

ILLUMINATION AND THE ADSORPTION OF XANTHATE
IN THE FLOTATION OF GALENA AND MARMATITE

by

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B.Sc., University of Alberta, 1961

M.Sc., University of Alberta, 1965

A thesis submitted in partial fulfilment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

in the Department of
Mineral Engineering

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November, 1968

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Date December 24, 1968

ABSTRACT

The changes in the adsorption characteristics of potassium ethyl xanthate (KEtX) on galena (PbS) and marmatite [(Zn,Fe)S] due to illumination have been investigated.

Studies by others have indicated that: (1) the amount of surfactant adsorbed by a semiconductor depends on its n-type or p-type character, (2) copper activation of sphalerite (ZnS) is required for flotation, (3) sphalerite is a semiconductor with an energy gap of 3.6 eV whereas galena is a semiconductor with an energy gap of 0.37 eV.

The amount of xanthate adsorbed from aqueous solution on galena and marmatite was found to depend on both the intensity and photon energy (0.5 to 3.5 eV) of the incident light. In the galena system, increasing the light photon energy above the energy gap value increased adsorption of xanthate. The amount of xanthate adsorbed by the p-type galena was three times the amount adsorbed by the n-type galena. This suggested that the reaction

may involve the transfer of an electron from the adsorbate to the adsorbent. The effect of the presence of an oxide film on the surfaces of galenas was also investigated and appeared to be less significant than the type of charge carrier originally dominant in the mineral.

When copper-activated marmatite was illuminated by light with photon energies lower than the intrinsic gap (3.6 eV), adsorption of xanthate was less than when the mineral was kept in darkness. Similar "photodesorption" effects have been reported in the literature. These were explained by excitation of electrons from traps to the conduction band and subsequent recombination with holes in the valence band. Fewer charge carriers would then have been available to participate in the adsorption reactions. Flotation experiments agreed with the adsorption results above. Flotation recovery of activated marmatite dropped ca. 10% when the mineral was illuminated with a high intensity of 0.6 eV photons as compared to the recovery in daylight.

A model that takes into account the surface concentration of electrons and the type and concentration of impurities is discussed. The activity and selectivity of surface reactions are explained in terms of the electrochemical potential, i.e. the Fermi energy level,

the actual position and/or displacement of which is affected by the impurities present.

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ACKNOWLEDGEMENT

I wish to express my deep gratitude and sincere appreciation to Dr. J. Leja for his guidance and useful criticism throughout the course of this investigation.

My thanks are also due to all the members of the Department of Mineral Engineering, in particular to Dr. G.W. Poling and Dr. H. Majima and all the graduate students for their useful suggestions and discussions.

I wish also to thank Mr. M. Clegg for spending many hours in technical discussions and meticulous proof-reading of the manuscript.

Unlimited appreciation goes to my wife who, during all my university years, displayed a great deal of patience and tolerance while accepting the major responsibility of bringing up a family.

I am indebted to Syncrude of Canada Limited, and the National Research Council of Canada for their financial support without which this study would have not been possible.

CHAPTER 1

INTRODUCTION

The primary requirement for the successful flotation of a hydrophilic mineral is the adsorption of a surfactant at the solid/liquid interface in a form that will lead to a subsequent particle-bubble attachment. While the fundamental mechanism of adsorption still requires further elucidation, the role of the substrate in adsorption is becoming increasingly apparent as some investigators^(1,2) have found that irradiation may be used successfully to increase the recoveries of the minerals floated.

In general, solid-state photochemistry has not received the amount of quantitative effort dedicated to liquid and gaseous systems because of the inherent difficulties peculiar to the solid system. These include profound differences in chemical behaviour as a result of crystal defects (impurities, lattice imperfections, ion vacancies), non-homogeneous absorption of light and a change in the adsorption characteristics of the adsorbing species on illumination. These changes may result in either photodesorption or photoadsorption. Cadmium sulphide shows less affinity for phenolphthalein when irradiated in

an aqueous solution of ethanol than when not exposed to illumination⁽³⁾, whereas the red form of mercuric sulphide shows the reverse effect. As a direct consequence, the results of studies of a given system by different investigators are often in direct disagreement.

In an attempt to correlate the energy structure of minerals with their flotation properties, Plaksin et al⁽¹⁾ considered the electrophysical properties of the solid phase as a base on which to construct a satisfactory theory of the flotation process. These authors showed that the flotation recovery of zircon is strongly affected by exposure of the solids to γ -radiation. In another work Plaksin and Shafeev⁽²⁾ analyzed the effect of light from a 175 watt bulb on the adsorption characteristics of oleic acid on ilmenite and found that the flotation recovery increased by 12%. Since the photoelectric effect in semiconductors is well known^(4,5,6) and all sulphide minerals are semiconductors⁽⁷⁾, it is conceivable that a photon energy of a few electron volts could cause the necessary electronic transitions that may enhance or retard the adsorption of surfactants.

The purpose of the present research was to investigate the effects of photon energies of 0.5 to 3.5 eV on the adsorption of xanthate on copper activated marmatite and on both p-type and n-type galena. A further objective was to correlate the electrophysical properties

of the substrate with the adsorption of xanthate at a constant illumination level. In order to achieve these objectives, electrophysical as well as adsorption experiments were required. The physical characteristics given by the Hall coefficient on solid samples were supplemented by measurements of the thermoelectric power on pelletized powders. Kinetic measurements of the adsorbed quantities of xanthate were obtained by circulating a xanthate solution in a closed system with the powder retained between two fritted discs. The adsorption characteristics of the xanthate on the various sulphides are presented as a function of the energy of illumination, illumination intensity, added impurities, oxidation and flotation. The resulting effects are further correlated in terms of the measured surface area.

The adsorption characteristics of galena and marmatite depend strongly on the electronic distribution in the substrate. The n-type or p-type character dominates the adsorption behaviour more so than the effect of illumination. The latter is readily detectable by kinetic measurements but is not so evident under normal flotation conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Xanthate anions chemisorb readily on most sulphide minerals^(8,9) but the relative amounts adsorbed vary depending on the individual characteristics of the solid substrate. Since all sulphide minerals are semiconductors⁽⁷⁾, the effects of illumination on the adsorption of xanthate at a solid/liquid interface involve both an a priori knowledge of the electrophysical characteristics of the semiconductor and an understanding of the changes in the electronic distribution caused by the absorption of photons. It is this change in the electronic distribution that has been utilized in the most recent developments in flotation recovery.

2.2 Solid Semiconductors

The crystal structure of semiconductors is currently described in terms of the band theory of solids. In this theory^(4,10), the lattice ions are considered to affect the movement of electrons only by causing exclusion

of bands (energy gaps, E_g) from the possible electronic states of motion. The density of charge carriers ($\sim 10^{15}/\text{cc}$) is lower than that for metals ($\sim 10^{22}/\text{cc}$) hence electric fields in the surface plane caused by surface dipoles extend for a distance of many atomic layers into the bulk material, forming a space charge region below the surface. The depth of the effective space charge layer, or the Debye length, can be as great as 10,000 Å for semiconductors. Usually semiconductors are classified as n-type or p-type depending on whether the charge carriers are electrons or free quantum states (holes). Fig. 1 shows the basic structure of both n-type and p-type semiconductors with particular emphasis on the form of the Fermi distribution function $[f(E)]$ as impurities are added to the existing structure. In Fig. 1a if an electron is excited from a donor level into the conduction band, the semiconductor behaves as a metal. In this case, the electrical conductivity is due to the free movement of electrons (n-type conductance). A p-type conductance is shown in Fig. 1b when an electron is moved into an acceptor level leaving behind a hole free to migrate. If both donor and acceptor levels are present then the semiconductor is of the mixed type. Pure sphalerite is reported to be an n-type semiconductor while galena can have either p or n-type properties⁽¹¹⁾.

The semiconducting properties of pure sphalerite

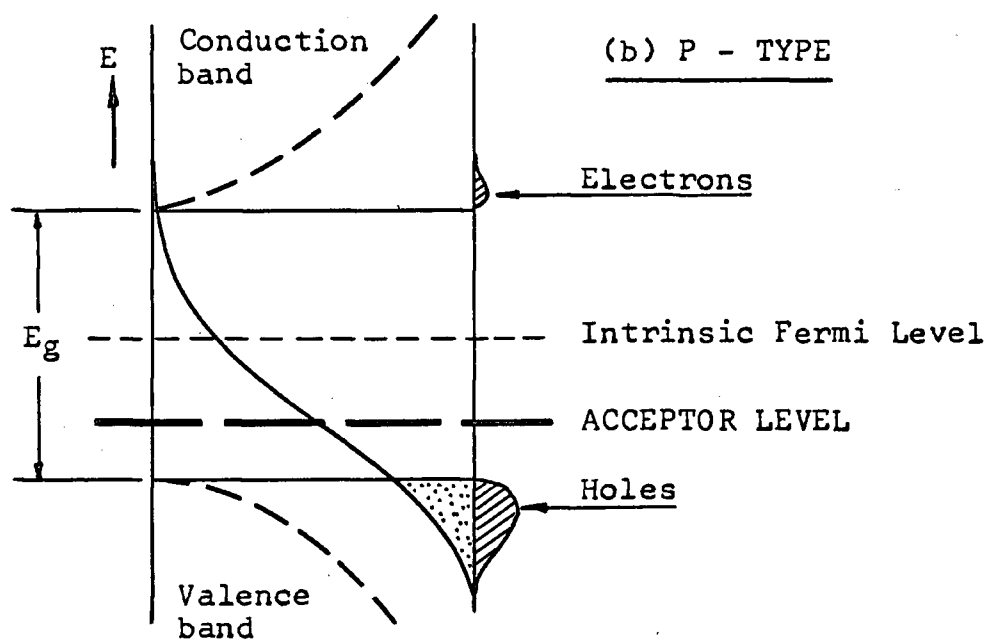
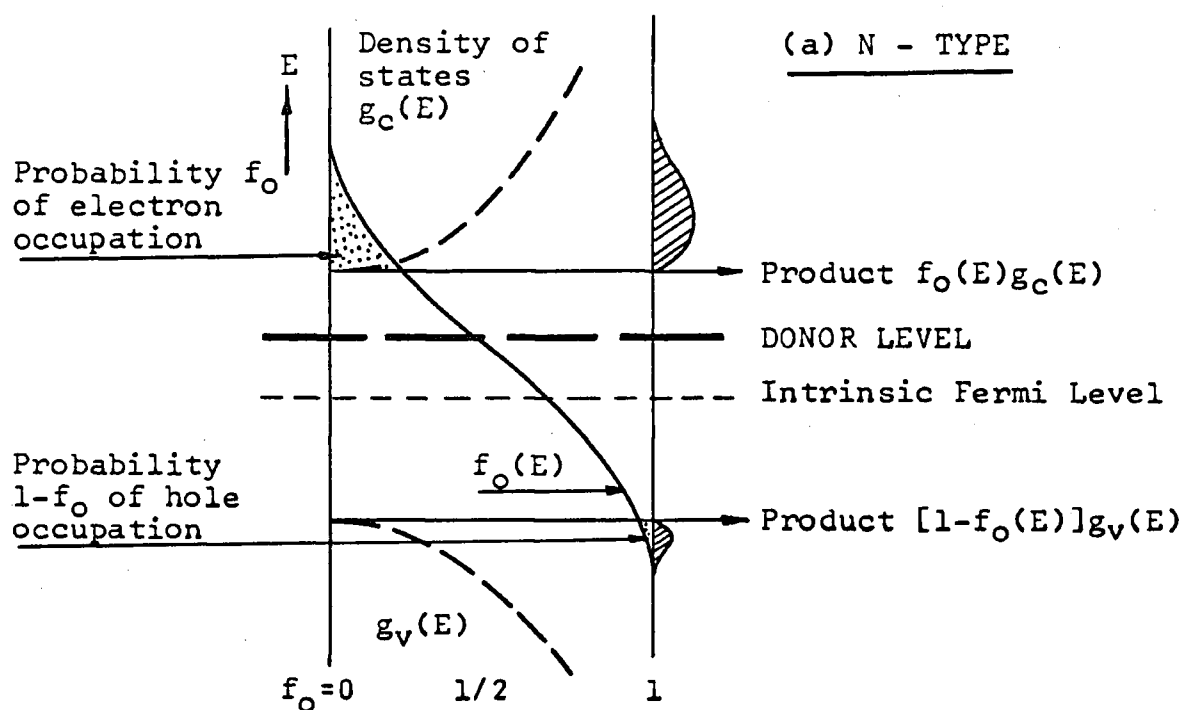


Fig. 1 - Distribution function and electron and hole population for impurity semiconductors (after McKelvey⁴).

are well known even though at the standard conditions of temperature and pressure the mineral is a non-conductor. To promote conducting properties, a suitable amount of energy must be supplied to transfer electrons from the valence band to the conduction band. Gudden and Pohl⁽¹²⁾ measured the photoconductivity of sphalerite and showed that the absorption peak corresponds to a photon energy of approximately 3.7 eV in agreement with the fundamental absorption edge. Cheroff and Keller⁽¹³⁾ attributed the photoconductivity effect at longer wavelengths to the presence of impurities in the crystal lattice.

Low and Weger⁽¹⁴⁾ investigated the effect of iron in sphalerite. For an iron content as low as 0.03% they recorded three strong peaks at approximately 7,000 Å (1.8 eV) and a strong absorption band at 3 microns (0.4 eV). The effect of manganese has been investigated by McClure⁽¹⁵⁾ who noted a number of peaks in the 3,900-5,000 Å region. The absorption below these regions increased steadily culminating in what is commonly referred to as the fundamental absorption edge. Because of the gradual increase in absorption there is a discrepancy in the assignment of a particular wavelength to the fundamental frequency. Beun and Goldsmith⁽¹⁶⁾ and Curie⁽¹⁷⁾, as well as most of the other investigators, agree that the absorption edge lies in the 3,400 Å region and that it is a measure of the energy gap. Thus, for sphalerite, the photon energy of

the forbidden gap is of the order of 3.6 eV equivalent to 83 Kcal/mole. Bube⁽¹⁸⁾ investigated the ZnS phosphors at room temperature and proposed a tentative energy level diagram for the measured electronic transitions involving absorption, excitation, emission, trapping and photoconductivity processes. The materials studied included pure ZnS, ZnS with Cu and ZnS with Ag as added impurities, together with other impurities, including Mn, Mg and Na. The author showed that there were five major trapping levels common to all ZnS phosphors regardless of the impurity. Fig. 2 shows the proposed energy level diagram for excitation and emission transitions. Optical trap emptying by visible light, like thermal trap emptying, involves a process of stimulation in which trapped electrons are raised into the conduction band before returning to luminescence centers to produce emission.

Natural galena is normally an n-type semiconductor⁽¹⁹⁾ with an energy gap of the order of 0.37 eV or 8.5 Kcal/mole. Amphoteric properties have been attributed either to impurities or to non-stoichiometric proportions of Pb and S in crystals, both n-type and p-type being the object of more recent investigations. In general, the electrical properties of partially ionic semiconductors may be attributed to the presence of donor and acceptor levels produced either by foreign atoms or by deviations from stoichiometric proportions. The crystal can exist as a single phase over

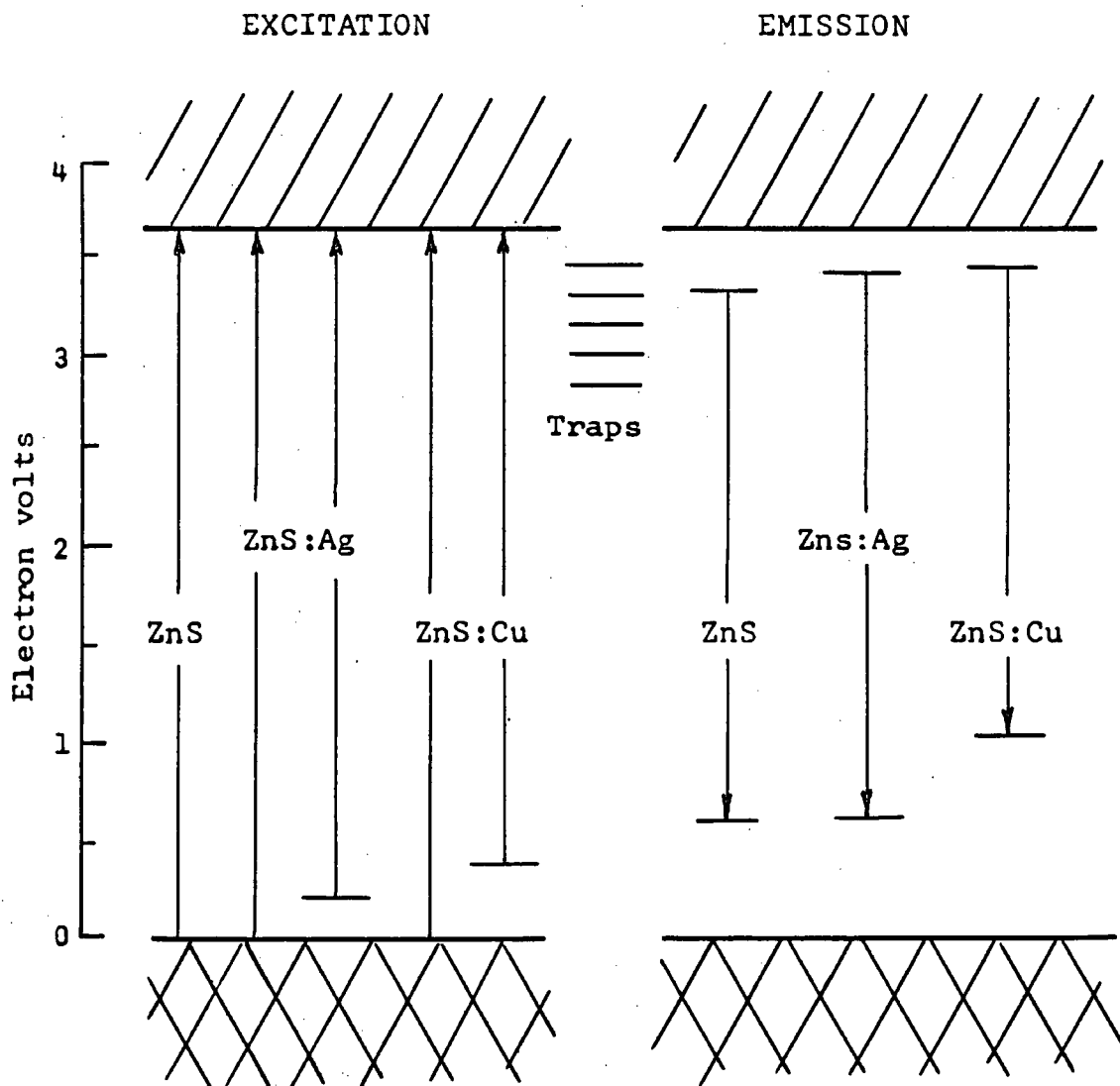


Fig. 2 - Tentative energy level diagram for the excitation and emission transitions in ZnS phosphors (after Bube¹⁸).

a range of composition through the inclusion of interstitial atoms and/or vacant lattice sites. Wide variations in the absorption characteristics of various samples of galena have been observed by Paul and Jones⁽²⁰⁾ even though the impurity content was too small to be detected by normal chemical procedures. Brebrick and Scaulon⁽²¹⁾ investigated the electrical properties of galena of near stoichiometric composition prepared by controlling the temperature and vapour pressure of sulphur. The impurity energy gap that they calculated from their experimental results was 0.03 eV for an n-type crystal and 0.001 eV for a p-type crystal.

The fact that galena does not show a sharp absorption edge is attributed by Gibson⁽²²⁾ to the absorption of radiation with energy less than 0.37 eV resulting in an electronic transition within the conduction band.

In a recent study on the photoconductivity of lead sulphide films, Fleming and Alberg⁽²³⁾ proposed that their films were composed of both n-type and p-type material, the p-type regions consisting of the intercrystalline layers and the outer portions of the crystallites which had become oxidized during the preparation of the film. Plaksin and Shafeev⁽²⁴⁾ described the action of oxygen as the take-up of electrons during ionization of the adsorbed oxygen molecules. This resulted in a lowering of the height of the potential barrier at the mineral surface. The

chemical potential gradually fell off and the probability of the xanthate anions overcoming the potential barrier gradually increased.

2.3 Recent Approaches to Flotation

As early as 1959, Plaksin⁽²⁵⁾ emphasized the role of oxygen and other gases in flotation. According to this author, oxygen promotes dehydration of the mineral surface and facilitates the penetration of xanthate groups thus assisting their fixation. Using an infrared multiple reflectance technique, Poling and Leja⁽²⁶⁾ found no interaction between galena and xanthate ions solutions in the absence of oxygen. Tolun and Kitchener⁽²⁷⁾ confirmed these results and suggested that oxygen not only reacts with the galena surface forming a thin layer of basic thiosulphate, which in turn reacts with xanthate to form lead xanthate, but also raises the electrochemical potential of galena modifying its form from n-type to p-type. These suggestions support the latest theory proposed by Plaksin and co-workers⁽⁷⁾ who invoked semiconductor principles to explain the xanthate-sulphide interactions. Since all sulphide minerals are semiconductors with electronic and hole conductivity, a strong chemical bond will result from the transition of an anion electron to a free (anodic) vacant site. They proposed that the separation of sulphide minerals from non-sulphide

ones is based on the following principles: a) potential energy of the surface and b) energy necessary to create an adsorption bond between a surfactant and the mineral surface. The mosaic distribution of reagents on the surface is theoretically explained by the non-uniform potential of the surface and experimentally proven by radiographic studies of minerals treated with radioactive surfactants. According to these authors, the surface properties of mineral particles can be modified by either changing the oxidation-reduction potential of the medium or by the addition of ions that behave as donors or acceptors.

Natural sphalerite does not float when short chain xanthates are used as collectors, but flotation is first achieved with amyl xanthate and continues with higher chain homologues⁽⁸⁾. A short chain xanthate can be used effectively to collect sphalerite if the mineral has been effectively activated with copper. In a recent review Yonezawa⁽²⁸⁾ found a consistency between the extraction of copper ions by sphalerite and the subsequent adsorption of xanthate. From experimental data of xanthate and copper abstraction from solution, the surface area of the ground sphalerite, the parking area of a copper atom ($10.4 \text{ \AA}^2$) and the cross sectional area of the xanthate radical ($25 \text{ \AA}^2$), this author showed that the ratio of copper to xanthate ions adsorbed was close to the ratio of their respective cross sectional areas when the surface coverage of copper

ions is about 100 per cent. Gaudin et al⁽²⁹⁾ investigated the activation of sphalerite with Cu⁶⁴ and described the activation as a rapid chemical exchange of Cu⁺⁺ for Zn⁺⁺ until three layers of Zn⁺⁺ have been replaced.

The flotation of galena with potassium ethyl xanthate is well known, 25 mg/l being sufficient for collection up to a critical pH value of 10.4 where flotation ceases⁽⁸⁾. Klassen and Mokrousov⁽³⁰⁾ indicate that only 20 to 40 percent coverage is required to float the mineral. Obviously these values can only indicate a trend since they are based on a hypothetical uniform distribution and vertical orientation of the collector on the surface.

Plaksin and Shafeev⁽²⁾ made an unusual contribution to flotation by correlating absorption of photons and collection. Illumination of ilmenite with a common light bulb increased the mineral recovery by 12%. Using γ -irradiation Plaksin et al⁽¹⁾ effectively separated zircon from pyrochlore in a flotation system, thus indicating the improved technology resulting from the change of the ratio of electron concentrations and electron vacancies in the mineral.

2.4 Illumination

The effect of illumination is to change the electronic distribution and thus to change the Fermi energy

level⁽⁴⁾. Of particular importance is the number of electrons in the conduction band because these electrons can directly participate in the formation of a chemical bond.

Their distribution is given by:

$$n = \int_0^{\infty} f(E) N(E) dE \quad (2.4-1)$$

where $f(E)$ is the Fermi distribution function and $N(E) dE$ the density of energy levels in the energy range dE . The integration is carried out over the lower part of the conduction band. The density of states, that is the number of energy states per unit volume lying between E and $E+dE$ taking into account the states for both spins is:

$$\begin{aligned} dN &= 4\pi/h^3 (2m^*)^{3/2} E^{1/2} dE \\ &= N(E) dE \end{aligned} \quad (2.4-2)$$

where m^* is the effective mass of the electron. By substituting and integrating Many et al⁽³¹⁾ obtained the following expression:

$$n = 2(2\pi m^* kT/h^2)^{3/2} \exp(E_F - E_C)/kT \quad (2.4-3)$$

or

$$n = N_C \exp(E_F - E_C)/kT \quad (2.4-3a)$$

where N_C is the density of states, E_C the energy value of the conduction band and E_F the Fermi energy level. A similar equation can be derived for holes.

It is this electronic density that can be modified by providing the reactants with the necessary quanta of electromagnetic energy. In general, wavelengths varying from 1,000 to 10,000 Å or, in terms of energy of quanta, from about 1 eV to 10 eV (23 to 230 Kcal per mole), are sufficient to cause the necessary electronic transitions or recombinations between the valence band and conduction band. Since these energies are of the same order of magnitude as those of chemical bonds, definite effects can be expected from the absorption of these photons.

Absorption of light by an atom in the line-spectrum region results in an excited atom whereas in the continuum it produces a dissociation (an ion plus an electron). These transitions occur in accord with the Frank-Condon principle that electronic excitations occur without affecting the positions of the nuclei.

In this way, light absorption may cause the excited molecule to follow one of these alternatives:

- a) Re-emission of a quantum of the same or different frequency (luminescence).
- b) Collision with another molecule either transferring energy to cause a reaction in the other molecule or degrading the energy into heat.

- c) Reaction with another molecule.
- d) Spontaneous decomposition (predissociation).

The phenomenon of luminescence is well known in the case of sphalerite. Luminescent solids have been classified as pure and impurity activated. Zinc sulphide is a typical impurity activated solid. Pure sphalerite displays no luminescence but, if the material is heated, a dissociation takes place and there is an excess of zinc atoms interstitially dissolved in the zinc sulphide matrix. When this material is illuminated with light of wavelength approximately 3,400 Å, phosphorescence is displayed and the solid becomes a better conductor of electricity (photo-conductivity). A simple explanation consists of the absorption of a quantum of radiation sufficient to drive an electron from the valence band to the conduction band leaving a hole behind. In pure zinc sulphide the electron and the positive hole will recombine without the emission of light but with dissipation of heat. In the impurity activated zinc sulphide, the impurity centers provide a mechanism by which the excitation energy can be re-emitted as light. Electron traps, from which transitions to the ground state are forbidden, are present in both pure and impurity activated sphalerite. Thus when thermal energy is supplied an electron can move back to the conduction band and eventually emit the phosphorescent radiation by falling to a lower energy level.

A transition model of luminescence was first proposed by Schon⁽³²⁾ and later modified by Klasens⁽³³⁾. According to these authors the luminescence is caused by an electronic transition from the conduction band to a localized level above the valence band (Fig. 3a).

The Lambe and Klick⁽³⁴⁾ model attributes the luminescence to a hole transition from the valence band to a level located below the conduction band to account for the different value of the decay constant between photoconductivity and luminescence, the latter being the smaller of the two (Fig. 3b).

Prener and Williams⁽³⁵⁾ considered necessary the association of acceptors of group Ib (Cu, Ag, Au) and donors of Group VIIb (Cl, Br, I) or IIIb (Al, Ga, In) for the appearance of luminescence thus proposing that the transition takes place from the excited state of the donor to the ground state of the acceptor in an associated pair (Fig. 3c).

In actual fact, luminescence is far more complicated than these simple models describe, being affected by other factors such as impurities, defects, thermoluminescence decay and optical stimulation.

Of particular interest is the case when impurity cations are present in the crystal lattice. The emission spectra of the luminescence in sphalerite when other cations are present in the crystal lattice have been investigated by Shionoya et al⁽³⁶⁾. Fig. 4, abstracted from their work,

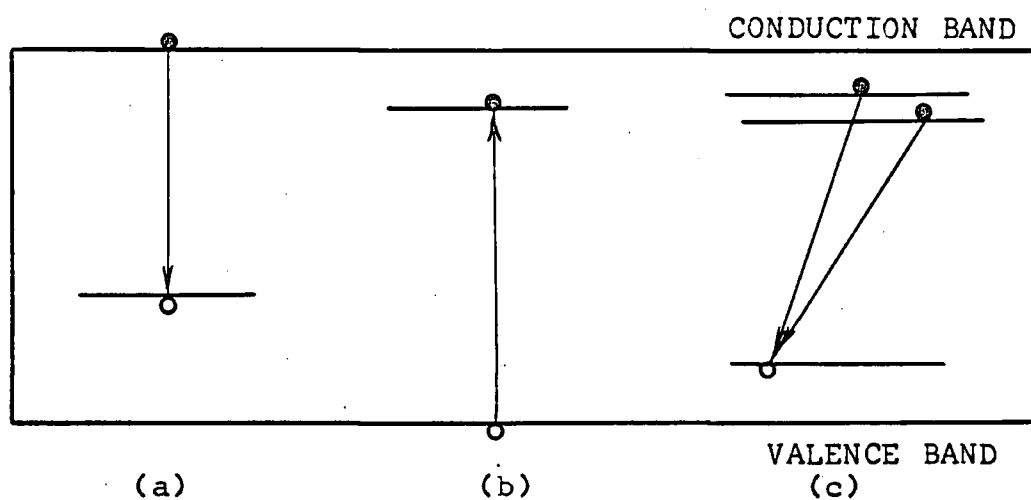


Fig. 3 - Models of luminescence according to: (a) Schon-Klasen; (b) Lambe-Klick; (c) Prener-Williams.

