

STUDIES ON THE DEPRESSIVE ACTION OF CHROMATE
AND DICHROMATE SALTS ON GALENA

by

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ABSTRACT

In the course of the experimental work conducted it was found that when galena was treated with chromate salts or dichromate salts in an aqueous solution, lead chromate identified by infrared spectroscopy was the main species adsorbed on the galena surface. The formation of chromium hydroxide or chromium oxide was not observed. Thermodynamic considerations of the Pb-Cr-S-H₂O bulk system indicate the very stable character of lead chromate as shown in the potential-pH diagram constructed in this study. It is also seen that no stable domain of lead dichromate exists. The adsorption rate as well as adsorption amount of dichromate at the pseudo-equilibrium condition increases with the decrease in pH value. This phenomenon supports the fact experienced in galena flotation that a dichromate salt is a much more efficient depressant than is an equivalent chromate salt.

The desorption of xanthate from galena surfaces covered with more than a monolayer thickness of xanthate was found to be possible by adding chromate salt to the system, whereas chromate desorption from galena surfaces due to xanthate addition was not observed.

It was found that under comparable conditions xanthate adsorbed on lead chromate surfaces oxidized to dixanthogen much more readily than xanthate adsorbed on galena surfaces.

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INTRODUCTION

In the flotation of complex sulfide ores containing galena, chromate or dichromate salts are commonly used as depressants. The history of studies involving the use of chromate in flotation circuits date to 1912, when Lowry and Greenway [1] introduced what would now be termed a "depressant" for the lead mineral by using one per cent sodium dichromate.

The dezincing operation for lead concentrates is important as a method of improving lead concentrate quality and increasing zinc extraction into zinc concentrate in zinc lead ore flotation. For example, at the Sullivan Concentrator, dichromate salt had been used for the depression of galena in the selective flotation circuit. According to the example at the Sullivan Concentrator, the lead concentrate was conditioned with dichromate, then with lime, xanthate, frother and copper sulphate. Galena was depressed under these conditions when the material was heated to 30-35°C. One of the examples of operation results [2] were: the grade of initial lead concentrate, 58.1% Pb, 9.19% Zn, 9.72% Fe, the grade of zinc froth product 29.3% Pb, 34% Zn, 9.72% Fe and those for final lead concentrate 62.45% Pb, 5.55% Zn, and 9.72% Fe.

Even though this type of reagent has almost lost practical importance in milling operations, it is still

one of the most interesting topics on the depression of sulfide minerals. A large number of papers concerned with the depression of galena and pyrite with chromate or dichromate salts have been presented. The main results obtained on galena by the previous researches are summarized as follows:

- (1) When galena is treated with a chromate or a dichromate solution, the hydrophilic film formed on galena is lead chromate. However, some researchers suggest that depression occurs as a result of formation of an oxide film.
- (2) The chromate is adsorbed irregularly at the mineral surface, and the chemical attachment of chromate ions to mineral is independent of xanthate ion attachment, and apparently takes place in a different area.
- (3) The chromate adsorption on the mineral surface is described by the Freundlich equation.
- (4) The adsorption of chromate on galena increases with an increase in the concentration of the solution up to pH 6 and becomes almost constant above this pH value.
- (5) The increase of the chromate adsorption creates a proportional decrease in the yield of galena by flotation.

- (6) Dichromate is a much more efficient depressant for galena than chromate. On the contrary it is also said that galena depression is most effective at pH 5-6 and above 8.
- (7) Galena depression occurs when a depressant adsorption layer, approximately equal to a monolayer, is formed; at this point adsorption of xanthate remains the same as without the depressant.
- (8) The potential of a galena electrode decreases when xanthate is added and the addition of dichromate causes an increase in potential proportional to the logarithm of its concentration. A galena electrode treated with concentrated dichromate solution shows no significant potential change by the addition of xanthate.

As mentioned above, in the detailed mechanisms of galena depression with chromate or dichromate salt, some problems are yet unsolved. Firstly, it seems that there is a discrepancy in the proposed reaction product which causes galena depression. Secondly, Plaksin et al. [3] stated that the increase of the chromate adsorption created the proportional decrease in flotation yield, and it is also well known that dichromate is much more effective for galena than chromate. On the other hand Bagdanov and Podnek [4] showed that galena depression by chromate salt was most effective at pH 5-6 and above 8. Furthermore, in the system

of galena, xanthate, and chromate, the behaviors of xanthate and chromate species on galena surface are not fully understood.

Considering these points, in the present work some experimental studies and a thermodynamic investigation were made in order to get a better understanding of the depression of galena. For these purposes an infrared spectrometer as well as ultraviolet spectrophotometer were used to identify the surface products on galena. The principal experiments were the adsorption tests of chromate, dichromate, and/or xanthate ions on the galena surface. Besides these experimental studies, thermodynamic studies were made of the possibility of the formations of lead chromate and chromium oxide. For this purpose, a potential-pH diagram was constructed for the system of Pb-Cr-S-H₂O, and the stable domains of lead chromate and chromium oxide were presented graphically.

LITERATURE SURVEY

As mentioned before, the history of studies involving the use of chromate or dichromate salt in flotation circuits date to 1912, when Lowry and Greenway [1] introduced what would now be termed "depressant" for the lead minerals by using one per cent sodium dichromate.

Gaudin and his co-workers [5] studied the system, in which galena was depressed with potassium dichromate in the presence of iso-amyl xanthate. They also studied the separation of galena from sphalerite. The flotation experiment was performed with the synthetic mixture of galena and sphalerite both sized to be -100+600 mesh. Galena was well depressed, while sphalerite was not. They assumed that galena was depressed by dichromate salt because the insoluble coating of lead chromate was formed on the galena surface. Coating may be responsible for the failure to float.

A few years later, however, Wark and Cox [6] showed that lead chromate, the mineral crocoite, was floated by ethyl xanthate, indicating that the interpretation given by Gaudin et al. was not satisfactory.

Plaksin and Myasnikova [7], [8] employed radioactive chromium, Cr^{51} , for the study of the effect of chromate on the flotation of galena and pyrite. Their results are summarized as follows: (1) The chromate

adsorption on the mineral surface is given with sufficient accuracy by the Freundlich equation: $a = kC^{1/n}$ (a = adsorbed chromate amount, C = equilibrium concentration of the chromate solution, k = constant with the value of 2.95 for PbS and 2.12 for FeS_2 , $1/n$ = constant with value of 0.42 for PbS and 0.83 for FeS_2 . (2) The increase of the chromate adsorption creates a proportional decrease of the yield of mineral by flotation. (3) The adsorption increased with the increase of the concentration of the solution up to pH 6 and becomes almost constant at this value and values above. (4) The chromate is adsorbed irregularly on the mineral surfaces, taking probably the free places in the crystal lattice. From these experimental results, they concluded that the depressive effect of chromate ions took the form of chemical attachment to the mineral surfaces, as a result of which the mineral surface became hydrated; under these conditions, surface hydration was so great that the mineral could no longer be floated in spite of the presence of a xanthate adsorption layer on its surface of a density up to 30-33 per cent of a complete monolayer.

The depressive effect of potassium chromate and potassium dichromate is regarded as due to adsorption of chromate anions on the surface of galena and pyrite; these anions attach themselves chemically to the mineral surfaces. According to the results obtained by Plaksin and Myasnikova from studying the depressive action of chromate ions on

pyrite and galena by means of trace microradiography, the chemical attachment of chromate ions to mineral is independent of xanthate ions attachment and apparently takes place in different areas [3]. The study of the depressive action of chromates on galena and pyrite, which was carried out at the Mekhanobr Institute of U.S.S.R. [9], supports the hypothesis given by Plaksin et al.

Plaksin and Myasnikova [10] studied the depressive action of chromate on galena and pyrite by using Cr^{51} isotope, with ethylxanthate as the flotation agent and pine oil as the foaming agent. They found that the maximum chromate ion adsorption on the sulphide mineral surface resulted in a minimum of their extraction. In the contrast to references [7] and [8] the chromate adsorption was affected by the pH of the solution, was zero at pH 0, and reached 0.2 mg/g at pH above 6, after which it remained constant. They hypothesized that the depressive action of chromate ion was attributed to the formation of very slightly soluble normal or basic chromates on the mineral surface.

Bogdanov and Podnek [4] also examined the effect of potassium chromate on galena and copper sulphides. Experiments on galena flotation with variable chromate salt consumption showed the total galena depression occurs when a depressant adsorption layer, approximately equal to a monolayer, is formed; at this point adsorption of butylxan-

thate remains the same as without a depressant. Depression of galena by potassium chromate was explained by the hydrophilization effect of chromate ion, which covers the hydrophobilization effect of xanthate ions on the surface.

