -3.09$

If $a_{Pb^{++}} = 10^{-3}$, $pH = -1.59$

(l) $Pb^{++} + 2e^- \rightleftarrows Pb^0$

If $a_{Pb^{++}} = 10^0$, $E_h = -.126$

If $a_{Pb^{++}} = 10^{-3}$, $E_h = -.218$

(m) $PbSO_4 + 8H^+ + 6e^- \rightleftarrows Pb^{++} + S^0 + 4H_2O$

If $a_{Pb^{++}} = 10^0$, $E_h = .279 - .0788\ pH$

If $a_{Pb^{++}} = 10^{-3}$, $E_h = .309 - .0788\ pH$

APPENDIX B

TABLES OF MATERIAL ASSAYS

TABLE II

SPECTROGRAPHIC ANALYSIS OF GALENA SAMPLES
"X" AND "Y" AS DETERMINED BY
COAST ELDRIDGE ENGINEERS

	Percent by weight						
Samples	Ca	Fe	Mg	Si	Ag	Ti	Zn
"X"	.003	.001	.001	.001	T	<.001	<.01
"Y"	.001	<.001	N.D.	N.D.	T	T	<.01

Elements other than Pb, S and not listed above were not detected.

N.D. = Not detected.

T = Trace

TABLE III

TYPICAL ASSAY OF PINE POINT GALENA CONCENTRATE USED IN LEACHING EXPERIMENTS

Element	%
Pb	78.0
Zn	1.7
Fe	3.0
S	16.1

APPENDIX C

TABLES OF EXPERIMENTAL RESULTS

TABLE IV

STOICHIOMETRY OF THE ANODIC DISSOLUTION OF GALENA AT pH = 0

E_h (volts)	Apparent Surface Area (cm^2)	Coul. Passed	Ratio Faradays/ gm-ion Pb^{++}
0.50	3.40	10.1	1.93
0.50	1.79	30.15	1.99
0.60	3.40	10.0	2.05
0.70	1.79	32.5	1.90
0.80	3.40	12.6	2.04
0.90	3.40	10.0	1.98
0.90	1.79	31.4	2.02
1.00	.20	10.0	2.22
1.10	.20	10.3	2.19
1.20	.20	12.1	2.33

TABLE V

CURRENT EFFICIENCY OF THE CATHODIC REACTION OF GALENA AT pH = 0

Eh (volts)	Faradays	H_2S (moles)	Ratio F/H_2S	Current Effic. (%)
-0.30	1.036×10^{-3}	4.52×10^{-4}	2.29	87.2
-0.40	1.605×10^{-4}	6.45×10^{-5}	2.49	80.2
-0.40	1.036×10^{-3}	4.24×10^{-4}	2.44	81.7
-0.50	3.54×10^{-3}	1.69×10^{-3}	2.10	95.5
-0.60	5.28×10^{-4}	2.54×10^{-4}	2.08	96.1
-0.80	1.056×10^{-3}	5.05×10^{-4}	2.09	95.7
-0.90	1.056×10^{-3}	5.07×10^{-4}	2.08	96.1
-1.00	1.056×10^{-3}	5.22×10^{-4}	2.02	98.5

Electrode XS Area = 2.47 cm^2

TABLE VI

THE ANODIZATION OF GALENA AT pH > 0 AND THE MEASURED REST POTENTIAL

Solution	pH	Pb^{++} M/L	$E_{cal.}$ (corrected) (volt)	Eanodizing (volt)	E_{rest} (volt)
A	-0.2	10^{-1}	.214	.4,.7,1.0	.327
A	-0.2	10^{-3}	.214	.4,.7,1.0	.245
B	-0.3	10^{-1}	.214	.7,1.0	.361
B	-0.3	10^{-3}	.206	.7,1.0	.260
A	1.9	10^{-1}	.244	.4,.7,1.0	.325
A	1.9	10^{-3}	.244	.4,.7,1.0	.302
C	4.1	10^{-1}	.238	.4,.7	.295
				1.0	< .266
C	3.8	10^{-3}	.238	.4,.7	.266
				1.0	< .228
D	3.8	10^{-1}	.244	.4,.7	.286
				1.0	.278
D	3.9	10^{-3}	.242	.7	.230
				1.0	.202

Solution	Composition
A	$HClO_4$, $Pb(ClO_4)_2$
B	$HClO_4$, $Pb(C_2H_3O_2)_2$
C	$HC_2H_3O_2$, $NaC_2H_3O_2$, $Pb(ClO_4)_2$
D	$HC_2H_3O_2$, $NaC_2H_3O_2$, $Pb(C_2H_3O_2)_2$

APPENDIX D

ANALYTICAL PROCEDURE FOR H_2S DETERMINATION

Reagents:

Silver Nitrate Solution (.001M)

Analytical grade $AgNO_3$ was dried at 120°C for two hours and allowed to cool in a desiccator. 8.496 gm. was weighed out, dissolved in water, and made up to 500 ml. in a volumetric flask, to give a .100M solution; 10.0 ml. of this solution was pipetted and further diluted to 1000 ml. to give a .001M solution.

Procedure:

The H_2S, which exists in strongly basic solution as $S^=$, was trapped in a 400 ml. solution of molar sodium hydroxide. After a run, this solution was made up to 500 ml. and 100 ml. aliquots taken for analysis. The aliquot was titrated with the silver nitrate solution, as prepared above, while recording the potential with a sulphide-ion sensitive electrode (Orion Model 94-16) and a sleeve-type calomel electrode.

Extreme care was required to exclude air from the caustic solution by working under an argon atmosphere, since it was found that upon exposure to air, the titration endpoint changed rapidly with time. This was probably due to slow oxidation of $S^=$ to $S_2O_3^=$ by oxygen. To obtain a sharp endpoint, it was found necessary to perform the titration immediately after the run.

APPENDIX E

ANALYTICAL PROCEDURE FOR LEAD DETERMINATION

Reagents:

(a) Xylenol Orange Indicator

About 100 mg. of xylenol orange was made up to 100 ml. with a 1:1 ethanol/H_2O solution.

(b) E.D.T.A. Solution (0.05N)

18.61 gm. of disodium ethylenediaminetetraacetate was made up to 1000 ml. with distilled water.

(c) Buffer Solution (pH ~ 5)

100 ml. of 0.1M acetic acid was mixed with 200 ml. of 0.1M sodium acetate.

Procedure:

Depending on the lead concentration, between 2.0 and 5.0 ml. samples of solution were pipetted into a beaker containing 75 ml. of water and 10 ml. of buffer solution. Several drops of indicator were added and the solution was titrated with .05N E.D.T.A. solution until the color changed from red to yellow.

1 ml. E.D.T.A. solution = 10.36 mg. Pb.