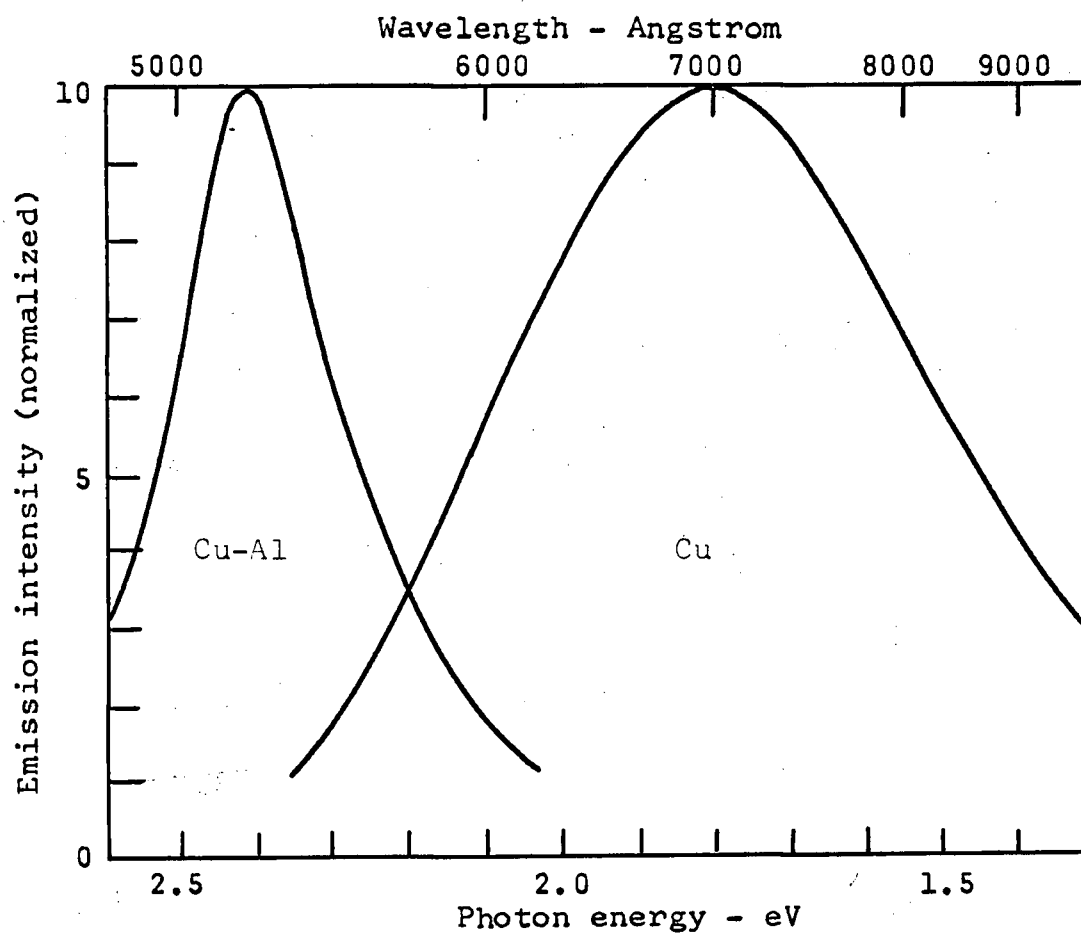


Fig. 4 - Emission spectra of luminescence in ZnS (after Shionoya et al. ³⁶)

clearly indicates that the presence of copper alone gives a peak at 1.77 eV while the copper-aluminum produces a shift in the peak which now rests at 2.41 eV.

2.5. Sources of Radiant Energy

The electromagnetic spectrum of interest to this study can be arbitrarily divided into three regions: ultraviolet, visible and infrared. The conventional wavelength range of each of these regions is given in the following table⁽³⁷⁾:

TABLE I - ELECTROMAGNETIC SPECTRUM
(After Strong³⁷)

<u>Spectral Region</u>	<u>Wavelength Limits</u>
Extreme UV	.050 to .200 microns
UV	.200 to .400 microns
Visible	.400 to .720 microns
Near IR	0.72 to 20 microns
Intermediate IR	20 to 40 microns
Far IR	40 to 400 microns

The most important natural source of continuous radiant energy is the sun. Many spectroradiometric measurements have been made by various investigators but, because

of instrumental problems and varying atmospheric conditions, only a fair agreement exists between the spectral energy distributions reported.

In general the luminous efficiency of the sun is equivalent to that of a lamp with an output of 80 lumens/watt. The energy distribution in the solar spectrum is closely approximated by that of a black body at 5,400°K. A black body, sometimes called a full radiator, is an imaginary object that, when heated, emits radiation in the form of a continuous spectrum. At room temperature radiation is in the invisible infrared region, but at higher temperatures the radiation frequency increases and covers the visible regions. As illustrated in Fig. 5, black body colour is precisely related to temperature in degrees Kelvin⁽³⁸⁾.

The efficiency of a tungsten lamp is approximately 11 lumens/watt and its spectrum is limited by the transmission of glass, namely from 0.31 microns to 3 microns for a thickness of 0.25 mm. Fig. 6 shows the transmittance limits of some glasses and water. If a tungsten light is provided with a quartz bulb (50 amp tungsten at 3,400°K) the spectrum easily extends into the ultraviolet.

Addition of iodine to the filling gas of a tungsten lamp starts a regenerative iodine cycle and the new lamp is properly called quartz iodine. The evaporated tungsten is deposited on the walls of the lamp and converted into a volatile iodide which, in turn, is decomposed

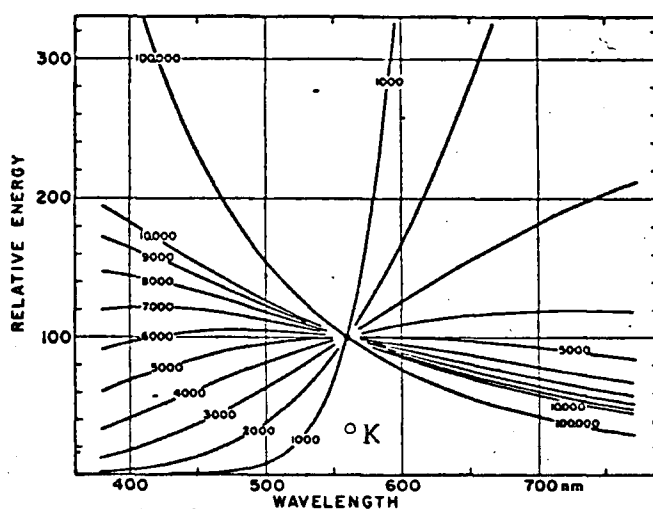


Fig. 5 - Relative spectral energy distribution of the black body radiator normalized at $\lambda=560$ millimicrons (after Wyszecki³⁸).

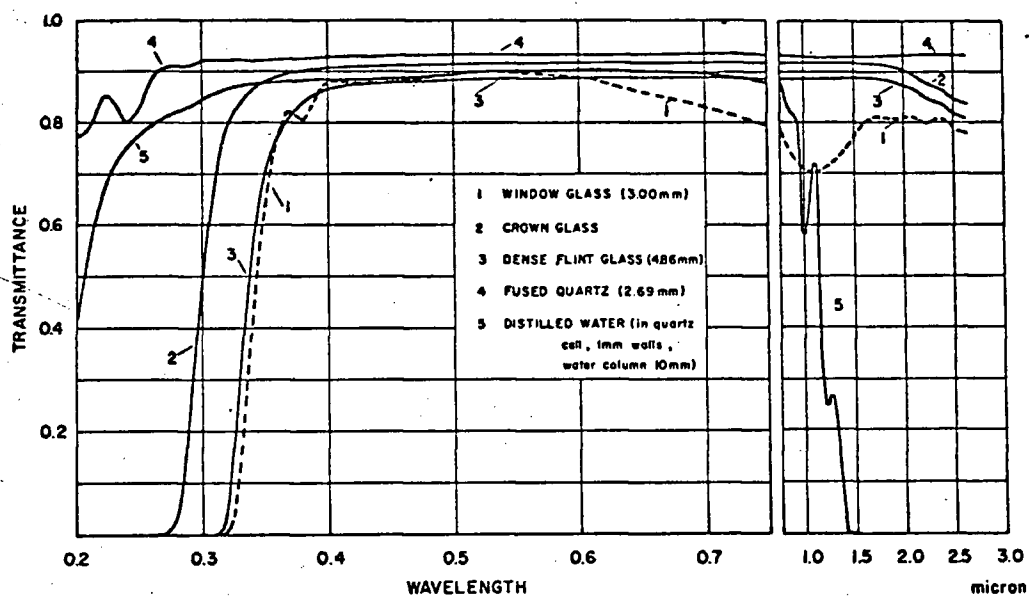


Fig. 6 - Spectral transmittances of absorption filters (after Wyszecki³⁸).

by the high temperature of the filament and thus completes the cycle. Since all of the tungsten is returned to the filament, it is possible to increase the operating temperature and the lamp efficiency.

Mercury arcs give several strong lines in the visible, ultraviolet and infrared region but lack a good spectrum continuity.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 General Approach

The materials used in this study were PbS, (Pb,Ag)S and copper activated (Zn,Fe)S. The original samples were crushed, ground, sized, cleaned and stored in a desiccator. The surface areas of the powders were evaluated from measurements of nitrogen adsorption by a continuous flow method. Further characterization of the materials included measurements of the Hall voltage for solid specimens and of the Seebeck effect for pelletized powders.

The kinetics of adsorption of high purity K₂EtX on the individual solids under various conditions of illumination were measured by determining the difference between the initial concentration and the concentration at time t . Samples of solution were removed at predetermined intervals for U.V. spectroscopic analysis and immediately returned to the circulating system. The adsorption apparatus normally contained 600 ml of solution at $20 \pm 0.1^\circ\text{C}$. The solution was circulated once every 30 seconds through a

fluidized bed of 10 or 20 g of powders.

The major portion of the experimental work was completed on 100/150 mesh powders. In the case of (Zn,Fe)S other size fractions had to be used because of the limited amount of material available; some tests were carried out on a 65/100 mesh fraction whilst all of the flotation experiments were performed on a 150/200 mesh fraction.

3.2 Materials

(a) Marmatite [(Zn,Fe)S]. Various screened fractions of the mineral were prepared from a selected sample received from The Zinc Corporation Limited, Broken Hill, Australia. The original material was crushed in a mortar and pestle and screened on a carefully cleaned set of stainless steel Tyler Sieves. All traces of free pyrrhotite were then removed from each fraction with a hand magnet prior to a final cleaning in a Frantz Isodynamic Magnetic Separator. Each fraction was subsequently washed with distilled water on the largest retaining screen to remove the fines attached to the larger particles. After a final rinse with doubly distilled water, the sample was dried in a vacuum desiccator, thoroughly mixed, and stored under nitrogen. An analysis of the major and minor constituents of the marmatite sample is reported in Table II.

TABLE II - ANALYSIS OF MARMATITE SAMPLE

(by Coast Eldridge, Vancouver, B.C.)

<u>Chemical Analysis of major constituents-%</u>		<u>Spectrographic Analysis of minor elements-%</u>	
Zn:	54.05	Co:	0.01
S:	33.46	Mo:	0.003
Fe:	11.63	Ca:	0.003
Cu:	0.31	Mg:	0.0005
Cd:	0.18	Si:	0.03
Mn:	0.14	Mn:	0.2
Insol.:	<u>0.15</u>		
99.92			

Pure zinc sulphide consists of 67.09% zinc and 32.91% sulphur.

Copper activated marmatite was prepared by immersing the mineral for 45 minutes in a 9.97×10^{-4} M copper sulphate solution at room temperature. The weight ratio of solid to liquid was 1 to 10. Since the uptake of copper ions was almost instantaneous⁽⁹⁾, the time selected to reach equilibrium was more than ample. A separate investigation of the effect of varying initial concentrations on the total amount of copper abstracted was also carried out and will be described with the adsorption results. Further preparation of the activated powders included repeated washing with doubly distilled water, filtering, drying and storing under nitrogen.

(b) Galenas [(PbS) and (Pb,Ag)S]. A high purity sample of galena from Pine Point (N.W.T.) was available in this Department. This was re-screened prior to storage in a desiccator. A complete analysis is presented in Table III.

TABLE III - ANALYSIS OF GALENA SAMPLE

Chemical Analysis of major constituents-% (by Cominco)		Spectrographic Analysis of minor constituents-% (by Coast Eldridge)	
Pb:	84.7	Si:	0.05
S:	14.1	Ca:	0.001
Zn:	0.7	Fe:	0.003
Fe:	<u>0.4</u>	Cu:	0.0005
	99.9	Mg:	0.0007
		Au,Ag:	traces

The theoretical contents of PbS are 86.6% lead and 13.4% sulphur.

Another sample of galena containing 0.28 oz/ton of silver [hereafter referred to as argentiferous galena, (Pb,Ag)S] was crushed in a porcelain mortar and pestle and screened for immediate use in a series of tests where excessive oxidation of the surface was to be avoided.

(c) Potassium ethyl xanthate (KEtX). A fresh sample of potassium ethyl xanthate was prepared for this series of experiments. Redistilled ethyl alcohol was mixed with pure potassium hydroxide (Fisher Certified Reagent) to

which carbon disulphide (Fisher Certified Reagent-Infrared Spectranalyzed) was added slowly at low temperature to avoid decomposition of the mixture. The product was then recrystallized from acetone five times and stored in a vacuum desiccator. At weekly intervals, the xanthate was washed several times with ether to remove any dixanthogen formed on oxidation.

(d) Water. Low conductivity doubly-distilled water was used in all experiments. Typical values of the specific conductance taken from the storage pyrex bottles ranged between 0.9×10^{-6} and 1.0×10^{-6} ohms⁻¹ cm⁻¹.

(e) Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Certified ACS reagent grade copper sulphate supplied by Fisher Scientific Company of Vancouver was used for all experiments.

3.3 Surface Area Measurements

The surface areas of the 100/150 mesh size of the three powders have been measured by a continuous flow method⁽³⁹⁾. Nitrogen was adsorbed by the sample at liquid nitrogen temperature from a gas stream of nitrogen and helium and eluted upon warming the sample. The nitrogen liberated is measured by thermal conductivity. With this method, materials of low specific area (well below one square meter per gram) can be measured with a precision of $\pm$ one

per cent at the 95 per cent confidence level⁽⁴⁰⁾.

Fig. 7 shows a schematic diagram of the apparatus for surface area measurements made available by the Department of Chemical Engineering.

The experimental procedure was initiated with the introduction of a known weight (approximately 1g) of sample to a U-tube. The sample tube was then placed in the circuit as indicated in Fig. 7. When all the air was flushed out by the mixture of nitrogen and helium (5, 10 or 15% N₂) the thermal conductivity detector was switched on and the bridge balanced to zero output. The sample was then cooled slowly in the liquid nitrogen and at the same time the adsorption peak was recorded. In order to take advantage of the full range of the recorder scale, the polarity switch was reversed prior to desorption of nitrogen. Desorption was achieved by rapid immersion of the U-tube in warm water. The complete sequence of adsorption was repeated three times to show consistency of results. In addition, a calibration of the volumes eluted was achieved by injecting known volumes of purified nitrogen into the system.

3.4 Electrical Conductivity and the Hall Effect

The electrophysical characteristics of the solid specimens have been investigated by the Hall effect. The Hall coefficient is given by the transverse voltage produced

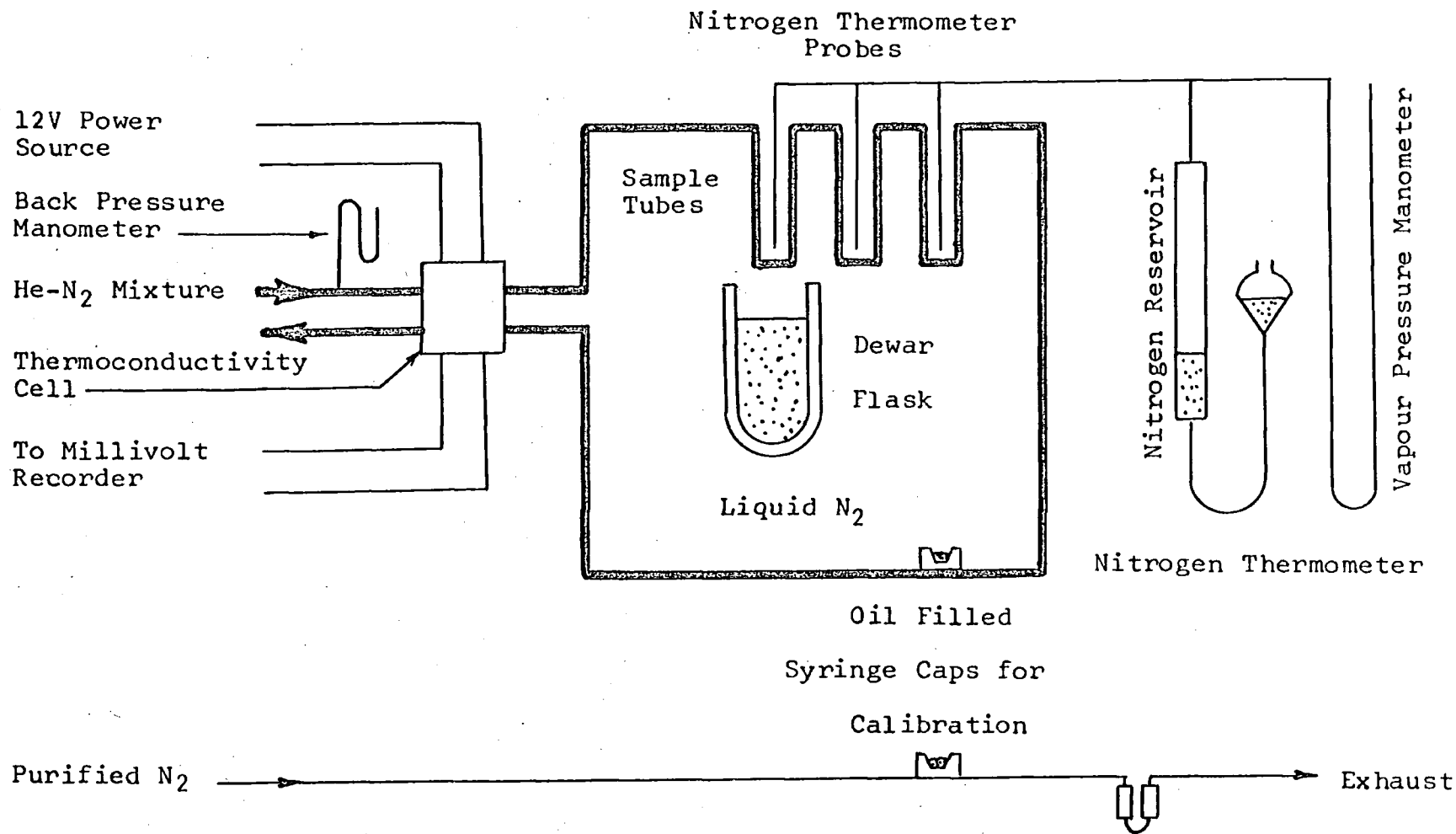


Fig. 7 - Schematic diagram of the apparatus for surface area measurements (courtesy of Mr. R. Orr).

when a current is passed through a conductor lying in a magnetic field at right angles to the current. The sign of voltage produced depends on the material under investigation. This voltage is proportional to the current (I) in amperes, to the magnetic field (H) in oersteds and inversely proportional to the thickness (t) in cm measured in the direction of the magnetic field. The proportionality constant ($R=1/nqc$) is called the Hall coefficient:

$$V = R IH/t = IH/nqct \quad (3.4-1)$$

where n is the number of carriers, q their charge and c the velocity of light. A schematic diagram of the Hall effect is presented in Fig. 8. Converting to practical units and substituting the value of c (see Appendix A):

$$V = 10^{-8} IH/nqt = R_H 10^{-8} IH/t \quad (3.4-2)$$

indicating that the practical Hall coefficient, R_H , is equal to

$$R_H = \pm 1/nq \quad (3.4-3)$$

the plus or minus sign indicating hole or electron conductivity. From a knowledge of the conductivity ($\sigma = nqu$) the mobility (μ) can now be readily calculated by multiplying the Hall coefficient by the conductivity:

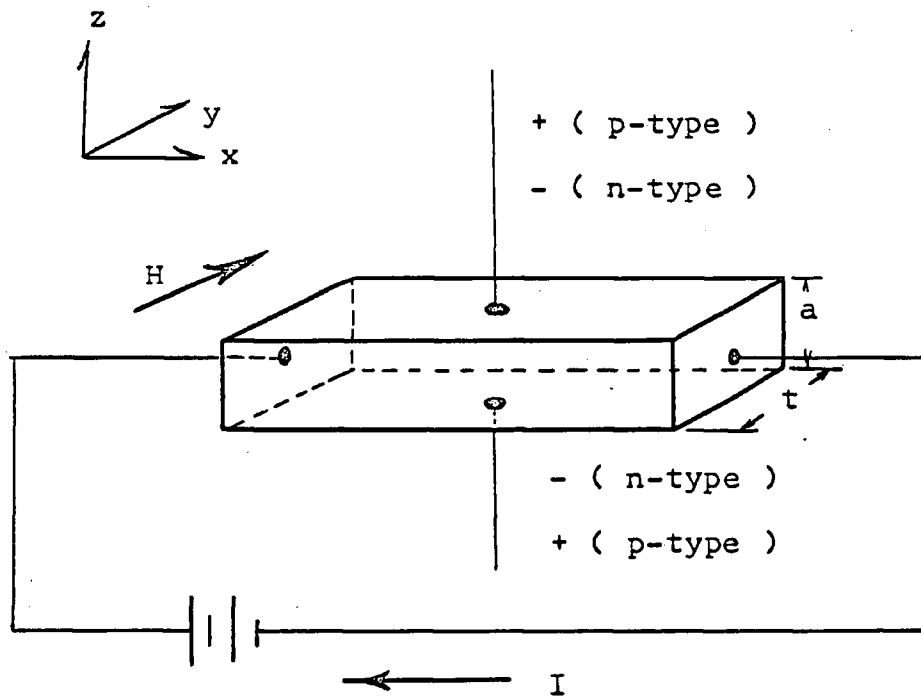


Fig. 8 - Schematic diagram of the Hall effect.

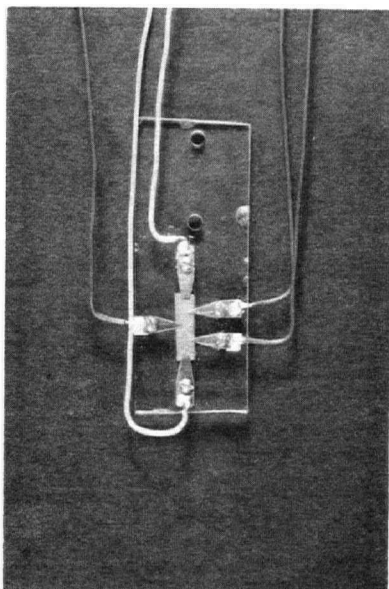
$$\mu = \sigma R_H \quad (3.4-4)$$

The samples of galena and sphalerite used in the measurements of the Hall coefficients were prepared from representative samples of solid specimens by (1) cutting thin sections with a diamond saw, (2) reducing the sections to the required size with a high speed carborundum wheel, and (3) mounting on plastic as shown in Fig. 9 and 10. The three-points voltage pick up is commonly used to avoid an ohmic voltage drop. When the potential contacts are not perfectly aligned and do not coincide with an equipotential line, in the absence of a static magnetic field an ohmic voltage drop proportional to the steady current will be measured in addition to the Hall voltage. Fig. 11 shows the origin of this ohmic voltage drop.

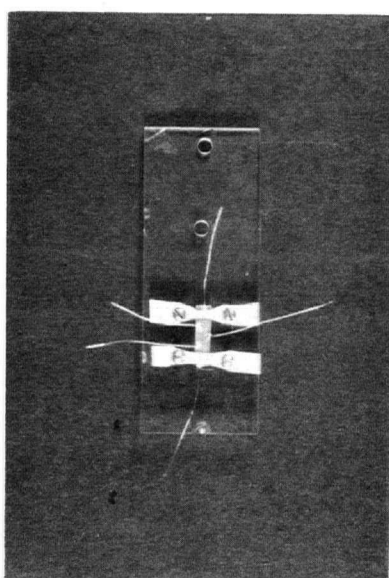
All measurements were made at room temperature using the facilities made available by the Physics Department of The University of British Columbia.

3.5 Seebeck Voltage Measurements

The Seebeck effect is a simple and efficient method for determining the conductivity type of a semiconductor from the sign of the potential produced. It is particularly useful for low mobility materials and for powder specimens where the Hall effect is difficult to

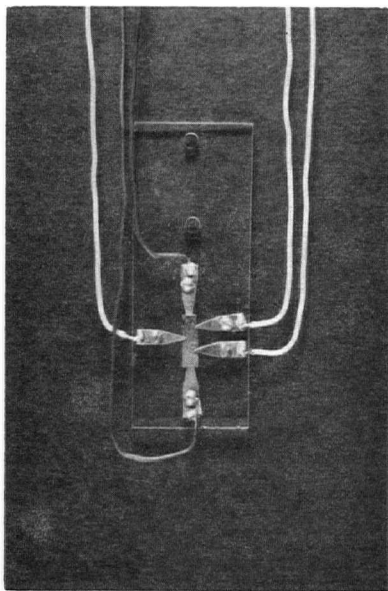


a) Pressure contacts

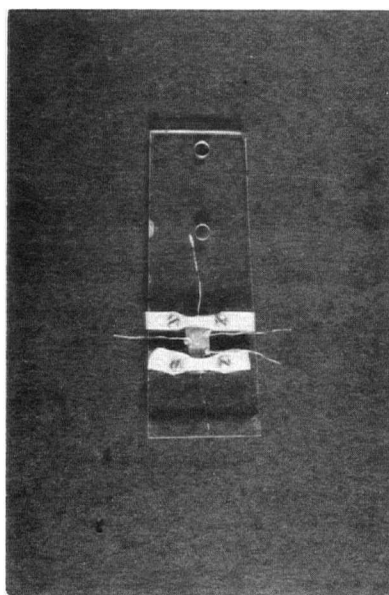


b) Indium contacts

Fig. 9 - Ohmic connections to marmatite specimens.



a) Pressure contacts



b) Solder contacts

Fig. 10 - Ohmic contacts to galena specimens.

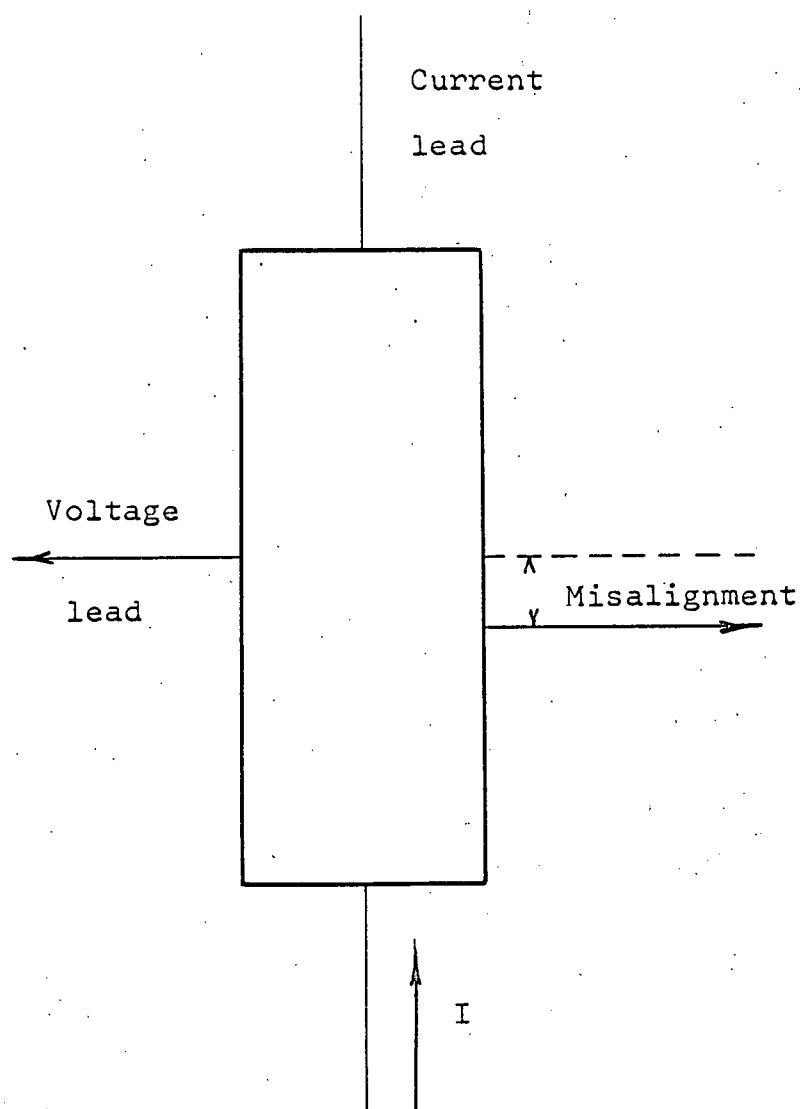


Fig. 11 - Origin of ohmic voltage drop due to misalignment when measuring the Hall coefficient.

measure⁽⁵⁾. A schematic diagram of the measurement of this thermoelectric power is shown in Fig. 12. The diagram indicates that when there is a temperature gradient between the ends of a specimen, an emf of $Q\Delta T$ in millivolts is produced where Q represents the thermoelectric power in units of millivolts/degree.

The Peltier effect which is the inverse of the Seebeck effect, arises when a current is passed through a semiconductor: the heat absorbed at one end of a semiconductor-metal junction is liberated at the other. The Peltier coefficient π in units of volts is expressed as joules of reversible heat absorbed or liberated per coulomb of charge passing through the junction. The physical representation of this effect in terms of energy levels for an n-type semiconductor is shown in Fig. 13. Under an applied potential, the energy levels slope to the right resulting in a current flow from right to left corresponding to an electron flow from left to right. Electrons from the metal entering the semiconductor from the left must possess an energy equal or greater than the energy barrier ($E_C - E_F$) but no barrier is present at the right, and semiconductor electrons with excessive thermal energy are easily added to the metal transferring heat from left to right. This heat transfer forms the basis of the Peltier effect since the mobile charge carriers diffuse from the hot to the cold junction imparting a potential of the same sign as

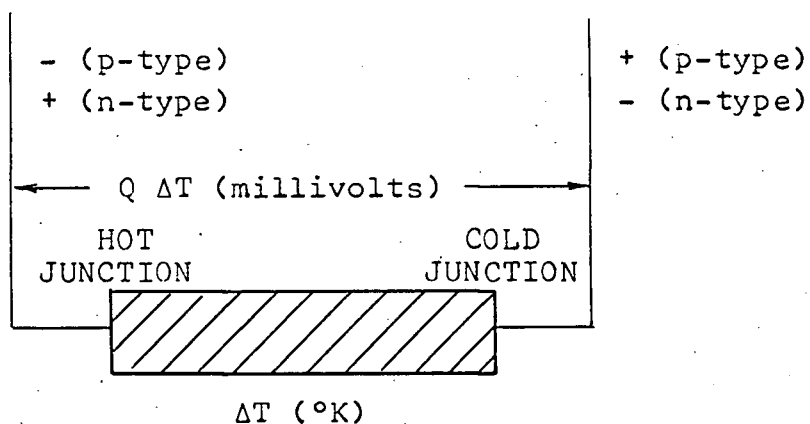


Fig. 12 - Schematic diagram of the Seebeck effect (after Hannay⁵).