Galena depression appeared most effective at pH 5-6 and above 8. The sharp impairment of galena flotation at above pH 8 was explained as due to the fact that in this region potassium chromate is in solution with chromate ions, forming lead chromate, and to the depressive action of hydroxyl ions.

Mitrofanov and Kushnikova [11] studied the adsorption of chromium compounds on sulphide minerals by using radioactive isotope Cr^{51} in the form of dichromate. The effect of various factors, such as pH, temperature, potassium dichromate concentration, contact time, etc. on the adsorption of chromium compounds on sulphide minerals. They found that the adsorption of chromium compounds on galena increases with the increase in temperature, concentration of potassium dichromate and contact time. They suggested that the adsorption of dichromate ion was evidently connected with HCrO_4^- and CrO_4^{2-} , rather than with Cr(OH)_3 because sorption was reduced by approximately half on minerals washed with HCl.

Contrary to the conclusion of Mitrofanov et al., Stepanov and Nagirnyak [12] suggested that the depression of galena and pyrite occurs as a result of formation of

oxide films on their surfaces. In the intermediate pH range, both dichromate and chromate ions are present in the solution, regardless of which chromate salt is added to the pulp; the effect of each of these ions is determined by its concentration in the pulp, and depends on the pH of the solution. They made the thermodynamic calculations for the oxidizing reactions of chromium salts on xanthates. According to their calculation, under standard conditions the lower xanthates are oxidized, and the higher xanthates are not oxidized.

Mitrofanov and Kushnikova [13], [14] have studied the effect of potassium dichromate and sodium sulphide on adsorption of an amine on sulphides of heavy metals in connection with their floatability. According to the experiments using potassium dichromate and tri-decylamine labeled with C^{14} , potassium dichromate increased the adsorption of tridecylamine on sphalerite and pyrite at all pH values; however, on galena, this increase was shifted toward alkaline pH values, with a maximum at about pH 10. Then, the following conditions for the separation of sphalerite from galena were determined: use of potassium dichromate 3-5 kg/ton, amine consumption 20 g/ton, pH 7.2, extraction of zinc into the zinc concentrate 68.0-72.0% and that into Pb concentrate 26.0-33.0%.

Yamasaki et al. [15] studied the action of potassium chromate on galena by means of electron diffrac-

tion. They observed the formation of lead chromate film on the galena surface when the galena specimen having 2mm x 2mm x 1mm was treated with 0.2 M/L of potassium chromate solution for 24 hours. An aggregate of fine polycrystalline lead chromate was suggested as the surface product.

An electrochemical survey of galena flotation was done by Pomianowski and Czubak-Pawlikowska [16]. They observed that the rest potential of galena electrode decreased when potassium ethyl xanthate was added, and that an addition of dichromate caused the increase of the potential proportionate to the logarithm of its concentration. Solov'eva and Khokhlova [17] also measured the electrode potential of galena in dichromate solutions. They found that the treatment of electrode with concentrated dichromate solution (1 g/L) resulted in the covering of electrode with a lead chromate film and no decrease of potential was observed after addition of xanthate. At 20 mg/L of dichromate solution, the addition of xanthate caused the decrease of potential, and it was especially large at pH around 7.

Poole reported the effect of dichromate in flotation at the Sullivan mill at the year of 1920 [18].

EXPERIMENTAL

Materials

The galena, from Galena, Kansas was supplied by Ward's Natural Science Establishment Inc. The mineral specimen grade of galena was ground in a mortar and pestle and screened into size fractions. Enough of the mineral for all the runs was ground initially and stored in a vacuum desiccator. Only - 200 + 270 mesh, - 270 + 325 mesh and - 325 + 400 mesh* size fractions were used for adsorption tests. Galena samples for infrared spectroscopy, were prepared by a further grinding in an agate mortar for 30 minutes.

Pure potassium ethyl xanthate was synthesized by a standard method using potassium hydroxide, methanol and carbon disulphide and purified three times by recrystallization with ethyl alcohol and ethyl ether [32]. Xanthate solution was always prepared just before every experiment. Dixanthogen preparation was achieved by oxidizing the aqueous solution of pure xanthate with iodine, extracting the product with ethyl ether and then drying it under reduced pressure [33].

Potassium chromate, potassium dichromate, potassium hydroxide, lead sulphide of reagent grade supplied

* Mesh sizes refer to Tyler standard screens.

from the Fisher Scientific Company were used. All solutions were made with distilled water. The perchloric acid was Baker and Adamson, 60%. Lead chromate used for the adsorption test of xanthate was precipitated by the reaction between lead nitrate and potassium chromate of reagent grade, followed by filtration, rinsing with distilled water and drying under reduced pressure. For the purging of dissolved oxygen from aqueous solutions, helium* or nitrogen gas** supplied by Canadian Liquid Air Company Limited, was used without further purification.

Analytical Equipment

A Perkin-Elmer Model 450 UV-VIS-NIR Recording Spectrophotometer and matched 1.0 cm Corex cells were used for the determination of xanthate, chromate and dichromate ion concentrations. The spectrophotometric determination of xanthate ion was based on its absorption peak at the wave length of 301 mμ.

Chromate and dichromate ions were quantitatively analyzed by measuring the optical densities at 370 mμ and 345 mμ, respectively.

The identification of adsorbed species of chromate or dichromate ions on galena, synthetic lead sulphide and xanthate ions of lead chromate was achieved by means of

* Helium: 99.995% , moisture <10 P.P.M., D.P. -76°F.

** G Grade Nitrogen: 99.5 to 99.8%, argon content included, oxygen 2-5000 P.P.M., moisture 128 P.P.M., D.P. -40°F.

infrared spectroscopy. A Perkin-Elmer Double-beam Infrared Spectrometer, Model 521 was used for this purpose.

The measurements of rest potential of galena electrode was done with a Beckman Electroscan Model 30 and a matched electrode assembly. The measurement of pH were made using the same equipment, but a combination electrode was used.

Experimental Procedures

(1) Adsorption and Desorption Tests

Adsorption and desorption tests were conducted in a cylindroconical glass vessel whose diameter was 4.5 cm. and the length of conical part was 7.0 cm. A bubbling tip for nitrogen gas or air flow was inserted to allow gas bubbles to agitate the galena samples gently. Some adsorption tests were carried out in a glove box under a controlled atmosphere. A certain amount of galena was put into the glass vessel, and the necessary amount of solution was added. Then the apparatus was put in a water bath whose temperature was kept at $25 \pm 0.5^{\circ}\text{C}$. Some experiments were done at room temperature when it was necessary. After a certain period of agitation, the solution was filtered using a Millipore filter or separated from galena particles by a centrifuge. Then the solution was subjected to a spectrophotometric determination of the concentrations of

xanthate, chromate or dichromate ions. Dixanthogen in a solution or formed on solid particles was also determined spectrophotometrically when it was necessary, after first extracting it with hexane. The amount of dixanthogen was sometimes checked by pyridine colorimetric method [19].

(2) Buffer Action Tests

In order to study the buffer action of galena, five grams of galena powder (- 200 + 270 mesh) was put in one hundred milliliters of distilled water adjusted at various pH values. The same glass vessel was used as used in adsorption tests. Then the change in pH of the solution was recorded for thirty minutes using a combination electrode. For pH adjustment, perchloric acid and potassium hydroxide solutions were used. Air and nitrogen gas were used to agitate the galena powders gently.

(3) Identification by Infrared Spectroscopy

Identification of adsorption products of xanthate and of chromate or dichromate on natural galena, synthetic lead sulphide, and lead chromate was made by infrared spectroscopy. Extremely fine powder of galena was made with an agate mortar to identify the adsorption products of dichromate on the galena surface.* One gram of the sample

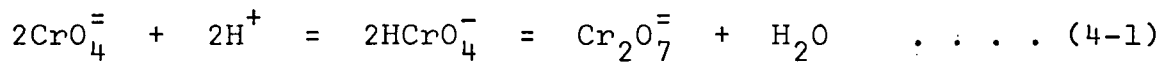
*The surface products on the surface of fine powder may be different from those on the surface of large particles, because the conditions of the surface are different.

powder was immersed in one hundred milliliters of 1.0×10^{-2} M/L potassium dichromate solution for one hour at 25°C. After filtration the sample was stored in a vacuum desiccator. Synthetic lead sulphide was also used to identify the surface products of chromate and dichromate on galena. Lead chromate and chromate-treated lead sulphide were exposed to a 1.0×10^{-2} M/L xanthate solution to identify the adsorption products of xanthate on lead chromate. One to two milligrams of these dried sample were then ground with five hundred milligrams of potassium bromide and pressed into pellets at five thousand psi, and subjected to IR identification.