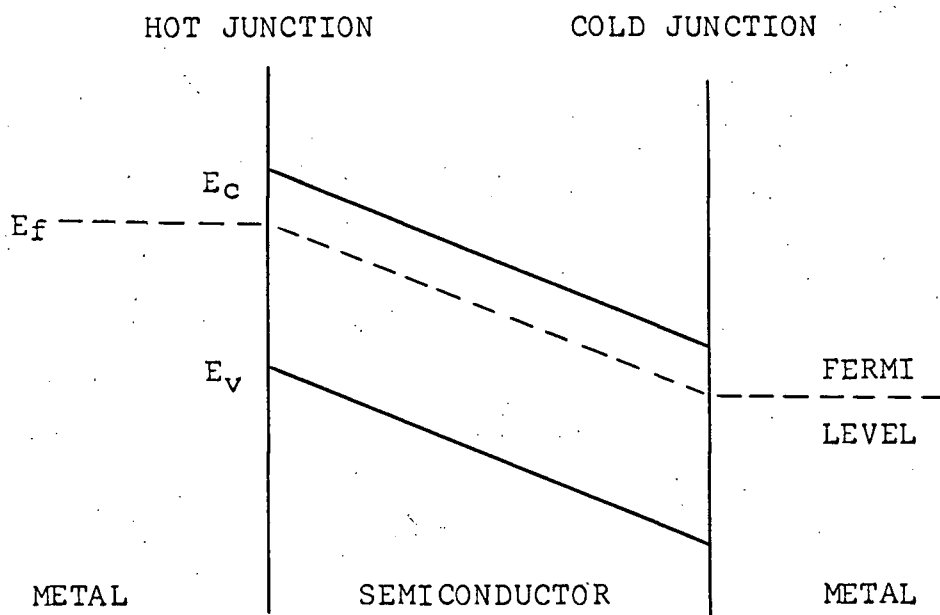


Fig. 13 - Origin of the Peltier effect for an n-type semiconductor (after Hannay⁵).

the carriers to the cold junction as indicated in Fig. 12. The energy transferred therefore is the energy required to overcome the energy barrier $[(E_C - E_F)]$ for an n-type semiconductor] plus a term for the kinetic energy transported by the carriers, or:

$$q\pi = qQT = (E_C - E_F) + 2kT \quad (3.5-1)$$

This equation indicates that the potential Q is related to the position of the Fermi level and by substituting in equation (2.4-3):

$$n \approx p \approx 2(2\pi m^* kT/h^2)^{3/2} \exp(E_F - E_C)/kT \quad (3.5-2)$$

the number of electrons (n) or holes (p) can be calculated.

A simple apparatus designed to investigate the type of semiconduction in low mobility materials is shown in Fig. 14. A photograph of the apparatus is shown in Fig. 15.

Solid specimens as well as pelletized discs, made by compressing powders in a standard press at 65,000 psi, were placed between the two copper discs maintained at constant temperature. The voltage produced was measured by a Keithley Electrometer (Model 610B).

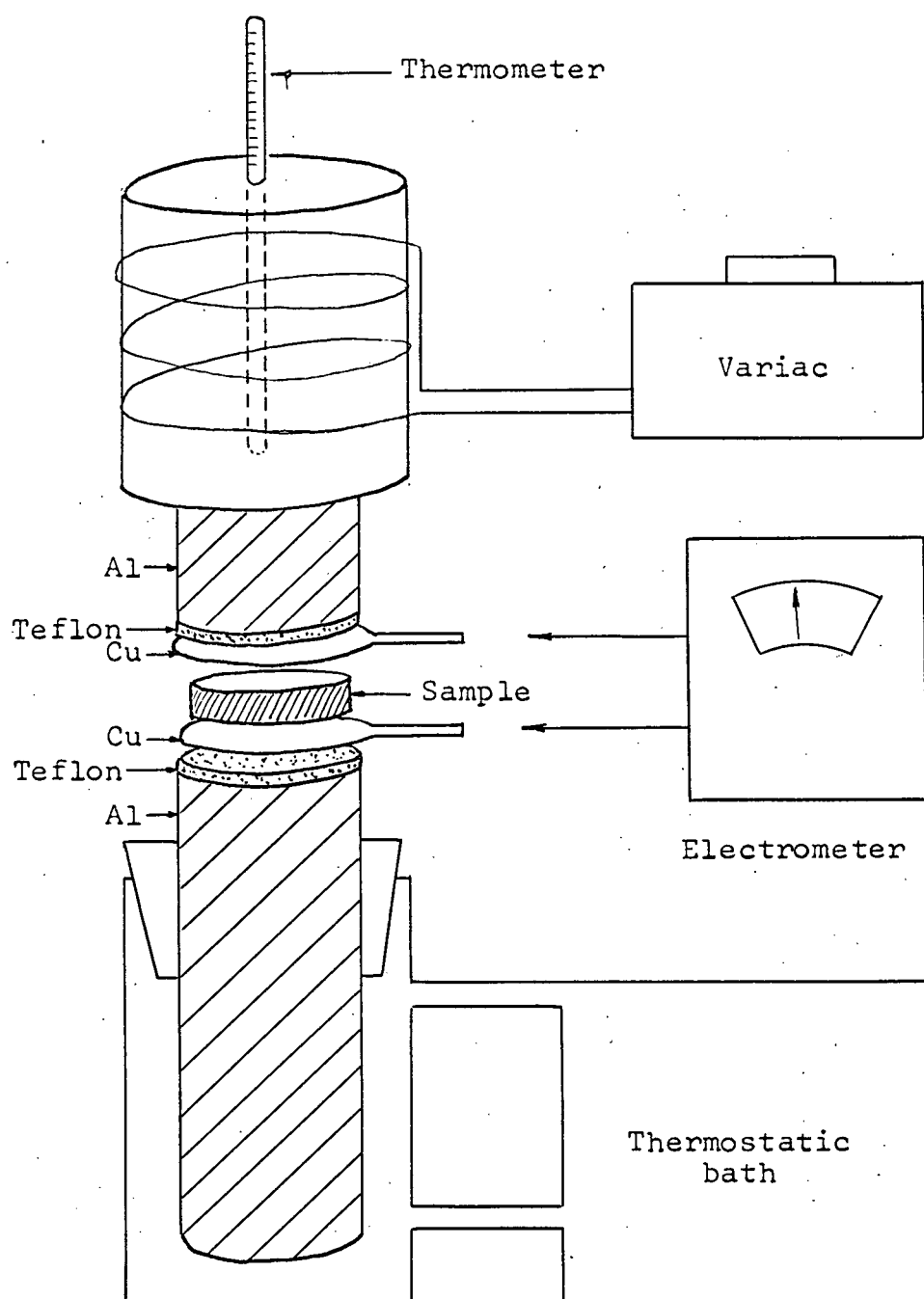


Fig. 14 - Schematic diagram of the apparatus for the measurement of the Seebeck voltage.

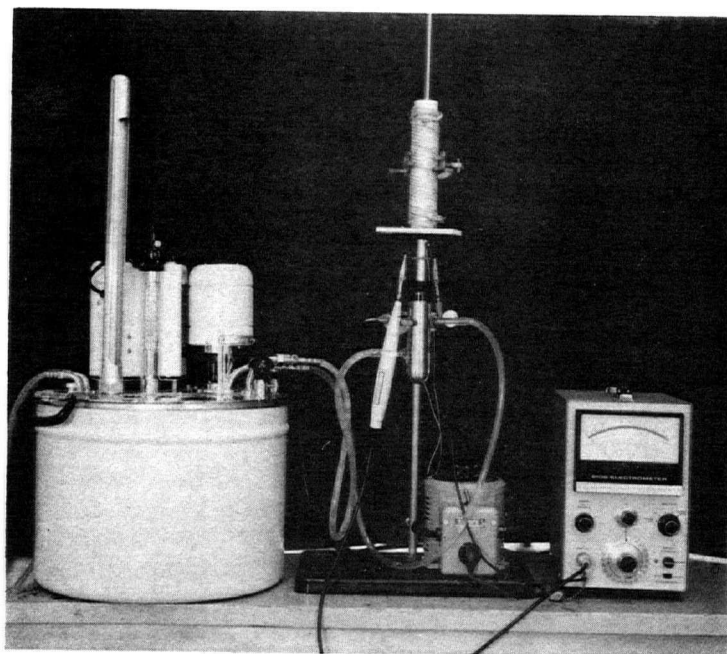


Fig. 15 - Apparatus for the measurements of the Seebeck voltage rearranged outside the Faraday cage.

3.6 Oxidation of Galena Powders

The role of oxygen in xanthate adsorption on sulphide minerals is well documented. Some investigators⁽³⁰⁾ propose that penetration of oxygen into the surface layer of the mineral weakens the surface bonds and increases the chemical activity of the surface. Others^(25,30) describe the effect of oxygen adsorption as one of surface dehydration that allows the subsequent penetration of surfactants. Other experimenters⁽²⁴⁾ postulate electrophysical changes from an n-type solid to a p-type through adsorption of oxygen. In this case, the p-type solid is described as being more susceptible to anionic adsorption. A fourth possibility is the oxidation of xanthate anions to dixanthogen^(9,26).

Since no complete agreement has been reached, it was decided to investigate the relative oxidation rates of the two galenas in order to differentiate between the effect of surface products, if any, and the bulk characteristics in subsequent adsorption tests.

The relative rates of oxidation of the two galena samples were analyzed with a Cahn RH Electrobalance made available by the Faculty of Forestry of The University of British Columbia. The galena powders were prepared by crushing large specimens in a porcelain mortar and pestle followed by screening the 100/150 mesh fraction in a dry box filled with purified premium nitrogen. The sealed

test tubes containing the powders were then transferred to the dry box protecting the electrobalance. For the tests without water vapour, the dry box was repeatedly evacuated and filled with helium. The remaining water vapour was then removed by drierite and sodium hydroxide. Approximately three grams of galena were removed from the test tube, placed on the balance and equilibrated by the addition of the appropriate weight to the other pan. The recorder was then allowed to run for a few minutes to establish a baseline. The dry box was then evacuated and as the oxygen was admitted the chart recorder was switched on simultaneously to measure the weight increase. For the tests with water vapour the same procedure was used but the desiccants were replaced by a beaker of water.

3.7 Adsorption from Solution

(a) Apparatus. The adsorption apparatus was designed to investigate the rate of adsorption of xanthate on different n-type and p-type minerals by continuously circulating the solution containing the surfactant through the solids in a closed system. The most critical features to be controlled were the energy of illumination, the inertness of the construction material and the presence of atmospheric oxygen.

The apparatus presented in Figs. 16 and 17, is

LEGEND:

- a) light source
- b) thermostatic bath
- c) thermometer
- d) sample chamber
- e) heat exchangers
- f) flow meter
- g) receiving vessel
- h) circulating pump

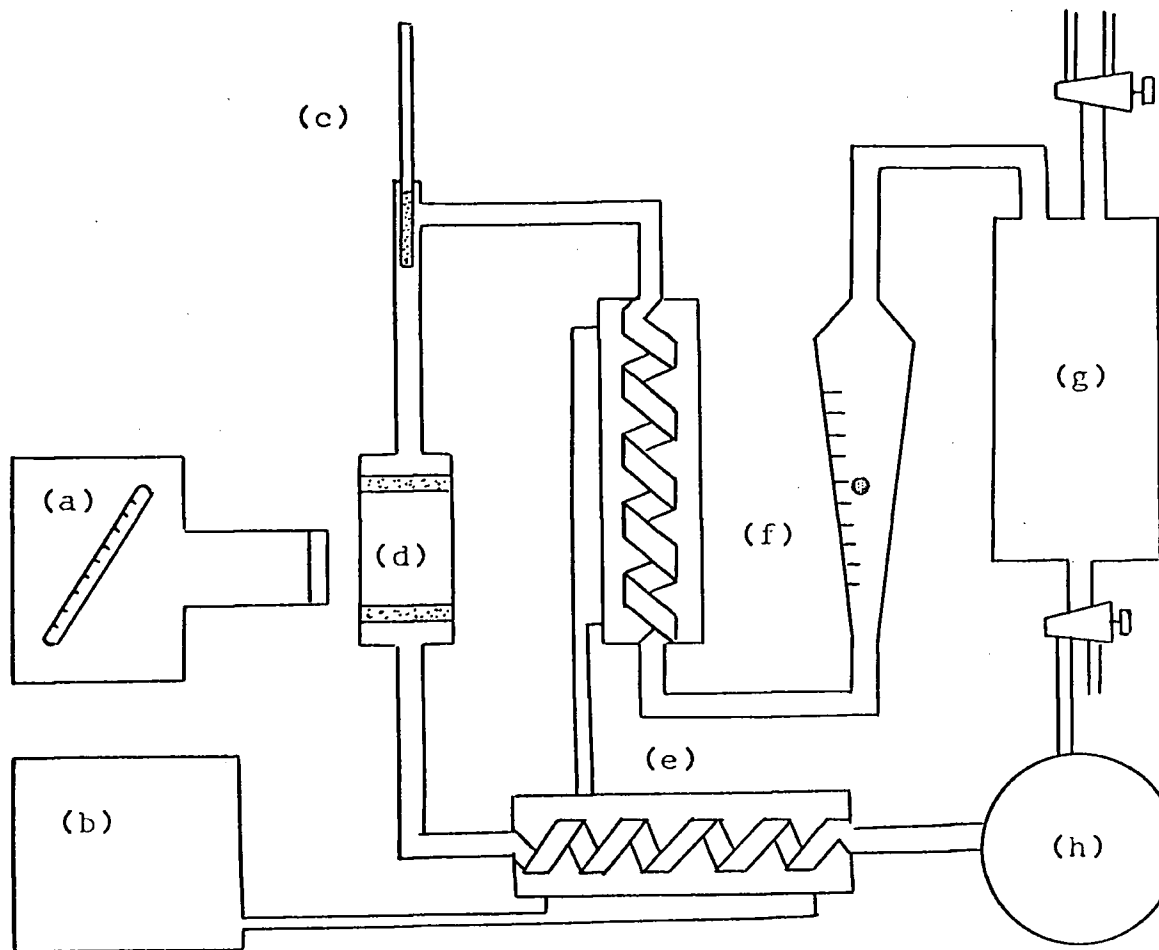


Fig. 16 - Schematic diagram of the adsorption apparatus.

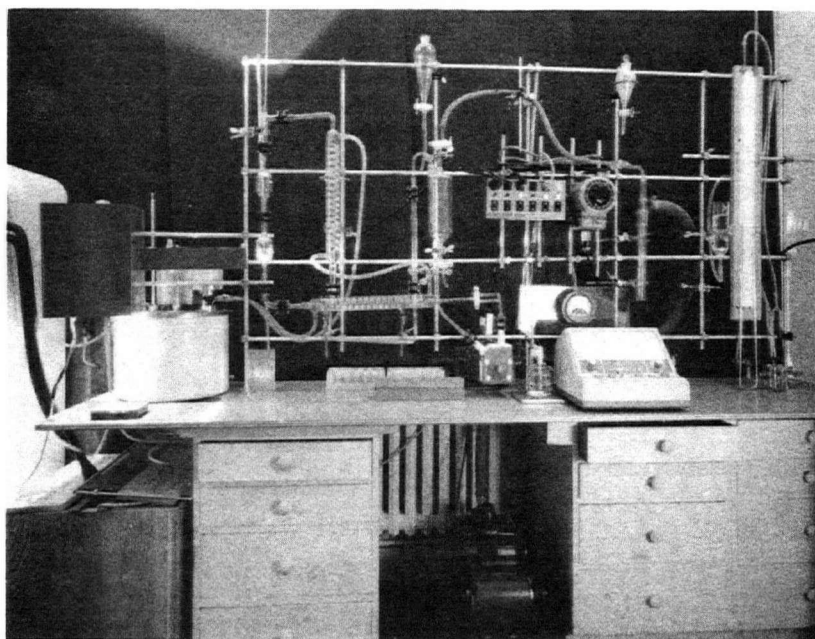


Fig. 17 - Adsorption apparatus complete with accessories and a semi-microflotation cell.

an improved version of that used by the author⁽⁴¹⁾ in a previous study.

The main features of the apparatus include: (1) localized illumination within an energy range of 0.5-3.5 eV, (2) ability to handle different amounts of solids and different volumes of solution, (3) fluidized mixing of the solids to reduce the production of fines and, consequently, changes in surface area, (4) elimination of fines removal during sampling, (5) elimination of solid abrasion of the pump liner, (6) ability to carry out tests in inert atmospheres, (7) ability to clean, wash and dry the system without dismantling the components, and (9) versatility, simplicity and reliability of design.

Two Sylvania Quartz-Iodine Lamps (No. 400 T4Q/CL/F and No. 500 T3 Q/CL/U) were used as a light source. Their characteristics are presented in Fig. 18. The particular lamp used in any one experiment was encased in a metal box open at both vertical ends to allow for the dissipation of heat. A protruding collimator was used to support the coloured glass filters at a reasonable distance to avoid absorption of heat. The nominal ratings of the lamps were given as 7,500 and 10,500 lumens for an approximate colour temperature of 3,000°K.

Temperature control of the solution at 20°C was achieved with a Colora Ultra-Thermostat Bath, Type NB, having a specified accuracy of $\pm 0.01^\circ\text{C}$. A precision

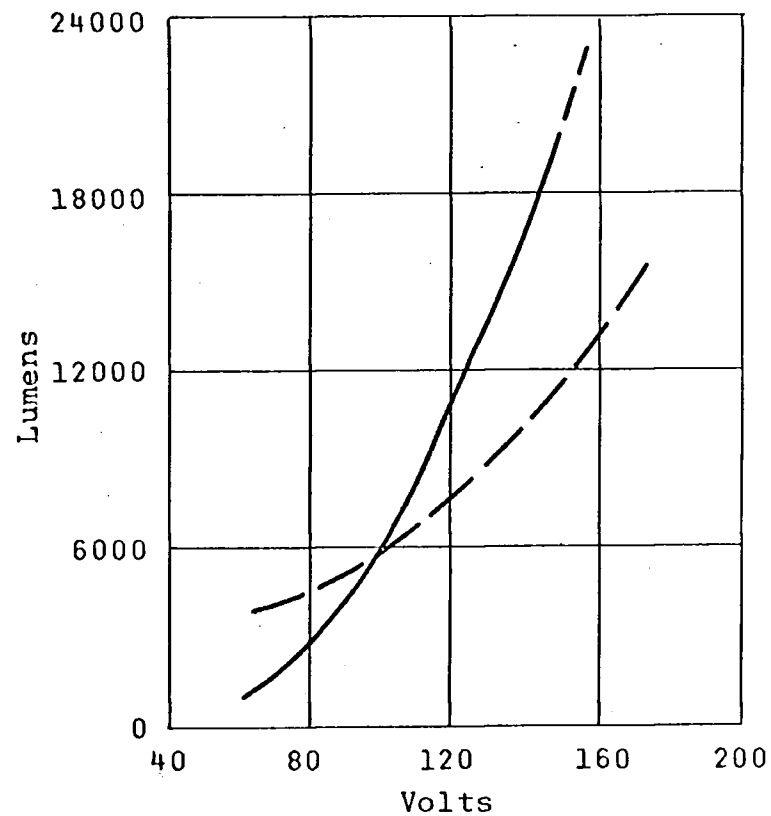
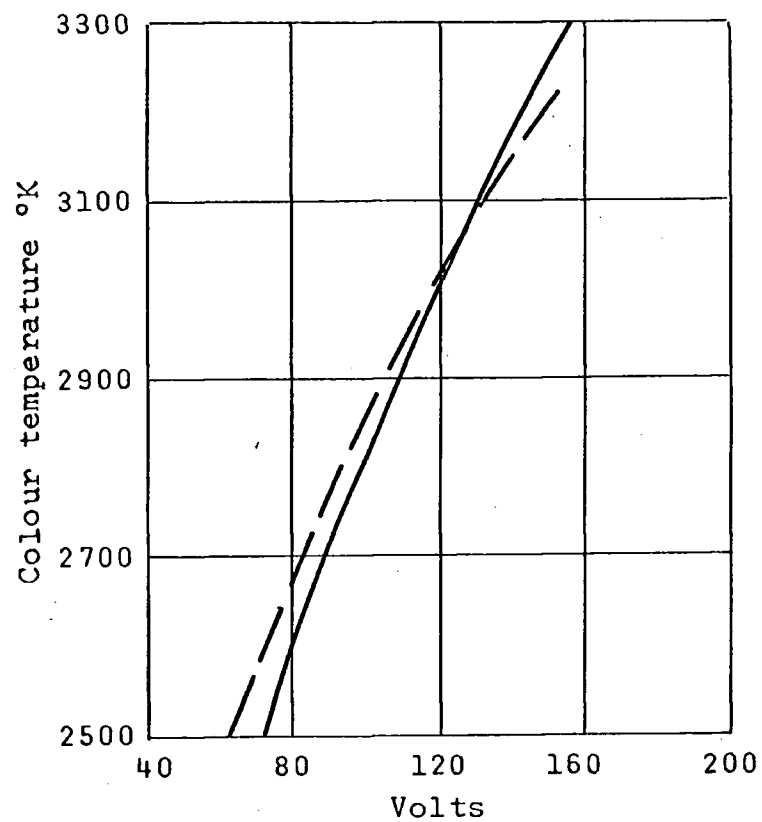


Fig. 18 - Characteristics of the Sylvania quartz-iodine lamps (Sylvania Electric Ltd.).

thermometer with a range of -1 to $+51^{\circ}\text{C}$ in subdivisions of $1/10^{\circ}\text{C}$ indicated that a constant temperature within $1/10^{\circ}\text{C}$ was attained within the sample chamber.

The sample chamber was constructed from a Buchner fritted glass (Pyrex) funnel of coarse porosity (60 microns). To provide illumination from all sides a U-type aluminum reflector (not shown in Fig. 17) was placed around the sample chamber.

The heat exchangers, the main receiving vessel and the flow meter (supplied by Manostat Corporation, New York) were all made of Pyrex Brand Glass.

A standard rheostat and an ammeter were used to control the speed of the circulating pump (Vanton Flex-I Liner) which was supplied by Vanton Pump and Equipment Corp., Hillside, N.J. The pump was equipped with a Kel-F liner (a polymonochlorotrifluoroethylene fluorocarbon) encased in a solid block of teflon (a polytetrafluoroethylene fluorocarbon).

All mechanical connections were made by squeezing a teflon gasket sheath between the tapered ends of QVF glass tubing [QVF Glass (Canada) Limited, Scarborough, Ontario], a borosilicate glass with the following typical composition:

Silica (SiO_2)	80.60%	Boric Oxide (B_2O_3)	12.60%
Sodium Oxide (Na_2O)	4.15%	Calcium Oxide (CaO)	0.10%
Aluminum Oxide (Al_2O_3)	2.20%	Magnesium Oxide (MgO)	0.05%
Iron Oxide (Fe_2O_3)	0.04%	Chlorine (Cl)	0.10%

The transmission curves for QVF glass in the ultraviolet and visible regions of the spectrum, as supplied by the manufacturer, correspond to that of Dense Flint Glass shown in Fig. 6.

In the present work the selection of spectral energies was achieved using colour glass filters 5-83, 5-75 and 7-86 manufactured by Corning Glass Works of New York. The transmittance curves for the filters in question were determined on a Model 450 Perkin-Elmer Spectrophotometer for the ultraviolet and visible regions and on a Model 521 Perkin-Elmer Spectrophotometer for the infrared region (Fig. 19). These narrow band filters were selected so that they cover approximately the same range of photon energy in different regions of the spectrum. The 5-83 filter covers the range of 0.340-0.380 microns (3.6-3.3 eV), the 5-75 filter extends from 0.440 to 0.490 microns (2.9-2.6 eV) while the 7-86 filter covers the 1.5-2.75 microns range (0.8-0.5 eV).

Ancillary equipment included a Beckman Zeromatic II pH Meter and a Cenco Hyvac 7 Vacuum Pump (from Central Scientific Company, Chicago, Ill.).

(b) Typical Adsorption Procedure. The following procedure used for the adsorption of xanthate on 10g of PbS at constant illumination is typical for all systems. The basic differences lie in the type and amount of solid

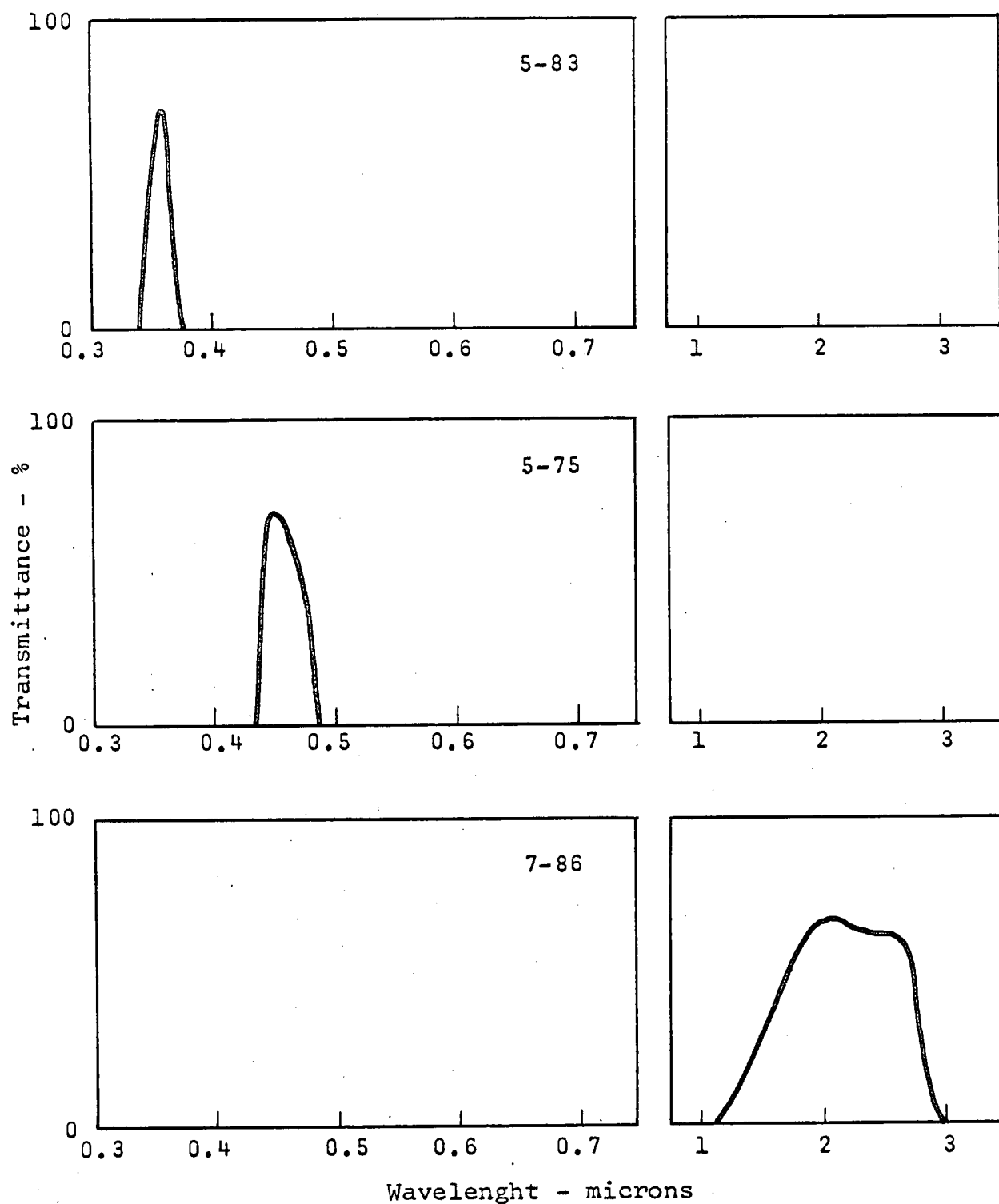


Fig. 19 - Measured transmittance of Corning Glass Filters.

material used in the test, the initial concentration and volume of xanthate solution and the illumination conditions. To minimize the variations in surface area caused by weighing, 10g of PbS were weighed, after coning and parting, on a Mettler H15 balance to within ± 0.001 g which corresponded to an accuracy of surface area of ± 1.8 cm²/10g. The material was transferred to the adsorption cell, all seals were carefully tightened and the whole system evacuated. At the same time the appropriate glass filter was placed in the collimator and the reflector positioned around the cell. Complete removal of interfering external irradiation was achieved by darkening the adsorption assembly with a black cloth. The light source and the thermostatic bath were then switched on. While the solids were being irradiated, 600 ml of approximately 10^{-4} M solution of KEtX were prepared and the exact concentration determined by a Perkin Elmer 450 Spectrophotometer. The solution was transferred to the evacuated apparatus while the circulating pump was operating. Thermal equilibrium was easily reached within the first two minutes, the maximum initial deviation never exceeding $\pm 2^{\circ}\text{C}$. At selected time intervals, 4 ml of solutions were removed to record the xanthate concentration and immediately returned to the circulating system. The differences in concentration represented the amount of xanthate abstracted by the mineral sample together with losses due to decomposition.

In connection with oxidation studies it was necessary to carry out adsorption tests in an inert atmosphere. In this case oxygen contamination had to be avoided in the preparation of materials as well as during adsorption. The powders were crushed in a porcelain mortar and pestle and screened in a dry box containing purified premium nitrogen. Ten grams of material were then weighed in the same dry box and transferred to the adsorption cell the ends of which were sealed off with removable teflon discs. The sealed chamber was reconnected to the main apparatus which was subsequently evacuated up to the teflon seals. These seals were removed while flushing the loosened connection with helium from the previously evacuated side. The whole apparatus was then evacuated. In the meantime the xanthate solution was prepared by adding deaerated doubly distilled water to the proper weight of xanthate in a volumetric flask, the procedure carried out in a portable dry box filled with helium. This solution was slowly added to the evacuated apparatus which was then pressurized with helium to atmospheric pressure. Before starting the circulating pump, other conditions being selected, four milliliters of solution were removed for UV analysis. The test was carried to completion in the manner previously described, except that the samples removed for UV analysis were not returned to the system.

(c) Analytical Procedure. In order to retain the constancy of circulating volume, a fast and reliable physical method of analysis was preferred to a chemical one. Ultraviolet spectroscopy offers these advantages since KETX displays a good spectrum with a sharp absorption peak that culminates at 301 mμ. The absorption of radiant energy at 301 mμ follows the well known Beer-Lambert Absorption Law. This law states that the amount of energy absorbed by the excited ions is proportional to the thickness and quality of medium traversed, or:

$$-dI/dx = aI \quad (3.7-1)$$

where I is the intensity of light, x a distance into the medium, and a the absorption coefficient. Integration at the boundary conditions ($I = I_0$ when $X = 0$) gives:

$$I = I_0 \exp(-ax) \quad (3.7-2)$$

In 1852 Beer showed that the coefficient a was proportional to the concentration c of the solute, therefore, rewriting:

$$I = I_0 \exp(-\epsilon cx) \quad (3.7-2a)$$

In this equation the symbol ε is known as the molar extinction coefficient, an intrinsic property that characterizes each substance. In the case of potassium ethyl xanthate, the

molar extinction coefficient used by Pomianowski and Leja⁽⁴²⁾ was 17,750, the value given by Majima⁽⁴³⁾ was 17,460. Assuming that these discrepancies may be caused by instrumental calibration, an independent determination of the molar extinction coefficient was carried out for the particular sample of KEtX used in these experiments (Appendix B). The extinction coefficient calculated from these data is equal to 17,500.

One of the major objections to the assumption that all of the reagent that disappears from solution is actually adsorbed by the mineral surface is that no consideration is given to the amount of surfactant precipitated, decomposed or evaporated from solution. In order to circumvent such a difficulty a number of curves labelled "Adsorption on Apparatus and Decomposition of Potassium Ethyl Xanthate" have been recorded to account, at least in part, for these effects. The curves are plotted in Fig. 20 and have been used to correct all subsequent adsorption measurements open to atmospheric oxygen. It should also be noted that the corrections apply to the total amount of solids present. For example, in the case of 20g of PbS, the correction is less than 4% at 10 minutes and 13% at 300 minutes. The change in volume from 1,000 ml. to 600 ml. was introduced after the preliminary experiments to increase the separation of the xanthate absorption lines on the UV recorder. It is most interesting to observe that

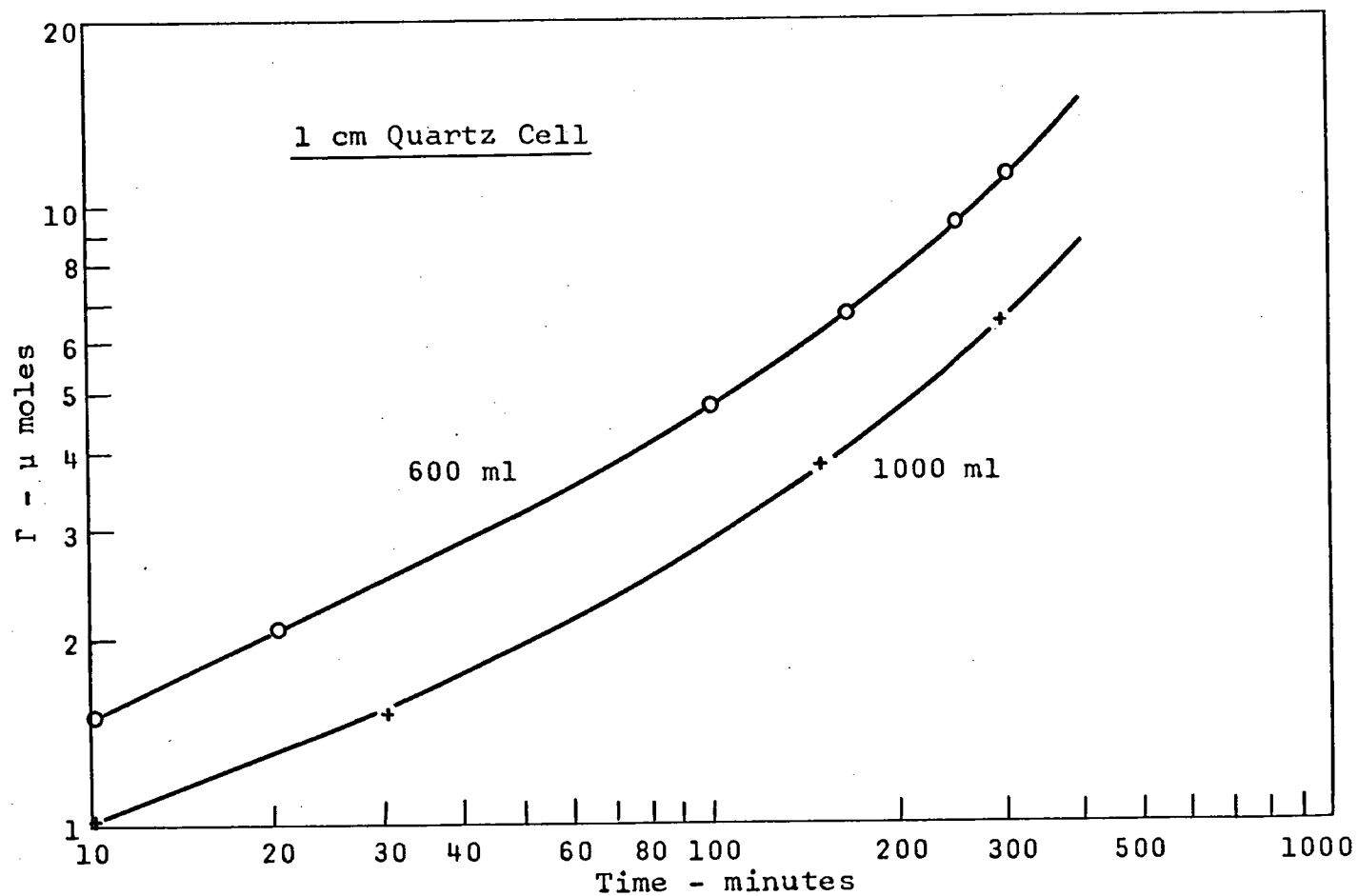


Fig. 20 - Adsorption on apparatus and decomposition of xanthate. Test conditions: KEtX ($10^{-4}M$), $20^{\circ}C$, illuminated with a 400W Q/I lamp.

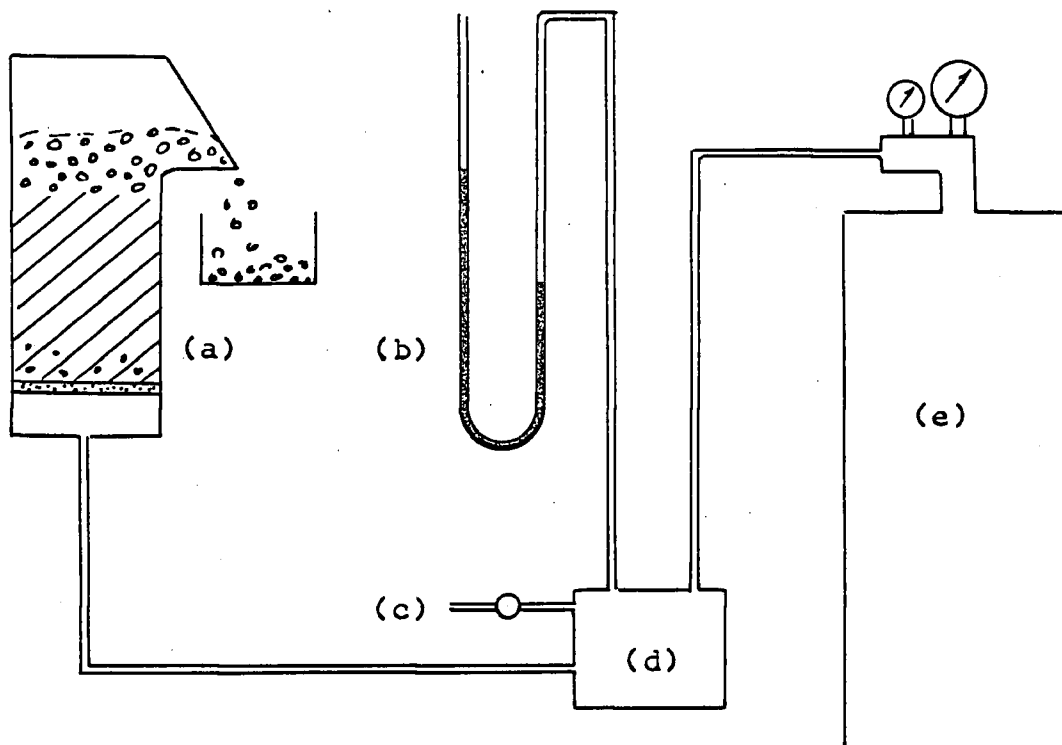
when the ordinate is changed to read in micromoles/l, the two lines of Fig. 20 display almost a perfect coincidence. This suggests that the majority of the correction can be attributed to decomposition since the internal surface area of the apparatus was a constant.

(d) Reproducibility. A major concern of all experimenters is to attain good reproducibility of results. To establish the degree of reproducibility relatively coarse marmatite (65/100 mesh) was selected for the tests using 1,000 ml volumes whereas galena was used for the tests using 600 ml volumes (Appendix C). The slight departure of the lines displayed by the marmatite sample can be attributed to varying light conditions and/or sample deviations from stoichiometry. A more remarkable reproducibility was obtained with the galena samples irradiated by a 400 W/QI lamp and by a 500 W/QI lamp. The choice of a 500 W/QI lamp for the last experiments emerged from necessity when the burnt out 400 W/QI lamp proved to be one of the first prototypes presently out of production. In the reproducibility tests as well as most of the subsequent experiments, the initial concentration of xanthate was 10^{-4} M. In the case of marmatite, the maximum error, at the beginning of the adsorption, was $0.08 \text{ moles/cm}^2 \times 10^{10}$. To assist in the logarithmic presentation, times of less than 10 minutes were omitted from the graphs. The linearity of adsorption

in the 1 to 10 minute region was well demonstrated in previous work⁽⁴¹⁾ and is shown for two tests from the present series in Fig. 34. Adsorption results below the one minute limit are not reliable with the present apparatus since it takes thirty seconds for the solution to circulate once through the mineral bed. Adsorption below this limit was investigated by several authors⁽³⁰⁾. In the case of galena, they observed that the adsorption on the active sites occurred within the first sixty seconds, a slower adsorption proceeding subsequently. In the present study the adsorption at times greater than one minute, was investigated by changing the surface characteristics of the mineral surface with illumination. Such a range was selected because it is more closely related to the actual flotation conditions in a plant operation.

3.8 Flotation

Flotation of the various minerals was investigated using a semi-micro flotation technique previously used by the author⁽⁴⁴⁾. This method was preferred to the Hallimond tube^(45,46) and to the cell devised by Purcell⁽⁴⁷⁾ for the ready adaptability of the design to the light attachment used in the adsorption tests. The semi-micro flotation cell, handmade from a Pyrex Glass fritted funnel of 60 microns porosity, is shown in Fig. 21.



LEGEND:

- (a) Pyrex semi-microflotation cell (capacity: 150 ml; porosity: 60 microns)
- (b) Mercury manometer
- (c) Needle valve bleed off
- (d) Constant pressure distribution chamber
- (e) Gas cylinder

Fig. 21 - Schematic diagram of the flotation arrangement.

The previously cleaned cell was filled with 150 ml of doubly distilled water while sufficient back pressure of nitrogen was maintained to avoid percolation through the fritted disc. A typical charge of 2g of closely sized solids [150/200 mesh in the case of (Zn,Fe)S] was weighed, after coning and parting, and added to the cell. Potassium ethyl xanthate was then added to give a typical concentration of $2.5 \times 10^{-7} \text{ M/l}$ (0.04 mg/l) using an Agla Micrometer Syringe. Following a conditioning time of 30 seconds, 0.02 mg/l of ethyl alcohol were added as a frother and the nitrogen pressure adjusted to 20.5 cm of Hg to produce intense but not violent agitation. The froth product was collected for 3 minutes. Both product and tailing were dried and their respective weights used to calculate the metallurgical recoveries under conditions of normal daylight illumination.

In the case where selected wavelengths were used, the procedure was essentially the same but more attention was focused on the preparation of solids. All solids were weighed in numbered beakers and kept in total darkness overnight. They were then added individually to the cell, the light source turned on and the solids illuminated for 15 minutes prior to addition of the xanthate. Subsequent steps were exactly the same as described above.

CHAPTER 4

EXPERIMENTAL RESULTS

The adsorption results are presented as the total amount adsorbed versus time. Such a presentation is preferred to the conventional equilibrium method because flotation per se is a non-equilibrium system and more information can be obtained at selected time intervals.

A detailed analysis of the rate constant, reaction order, activation energies and entropies of activation for a similar system has been presented by Guarnaschelli and Leja in a previous publication⁽⁴¹⁾. According to this, the reaction for the adsorption of xanthate is of the first order with an activation energy of about 18 Kcal/mole. This high value indicates strong chemisorption.

In the present work the results are discussed in terms of surface area coverages.

4.1 Surface Area Measurements

The physical adsorption of nitrogen on mineral surfaces can best be represented by the Brunauer, Emmett and Teller (BET) equation⁽⁴⁸⁾:

$$P/V_{ad}(P_0 - P) = [(C-1)/V_m C] (P/P_0) + 1/V_m C \quad (4.1-1)$$

where: P = partial pressure of nitrogen
 P_0 = saturated pressure of nitrogen at temperature of liquid nitrogen used
 V_{ad} = total volume of gas adsorbed
 V_m = monolayer volume of gas adsorbed
 C = constant

This is the equation of a straight line having $P/V_{ad}(P_0 - P)$ as ordinate and P/P_0 as abscissa. Then $(C-1)/V_m C$ is the slope of this line and $1/V_m C$ the intercept. For a linear BET plot, the value of P/P_0 should lie between 0.05 and 0.35. In order to work within these limits, mixtures of nominally 5, 15 and 25 per cent nitrogen in helium were used. The quantity V_m for each powder was calculated from the slope and intercept of the lines of Fig. 22. In this figure every point represents the arithmetic average of three independent measurements. The main parameters and surface areas of the three samples are summarized in Table IV. A detailed calculation of the surface area of marmatite is presented in Appendix D. The large surface area of the marmatite, four times the area reported for a similar size fraction⁽⁴⁹⁾, is the consequence of the presence of porous oxidation products due to the high iron content of the sample and the presence of inevitable fines (slimes).

From a knowledge of the measured surface area of the 100/150 mesh marmatite the areas of other screened fractions can be obtained from their average screen size.

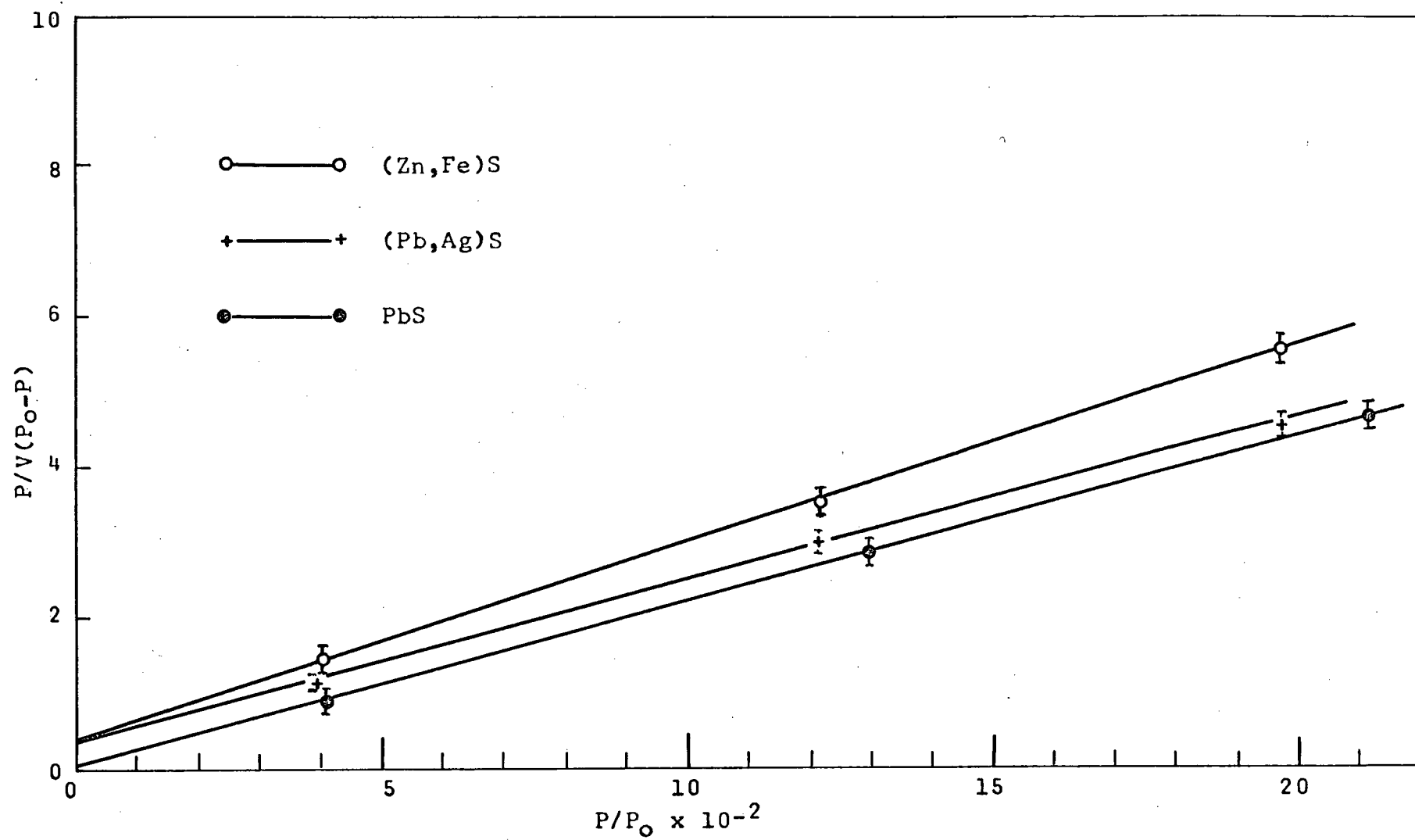


Fig. 22 - BET plots for 100/150 mesh mineral powders.

TABLE IV - BET AREAS OF POWDERS(100/150 MESH)

Sample	Size-g	Slope	Intercept	Vm-ml	Area-cm ² /g
(Zn,Fe)S	0.4600	25.4	0.4	0.0388	3675 [±] ₄₀₀
(Pb,Ag)S	1.5751	21.3	0.4	0.0460	1270 [±] ₂₀₀
PbS	1.0983	21.5	0.1	0.0464	1850 [±] ₂₀₀

TABLE V - CALCULATED SURFACE AREAS OF SCREENED
FRACTIONS OF MARMATITE

Mesh Size	Average Screen Size (microns)	BET Area of (Zn,Fe)S cm ² /g	Calculated Area cm ² /g
65/100	177	--	2600
100/150	125	3675	--
150/200	88	--	5200

These calculated areas are shown in Table V.

In addition the number of xanthate molecules and the equivalent in moles/cm² required to form a closely packed monolayer can be calculated in terms of the estimated parking area of 29 Å² for the xanthate radical⁽⁹⁾. The number of xanthate radicals per cm² is $10^{16} \text{ Å}^2 / 29 \text{ Å}^2 = 34.5 \times 10^{13}$ which divided by Avogadro's Number yields 5.7×10^{-10} moles/cm². This monolayer coverage is included in each of the adsorption figures.

4.2 Effects of Illumination

The results of the adsorption of xanthate on copper activated marmatite as a function of varying radiant energy are presented in Figs. 23 and 24. In Fig. 23 the amounts of xanthate adsorbed increased as higher energy was supplied to the system. Fig. 24 shows that marmatite adsorbed less xanthate when illuminated with 0.6 eV than when not illuminated. In the case of illumination with 0.6 eV there was a decrease in both the amount adsorbed at 10 minutes and the total amount adsorbed compared to the case of no illumination. This same trend towards a decreased adsorption is observed if the test with 2.9 eV illumination is compared to the test in darkness (Fig. 23 vs. Fig. 24).

The last effect can be explained in terms of

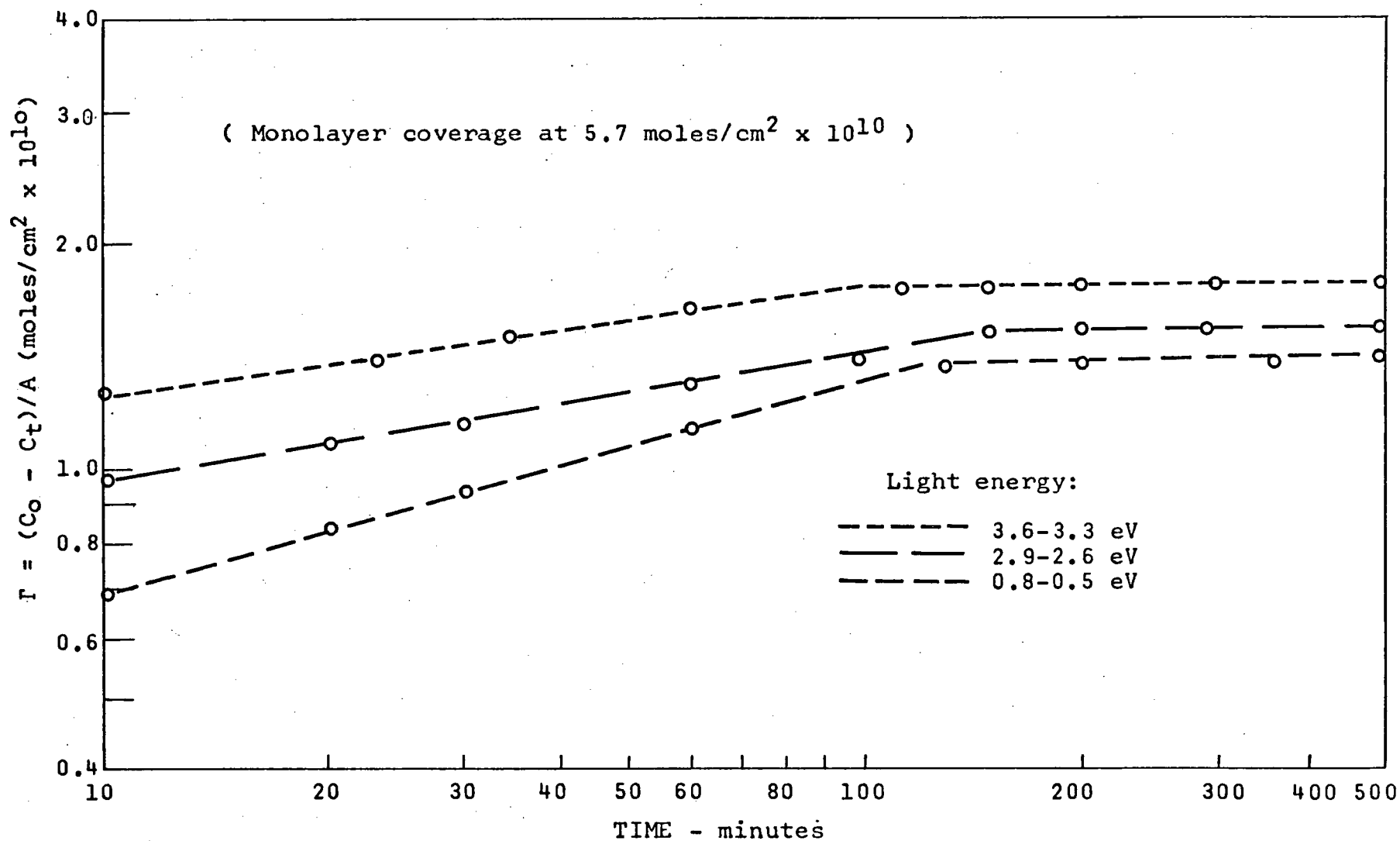


Fig. 23 - Adsorption of EtX^- from a solution of KEtX ($9 \times 10^{-5} \text{ M}$) on activated $(\text{Zn,Fe})\text{S}$ (100/150 mesh) at 20°C and natural pH (6.5) under controlled illumination, (20g).

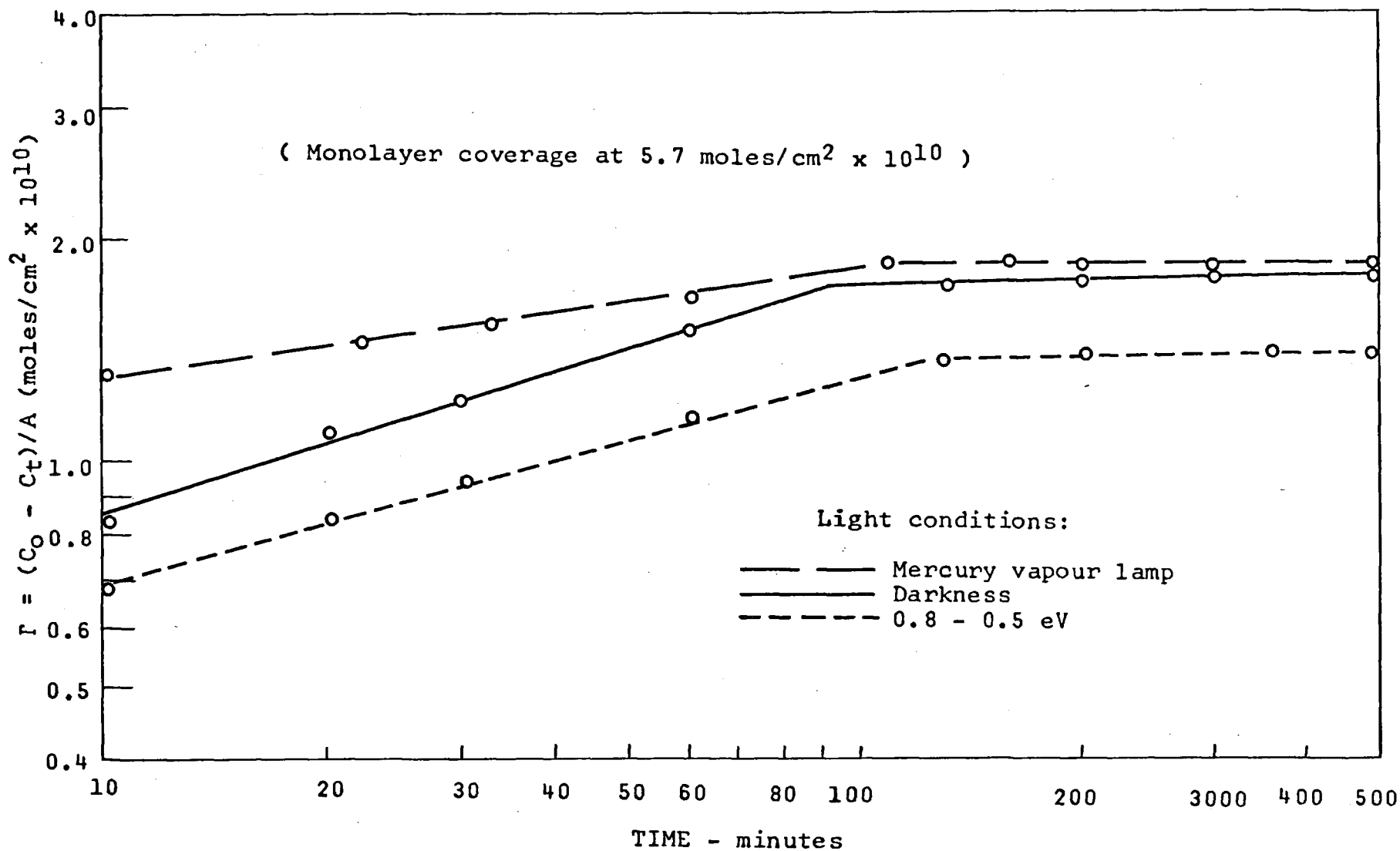


Fig. 24 - Adsorption of EtX^- from a solution of KEtX ($9 \times 10^{-5} \text{ M}$) on activated $(\text{Zn,Fe})\text{S}$ (100/150 mesh) at 20°C and natural pH (6.5) under controlled illumination, (20g).

electron-hole recombination by trapping. The traps, commonly associated with impurities and structural defects, provide localized energy levels lying deep within the forbidden energy gap (See Fig. 2). The addition of energy less than the energy gap value may be sufficient to raise the electron from a trap into the conduction band from which it can then recombine with a hole in the valence band. Therefore the function of energy less-than-the-energy-gap value is to promote these recombinations by supplying the required transition energies to the system. The net effect is to annihilate an electron-hole pair and consequently to decrease chemisorption. A limiting state will be reached when the energy supplied has promoted all the electrons from the traps to the conduction band. From the results of the present investigation it may be concluded that an energy of 0.6 eV is sufficient to raise an electron from the trap to the conduction band, and that 2.9 eV is sufficient to raise electrons from the valence band into the traps. The former process results in a combination and removal of holes and the latter results in both creation of electron-hole pairs and recombination. An energy of 3.4 eV appears to be sufficient to promote electrons from the valence band to the conduction band thus creating electron-hole pairs.

The existence of different equilibrium adsorption values after about two hours is somewhat disconcerting.

The atomistic approach with its "dangling valence bonds" or active sites has been quite useful in explaining similar experimental results up to a monolayer value. Preferential adsorption on surfaces of different crystallographic orientation would be difficult to measure in the case of the mineral powders used in the present study. Furthermore adsorption slightly above the monolayer value is difficult to visualize from the concept of dangling valence bonds. The function of illumination is to produce more photoactive sites, resulting in different equilibrium adsorption values. In the only case where the results indicated adsorption greater than the monolayer value, that of the p-type galena, the strong attraction of xanthate could be attributed to the larger number of strongly anodic sites⁽²³⁾. However the rate of adsorption would be expected to decrease at the monolayer coverage. In view of the fact that the indicated surface coverage was not much greater than a monolayer, this excess could, on the other hand, arise from the experimental error of the surface area measurement. If the surface area is assumed to be correct, then the most satisfactory alternative is to describe the experimental results in terms of the position of the Fermi level.