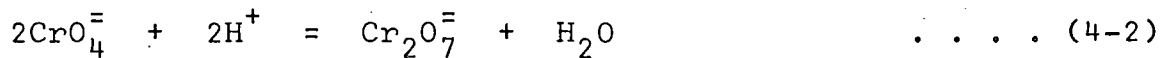
EXPERIMENTAL RESULTS

A. Effect of pH on the Concentrations of Chromate and Dichromate Ions, and the Effect of the Addition of Chromate on Xanthate Stability

In the flotation of sulphide ores containing galena, both chromate and dichromate are used as depressants. However, the relationship between chromate and dichromate ions can be expressed as,



The equilibrium condition of the reaction (4-2) can be calculated as Equation (4-3), using the necessary thermodynamic data given in Latimer's book [20].



$$\text{pH} = 7.3 + \log (\text{CrO}_4^{=2}) - 0.5 \log (\text{Cr}_2\text{O}_7^{=2}) \quad (4-3)$$

Similarly the reaction (4-4) has the equilibrium condition which can be expressed by Equation (4-5).



$$\text{pH} = 6.46 - \log (\text{HCrO}_4^{-}) + \log (\text{CrO}_4^{=2}) \quad (4-5)$$

In order to confirm such a relationship, spectrophotometric determinations were made for chromate ion and dichromate ion concentrations. Figure 1 shows absorption spectra of chromate solution as well as dichromate solution. The peak of absorption band of chromate ions was found at the wave length of 370 mμ and that of dichromate ions at 345 mμ, thus the concentrations of each species can be determined by measuring the optical densities at the wave length of 345 mμ and 370 mμ.

$$A_{345} = \epsilon'_c C_c + \epsilon_d C_d \quad (4-6)$$

$$A_{370} = \epsilon_c C_c + \epsilon'_d C_d \quad (4-7)$$

Where A_{345} and A_{370} are absorbance at 345 mμ and 370 mμ respectively, C_c and C_d are concentrations of chromate ion and dichromate ion, ϵ_c and ϵ'_c * are the molar extinction coefficient of chromate at 370 mμ and 345 mμ, and ϵ_d and ϵ'_d ** are the molar extinction coefficient of dichromate at 345 mμ and 370 mμ. The concentrations of chromate and dichromate ions were determined at the different levels of pH and were depicted in Figure 2. The stability of each ions can be shown graphically as in Figure 2, and in the neutral solution, both ions coexist in solution, regardless of which salt is used.

$$* \epsilon_c \text{ is } 0.482 \times 10^4 / M \text{ and } \epsilon'_c \text{ is } 0.240 \times 10^4 / M.$$

$$** \epsilon_d \text{ is } 0.315 \times 10^4 / M \text{ and } \epsilon'_d \text{ is } 0.112 \times 10^4 / M.$$

The molar extinction coefficients of chromate at pH 9.5 and dichromate at pH 1.0 were determined statistically using 1 cm Corex cells.

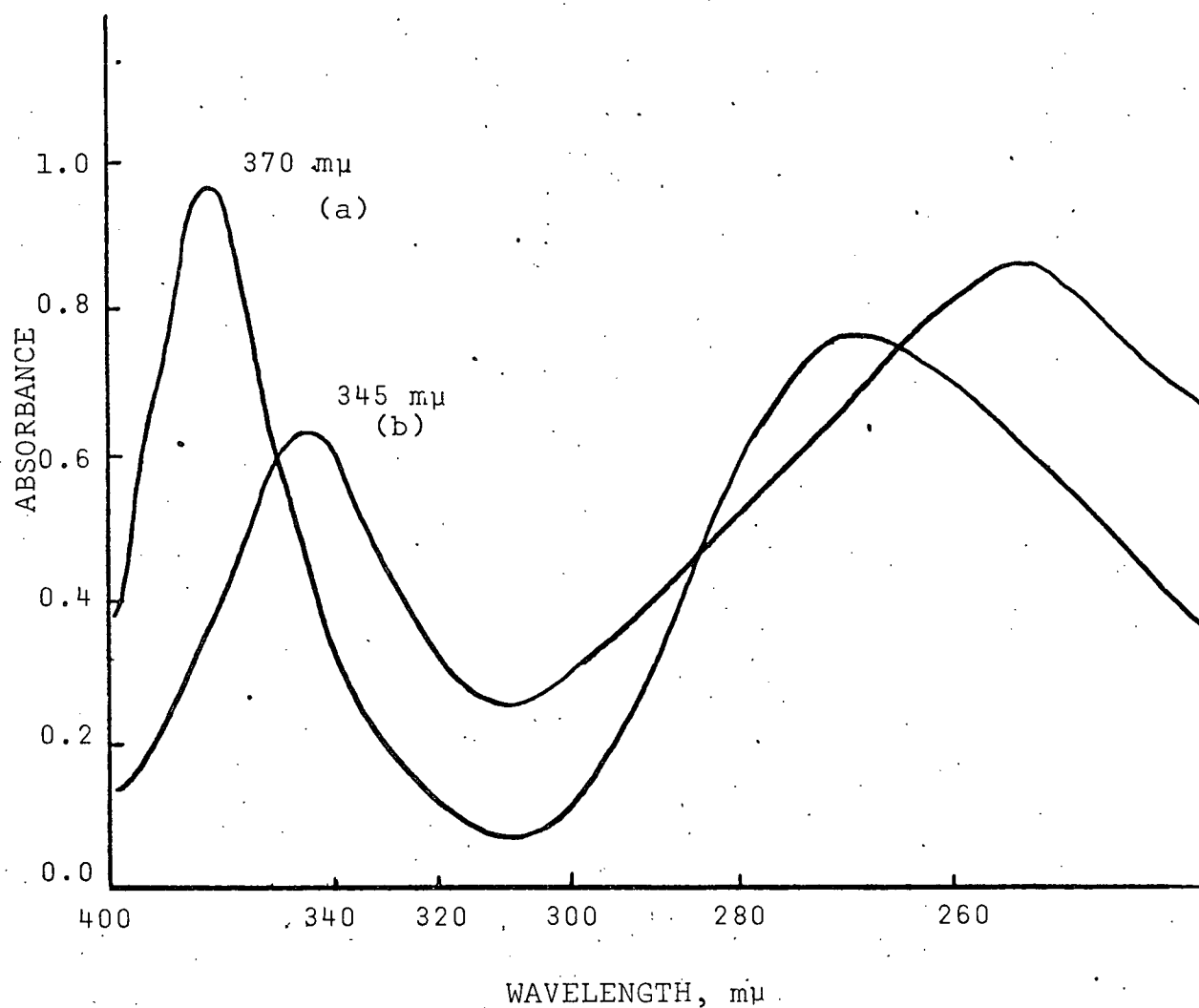


Figure 1 Absorption Spectra of (a) Potassium Chromate Solution (pH 11.5) and (b) Potassium Dichromate Solution (pH 4.3).

The absorption spectra of potassium ethyl xanthate potassium chromate, and their mixture in an aqueous solution are shown in Figure 3. The concentration of potassium ethyl xanthate was 6.0×10^{-5} M/L, and that of chromate was 2.0×10^{-4} M/L. The spectrum of the mixture was taken forty minutes after mixing, and the pH of the solution was 9.81. At any wave length, the optical density of the mixture satisfied the relationship expressed by Equation (4-7).

$$A = C_x \epsilon_x + C_c \epsilon_c \quad (4-7)$$

where A is the absorbance of the mixture, C_x concentration of xanthate ions, C_c concentration of chromate ions, ϵ_c the molar extinction coefficient of chromate solution, and ϵ_x the molar extinction coefficient of xanthate solution. Therefore, the result indicates the satisfactory stability of the mixture of chromate and xanthate ions under these conditions.