When a semiconductor is in thermal equilibrium, the Fermi energy level assumes a certain value. Upon illumination, the quasi-Fermi levels for electron and holes

depend on the amount of photon energy supplied to the system. The higher the light intensity, the greater the probability of finding an electron in a surface trap and a localized hole in the depletion layer. This condition favours the chemisorption of xanthate anions. Since the charge density extends into the substrate, adsorption values slightly larger than a monolayer can be accommodated. While this explanation may not offer an exact description of the system, these considerations, like many others, are in a direction to fill a deficiency in the understanding of the chemisorption process.

When higher-than-the-energy-gap values of radiant energy are used in the tests, less difficulties are encountered in the interpretation of the results. In the case of galena, increasing energies always increase the amounts of xanthate adsorbed. This constant trend is clearly indicated in Fig. 25. Somewhat less regularity is displayed by the argentiferous galena in Fig. 26. In this graph, the adsorption values for the darkness and the one obtained with 0.5 eV are superimposed suggesting a minimum adsorption for the solid in question. A sudden increase in the amount adsorbed is displayed when 3.4 eV are used. In this case two effects must be taken into consideration: the original distribution of electrons in the substrate and the high energy value of illumination. Since the (Pb,Ag)S is predominantly an n-type semiconductor, less adsorption of

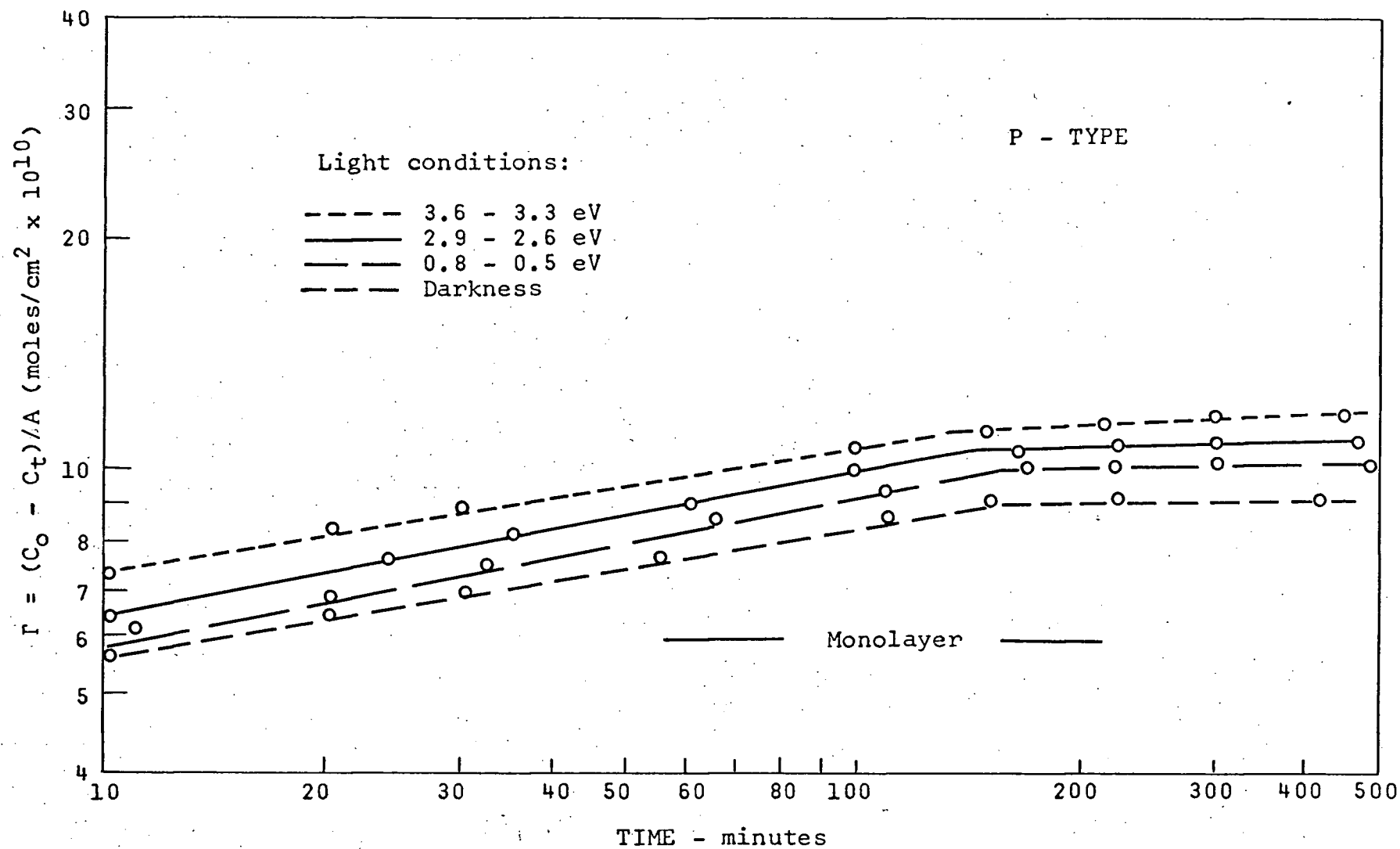


Fig. 25 - Adsorption EtX^- from a solution of KEtX ($9 \times 10^{-5} \text{ M}$) on PbS (100/150 mesh) at 20°C and natural pH under controlled illumination; 20g.

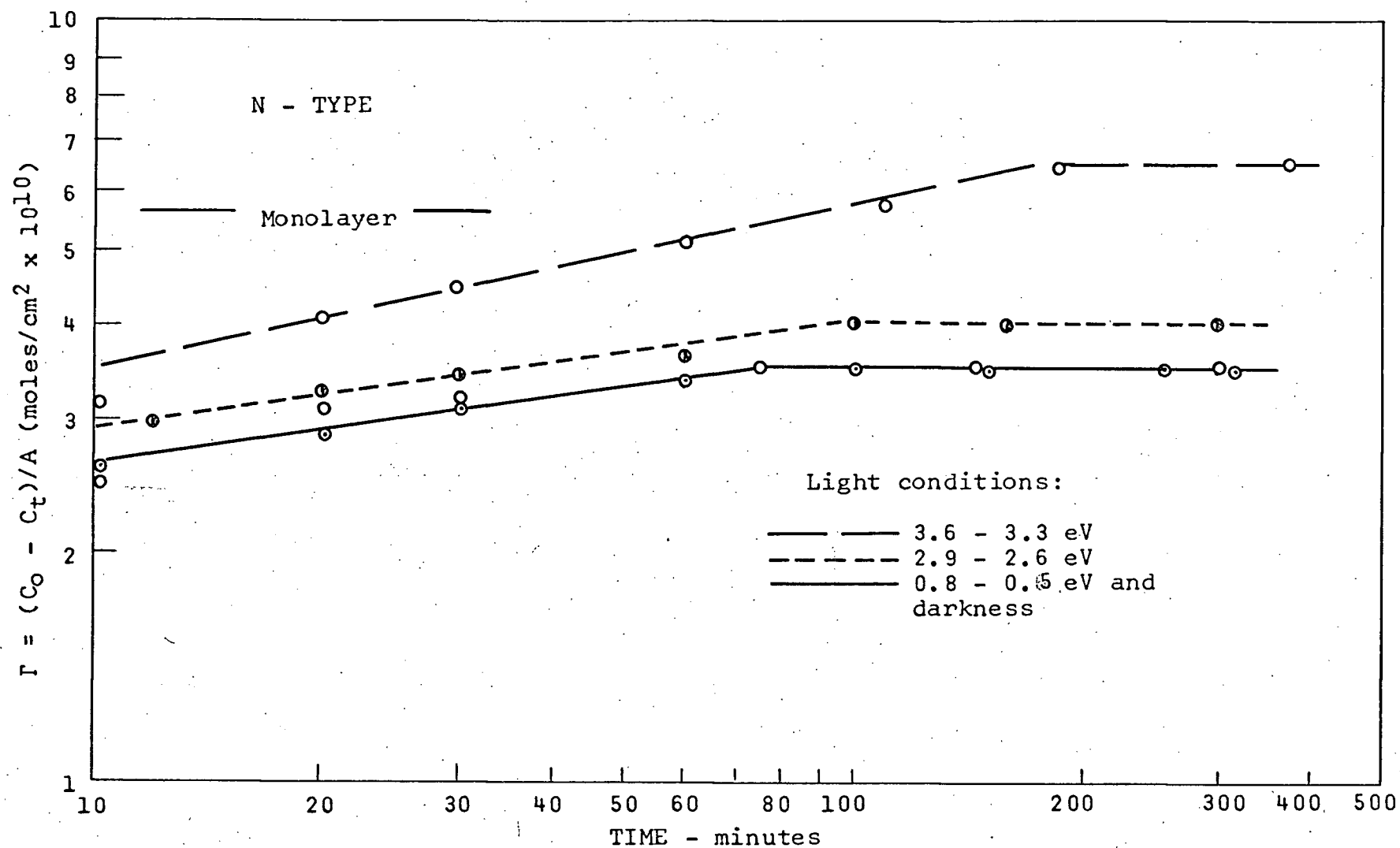


Fig. 26 - Adsorption of EtX^- from a solution of KEtX ($5 \times 10^{-5} \text{M}$) on argentiferous galena (100/150 mesh) at 20°C and natural pH under controlled illumination; 20g.

xanthate anions is to be expected, as will be discussed subsequently. The effect of illumination is then to change drastically the electron-hole distribution resulting in preferential adsorption.

A comparison between Fig. 25 and 26 shows a two-fold difference in the amount of xanthate abstracted by the two samples of galena. This effect may be attributed to either oxidation or to the electrophysical characteristics of the original samples and will be discussed under these headings.

4.3 Effect of Oxidation on Adsorption

The results presented in the previous section suggest that xanthate adsorption may be influenced either by the electrophysical characteristics of the original surface or by the presence of an oxidation product on the mineral surface. Two sets of experiments were carried out in order to differentiate between the two alternatives. The experiments were: (1) oxidation rates of galena surfaces and (2) adsorption of xanthate on unexposed surfaces in the absence of oxygen.

In the first case the relative rate of oxidation of the two galena samples is expected to indicate which sample is the most likely to form a thicker layer of oxides and, by comparison to the previous adsorption tests, the

influence of this layer on the fixation of xanthate anions. The test results are summarized in Tables XIII, XIV and XV (Appendix E). In these tables a column has been added to indicate the amount of oxygen uptake in terms of unit area. In the first two tables duplicate runs prove that the experimental procedure is quite reproducible. This can be seen in the graphical representation of Fig. 27. A comparison between Fig. 27 and Fig. 28 shows the effect of water vapour on the weight increase. Regardless of the atmosphere, the weight gain of the argentiferous galena (n-type) is approximately double that of the p-type galena at the arbitrary value of 30 minutes.

As described previously in section 3.7b adsorption of xanthate anions was studied on two samples of galena which were specially prepared and tested in an inert atmosphere. These results are presented in Fig. 29. In this graph the ranges of the previous adsorption results, when samples and solution were exposed to atmospheric oxygen, are shown as shaded areas. The effect of oxygen is quite pronounced in the case of the argentiferous galena. The increase in adsorption due to oxidation of the n-type galena was approximately one half of the difference in adsorption of p-type compared to n-type galena. This fact correlates quite well with the previous oxidation experiments since the argentiferous galena is the one that oxidized more readily.

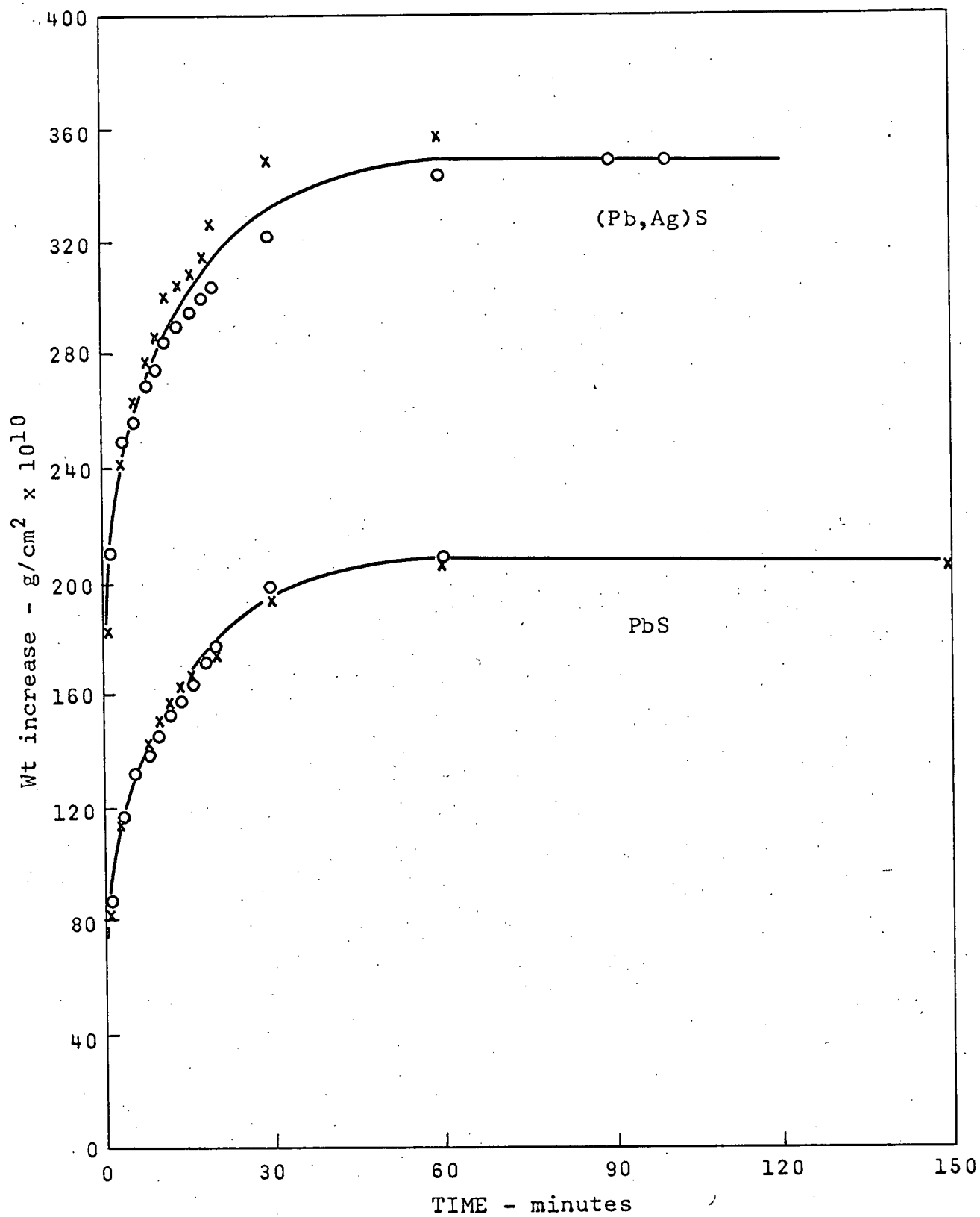


Fig. 27 - Oxidation rate of galena in oxygen in the presence of water vapour.

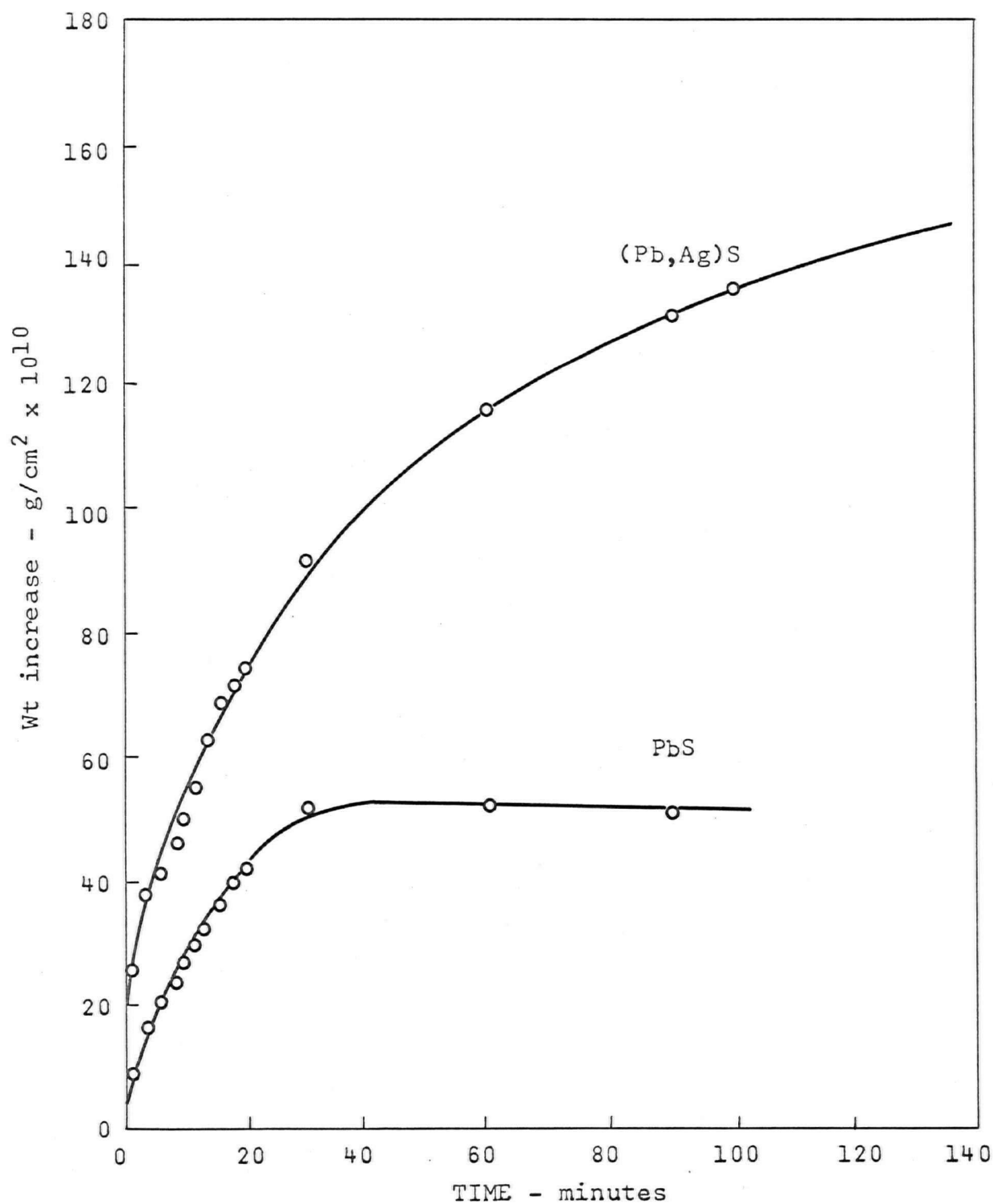


Fig. 28 - Oxidation rates of galena in a dry atmosphere of oxygen.

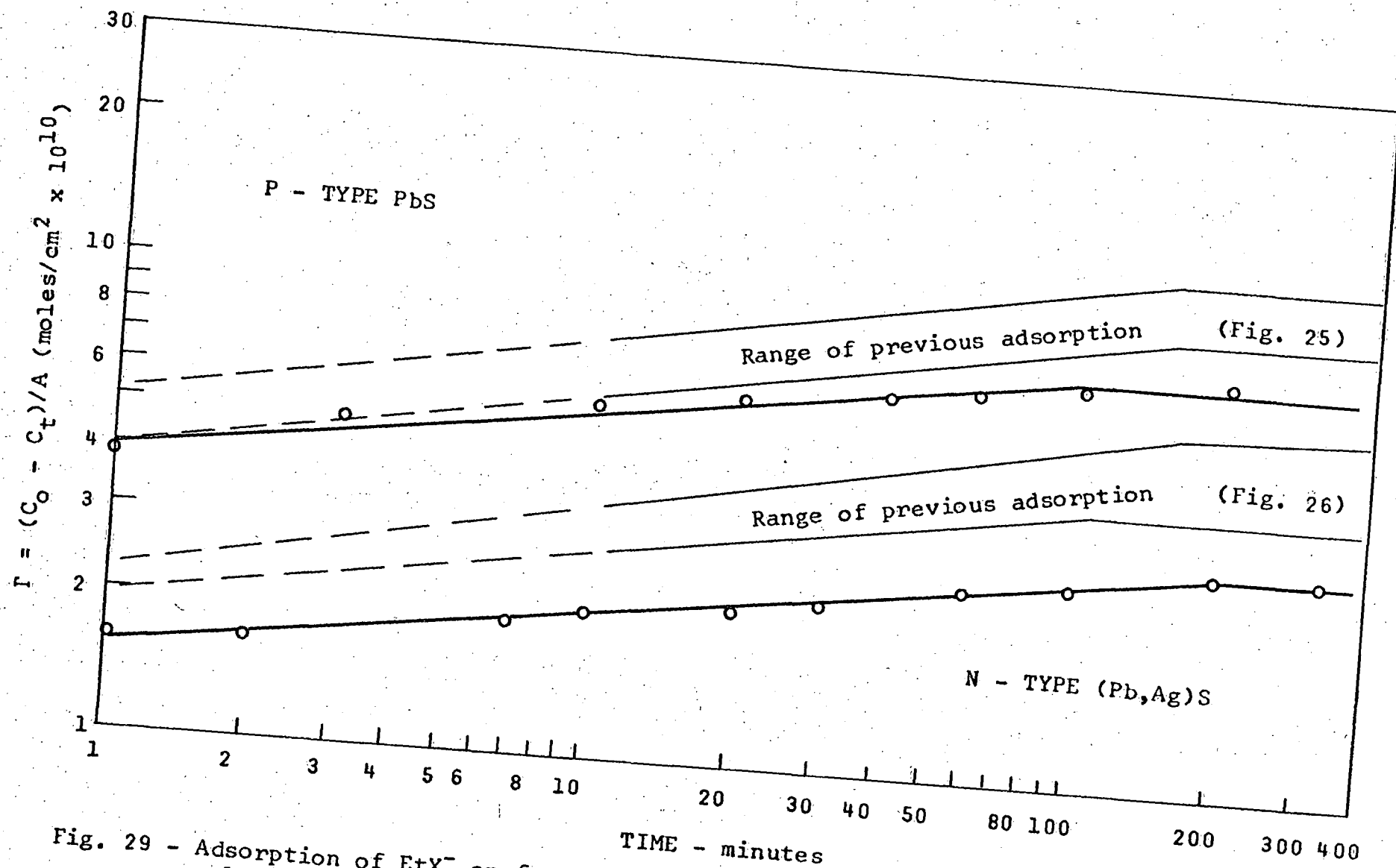


Fig. 29 - Adsorption of EtX^- on freshly prepared surfaces of galena (100/150 mesh) from a solution of KEtX in a helium atmosphere at 20°C , natural pH and constant wavelength (.340-.380 microns, 3.6-3.3 eV).

4.4 Effect of Surface Characteristics on Adsorption

Apart from the effects of oxidation and illumination there is still a basic difference in the adsorption behaviour between the p-type and n-type samples. This behaviour can be analysed in terms of the electrophysical characteristics of the solids.

Since the uptake of an adsorbate is accelerated by the presence of free quantum states (holes), a p-type solid is expected to favour the chemisorption of xanthate. The reverse is true for a solid of the n-type. Fig. 29 shows that the order of magnitude of this effect is larger than that of either illumination or oxidation. In terms of surface coverage, the amount of xanthate adsorbed in the first 10 minutes by the p-type galena reaches that of a monolayer whereas in the case of the n-type solid, the coverage is approximately one half of the monolayer value.

To summarize, the combination of the rate of oxidation and the presence of oxidation products on the adsorption of xanthate anions leads to some interesting conclusions. Since (Pb,Ag)S oxidizes more rapidly than PbS, the former should have changed to a p-type semiconductor in a relatively short period⁽²⁴⁾. That this transition did not take place is evidenced by the Seebeck Effect (n-type), discussed subsequently in section 4.7, and by the lower affinity of (Pb,Ag)S for EtX^- than that dis-

played by PbS (p-type) in the adsorption experiments. Without refuting the effects of oxygen on adsorption, the present results strongly suggest that the original n-type or p-type character of the solids is the more important factor.

4.5 Effect of Illumination Intensity on Adsorption

The dependence of the adsorption on the intensity of light of a constant wavelength in the system xanthate-activated marmatite was investigated and results are shown in Fig. 30. The system is characterized by a strong photo-adsorption effect which depends on the intensity of the light. When the maximum intensity was irradiated on the sample, the amount of xanthate adsorbed in the first 10 minutes was twice the amount adsorbed by the sample kept in total darkness. These points as well as those for intermediate intensities are presented in Fig. 31. In these figures the light intensity was calculated using the mean emf of a calibrated thermopile* and the reading of a high-impedance microvoltmeter (Fluke, Model 845-AB). All measurements refer to the light values after filtering as present at the outside walls of the adsorption chamber.

* Eppley Thermopile Serial No. 8824, The Eppley Laboratory Inc., Newport, R.I.

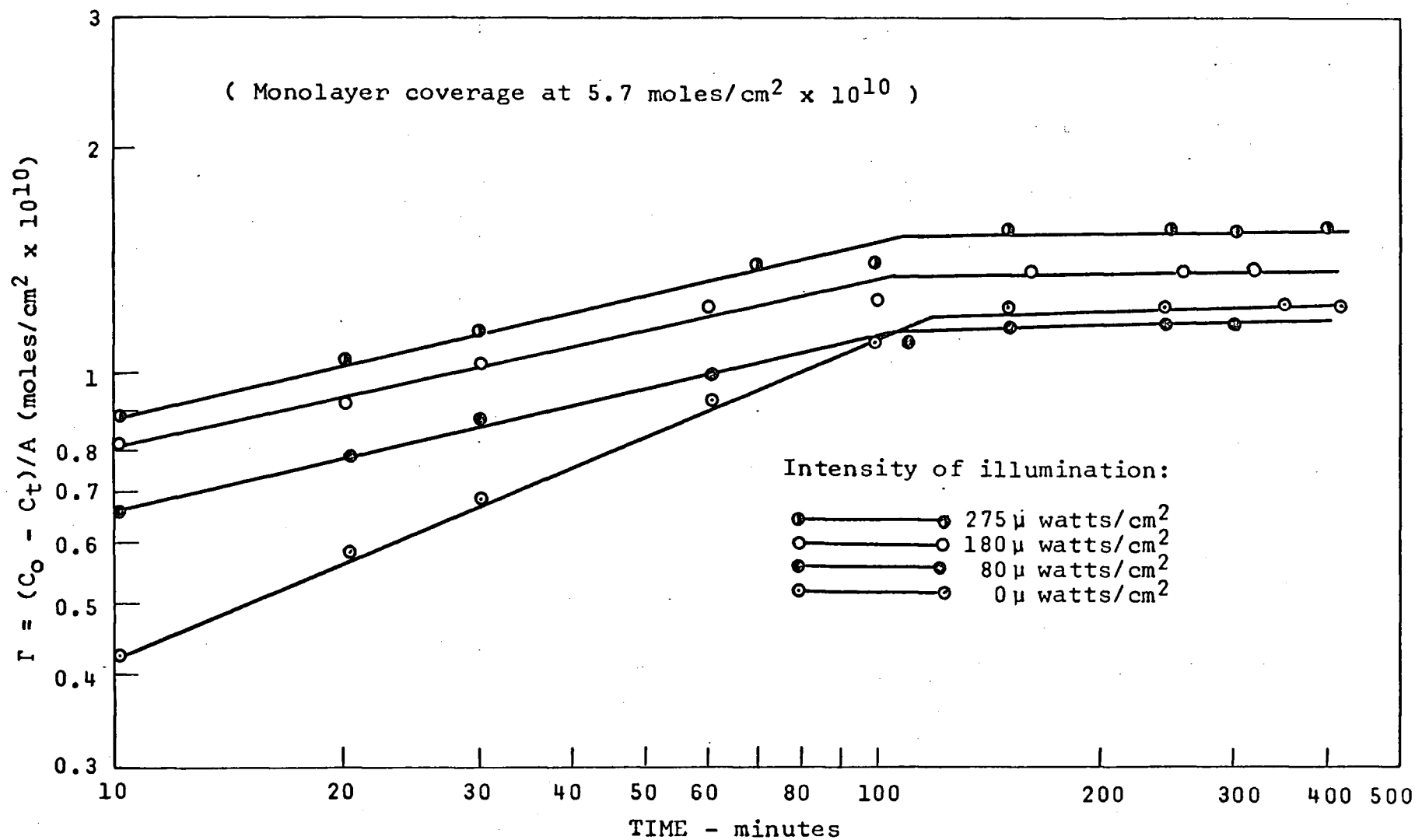


Fig. 30 - Adsorption of EtX^- on activated $(\text{Zn,Fe})\text{S}$ (150/200 mesh) at 20°C and natural pH using various intensities of illumination at a constant wavelength (.340-.380 microns) from a 400 W/QI lamp; 10g.

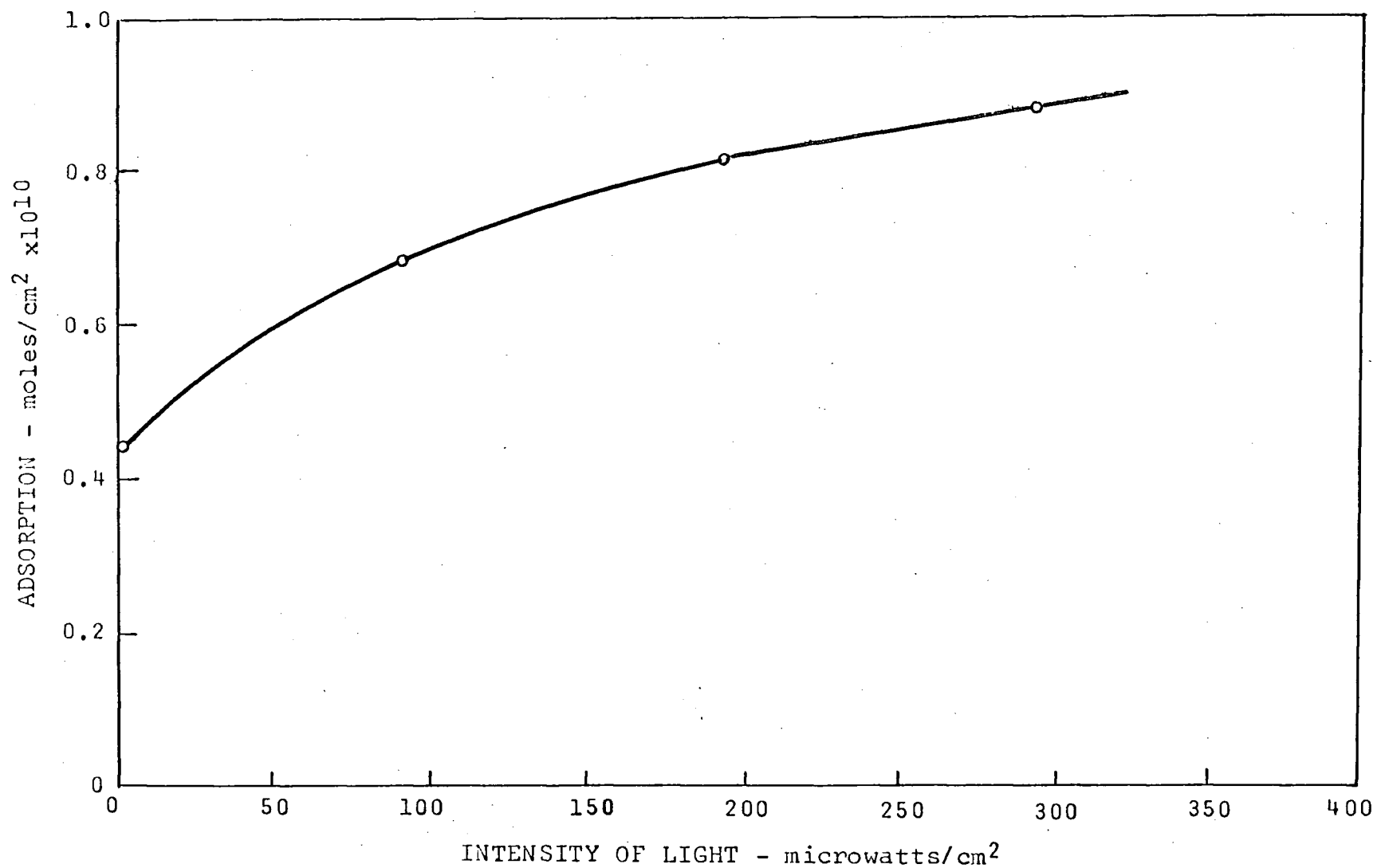


Fig. 31 - Variation on the amount of xanthate adsorbed as a function of light intensity for a constant energy (3.6-3.3eV) at 10 minutes.

TABLE VI

ELECTROPHYSICAL CHARACTERISTICS OF ACTIVATED
MARMATITE AFTER ADSORPTION OF EtX^- AS
A FUNCTION OF ILLUMINATION INTENSITY.

Light Intensity μ watts/cm ²	Type of Semiconductor	Thermoelectric Power $\mu\text{V}/^\circ\text{C}$	Fermi Level ($E_C - E_F$) eV
0	P	34	0.97
80	P	21	0.58
180	P	24	0.67
275	P	26	0.73

The electrophysical characteristics of pelletized samples of activated marmatite after exposure to illumination and adsorption were determined as described previously. These are summarized in Table VI. A sample calculation of the Fermi energy level from thermoelectric power measurements is presented in Appendix F. In all cases, the Fermi energy level was raised after adsorption of the donor adsorbate (EtX^-).

4.6 Copper Activation

Copper activation of marmatite is normally required for flotation. The effect of initial copper ion concentration on the activation of marmatite and subsequent adsorption of xanthate ions was investigated using a constant illumination. The results are shown in Fig. 32. Concentrations of 10^{-4} and 10^{-3} M/l of copper sulphate had a definite effect on the adsorption of xanthate whereas a concentration of 10^{-5} M/l showed but little improvement over the non-activated marmatite. At the higher concentrations of copper sulphate the rate of xanthate adsorption was of the same order of magnitude as in the previous tests. At the low concentration, xanthate adsorption appeared to reach equilibrium at a low surface coverage. Coverages by copper atoms were determined from the differences between the initial and final concentration of copper in solution

in the activation step, assuming the parking area of the copper atom to be $10.4 \text{ \AA}^2$ (28). All concentrations were measured by an EEL Atomic Absorption Spectrophotometer. The results of Table VII together with Fig. 32 indicate that a concentration of 14% or more of the monolayer value promotes adsorption of xanthate, whereas a coverage of 2% is insufficient. Stoichiometrically, the value of 14% is in excellent agreement with the calculated coverage by xanthate (13%) after the first 10 minutes, a common retention time used by flotation plants.

The effects of washing, non-washing and washing followed or not by drying on the adsorption of xanthate on copper activated marmatite are shown in Fig. 33. Identical results were obtained with or without drying of the washed marmatite prior to adsorption of xanthate. When the sample was not washed more xanthate was adsorbed. In this case the high xanthate abstraction was due to the precipitation of cuprous ethyl xanthate. In the absence of washing extra copper was present in the system as an aqueous film around each mineral particle.

Table VIII summarizes the electrophysical characteristics of the powders prior to and after xanthate adsorption. If the results are grouped in pairs the correlation of Table VIII with Fig. 32 is quite evident. Following activation in low copper concentrations the resistance stays

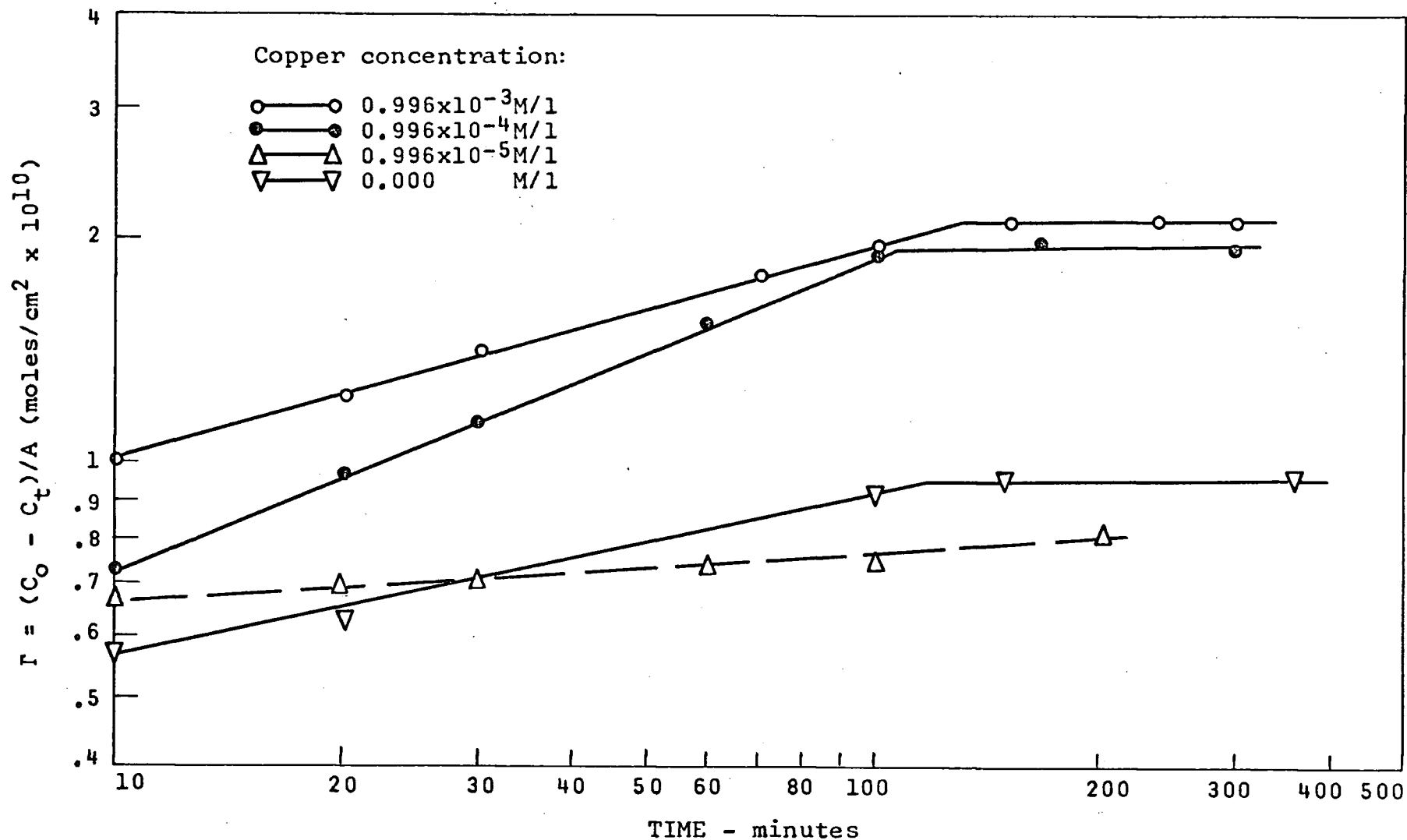


Fig. 32 - The effect of copper activation on the adsorption of EtX⁻ from a solution of KEtX (5x10⁻⁵M) on (Zn,Fe)S (65/100 mesh) at 20°C and natural pH, illuminated with light of 3.6-3.3 eV; 10g.

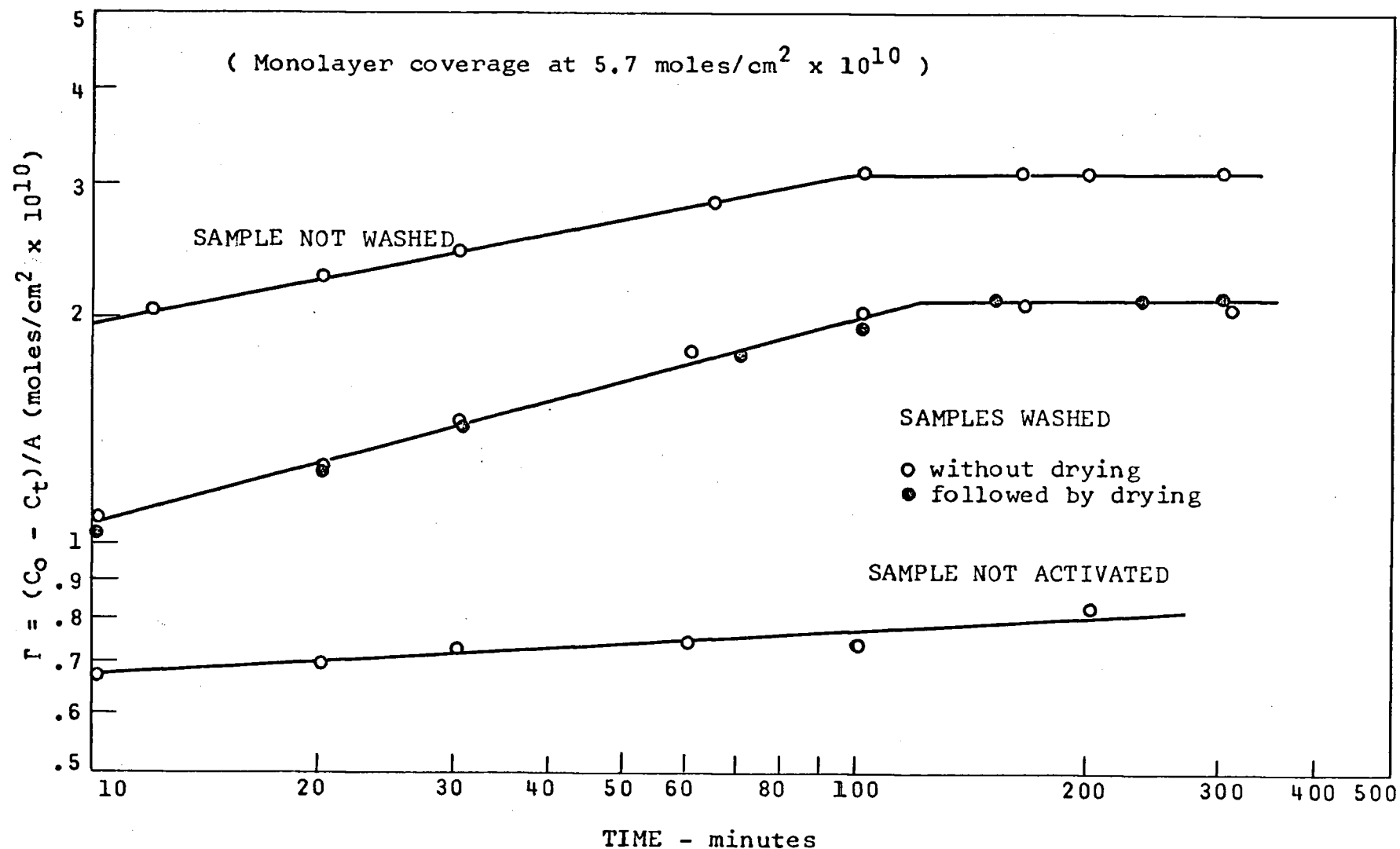


Fig. 33 - The effect of washing the marmatite after copper activation, 10g of (Zn,Fe)S (65/100 mesh) with 100 ml of a $0.996 \times 10^{-3} \text{ M}$ solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on the subsequent adsorption of EtX^- at 20°C and natural pH, illuminated with light of 3.6-3.3 eV.

TABLE VII - ADSORPTION OF COPPER ON
MARMATITE (65/100 MESH)

Initial Concentration of Copper $\times 10^{-5}$ M/l	Final Concentration of Copper $\times 10^{-5}$ M/l	Adsorbed Copper $\times 10^{-7}$ M/l	Calculated Surface Coverage %
0	0	0	0
0.996	traces	0.9	2
9.96	3.95	6.0	14
99.6	55.9	43.7	105

TABLE VIII

CHANGES IN THE ELECTROPHYSICAL CHARACTERISTICS
OF (Zn,Fe)S ON ADDITION OF VARIOUS
 Cu^{++} CONCENTRATIONS

Initial Copper Concentration- M/l	Prior EtX^- Adsorption			After EtX^- Adsorption		
	Type of Semic.	μ V/ $^{\circ}\text{C}$	Ω cm	Type of Semic.	μ V/ $^{\circ}\text{C}$	Ω cm
0	p	174	2×10^8	p	155	2×10^8
0.996×10^{-5}	p	155	4×10^8	p	139	2×10^8
0.996×10^{-4}	p	65	4×10^6	p	66	4×10^7
0.996×10^{-3}	p	14	1×10^6	p	46	2×10^7

approximately the same before and after adsorption (Table VIII). This effect is paralleled by low adsorption rates of xanthate in Fig. 32. Following activation in high copper concentrations the resistance of the powders before adsorption is less than in the previous case and increases slightly after adsorption (Table VIII). This trend is again clearly indicated in Fig. 32 by the higher adsorption rate and total adsorption of this pair.

4.7 Electrophysical Measurements

In the previous two sections some pertinent electrophysical measurements were introduced. In this section, some basic electrophysical characteristics of as-received solid and powder specimens are presented. These include a study of carrier type and concentration, from both the Hall coefficient and the Seebeck effect.

Table IX shows the results obtained on solid specimens by measuring the Hall voltage. A detailed calculation of one of the measurements is shown in Appendix G. In the case of galena reliable results were obtained with pressure contacts, solder contacts yielding similar results. Since no measurement could be made on the ground marmatite from Broken Hill, a solid sample of British Columbia sphalerite was prepared as a possible alternative. Because of its high resistance, measurements with either

TABLE IX - ELECTROPHYSICAL CHARACTERISTICS
OF SOLID SPECIMENS

Sample	Semic. Type	Resistivity Ω cm	Hall Coeff. cm^3/coul	Carriers Concentr'n cm^{-3}	Mobility $\text{cm}^2/\text{volt cm}$
PbS	p	0.4	280	2.2×10^{16}	700
(Pb,Ag)S	n	1.3×10^{-7}	0.013	6×10^{17}	10^5

TABLE X - SEEBECK EFFECT ON SOLID AND
POWDER SPECIMENS

Sample	Semiconductor Type	Q Millivolts/degree	Resistivity Ω cm
PbS			
powder	p	0.0018	56
solid	p	0.0012	20
(Zn,Fe)S			
act. powder	p	0.0028	1×10^6
non act. powder	p	0.0012	2×10^8
(Pb,Ag)S			
powder	n	0.0031	5×10^{-4}
solid	n	0.0026	2×10^{-5}

pressure or indium solder contacts were not successful. No further work was warranted on this particular sample.

Table X summarizes the results obtained on both solid and powder specimens. A sample calculation of the carrier concentration is presented in Appendix H. The value obtained, 5.1×10^{18} holes/cm³, is not in agreement with the value previously calculated from the Hall voltage, 2.2×10^{16} , as is commonly found when using thermoelectric power data. Similar discrepancy has been attributed to an interaction between the anisotropic lattice vibrations, due to the thermal gradient, and the mobile charge carriers⁽⁵⁰⁾. The carriers are preferentially scattered toward the cold end of the sample by the non-equilibrium phonon distribution thus enhancing the electrostatic field. Furthermore, in Appendix H the effective mass of the electron has not been measured in the galena specimens and has been assumed to be 0.3 the mass of the electron, a value previously used by Slater⁽⁵¹⁾. Because of these uncertainties, the application of the Seebeck effect has been confined to the differentiation of n-type and p-type specimens.

4.8 Correlation of Adsorption Results

The individual behaviour of galena and marmatite has been characterized by adsorption and electrophysical measurements under various conditions of illumination. To

be able to compare the adsorption effects with each other, a common base had to be selected. The most logical choice was that of percentage surface area coverage. Then the surface covered by the surfactant could be used to represent the tendency for the adsorption to take place. This tendency has been expressed as percent of monolayer coverage.

Table XI is a compendium of surface coverages for the various systems investigated. The main trends are quite apparent. Namely, the p-type galena adsorbs a monolayer of xanthate in the first 10 minutes whilst the n-type galena adsorbs only one half of its monolayer value. Moreover, the amount of xanthate adsorbed by the two galenas differs largely from the amount of xanthate abstracted by the marmatite. The latter shows an adsorption that never exceeds an equivalent coverage of 23% under the most favourable conditions.

These trends strongly indicate that the electro-physical characteristics of the substrate are of paramount importance in adsorption. Since the adsorption of xanthate is a p-type reaction it is accelerated by free quantum states and the p-type galena is expected to adsorb a monolayer of xanthate in a relatively short time. When the p-type galena is compared to the p-type marmatite the difference in the adsorption characteristics can be attributed to the difference in the energy gaps. If the tests with 0.6 eV are chosen in each case, the ratio between the theoretical

TABLE XI - ADSORPTION RESULTS IN TERMS
OF XANTHATE COVERAGE

Material	Conditions for Adsorption	Monolayer Coverage-%	
		at 10 min.	at equilibrium
(Zn,Fe)S	Hg lamp	23	31
"	Darkness	14	30
"	3.6-3.3 eV	22	30
"	2.9-2.6 eV	17	26
"	0.8-0.5 eV	12	24
"	7000 lumens	15	26
"	5600 lumens	14	22
"	2450 lumens	11	21
"	Darkness	7	20
"	Cu ⁺⁺ -10 ⁻⁵ M/l	19	37
"	Cu ⁺⁺ -10 ⁻⁴ M/l	13	35
"	Cu ⁺⁺ -10 ⁻³ M/l	11	18
"	Cu ⁺⁺ -0 M/l	12	13
PbS	400 W-QI	115	180
"	500 W-QI	115	200
"	3.6-3.3 eV	115	190
"	2.9-2.6 eV	105	175
"	0.8-0.5 eV	95	165
"	Darkness	90	150
PbS	Unox-3.4 eV	88	110
(Pb,Ag)S	Unox-3.4 eV	35	50
(Pb,Ag)S	3.6-3.3 eV	62	120
"	2.9-2.6 eV	53	72
"	0.8-0.5 eV	44	63
"	Darkness	44	63

values of the energy gaps is in good agreement with the ratio of their surface coverages at the ten minute value and at equilibrium. Namely, the theoretical energy gap ratio of 10 compares favourably with the ratios of 8 and 7 for the experimental coverages. The test with 0.6 eV has been chosen because with this energy the traps are emptied and the marmatite more closely resembles the intrinsic semiconductor. Under these conditions it was acceptable to use as the theoretical energy gap value the published figure for sphalerite.

The same trend towards increased adsorption is observed when the unoxidized forms of galena are compared with the oxidized. The unoxidized p-type galena adsorbs 88% of a monolayer in the first 10 minutes instead of a full monolayer. The unoxidized n-type galena adsorbs approximately 1/4 of a monolayer rather than one half of a monolayer during the same period of time. Thus a 50% difference between the adsorption behaviour of the two forms of galena is still apparent whether or not they are oxidized.

When the individual marmatite systems are taken into consideration, it is noted that in the first ten minutes the amount of xanthate adsorption increases as the illumination energy, light intensity or copper concentration increases. At the equilibrium conditions, a similar increase is observed but to a lesser extent in the case of photoexcitation. In the case of copper activation at

equilibrium conditions a greater adsorption of xanthate was observed.

The effect of illumination on each variety of galena was to increase adsorption. However during the first 10 minutes, the amount of xanthate adsorbed by PbS was enhanced by 25% whilst the increase in adsorption displayed by the (Pb,Ag)S was only 18%.

Thus the original electrophysical characteristics of the substrate are more significant than the effects of illumination on the adsorption of xanthate.

4.9 Flotation Experiments

The differences in the adsorption rates of xanthate anions on galena and marmatite suggest the possibility of utilizing controlled illumination in the practical separation of the two minerals. The actual application has been investigated using a semi-micro flotation technique described in section 3.8.

At the beginning it was decided to give the same statistical probability of particle to bubble attachment to both minerals by using the same number of particles in all tests (Appendix I). As soon as the first series of tests had been completed (Appendix J), it became apparent that it was extremely difficult to detect significant differences between tests of varying light energies since comparable

high recoveries were obtained in all tests. To circumvent this difficulty, starvation quantities of surfactant were calculated as follows. Since only 10% of the surface of marmatite is covered by xanthate (present work) it is not necessary to have more than this equivalent amount in solution. In the case of galena 20 to 40% coverage is required for flotation⁽³⁰⁾. Using 150 ml of solution and 2g of 150/200 mesh marmatite ($5,200 \text{ cm}^2/\text{g}$), 0.04 mg/l are required for a surface coverage of 9%. In the case of PbS, again using 150 ml of solution and 2g of 100/150 mesh fraction ($1,850 \text{ cm}^2/\text{g}$), 0.08 mg/l are required for a surface coverage of 32%. The fact that two different reagent concentrations were required, necessitated an individual treatment of the minerals.

A summary of the flotation results is presented in Table XII. The data indicate that the flotation of galena was not significantly different when either daylight or light of 2.5 microns wavelength was used in the experiments. A definite trend towards lower recoveries was present when marmatite was investigated under equivalent test conditions. The recovery of marmatite decreased by 11% when irradiated with light of 2.5 microns wavelength compared with that in daylight. The trend of the previous adsorption experiments was thus confirmed even though a practical separation of the mixed minerals would be extremely difficult to achieve since different initial concentra-

TABLE XII - SUMMARY OF FLOTATION RESULTS

Sample	FLOTATION CONDITIONS			DISTRIBUTION (Arith. Ave. of 5 tests)		Standard Deviation	Confidence Limit (68.27% level) %
	Light	KEtX mg/l	Ethanol mg/l	Float	Tails		
PbS (100/150)	Daylight	0.08	0.03	37.0	63.0	3.0	37.0+ <u>3.0</u>
PbS (100/150)	2.5 μ	0.08	0.03	39.7	60.3	2.7	39.7+ <u>2.7</u>
(Zn,Fe)S (150.200)	Daylight	0.04	0.02	73.2	26.8	2.2	73.2+ <u>2.2</u>
(Zn,Fe)S (150.200)	2.5 μ	0.04	0.02	62.2	37.8	3.3	62.2+ <u>3.3</u>
(Zn,Fe)S (150/200)	150 W	0.04	0.02	72.5	27.5	2.9	72.5+ <u>2.9</u>

tions of xanthate were required. Furthermore, inconclusive results were obtained with marmatite when tests conducted in daylight were compared with tests where a 150 watt light bulb was used. Similar recoveries suggest that the optical excitation was of the same order of magnitude in both cases.

CHAPTER 5

DISCUSSION OF RESULTS

5.1 Adsorption

In the present study two distinct adsorption stages can be identified: (a) a rate dependent stage that extends from 1 to approximately 100 minutes and, (b) a stage above the 100 minutes where the rate is greatly diminished. Another region where adsorption takes place in less than 1 minute has been previously described by other investigators⁽³⁰⁾. No investigation of the kinetics below one minute could be made because of the inherent limitations of the equipment used nevertheless, a short discussion must be included since the mode of adsorption in this region constitutes the basis for subsequent adsorption.

The kinetics of adsorption below the one minute level vary depending on monolayer or multilayer coverages⁽³⁰⁾. The supporting data indicate that the rate of collector adsorption depends on the concentration of reagent in solution. These results with 50g/ton (≈ 20 mg/l) agree with monolayer coverages whereas the results with 1000g/ton (≈ 300 mg/l) agree with multilayer adsorption. Presumably these coverages

refer to the hypothetical orderly arrangement of the surfactant on the mineral surface. This is of paramount importance because the main indication of multilayer adsorption comes from the calculation of the amount adsorbed on the unit area of the mineral surface. Calculations of multilayer coverages are not correct because of the non-uniform distribution of reagents on the mineral surface, the difference between the uniform and non-uniform distribution accounting for the multilayer coverage. Thus adsorption at low concentrations and within the first sixty seconds may be visualized as a "monomolecular gaseous" film residing entirely at the active sites with random orientation of non-polar radicals. In the present experiments multilayer adsorption should not have occurred with the low concentration of xanthate used for the adsorption (≈ 15 mg/l). These predictions were confirmed by the experiments where the calculated monolayer values appeared only around the two hour limit.

In the 1-to-100-minute region the rate of adsorption was found to vary according to the specific experimental conditions. A study of these variations was the main objective of this investigation since enhanced or reduced adsorption resulted on changing the electron-hole distribution of the substrate with illumination. When more active sites were induced in the substrate more xanthate could be adsorbed by the increased electrostatic attraction.

At this stage the molecules have a strong tendency to orient themselves on the mineral surface forming the equivalent of a two dimensional "liquid film". Two effects are apparent: (1) increased adsorption due to an increase in the number of surface sites and/or an increase in the electrostatic attraction with more holes localized at the active sites, and (2) adsorption facilitated by the association between hydrocarbon chains. Furthermore, multilayer formation in this region may be accompanied by a physical adsorption of metal xanthate molecules and dixanthogen molecules previously formed in the electrical double layer surrounding the mineral particles. In this case extensive adsorption of neutral molecules would occur through interaction of hydrocarbon chains but without electrostatic repulsion since the polar heads are uncharged.

In the region above 100 minutes the results indicate that the adsorption rate is negligible. Because chemisorption is responsible for the main adsorption of xanthate on galena, only physical adsorption may be operative in this region. When chemisorption occurs, it is usual for the surfactant to react completely unless the solid surface becomes saturated. It is difficult to understand why this does not occur in the xanthate-galena system. It could be postulated that the reaction is very slow at a particular concentration of xanthate but speeds up at higher concentration being controlled by a diffusion

rate through a film of products. Alternatively the reaction could be due to the presence of a very low concentration of another reactant which becomes exhausted or diffuses slowly through a continuous film of adsorbed xanthate (i.e. oxygen in solution). In either case the resulting effect would be an extremely low adsorption, an effect which was observed experimentally.

5.2 Photochemical Effects

The concentrations of electrons and holes for an illuminated crystal vary from those of a crystal kept in total darkness. The new distribution is expected to influence the subsequent adsorption of surfactants. Photoadsorption or photodesorption, therefore, may be observed depending on the position of the Fermi level, presence of impurities etc. Theoretically, the presence of an acceptor impurity that lowers the Fermi level, other conditions being equal, should result in photoadsorption.

In the case of galena, an easily oxidized mineral, the chemisorbed oxygen present at the surface may take part in an electronic interaction by lowering the electronic energy barrier and thus reducing the value of the photon energy of activation required for the adsorption of xanthate. The results of Fig. 25, 26, 29 confirm these predictions. Furthermore, oxidation of the n-type galena increased the adsorption of xanthate by 50% (Fig. 29) in

contrast with the lower adsorption of the p-type galena which was less readily oxidized.

In the case of marmatite a photon energy of 0.6 eV is capable of causing a captured electron to recombine with a hole in the valence band but is not sufficient to create an electron-hole pair. A depletion of electrons and holes results in a lowering of the amount of reagent adsorbed, an effect which is readily observed in Fig. 24. Furthermore the energy capable of causing these recombinations is of the same order of magnitude as the Lambe and Klick stimulation band [quoted as 2.6 microns (0.5 eV)¹⁷] as previously indicated in Fig. 3b. An alternative explanation of this effect is an emission transition as proposed by Bube⁽¹⁸⁾ and presented in Fig. 2. The practical result was an 11% reduction in the flotation recovery (Table XII), a result which was paralleled by Plaksin⁽¹⁾ in the flotation of zircon and pyrochlore; on irradiation, the flotation of pyrochlore was reduced by 40%.

In terms of photochemical effects, the results of the present study indicate that: (1) photoadsorption is the result of illuminating a semiconductor with energy higher-than-the-energy-gap whilst (2) photodesorption is the result of illuminating the semiconductor with energy lower-than-the-energy-gap.

5.3 Carrier Behaviour

Measurements of the Hall coefficient could only be carried out on galena specimens, the high resistance of the marmatite being outside the working limits of the available equipment. These measurements and limitations are in accord with the results of Putley⁽⁵²⁾ and Saito⁽⁵³⁾. The work of this last investigator is of particular interest because his results indicate that the transition from n-type to p-type may be followed through a change in resistance, a relatively simple measurement to carry out. Increased resistance has been emphasized also by Mark⁽⁶⁾. The tendency for the resistance of activated marmatite to increase after adsorption is evident from Table VIII.