B. Changes in pH of the Solutions Containing Galena

(1) Changes in pH of Aqueous Solutions Containing Galena

An attempt was made to determine the stoichiometry of the adsorption reaction of chromate ions on galena by analyzing chromate ion concentration and measuring pH. However, the change in pH of the solution containing galena

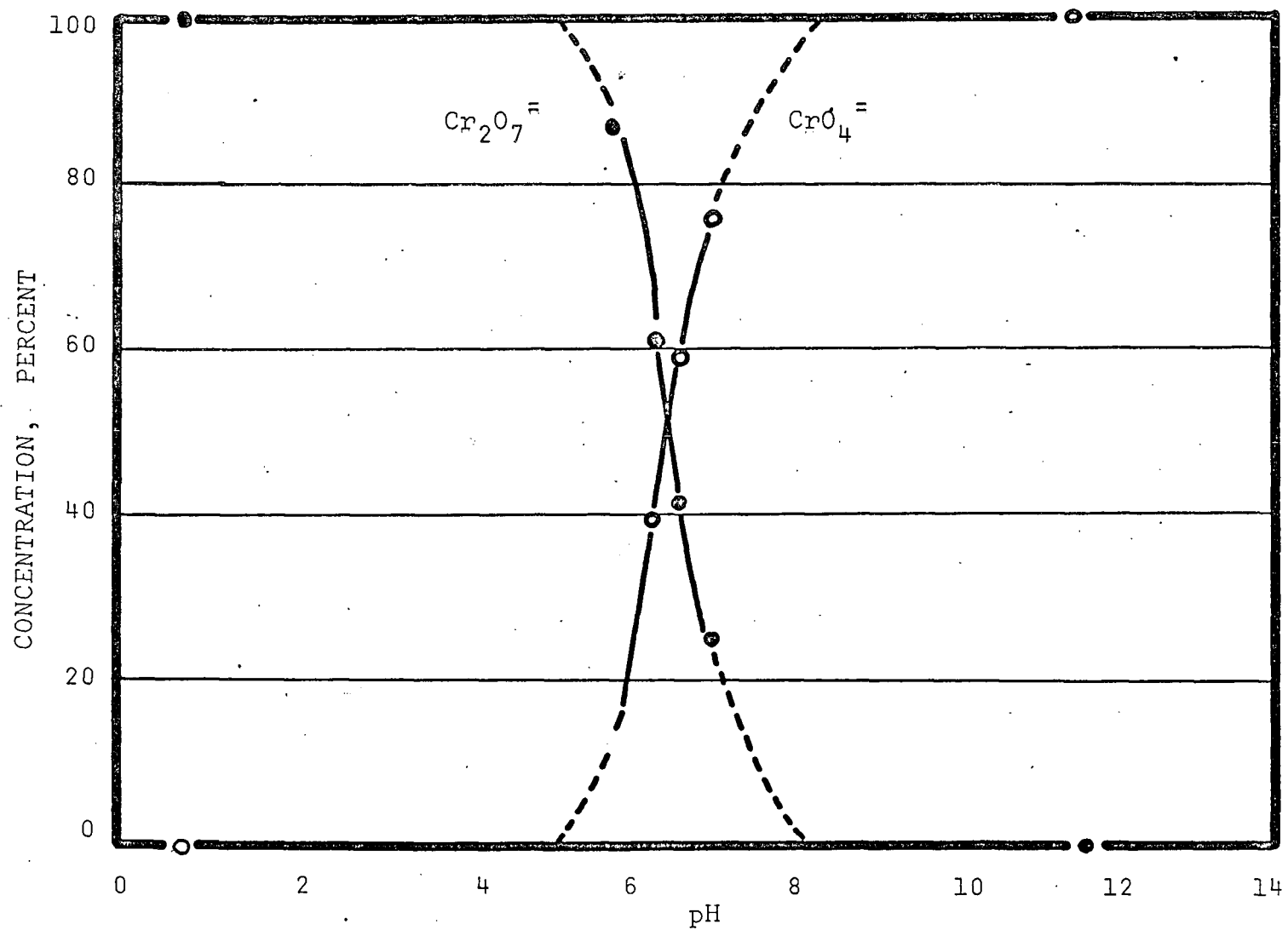


Figure 2 Stability of Chromate Ion and Dichromate Ion as a Function of pH

alone was found to be very large in the presence of oxygen. Both the changes in pH and the amount of chromate ions adsorbed on galena surface were larger when oxygen was present in solution than in the absence of oxygen as mentioned later. From these observations it would appear that the reaction system is rather complicated. In fact, because the ratios between chromate ions adsorbed and hydrogen ions consumed were not found to be a constant for the different levels of initial pH and of initial concentration of chromate ions, the stoichiometric determination of adsorption reaction of chromate ions on galena surface was unsuccessful.

Therefore, first of all, the change in pH of water containing galena was studied. Five gram quantities of galena (- 270 + 325 mesh) were put in one hundred milliliters of double distilled water of various pH adjusted by perchloric acid, and the changes in pH with time were measured continuously during gentle agitation. Figure 4 shows the changes of pH of water containing galena in the presence of oxygen. The value of pH shifted toward 7, regardless of the initial pH. Similar experiments were carried out under the same experimental conditions but with galena prepared in a glove box under a nitrogen atmosphere. The water used was deaerated by nitrogen gas bubbling. The result obtained are shown in Figure 5. In the acidic range, the changes in pH were similar to those in the presence of oxygen, but the changes in the alkaline region were not so large.

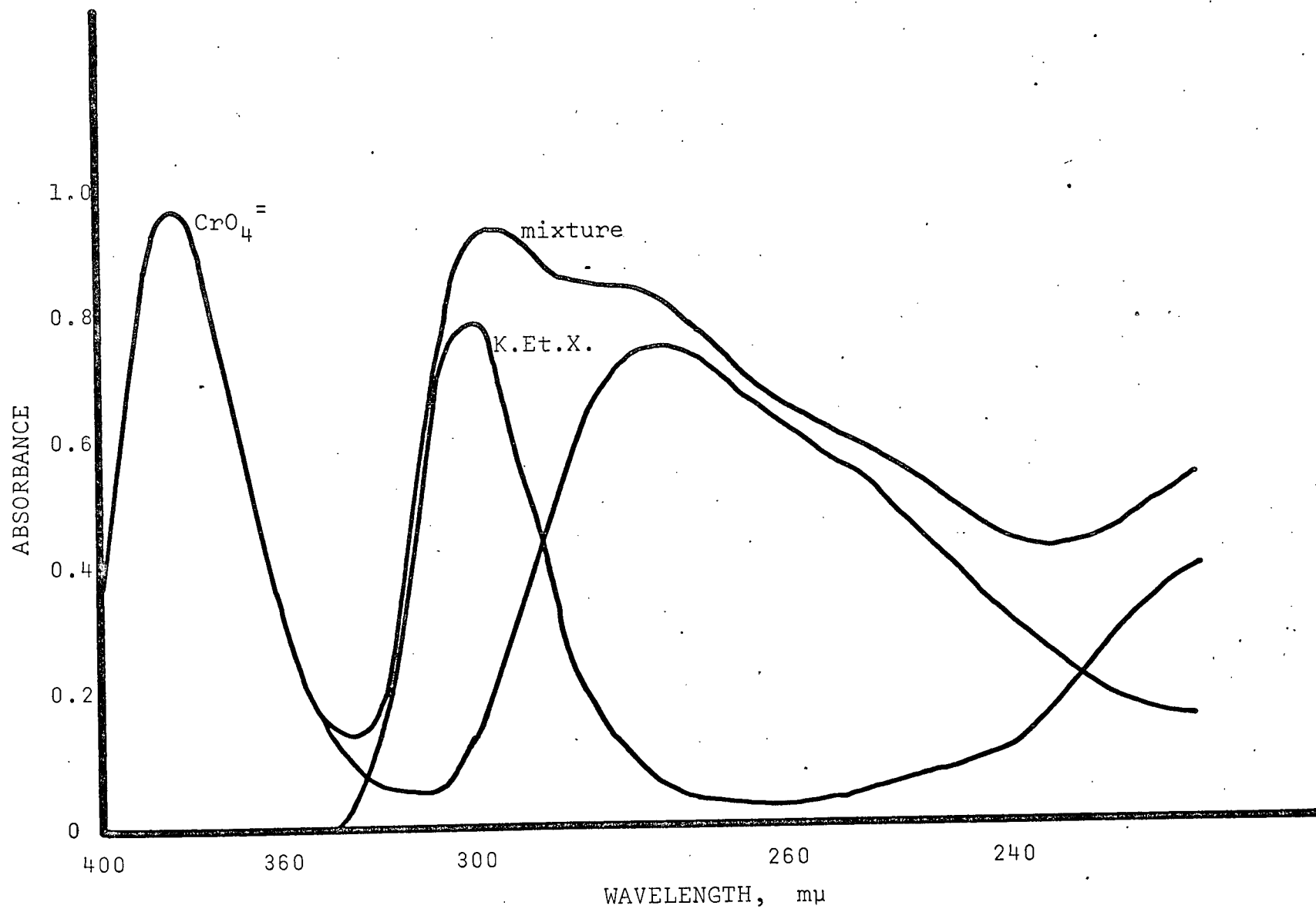


Figure 3 Absorption Spectra of K_2CrO_4 , K.Et.X. and Their Mixture in an Aqueous Solution (pH 9.8).

In order to obtain a better understanding of the way in which galena is responsible for the pH of the solution, titration experiments were designed. One hundred milliliters of double distilled water containing five grams of galena was adjusted to pH 3 by perchloric acid, and was titrated with 0.01 N sodium hydroxide. The results are shown in Figure 6. Curve (a) shows a titration in the presence of oxygen, while curve (b) shows corresponding results without oxygen. The former has a simple shape compared to the latter.

All experiments mentioned above were carried out without removal of oxygen contained in the nitrogen gas used. Since the oxidation of a galena surface by oxygen contained in nitrogen gas might occur, one must leave room for some variation. It would be very interesting to examine the change in pH of the solution avoiding oxygen contamination as completely as possible, however, further experiments were not done in this work.

(2) Changes in pH of a Chromate Solution Containing Galena

Similar experiments as mentioned above were carried out using 2×10^{-4} M/L potassium chromate solution. The results obtained in the presence and absence of oxygen are shown in Figure 7 and Figure 8, respectively. In the presence of oxygen, when starting pH values were 9.9 and 10.9, pH values did not change significantly after thirty minutes

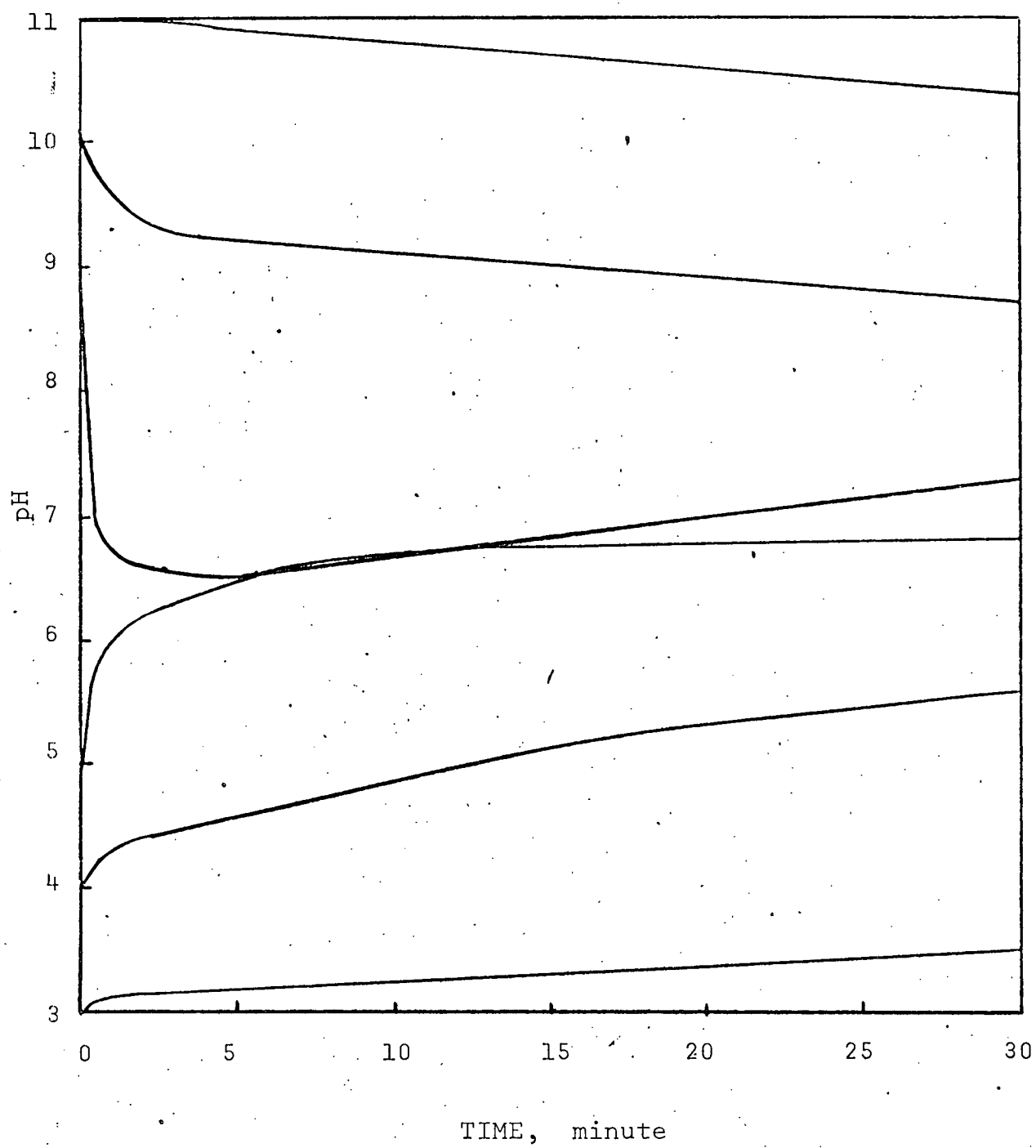


Figure 4 Time Dependence of H_2O with Galena Suspension

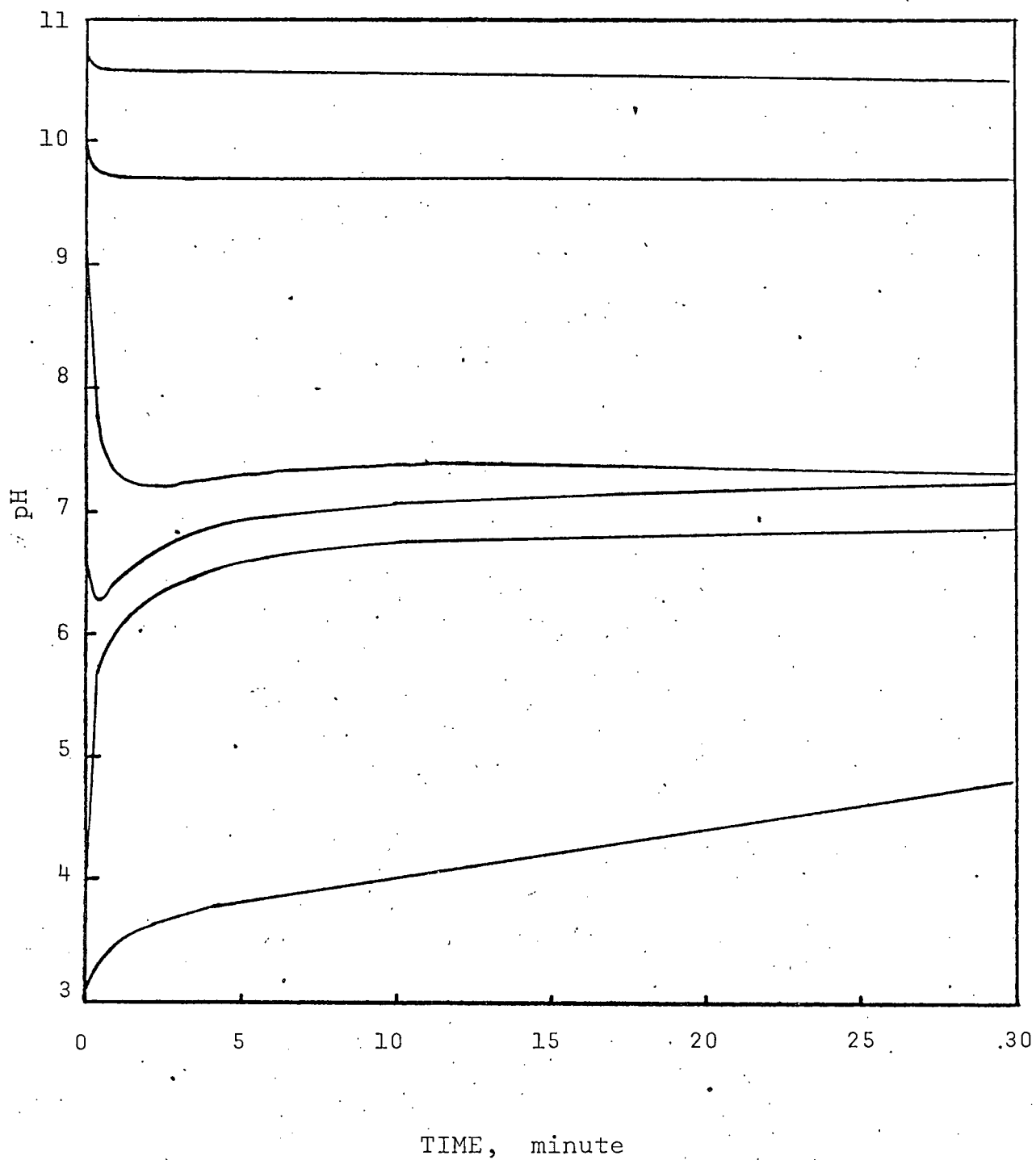


Figure 5 Time Dependence of pH of the Solution Containing Unoxidized Galena

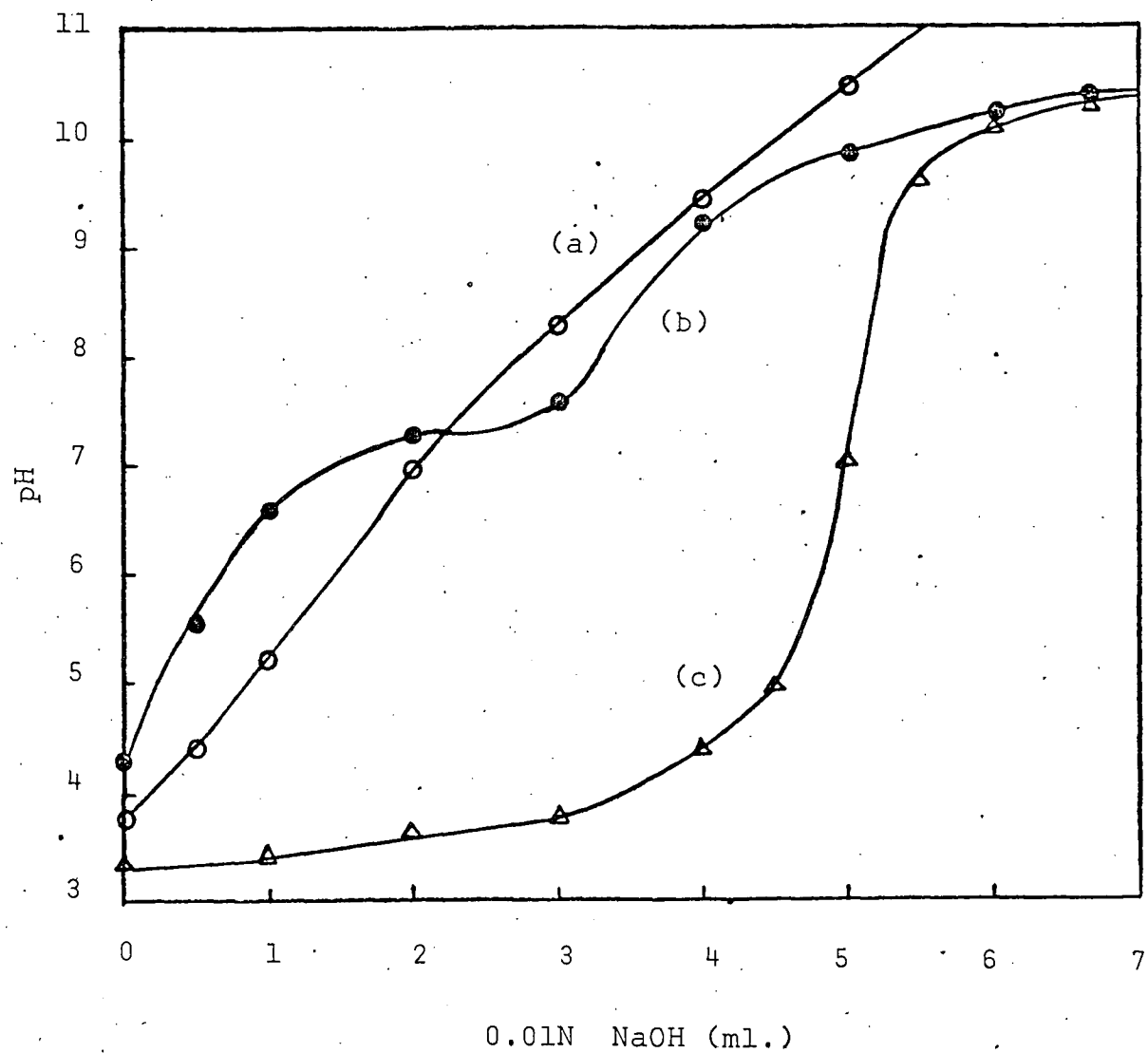


Figure 6 Titration Curves
(a) Oxidized Galena
(b) Unoxidized Galena
(c) Water Only