The Seebeck effect has been used successfully in measuring the n-type or p-type character of the pressed powders. The most important application is presented in Fig. 29 where the amount of xanthate anion adsorbed is drastically reduced in the case of the n-type semiconductors. Without the possibility of measuring the electronic character of the powders, it would have been impossible to interpret the experimental results.

The position of the Fermi level within a crystal and the degree of curvature of the energy bands establish the electrical conductivity of a semiconductor. The closer the Fermi level is to the conduction band, the larger is

the value of the electron density and the more pronounced are the n-type characteristics of the semiconductor. Thus semiconductors are classified as n-type or p-type when the hole component or electronic component respectively is negligible. The concentration of free charge carriers that take part in the reaction must be responsible for the reaction rate. A p-type reaction (donor) is one which is accelerated by free quantum states and an n-type reaction (acceptor) is one which is accelerated by electrons. Since the measurements of the Hall coefficient and the Seebeck effect indicate that the galena is a p-type semiconductor, the increase in electrical conductivity when the solid is illuminated and a parallel increase in adsorption rate suggest that the reaction is of the p-type. This is in agreement with the structure of the negative xanthate anion that requires a free quantum state or hole, and with the mechanism of photoconductivity originally described by Slater⁽⁵¹⁾. This author recognizes n and p-type regions in the galena structure and the excitation of an electron to the conduction band when light is absorbed anywhere in the crystal, leaving a hole in the valence band. The electron so introduced into the conduction band will now tend to fall to the lowest possible energy, or into an n-type region, and a hole will in a similar way find its way into a p-type region. The presence of extra electrons in the n-type region, extra holes in the p-type region, will

neutralize some of the potential barriers. Thus the barriers will be lowered and, in agreement with Plaksin et al⁽⁷⁾, the xanthate adsorption will be enhanced. This fact has been demonstrated repeatedly in the present work with the effect of illumination on adsorption, an effect that provides a good correlation between photoconductivity and adsorption.

5.4 Impurities and Reaction Mechanism

In this section emphasis is placed on the activation of marmatite, namely the role of copper in adsorption. In general the amount and type of impurity, which govern the surface concentration of electrons, regulate also the amount of xanthate adsorbed by the substrate. Any impurity (dislocations, vacancies, interstitials and substitutional foreign atoms), depending on the type and concentration, displaces the Fermi level causing either an acceleration or a retardation of the adsorption reaction.

Impurities, therefore, can be of two types: acceptors or donors. Acceptor impurities always lower the Fermi level, while donor impurities raise it. In terms of n-type and p-type reactions, an acceptor reaction then will be retarded by an acceptor impurity and accelerated by a donor impurity whereas a donor reaction will be accelerated by an acceptor impurity and retarded by a donor

impurity. Thus a given impurity may act as a promoter for one reaction and as a poison for another. It has been shown in the present study that marmatite activation by copper ions results in enhanced adsorption, that is, the adsorption reaction is promoted by copper. This may be caused by an increase in concentration of free quantum states (or holes), a fact which indicates that this particular type of impurity imparts acceptor properties to the mineral surface. This conclusion is in agreement with the proposed energy level diagram of Bube (Fig. 2) and with Plaksin⁽¹⁾ who offers an additional explanation for the activating effect of copper ions by describing a removal of electrons from the surface layer as the copper ions diffuse into the lattice.

Impurity concentration is another important parameter that regulates the position of the Fermi level. For an n-type semiconductor as the acceptor impurity concentration increases, the n character is diminished until it is changed to a p-type, increasing thereafter. For a donor reaction (p-type) the net result is a continuous increase in the reaction rate. Thus, again, the position of the Fermi level uniquely describes the poisoning or promoting characteristics of a semiconductor on an adsorption reaction, the type of impurity being the cause of the shift of the Fermi level. Fig. 32 and Table VIII show how the adsorption of xanthate is affected by different

levels of copper activation, as well as the minimum copper concentration for activation of xanthate adsorption. This implies that in a flotation system it is possible to regulate not only the reaction rate (activity) but also the selectivity of the float by controlling the concentration of effective impurities.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The basic purpose of this investigation was to study the effect of illumination on the adsorption of xanthate on galena and marmatite and to present experimental evidence on the role of the electronic character of solids in flotation.

The experimental results indicate that:

1. Absorption of 0.6 eV photons by copper-activated marmatite causes a decrease in the amount of xanthate adsorbed as well as a decrease in the adsorption rate. These effects can be explained by the excitation of electrons from traps to the conduction band and subsequent recombination with holes in the valence band.
2. In the case of galena, illumination by energies higher than the energy gap (0.37 eV) increases the amount adsorbed.
3. At constant wavelength of illumination, the

light intensity from darkness to 275 microwatts per cm^2 is to double the adsorption of xanthate on the activated marmatite.

4. Under conditions of constant energy of illumination, temperature and initial xanthate concentration, the amount of xanthate adsorbed on the p-type galena is three times the amount adsorbed on the n-type, suggesting that the adsorption reaction may depend on the transfer of an electron from the xanthate anion to the substrate.

The results of treating the particular marmatite with various copper solutions of concentrations incremented by a factor of 10 indicate that solutions of 10^{-4}M produce a pronounced increase in both adsorption rate and amount of xanthate adsorbed as compared to the activation with a 10^{-5}M copper solution.

Flotation tests using starvation quantities of xanthate indicate that lower recoveries may be expected when marmatite is irradiated with light of 0.6 eV compared with those in daylight.

On the basis of the results discussed above it is suggested that the electronic distribution in the substrate plays a vital role in surface reactions. It is postulated that the position of the Fermi level may control the adsorption rate and that this could be modified

by a judicious control of the impurity concentration. The application of photo-induced adsorption to a flotation system may be warranted when high recoveries are required or when selectivity is the main objective of the operation.

SUGGESTIONS FOR FURTHER WORK

An investigation of the surface charge and the function of donor and acceptor particles would be of interest. Experimentally, two effects could be observed: (1) a change in the work function; (2) a change in the electrical conductivity.

Another aspect that could be further investigated is the effect of quality and quantity of added impurities on the activity and selectivity of a flotation process. Depending on the type of semiconductor, the concentration of an impurity can control the reaction either by adding or removing excess quantities of electrons (selectivity).

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APPENDIX A

Hall Coefficient: Conversion of cgs units to Practical Units.

The following equation is expressed in cgs units:

$$V = \frac{1}{nqc} \frac{IH}{t}$$

Since: 1 electrostatic cgs unit = 300 volts

1 amp = 3×10^9 electrostatic cgs units

1 coulomb = 3×10^9 electrostatic cgs units

$$\frac{V}{300} = \frac{(I \times 3 \times 10^9) H}{n (q \times 3 \times 10^9) (3 \times 10^{10})}$$

$$V = \frac{1}{nq} 10^{-8} \frac{IH}{t}$$

$$V = R_H 10^{-8} \frac{IH}{t}$$

APPENDIX B

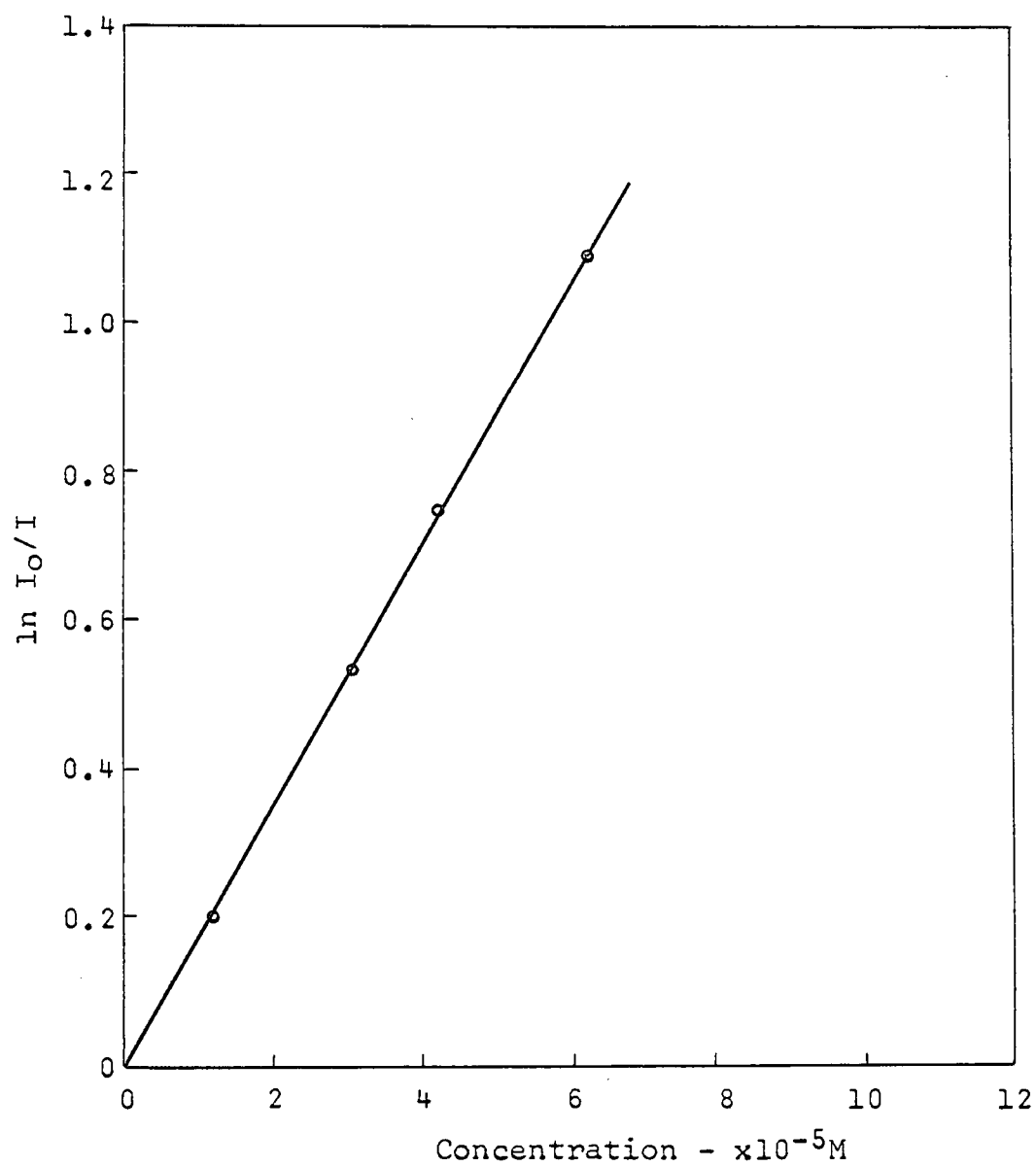


Fig. 34 - Beer's Law for potassium ethyl xanthate using a 1 cm quartz cell.

APPENDIX C

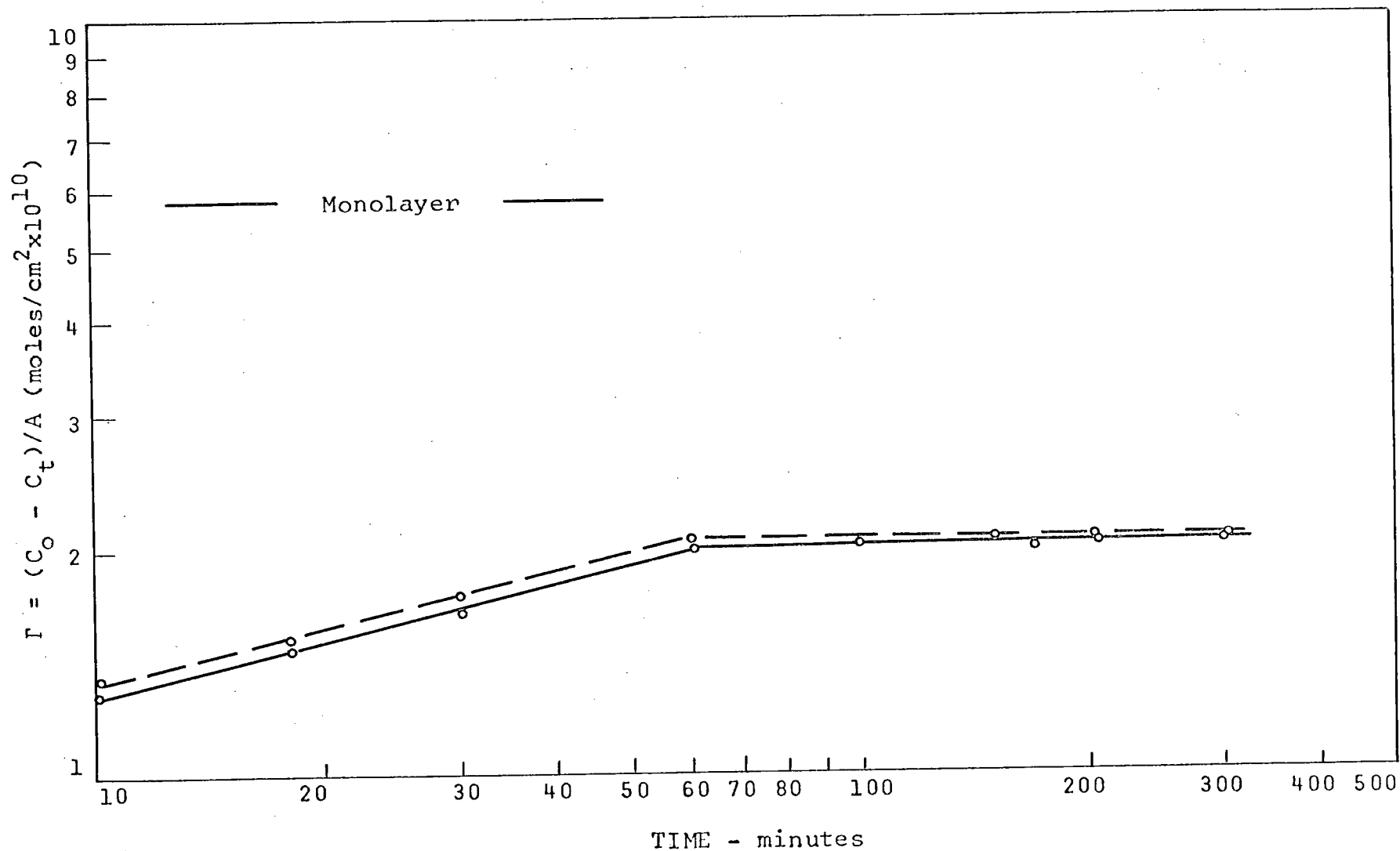


Fig. 35 - Reproducibility of testing procedure using marmatite. Test conditions: daylight, 10g of activated (Zn,Fe)S (65/100 mesh), 20°C, pH = 6.5, 1000 ml of 10^{-4}M KETX.

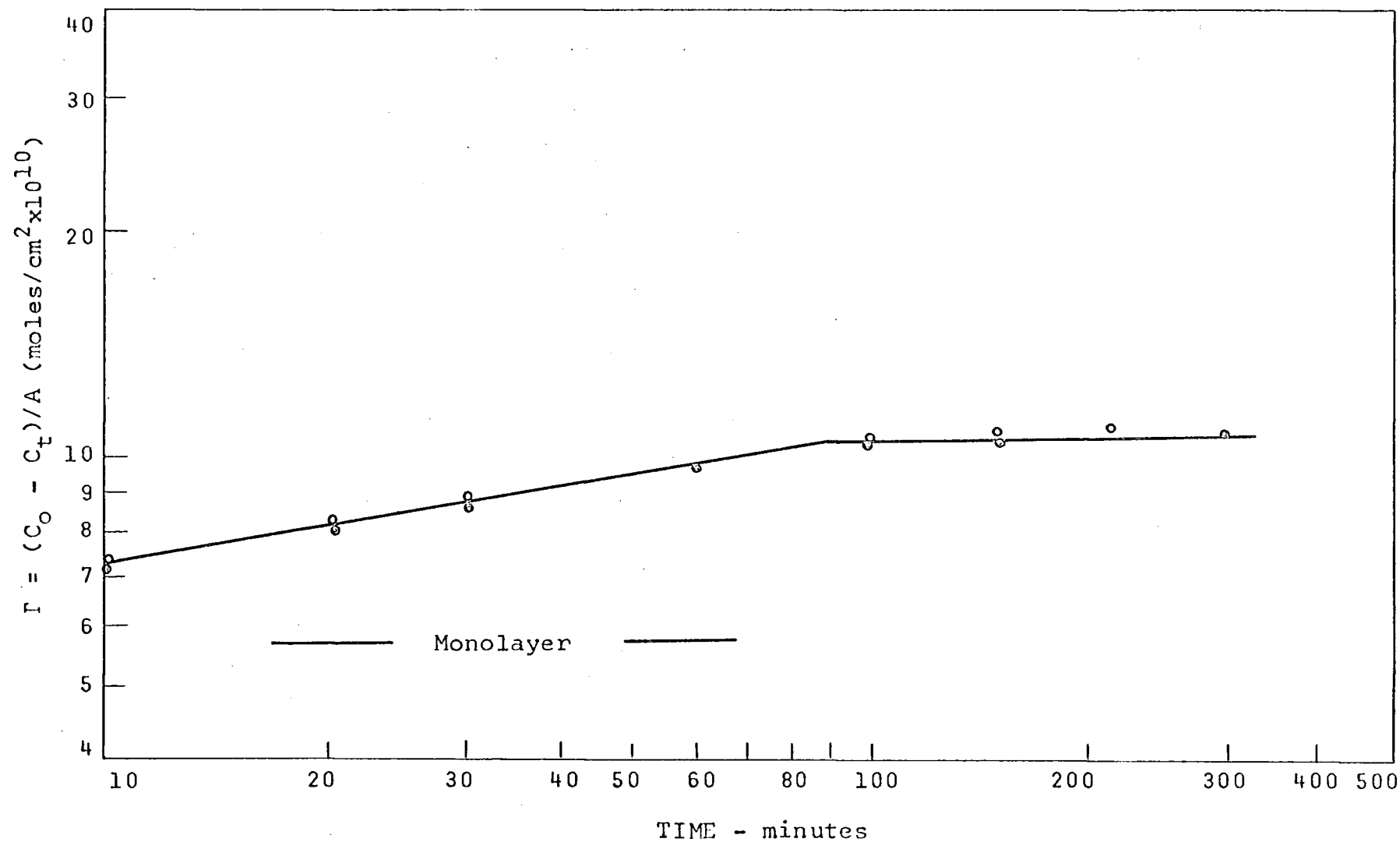


Fig. 36 - Reproducibility of testing procedure using galena. Test conditions: 400 W QI lamp, 20g of PbS (100/150 mesh), 20°C, 600 ml of 10⁻⁴M KEtX.

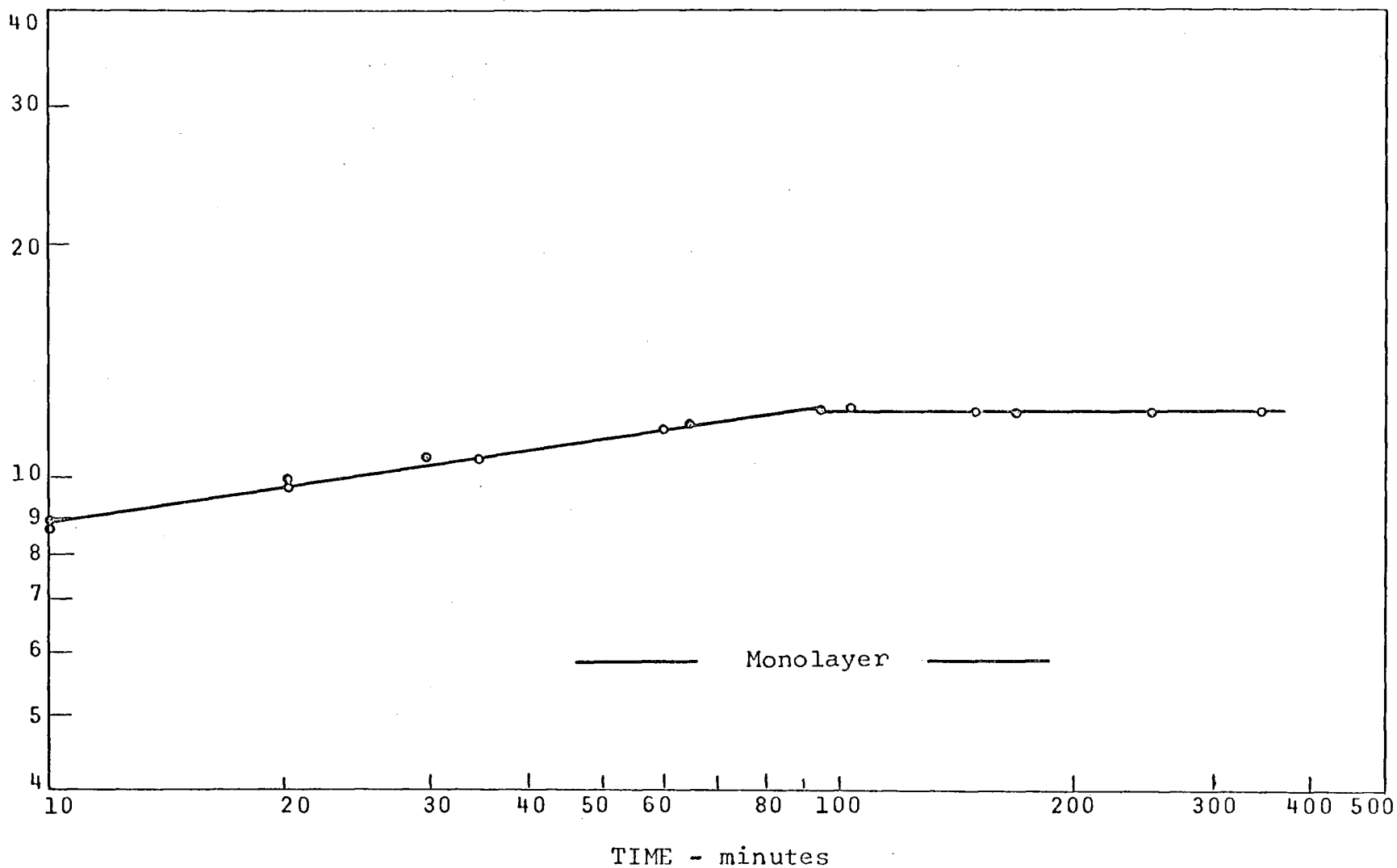


Fig. 37 - Reproducibility of testing procedure using galena. Test conditions: 500 W/QI lamp, 20g of PbS (100/150 mesh) 20°C, 600 ml of 10^{-4} M KEtX.

APPENDIX D

Detailed calculation of the BET isotherm for marmatite

A plot of the electronic integration areas vs. volumes injected is shown in Fig. 38. Using the desorption areas obtained in each run, the equivalent volumes adsorbed can be read directly from the graph.

For a 5.0585% nitrogen mixture:

$$V_o = \frac{V_1 P_1 T_o}{T_1 P_o} = \frac{31 \times 757.4 \times 273}{295.1 \times 760} = 29 \mu\text{l at STP}$$

$$P/P_o = (0.050585 \times 757.4) / (757.4 + 198) = 4.01 \times 10^{-2}$$

$$P/V_m (P_o - P) = 38.3 / 0.029 \text{ ml } (955.4 - 38.3) = 1.44$$

For a 15.598% nitrogen mixture:

$$V_o = \frac{P_1 P_1 T_o}{T_1 P_o} = \frac{43 \times 757.4 \times 273}{295.2 \times 760} = 40 \mu\text{l at STP}$$

$$P/P_o = (0.15598 \times 757.4) / (757.4 + 215) = 12.15 \times 10^{-2}$$

$$P/V_m (P_o - P) = 118 / 0.040 (972.4 - 118) = 3.45$$

For a 25.3807% nitrogen mixture:

$$V_o = \frac{V_1 P_1 T_o}{T_1 P_o} = \frac{48 \times 754.8 \times 273}{296.5 \times 760} = 44 \text{ } \mu\text{l at STP}$$

$$P/P_o = (0.253807 \times 754.8) / (754.8 + 215) = 19.75 \times 10^{-2}$$

$$P/V_m (P_o - P) = 191 / 0.044 (969.8 - 191) = 5.57$$

From Fig. 22, the slope is 25.4 and the intercept is equal to 0.4 or:

$$0.4 = \frac{1}{V_m C} \quad \text{and} \quad 25.4 = \frac{C-1}{V_m C}$$

solving for V_m : $V_m = 0.039 \text{ ml}$

$$\begin{aligned} \text{Total surface area of} &= \frac{0.039 \text{ ml} \times 6.023 \times 10^{23} \text{ molec/mole} \times 16.2 \text{ } \text{\AA}^2/\text{molec}}{10^{16} \text{ } \text{\AA}^2/\text{cm}^2 \times 22414.6 \text{ ml/mole}} \\ 0.4600 \text{ g} & \end{aligned}$$

$$= 1690 \text{ cm}^2$$

$$\text{Surface area} = 3675 \text{ cm}^2/\text{g}$$

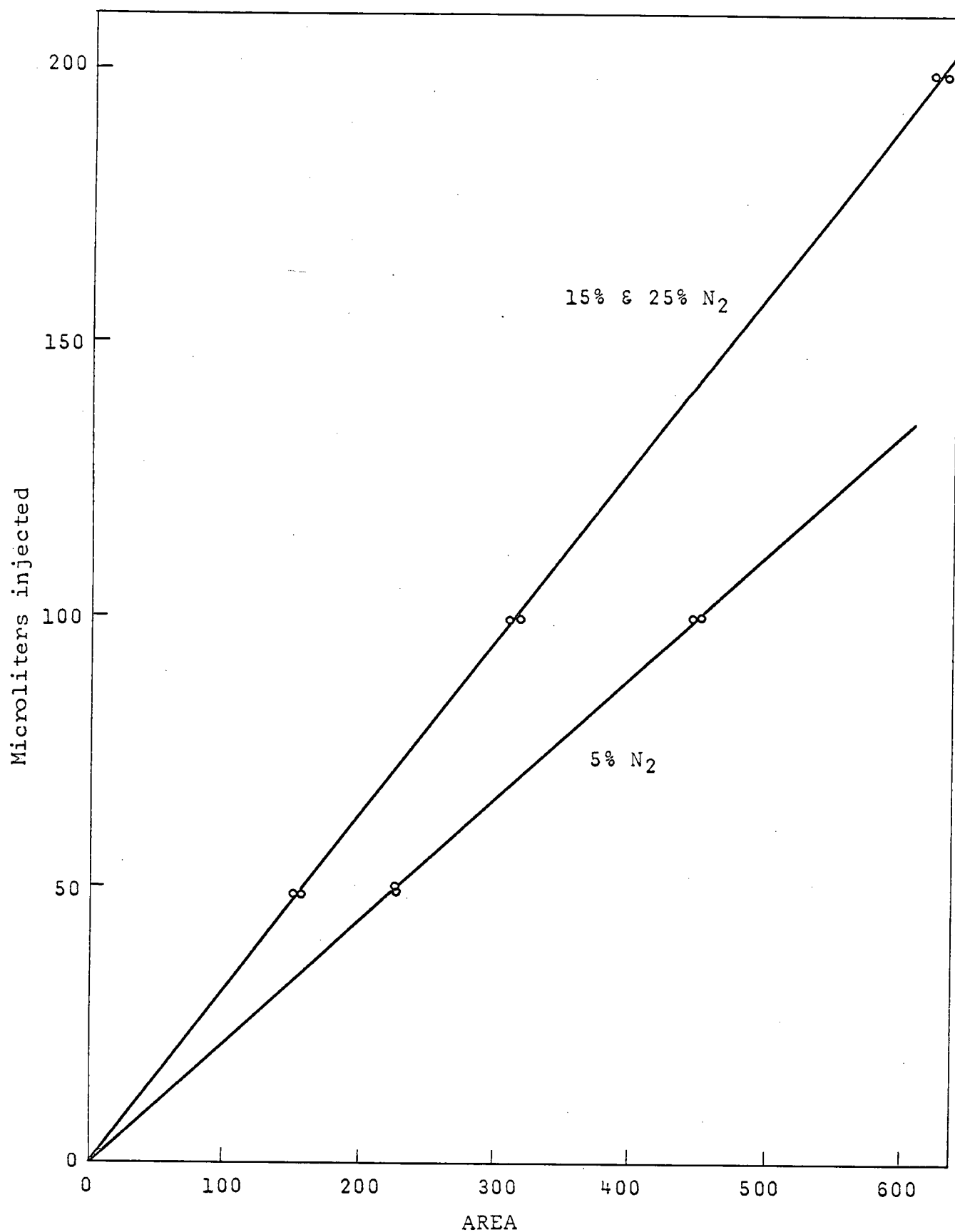


Fig. 38 - Electronic integrator areas of volumes of N₂ injected.