agitation, but when initial pH was below 9, pH of the solution increased with time. In the previous experiments, pH of the solutions which did not contain chromate salt changed from 3 to 3.5 and 4 to 5.6 after thirty minutes standing, but in those experiments, pH shifted from 3 to 4.5 and from 4 to 7, respectively. This indicates that pH shift of the solutions containing chromate salt was larger than that of the solutions without chromate salt. Similar phenomena were observed when the oxygen was excluded. The pH values of the solutions which did not contain chromate salt increased gradually, whereas that of the solutions containing chromate salt increased rapidly, when initial pH was 3. Figure 9 shows a titration curves for a chromate solution and for a chromate solution containing galena.

C. Adsorption Rates of Chromate and Xanthate Ions by Galena

Planksin and Myasnikova [4], and Bogdanov and Kakovskii [9] reported that the chemical attachment of chromate ions to minerals, such as pyrite, galena, etc., was independent of xanthate ion attachment and apparently took place in different areas.

In order to obtain an understanding of the adsorption of chromate and xanthate on galena surface, in the system of galena-xanthate-chromate experiments were conducted to investigate the competitive adsorption between chromate

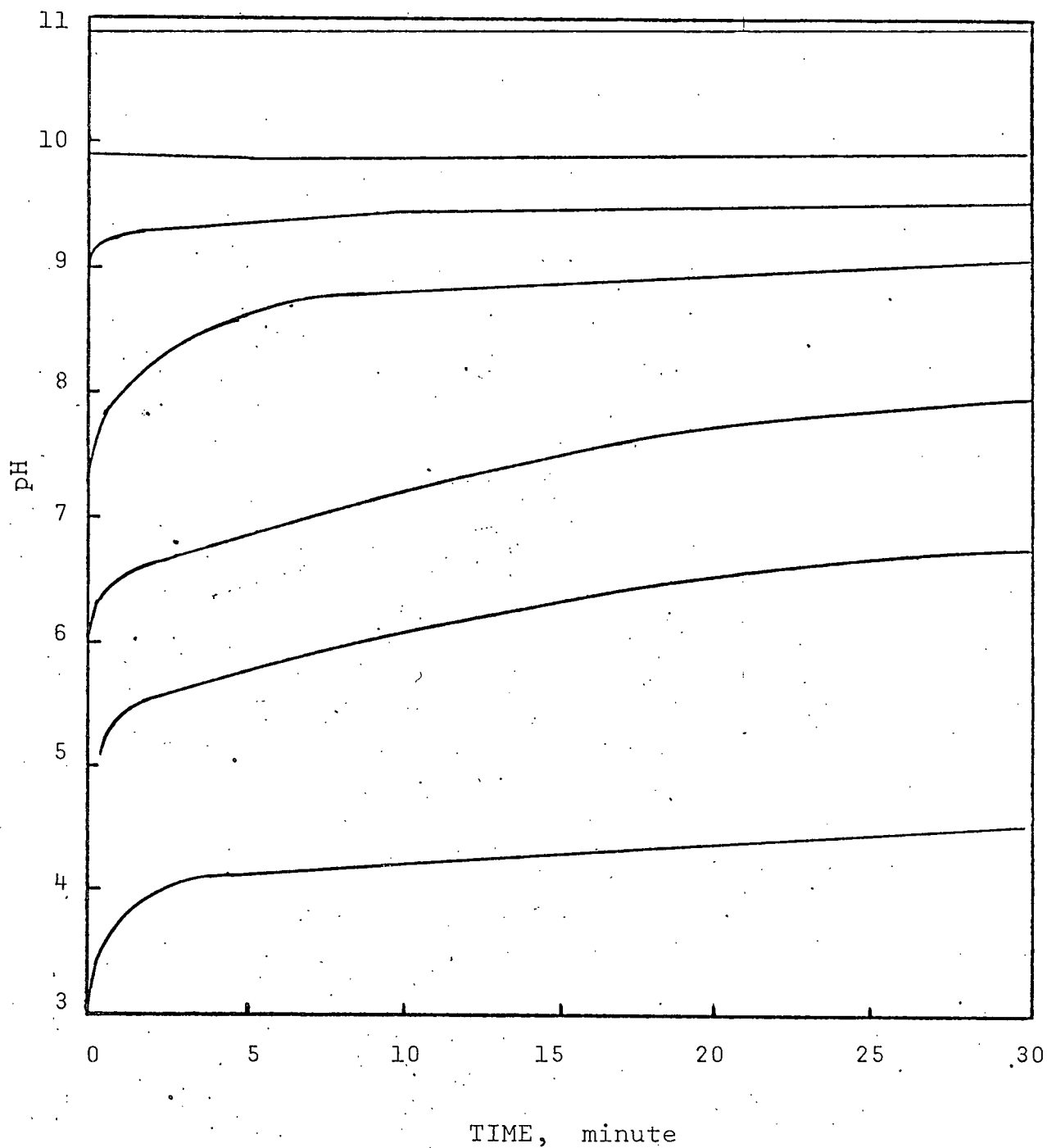


Figure 7 Time Dependence of pH of 2.0×10^{-4} M/L Potassium Chromate Solution Containing Galena