APPENDIX E

TABLE XIII

OXIDATION RATES OF GALENA (COMINCO)
IN THE PRESENCE OF WATER VAPOUR

TIME min.	Run No. 1		Run No. 2	
	Wt increase- μ g ($W_0 = 3.007535g$)	Amt. Ads. $g/cm^2 \times 10^{10}$	Wt increase- μ g ($W_0 = 2.999612g$)	Amt. Ads. $g/cm^2 \times 10^{10}$
0	--	--	--	--
2	46	83	48	86
4	64	115	65	117
6	73	131	73	131
8	79	142	77	138
10	84	151	81	145
12	88	158	85	153
14	91	163	88	158
16	93	167	92	166
18	95	171	95	171
20	97	174	99	178
30	107	192	110	198
60	115	206	115	209
150	112	201		

TABLE XIV

OXIDATION RATES OF ARGENTIFEROUS GALENA
IN THE PRESENCE OF WATER VAPOUR

TIME min.	Run No. 1		Run No. 2	
	Wt increase- μ g ($W_0=2.999466$ g)	Amt. Ads. $\text{g}/\text{cm}^2 \times 10^{10}$	Wt increase- μ g ($W_0=2.999148$ g)	Amt. Ads. $\text{g}/\text{cm}^2 \times 10^{10}$
0	--	--	--	--
2	69	181	80	210
4	92	241	93	244
6	100	262	97	255
8	106	278	102	268
10	109	286	104	273
12	114	300	108	283
14	116	304	110	289
16	118	309	112	294
18	120	315	114	299
20	123	323	115	302
30	133	349	122	320
60	136	357	131	343
90			133	349
100			133	349

TABLE XV

OXIDATION RATES OF GALENA IN A
 DRY ATMOSPHERE OF OXYGEN

TIME min.	Ag-PbS		PbS	
	Wt increase- μ g ($W_0 = 2.983964$ g)	Amt. Ads. $\text{g/cm}^2 \times 10^{10}$	Wt increase- μ g ($W_0 = 3.001441$ g)	Amt. Ads. $\text{g/cm}^2 \times 10^{10}$
0	--	--	--	--
2	10	26	5	9
4	14	37	9	16
6	16	42	11	20
8	18	47	13	23
10	19	50	15	27
12	21	55	16	29
14	24	63	18	32
16	26	69	20	36
18	27	71	22	40
20	28	74	23	41
30	35	92	29	52
60	44	116	29	52
90	50	132	28	51
100	52	137		
250	64	169		
300	65	171		
500	74	195		

APPENDIX F

Sample Calculation of the Fermi Energy Level from Thermo-electric Power

$$q QT = (E_C - E_F) + 2kT$$

$$(\text{coul})(\text{millivolts/degree})(\text{degrees}) = (E_C - E_F) + 2kT$$

Changing to electronvolts:

$$\frac{(Q)(1.6 \times 10^{-19})(10^3)(300)(10^7)}{1.6 \times 10^{-12}} = (E_C - E_F) + \frac{2(1.38 \times 10^{-16})(300)}{1.6 \times 10^{-12}}$$

$$\text{coul} \frac{\text{volts}}{\text{degree}} \text{ degree} \frac{\text{erg}}{\text{coul volt}} \frac{\text{ev}}{\text{erg}} = (E_C - E_F) + \frac{\text{ergs}}{\text{degree}} \text{ degree} \frac{\text{ev}}{\text{ergs}}$$

$$Q \cdot 30 = (E_C - E_F) + 0.0517 \text{ ev}$$

$$(E_C - E_F) = (Q \text{ millivolts}/^\circ\text{C}) 30 - 0.052$$

for $Q = 0.034 \text{ millivolts}/^\circ\text{C}$

$$(E_C - E_F) = 1.02 - 0.05$$

$$(E_C - E_F) = 0.97 \text{ ev}$$

APPENDIX G

Detailed Calculation of the Hall Coefficient, Carrier Concentration and Mobility

Dimensions of the galena specimen: $l = 1.30$ cm

$a = 0.25$ cm

$t = 0.10$ cm

Resistance of the sample measured at 10 mA:

$$R = 19.54 \pm 0.01 \text{ ohms}$$

$$\text{Resistivity} = \rho = \frac{Rat}{l} = \frac{19.54 \times 0.25 \times 0.10}{1.30} = 0.4 \text{ ohms cm.}$$

$$\text{Hall Resistance} = \frac{V}{I} = 0.280 \pm 0.005 \text{ ohms}$$

Semiconductor type: P (hole conductivity)

The Hall coefficient R_H is:

$$V = 10^{-8} R_H \frac{IB}{t}$$

$$R_H = \frac{Vt}{IB} \times 10^8 = \frac{0.28 \times 0.10 \times 10^8}{10^4} = 280 \frac{\text{cm}^3}{\text{coulomb}}$$

The number of positive carriers is:

$$R_H = \frac{1}{nq}$$

$$n = \frac{1}{R_H q} = \frac{1}{280 \times 1.6 \times 10^{-19}} = 2.2 \times 10^{16} \frac{\text{holes}}{\text{cm}^3}$$

Therefore the mobility μ is:

$$\begin{aligned} \mu &= R_H \sigma = \frac{1}{nq} \sigma = \frac{1}{nq\rho} \\ &= \frac{1}{(2.2 \times 10^{16}) (1.6 \times 10^{-19}) (0.4) \text{ coul ohms cm}} \frac{\text{cm}^3}{\text{cm}^3} \\ &= 700 \frac{\text{cm}^2}{\text{volt sec.}} \end{aligned}$$

APPENDIX H

Calculation of Carrier Concentration in PbS Using Thermo-electric Data

From Appendix B:

$$(E_F - E_V) = (\text{millivolts/degree}) \ 30 - 0.052$$

$$= 0.0030 \times 30 - 0.052$$

$$= 0.038 \text{ eV}$$

$$p = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \exp (E_F - E_V) / kT$$

since $m^* = 0.3 \text{ m}$ for galena:

$$p = 2 \left[\frac{6.28 \times 2.74 \times 10^{-28} \text{ g} \times 1.38 \times 10^{-16} \text{ erg/degree} \times 300 \text{ degree}}{(6.62 \times 10^{-27})^2 \text{ erg}^2 \text{ sec}^2} \right]^{3/2}$$

$$\times \exp (0.038 / 0.026)$$

$$p = 2 (0.6 \times 10^{12} \text{ g/erg sec}^2)^{3/2} e^{1.46}$$

$$p = 2 (0.6 \times 10^{12} \text{ g sec}^2 / \text{g cm}^2 \text{ sec}^2)^{3/2} \times 4.3$$

$$p = 5.1 \times 10^{18} \text{ holes/cm}^3$$

APPENDIX I

Calculation of the Proportionality Factor Required to
Correlate the Number of Particles to their Weight for
Galena and Marmatite

(a) If screened materials of the same mesh size are available, their weight is:

$$Wt = V\rho$$

where V is the volume and ρ the density.

Using the subscripts g for galena and s for sphalerite:

$$Wt_g = V_g \rho_g \quad Wt_s / V_s \rho_s$$

but $V_s = V_g = \text{same volume} = \text{same number of particles}$

$$Wt_g = Wt_s \frac{\rho_g}{\rho_s} = Wt_s \frac{7.5}{4.0}$$

$$Wt_g = 1.9 Wt_s$$

(b) If screened materials with the following mesh sizes are available:

PbS: 100/150 mesh (average diameter = 0.125 mm)

ZnS: 150/200 mesh (average diameter = 0.088 mm)

Assuming cubic particles:

$$\begin{aligned}
 V_{t_g} &= W_{t_s} V_{g\rho_g} / V_{s\rho_s} \\
 &= W_{t_s} (0.125)^3 \times 7.5 / (0.088)^3 \times 4.0 \\
 &= 5.3 W_{t_s}
 \end{aligned}$$

APPENDIX J

TABLE XVI - Flotation of Galena (100/150 mesh) in
Daylight Using KEtX and Dowfroth 250.

(a) KEtX = 30 mg/l

Dowfroth 250 = 130 mg/l

	Test 1		Test 2	
	Recovery		Recovery	
	Wt-g	%	Wt-g	%
Float	7.49	99.9	7.42	99.3
Tails	.01	.1	.05	.7
Total	7.50	100.0	7.47	100.0

(b) KEtX = 15 mg/l

Dowfroth 250 = 130 mg/l

	Test 1		Test 2	
	Recovery		Recovery	
	Wt-g	%	Wt-g	%
Float	7.48	99.8	7.45	99.5
Tails	.02	.2	.04	.5
Total	7.50	100.0	7.49	100.0

TABLE XVII - Flotation of Activated Marmatite (150/200 mesh) in Daylight Using KEtX and Dowfroth 250

(a) KEtX = 30 mg/l

Dowfroth 250 = 130 mg/l

	Test 1		Test 2	
	Recovery		Recovery	
	Wt-g	%	Wt-g	%
Float	3.96	99.1	3.95	99.2
Tails	.04	.9	.03	.8
Total	4.00	100.0	3.98	100.0

(b) KEtX = 15 mg/l

Dowfroth 250 = 130 mg/l

	Test 1		Test 2	
	Recovery		Recovery	
	Wt-g	%	Wt-g	%
Float	3.91	98.2	3.89	98.7
Tails	.07	1.8	.05	1.3
Total	3.98	100.0	3.94	100.0

TABLE XVIII - Flotation of Activated Marmatite (150/200 mesh) Using KEtX, Dowfroth 250 and Light of 2.5 Microns

(a) KEtX = 15 mg/l

Dowfroth 250 = 130 mg/l

	Recovery	
	Wt-g	%
Float	3.88	98.1
Tails	.07	1.9
Total	3.95	100.0

(b) KEtX = 5 mg/l

Dowfroth 250 = 130 mg/l

	Recovery	
	Wt-g	%
Float	3.89	98.2
Tails	.07	1.8
Total	3.96	100.0

APPENDIX K

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ (500 W)

Reagent: KEtX in 600 ml

Time	Abs.	Conc $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.54	8.80	--	--	--	--
10	0.55	3.14	56.6	55.1	1.65	8.9
20	0.43	2.46	63.4	61.3	1.84	9.9
30	0.35	2.00	68.0	65.5	1.96	10.6
65	0.21	1.20	76.0	72.2	2.17	11.7
95	0.16	0.91	78.9	74.6	2.24	12.1
170	0.11	0.63	81.7	74.9	2.25	12.1
250	0.08	0.46	83.4	74.2	2.24	12.1

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ (500 W)

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5}M$	Amt. Ads $\times 10^{-6}M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.62	9.24	--	--	--	--
10	0.66	3.77	54.7	53.2	1.59	8.6
20	0.53	3.03	62.1	60.0	1.80	9.7
35	0.43	2.46	67.8	65.1	1.95	10.5
60	0.32	1.83	74.1	70.5	2.11	11.4
105	0.22	1.26	79.8	74.8	2.24	12.1
150	0.16	0.91	83.3	75.1	2.25	12.1
350	0.09	0.51	87.3	75.2	2.25	12.1

Argentiferous galena

10g of 100/150 mesh

Temperature: 20°C

Radiant energy: 2-2.5 μ (500 W)

Reagent: KEtX in 600 ml

Time	Abs	Conc. $\times 10^{-5}M$	Amt. Ads. $\times 10^{-6}M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	0.95	5.42	--	--	--	--
10	0.83	4.74	6.8	5.3	0.32	2.5
20	0.81	4.62	8.0	5.9	0.35	2.8
30	0.79	4.51	9.1	6.6	0.39	3.1
60	0.76	4.34	10.8	7.6	0.43	3.4
100	0.73	4.17	12.5	7.3	0.44	3.5
155	0.72	4.11	13.1	7.2	0.44	3.5
255	0.68	3.88	15.4	7.4	0.44	3.5
310	0.67	3.83	15.9	7.2	0.43	3.4

Argentiferous galena

10g of 100/150 mesh

Temperature: 20°C

Radiant energy: 420-480 mμ (500 W)

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads. $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.02	5.82	--	--	--	--
12	0.88	5.03	7.9	6.3	0.37	2.9
21	0.86	4.91	9.1	7.0	0.42	3.3
30	0.85	4.86	9.6	7.1	0.43	3.4
60	0.82	4.69	11.3	7.7	0.46	3.6
100	0.79	4.51	13.1	8.3	0.50	4.0
160	0.76	4.34	14.8	8.3	0.50	4.0
300	0.72	4.11	17.1	8.3	0.50	4.0

Argentiferous galena

10g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ (500 W)

Reagent: KEtX in 600 ml

Time	Abs	Conc. $\times 10^{-5}M$	Amt. Ads. $\times 10^{-6}M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	0.95	5.42	--	--	--	--
10	0.81	4.62	8.0	6.5	0.39	3.1
20	0.76	4.34	10.8	8.7	0.52	4.1
30	0.74	4.22	12.0	9.5	0.57	4.5
60	0.70	4.00	14.2	10.6	0.64	5.1
110	0.65	3.71	17.1	12.1	0.73	5.8
185	0.59	3.37	20.5	13.5	0.81	6.4
375	0.51	2.91	25.1	13.4	0.81	6.4

Argentiferous galena

10g of 100/150 mesh

Temperature: 20°C

Radiant energy: darkness

Reagent: KEtX in 600 ml

Time	Abs	Conc. $\times 10^{-5} \text{M}$	Amt. Ads $\times 10^{-6} \text{M}$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	0.93	5.32	--	--	--	--
10	0.81	4.63	6.9	5.4	0.32	2.5
20	0.78	4.46	8.6	6.5	0.39	3.1
30	0.77	4.40	9.2	6.7	0.40	3.2
75	0.73	4.18	11.4	7.4	0.44	3.5
145	0.69	3.95	13.7	7.6	0.45	3.5
300	0.63	3.60	17.2	7.3	0.44	3.5

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Inert atmosphere: helium

Volume	Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	μ moles g	moles/cm ² $\times 10^{-10}$
600	0.0	1.57	8.95	--	--	--
596	1	1.15	6.57	23.8	0.71	3.8
592	3	1.03	5.89	30.6	0.90	4.9
588	10	0.97	5.54	34.1	1.00	5.4
584	20	0.91	5.20	37.5	1.10	5.9
580	40	0.87	4.96	39.9	1.15	6.2
576	60	0.84	4.80	41.5	1.19	6.4
572	100	0.80	4.57	43.8	1.24	6.7
564	200	0.74	4.23	47.2	1.32	7.1
560	300	0.72	4.12	48.3	1.35	7.3

Argentiferous Galena.

10g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Inert atmosphere: helium

Volume	Time	Abs.	Cong. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	μ mole g	moles/cm ² $\times 10^{-10}$
586	0	0.865	4.94	--	--	--
583	2	0.765	4.37	3.3	0.20	1.6
580	7	0.745	4.26	3.9	0.24	1.9
577	10	0.740	4.23	4.1	0.25	2.0
574	20	0.725	4.14	4.6	0.27	2.1
571	30	0.720	4.11	4.7	0.28	2.2
568	60	0.705	4.02	5.2	0.31	2.5
565	100	0.695	3.97	5.5	0.33	2.6
559	200	0.670	3.83	6.2	0.37	2.9
556	330	0.665	3.79	6.4	0.38	3.0

Non-activated Marmatite

10g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	0.95	5.42	--	--	--	--
10	0.87	4.97	4.5	3.0	0.18	0.69
20	0.86	4.91	5.1	3.0	0.18	0.69
30	0.85	4.86	5.6	3.1	0.19	0.73
60	0.83	4.74	6.8	3.2	0.19	0.73
100	0.81	4.63	7.9	3.2	0.19	0.73
220	0.74	4.23	11.9	3.5	0.21	0.81

Activated Marmatite ($0.996 \times 10^{-5} \text{ M Cu}^{++}$)

10g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Cong. $\times 10^{-5} \text{ M}$	Amt. Ads $\times 10^{-6} \text{ M}$	Corr. Value	$\mu \text{ mole}$ g	moles/cm ² $\times 10^{-10}$
0	0.95	5.43	--	--	--	--
10	0.88	5.03	4.0	2.6	0.15	0.58
20	0.87	4.97	4.6	2.7	0.16	0.62
30	0.85	4.86	5.7	3.2	0.19	0.73
100	0.80	4.57	8.6	4.0	0.24	0.92
150	0.77	4.40	10.3	4.2	0.25	0.96
360	0.71	4.06	13.7	4.1	0.25	0.96

Activated Marmatite ($0.996 \times 10^{-4} \text{M Cu}^{++}$)

10 g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{M}$	Amt. Ads $\times 10^{-6} \text{M}$	Corr. Value	μ mole g	moles/ cm^2 $\times 10^{-10}$
0	1.14	6.51	--	--	--	--
10	1.05	6.04	4.7	3.2	0.19	0.73
20	1.03	5.88	6.3	4.2	0.25	0.96
30	1.01	5.76	7.5	5.0	0.30	1.15
60	0.96	5.48	10.3	6.7	0.40	1.54
100	0.91	5.20	13.1	8.4	0.50	1.92
165	0.88	5.03	14.8	8.5	0.51	1.96
300	0.80	4.57	19.4	8.4	0.50	1.92

Activated Marmatite ($0.996 \times 10^{-3} \text{M Cu}^{++}$)

Filtered but neither dried nor washed

10g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{M}$	Amt. Ads $\times 10^{-6} \text{M}$	Corr. Value	μ mole g	moles/ cm^2 $\times 10^{-10}$
0	0.96	5.52	--	--	--	--
12	0.78	4.46	10.6	9.1	0.55	2.02
20	0.76	4.34	11.8	9.6	0.58	2.23
30	0.74	4.23	12.9	10.4	0.63	2.42
65	0.69	3.95	15.7	12.1	0.73	2.81
100	0.65	3.72	18.0	13.2	0.79	3.04
175	0.61	3.52	20.0	13.3	0.79	3.04
200	0.59	3.37	21.5	13.2	0.79	3.04
300	0.56	3.20	23.2	13.2	0.79	3.04

Activated Marmatite ($0.996 \times 10^{-3} \text{M Cu}$)

10g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{M}$	Amt. Ads $\times 10^{-6} \text{M}$	Corr. Value	$\mu \text{ mole}$ g	moles/ cm^2 $\times 10^{-10}$
0	0.89	5.08	--	--	--	--
10	0.78	4.46	6.2	4.7	0.28	1.08
20	0.75	4.34	7.4	5.3	0.32	1.23
30	0.73	4.17	9.1	6.4	0.38	1.46
60	0.69	3.94	11.4	7.8	0.47	1.81
100	0.66	3.77	13.1	8.6	0.52	2.00
165	0.63	3.60	14.8	8.8	0.53	2.04
310	0.58	3.31	17.7	8.7	0.52	2.00

Activated Marmatite ($0.996 \times 10^{-3} \text{ M}$)

10g of 65/100 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Cong. $\times 10^{-5} \text{ M}$	Amt. Ads $\times 10^{-6} \text{ M}$	Corr. Value	$\mu \text{ mole}$ g	moles/cm ² $\times 10^{-10}$
0	1.18	6.75	--	--	--	--
10	1.08	6.17	5.8	4.3	0.26	1.00
20	1.05	6.00	7.5	5.4	0.32	1.23
30	1.03	5.88	8.7	6.2	0.37	1.42
70	0.98	5.60	11.5	7.7	0.46	1.77
150	0.92	5.25	15.0	9.0	0.54	2.08
235	0.88	5.03	17.2	9.1	0.54	2.08
300	0.85	4.86	18.9	9.0	0.54	2.08

Activated Marmatite

10g of 150/200 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Intensity of light: 0 watts/cm²

Time	Abs.	Conc. x10 ⁻⁵ M	Amt.Ads x10 ⁻⁶ M	Corr. Value	μ mole g	moles/cm ² x10 ⁻¹⁰
0	1.03	5.72	--	--	--	--
10	0.92	5.26	4.6	3.6	0.22	0.42
20	0.89	5.09	6.3	5.0	0.30	0.58
30	0.87	4.97	7.5	6.0	0.36	0.69
60	0.82	4.69	10.3	8.2	0.49	0.94
100	0.78	4.46	12.6	9.7	0.58	1.12
150	0.74	4.23	14.9	11.1	0.67	1.29
245	0.71	4.06	16.6	11.1	0.67	1.29
310	0.68	3.88	18.4	11.2	0.67	1.29
350	0.66	3.77	19.5	11.0	0.66	1.28

Activated Marmatite

10g of 150/200 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Intensity of light: 80 μ watts/cm²

Time	Abs.	Conc. x10 ⁻⁵ M	Amt. Ads x10 ⁻⁶ M	Corr. Value	μ mole g	moles/cm ² x10 ⁻¹⁰
0	0.90	5.14	--	--	--	--
10	0.78	4.46	6.8	5.8	0.35	0.67
20	0.76	4.34	8.0	6.7	0.40	0.77
30	0.74	4.23	9.1	7.6	0.46	0.89
60	0.71	4.06	10.8	8.7	0.52	1.00
110	0.68	3.88	12.6	9.5	0.56	1.10
150	0.66	3.77	13.7	10.0	0.60	1.15
240	0.63	3.60	15.4	10.0	0.60	1.15
300	0.61	3.49	16.5	10.0	0.60	1.15

Activated Marmatite

10g of 150/200 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Intensity of light: 180 μ watts/cm²

Time	Abs.	Conc. x10 ⁻⁵ M	Amt. Ads x10 ⁻⁶ M	Corr. Value	μ mole g	moles/cm ² x10 ⁻¹⁰
0	0.91	5.20	--	--	--	--
10	0.77	4.40	8.0	7.0	0.42	0.81
20	0.75	4.28	9.2	7.9	0.47	0.91
30	0.73	4.17	10.3	8.8	0.53	1.04
60	0.69	3.94	12.6	10.5	0.63	1.21
100	0.67	3.83	13.7	10.8	0.65	1.25
160	0.63	3.63	15.7	11.7	0.70	1.35
255	0.60	3.43	17.7	12.0	0.72	1.38
320	0.58	3.31	18.9	12.1	0.72	1.38

Activated Marmatite

10g of 150/200 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Intensity of Light: 275 μ watts/cm²

Time	Abs.	Conc. x10 ⁻⁵ M	Amt. Ads x10 ⁻⁶ M	Corr. Value	μ mole g	moles/cm ² x10 ⁻¹⁰
0	0.90	5.14	--	--	--	--
10	0.75	4.28	8.6	7.6	0.46	0.88
20	0.71	4.11	10.3	9.0	0.54	1.04
30	0.69	3.90	12.3	10.0	0.60	1.15
70	0.65	3.72	14.2	11.9	0.71	1.37
100	0.64	3.65	14.9	12.0	0.72	1.38
150	0.60	3.43	17.1	13.3	0.80	1.54
245	0.56	3.25	18.9	13.4	0.80	1.54
300	0.56	3.20	19.4	13.1	0.79	1.52
400	0.53	3.03	21.1	13.5	0.81	1.56

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5}M$	Amt.Ads $\times 10^{-6}M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.68	9.60	--	--	--	--
10	0.86	4.91	46.9	45.5	1.37	7.4
20	0.74	4.23	53.7	51.5	1.55	8.4
30	0.67	3.83	57.7	55.2	1.66	9.0
100	0.44	2.52	70.8	65.8	1.97	10.6
150	0.38	2.17	74.3	67.8	2.03	11.0
215	0.30	1.71	78.9	70.9	2.12	11.5
300	0.24	1.37	82.9	71.9	2.21	12.0
450	0.18	1.03	85.7	71.9	2.22	12.0

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 435-480 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.80	10.28	--	--	--	--
10	1.10	6.28	40.0	38.5	1.18	6.4
24	0.93	55.31	49.7	47.5	1.42	7.7
35	0.85	4.86	54.2	51.5	1.51	8.1
60	0.73	4.17	61.1	56.5	1.69	9.1
100	0.62	3.54	67.4	62.4	1.87	10.1
165	0.51	22.91	73.7	66.7	2.00	10.8
220	0.45	2.57	77.1	68.6	2.06	11.1
295	0.38	2.17	81.1	71.1	2.13	11.5
470	0.29	1.66	86.2	71.0	2.13	11.5

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 2-2.5 μ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.63	9.30	--	--	--	--
11	0.95	5.43	38.3	37.7	1.13	6.1
20	0.82	4.74	45.6	43.5	1.27	6.9
32	0.77	4.40	49.0	46.4	1.39	7.5
65	0.60	3.43	58.7	55.0	1.65	8.9
110	0.50	2.86	64.4	59.2	1.78	9.6
170	0.41	2.34	69.6	62.6	1.88	10.4
220	0.36	2.06	72.4	64.2	1.93	10.5
300	0.30	1.72	75.8	64.6	1.94	10.5
490	0.22	1.26	80.4	65.0	1.95	10.6

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: darkness

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5}M$	Amt.Ads $\times 10^{-6}M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.46	8.34	--	--	--	--
10	0.83	4.74	36.0	35.0	1.05	5.7
20	0.72	4.11	42.3	40.1	1.23	6.6
30	0.66	3.77	45.7	43.2	1.29	7.0
55	0.54	3.08	52.6	49.1	1.47	7.9
110	0.41	2.34	60.0	55.0	1.65	8.9
150	0.37	2.11	62.3	56.2	1.71	9.2
220	0.30	1.71	66.3	57.8	1.73	9.3
420	0.20	1.14	72.0	58.0	1.74	9.4

Galena

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 400 W Qtz-I lamp

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{ M}$	Amt. Ads $\times 10^{-6} \text{ M}$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.69	9.65	--	--	--	--
10	0.89	5.09	45.6	44.0	1.32	7.1
20	0.79	4.51	51.4	49.4	1.48	8.0
30	0.72	4.12	55.3	53.0	1.59	8.6
65	0.58	3.31	63.4	59.6	1.79	9.7
100	0.49	2.80	68.5	63.5	1.90	10.3
150	0.41	2.34	73.1	66.6	1.98	10.7
305	0.27	1.54	81.1	71.1	2.14	11.5

Activated Marmatite

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 360-380 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{ M}$	Amt. Ads $\times 10^{-6} \text{ M}$	Corr. Value	$\mu \text{ mole}$ g	moles/cm ² $\times 10^{-10}$
0	1.56	8.90	--	--	--	--
10	1.26	7.20	17.0	15.5	0.46	1.25
23	1.22	6.96	19.4	17.2	0.51	1.39
35	1.19	6.79	21.1	18.4	0.55	1.50
60	1.15	6.56	23.4	19.8	0.59	1.61
115	1.10	6.28	26.2	21.0	0.63	1.72
150	1.07	6.08	28.2	21.5	0.64	1.74
200	1.09	5.94	29.6	21.6	0.65	1.77
300	0.98	5.60	33.0	22.0	0.65	1.77
505	0.92	5.25	36.5	22.0	0.65	1.77

Activated Marmatite

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: darkness

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} M$	Amt. Ads $\times 10^{-6} M$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.77	9.57	--	--	--	--
10	1.47	8.40	11.7	10.2	0.31	0.84
20	1.42	8.11	14.6	12.4	0.37	1.01
30	1.37	7.82	17.5	15.0	0.45	1.22
60	1.29	7.37	22.0	18.4	0.55	1.50
130	1.20	6.85	27.2	21.2	0.63	1.72
200	1.16	6.62	29.5	21.5	0.64	1.74
300	1.14	6.52	30.5	22.0	0.66	1.80
470	1.08	6.17	34.0	22.0	0.66	1.80

Activated Marmatite

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 2-2.5 μ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5}$ M	Amt. Ads $\times 10^{-6}$ M	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.62	9.25	--	--	--	--
10	1.45	8.28	9.7	8.2	0.25	0.68
20	1.40	8.00	12.5	10.4	0.31	0.84
30	1.38	7.88	13.7	11.2	0.34	0.93
60	1.31	7.49	17.6	14.0	0.42	1.14
130	1.22	6.97	22.8	16.8	0.50	1.36
200	1.19	6.80	24.5	17.0	0.51	1.39
355	1.11	6.34	29.1	17.1	0.51	1.39
495	1.07	6.12	31.3	17.2	0.51	1.39

Activated Marmatite

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: mercury lamp (UV)

Reagent: KEtX in 600 ml

Time:	Abs.	Conc. $\times 10^{-5} \text{M}$	Amt. Ads $\times 10^{-6} \text{M}$	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.58	9.03	--	--	--	--
10	1.27	7.26	17.7	16.2	0.49	1.33
22	1.23	7.03	20.0	17.8	0.53	1.44
33	1.20	6.86	21.7	19.1	0.57	1.55
60	1.16	6.63	24.0	20.5	0.61	1.66
110	1.09	6.24	27.9	22.9	0.68	1.85
160	1.04	5.95	30.8	22.4	0.67	1.83
200	1.01	5.77	32.6	22.8	0.68	1.85
300	0.96	5.49	35.4	22.9	0.68	1.85
500	0.87	4.97	40.6	23.0	0.68	1.85

Activated Marmatite

20g of 100/150 mesh

Temperature: 20°C

Radiant energy: 420-470 mμ

Reagent: KEtX in 600 ml

Time	Abs.	Conc. $\times 10^{-5} \text{ M}$	Amt.ads $\times 10^{-6} \text{ M}$	Corr. Value	$\mu \text{ mole}$ g	moles/cm ² $\times 10^{-10}$
0	1.62	9.25	--	--	--	--
10	1.38	7.88	13.7	12.2	0.36	0.98
20	1.35	7.74	15.1	13.0	0.39	1.06
30	1.33	7.60	16.5	14.0	0.42	1.14
60	1.28	7.31	19.4	15.8	0.47	1.28
100	1.23	7.05	22.0	17.0	0.51	1.39
150	1.18	6.67	25.8	18.4	0.55	1.50
200	1.15	6.57	26.8	18.8	0.56	1.53
295	1.09	6.25	30.0	19.0	0.56	1.53
495	1.02	5.83	34.2	18.5	0.56	1.53

Activated Marmatite

10g of 65/100 mesh

Temperature: 20°C (pH = 6.5)

Radiant energy: daylight

Reagent: KEtX in 1000 ml

Time	Abs.	Conc. $\times 10^{-5} \text{ M}$	Amt. Ads $\times 10^{-6} \text{ M}$	Corr. Value	$\mu \text{ mole}$ g	moles/cm ² $\times 10^{-10}$
0	1.64	9.37	--	--	--	--
10	1.56	8.91	4.5	3.5	0.35	1.35
18	1.55	8.86	5.1	3.9	0.39	1.50
30	1.53	8.78	5.9	4.5	0.45	1.73
60	1.51	8.63	7.4	5.3	0.53	2.04
100	1.50	8.56	8.1	5.2	0.52	2.00
150	1.48	8.46	9.1	5.3	0.53	2.04
200	1.46	8.34	10.3	5.3	0.53	2.04
300	1.44	8.23	11.4	5.3	0.53	2.04
500	1.40	8.00	13.7	5.3	0.53	2.04

Activated Marmatite

10g of 65/100 mesh

Temperature: 20°C (pH = 6.5)

Radiant energy: daylight

Reagent: KEtX in 1000 ml

Time	Abs.	Conc. $\times 10^{-5}$ M	Amt. Ads $\times 10^{-6}$ M	Corr. Value	μ mole g	moles/cm ² $\times 10^{-10}$
0	1.64	9.37	--	--	--	--
10	1.56	8.94	4.3	3.3	0.33	1.27
18	1.55	8.88	4.9	3.8	0.38	1.46
30	1.54	8.82	5.5	4.2	0.42	1.62
60	1.51	8.65	7.2	5.1	0.51	1.96
170	1.48	8.46	9.1	5.1	0.51	1.96
205	1.46	8.54	10.3	5.3	0.53	2.04
300	1.44	8.23	11.4	5.3	0.53	2.04
500	1.40	8.00	13.7	5.4	0.54	2.05