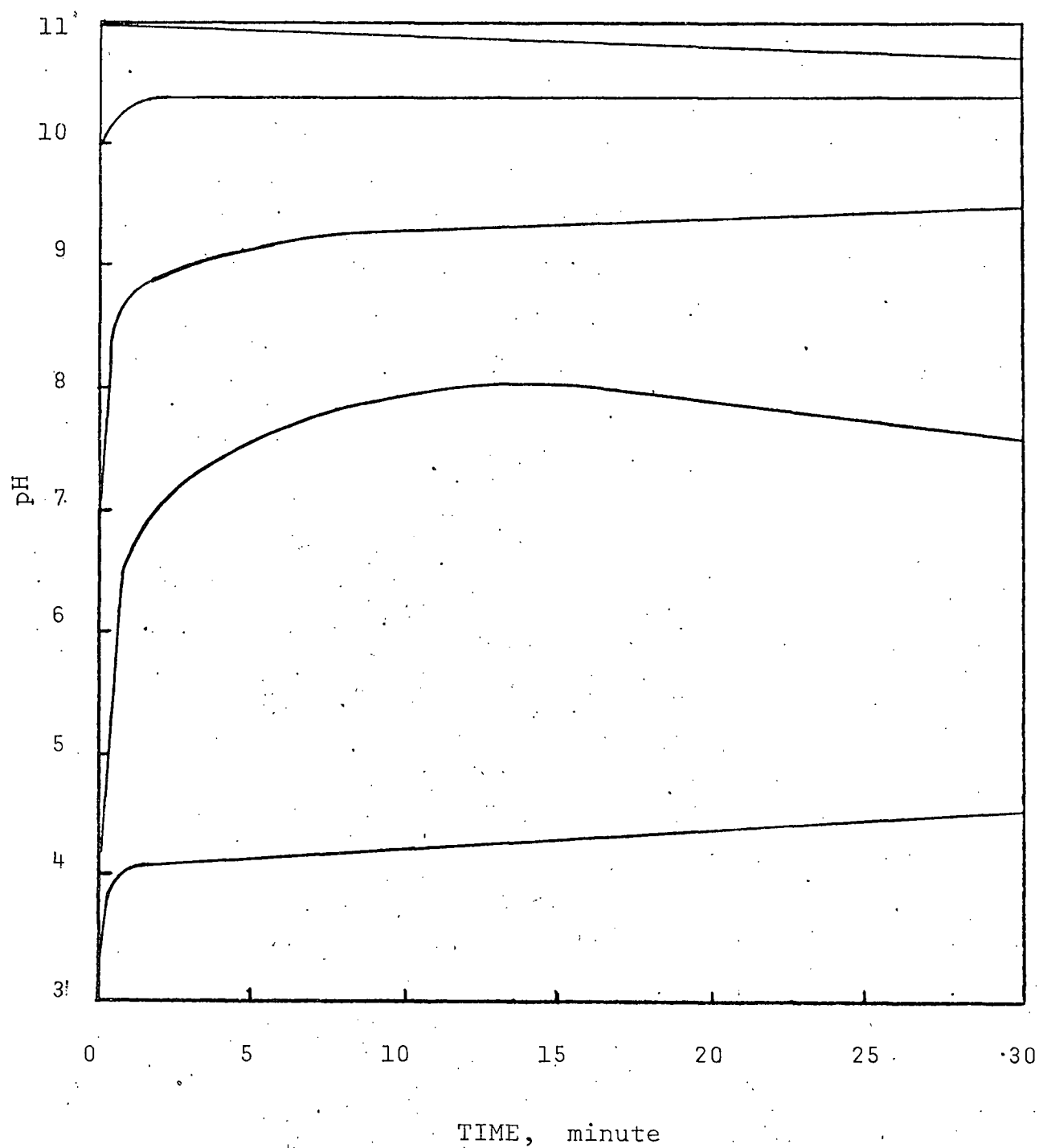


Figure 8 Time Dependence of pH of 2.0×10^{-4} M/L Potassium Chromate Solution Containing Unoxidized Galena

and xanthate ions, the desorption of chromate ions due to the adsorption of xanthate from galena pretreated with chromate, and the desorption of xanthate from galena surface pretreated with xanthate during the chromate adsorption test.

Prior to proceeding with such adsorption and desorption experiments, the adsorption rates of chromate and xanthate ions on galena were studied. The results obtained for the solutions containing 1.6×10^{-4} M/L xanthate and 4.0×10^{-4} M/L chromate respectively are shown in Figure 10.

Though the concentration of chromate ions was higher than that of xanthate ions the adsorption of chromate ions is fairly slow compared to that of xanthate ions. It is predicted from these results that xanthate adsorption is completed before chromate adsorption when galena is immersed in a solution containing both xanthate and chromate ions.

D. Adsorption of Chromate Ions and Xanthate Ions on Galena Surface

In order to understand the adsorption state of xanthate and chromate ions on galena, a competitive adsorption study may provide useful information. Three kinds of solutions, one containing potassium chromate alone, one containing potassium xanthate alone, and the other containing both chromate and xanthate ions, were used. The results obtained are shown in Table I.

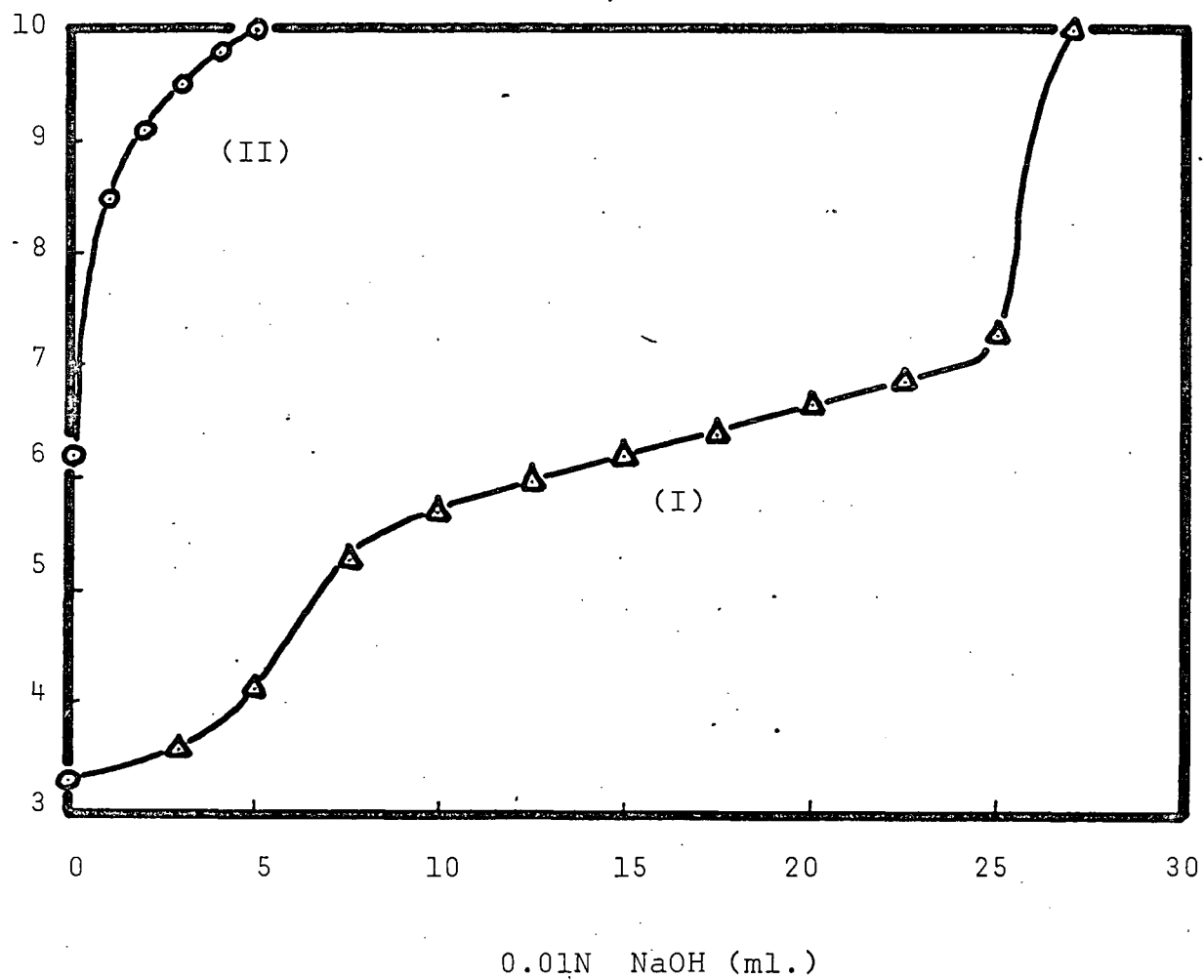


Figure 9 Titration Curves of Chromate Solutions
(I) Chromate Solution Only
(II) Containing Galena

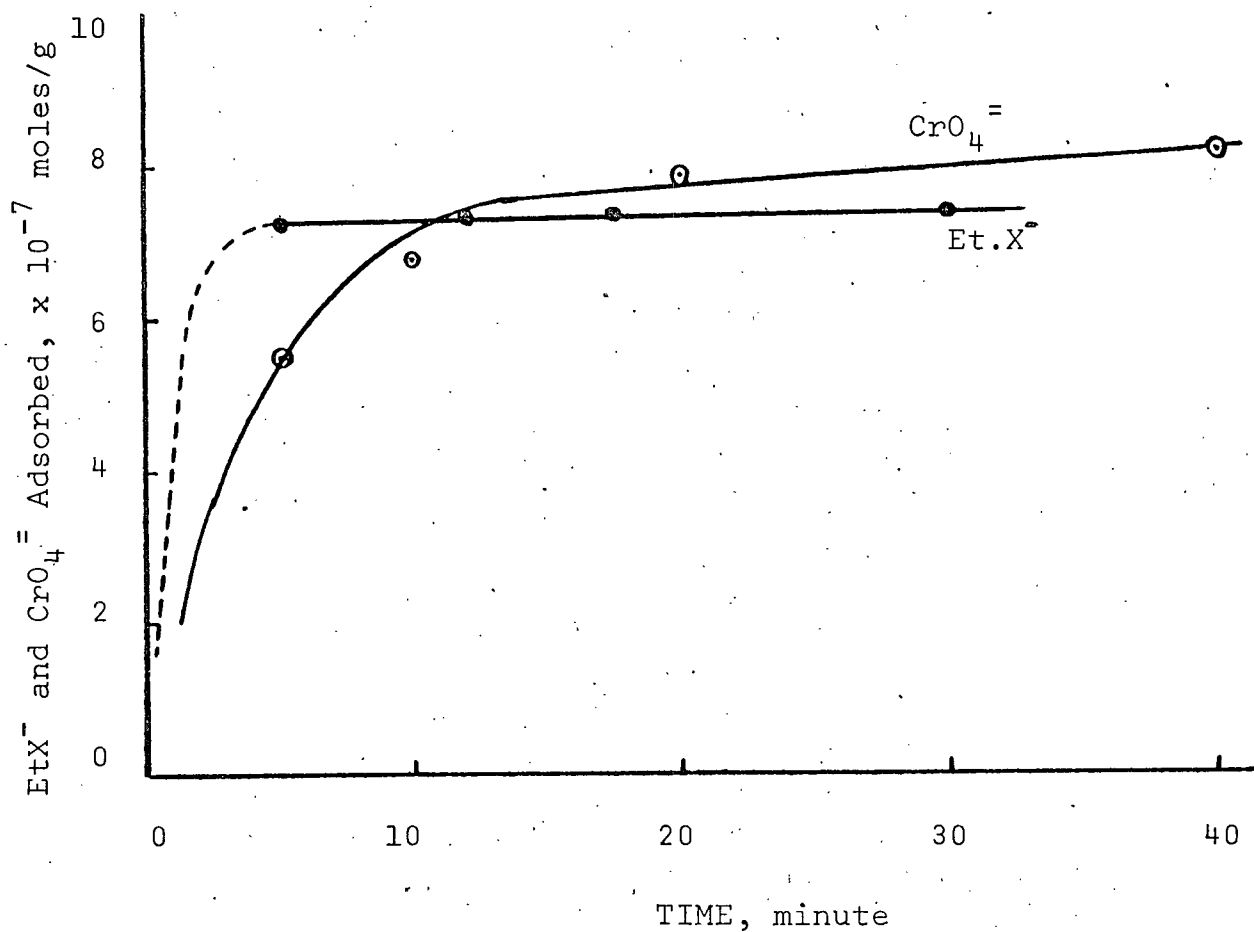


Figure 10 Adsorption Rates of Chromate and Xanthate on Galena at 25°C.

Galena (-325 + 400 mesh)	10 g.
K ₂ CrO ₄ (4.0 x 10 ⁻⁴ M/L)	50 mls., Initial pH 7.2
K.Et.X. (1.6 x 10 ⁻⁴ M/L)	50 mls., Initial pH 7.4

First of all, ten grams of galena (- 325 + 400 mesh) was put into fifty milliliters of 4.0×10^{-4} M/L potassium chromate solution and aerated for thirty minutes at 25°C. Initial pH of the solution was 7.35, and pH increased slightly to 7.56 after thirty minutes retention. The amount of chromate ions adsorbed by galena was 1.24×10^{-6} moles per gram galena.

The adsorption of xanthate by galena was studied using a neutral pH solution. When 8.0×10^{-5} M/L and 1.6×10^{-4} M/L xanthate solutions were used, xanthate ions adsorbed were 3.5×10^{-7} moles/g galena and 7.7×10^{-7} moles/g galena, respectively. It is seen that the amount absorbed almost doubled when the initial concentration of the solution was doubled.

In a solution containing 1.6×10^{-4} M/L potassium xanthate and 4.0×10^{-4} M/L potassium chromate, the adsorption of xanthate ions was 3.65×10^{-7} moles/g of galena while the chromate adsorption was 0.79×10^{-6} moles/g of galena. The pH value changed from 7.25 to 7.91 during the agitation. The adsorption of both chromate and xanthate were altered considerably under the competitive conditions. The decrease measured in the adsorption of chromate was 36 per cent, but in xanthate 53 per cent.

TABLE I
Adsorption of Chromate Ion and/or Xanthate
Ion on Galena Surface

Galena: -325+400 mesh 10.0 grams

Xanthate and/or Chromate Solutions: 50 mls.

Retention Time: 30 minutes

Temperature: 25°C.

Initial Concentration		Initial pH	Amount of Adsorption		Final pH
$\text{CrO}_4^{=}$ (M/L)	EtX^- (M/L)		$\text{CrO}_4^{=}$ (m/g)	EtX^- (m/g)	
4.0×10^{-4}	0	7.35	1.2×10^{-6}	0	7.56
0	8.0×10^{-5}	6.85	0	3.5×10^{-7}	6.98
0	1.6×10^{-4}	7.01	0	7.7×10^{-7}	7.03
4.0×10^{-4}	1.6×10^{-4}	7.26	0.8×10^{-6}	3.7×10^{-7}	7.73

Since the results obtained by U.V. spectrophotometer are accurate to within $\pm 1\%$. Considering the experimental accuracy, the concentrations of $\text{CrO}_4^{=}$, $\text{Cr}_2\text{O}_7^{=}$, EtX^- , and di-xanthogen, derived from U.V. absorbance data and presented in Tables I to VI, are corrected to two significant figures.

the adsorption test, helium bubbling was continued for agitation purpose. The concentration of the chromate solution was 4.0×10^{-4} M/L. After thirty minutes retention, the solution was separated from the galena particles and it was subjected to spectrophotometric analysis.

The other fraction, which weighed exactly the same as the first, was taken out from the glove box in order to investigate the oxygen effect. This sample was treated in a chromate solution with air bubbling for agitation purpose. The experimental conditions were all the same except for the air bubbling. Completion of the same experiment twice gave similar results and the averages of these results are shown in Table II.

Initial pH of a chromate solution was 7.60 (in air atmosphere). The amount of chromate ions adsorbed on galena surface was 1.27×10^{-6} moles per gram of galena in helium atmosphere and increased to 1.74×10^{-6} moles per gram of galena in air atmosphere. The adsorption of chromate for the latter case is about 1.4 times of that of the former. This fact supports the prediction that oxygen may be involved in the formation of lead chromate on galena surface. Such a phenomenon is reasonable from the thermodynamic point of view which will be discussed later.

TABLE II
Adsorption of Chromate Ion on Galena Surface
in the Presence or Absence of Oxygen

Galena: -270+325 mesh 5.0 gram

Potassium Chromate Solution: 4.0×10^{-4} M/L 50 mls.

Retention Time: 30 minutes

Initial Temperature: 25°C.

Atmosphere	Initial pH	Adsorption of $\text{CrO}_4^{=}$ (moles/g)	Ratio	Final pH
He	7.60	1.2×10^{-6}	1.0	7.72
Air	7.60	1.7×10^{-6}	1.4	7.80

F. Effect of pH on Chromate Adsorption on Galena

Figure 11 shows the effect of pH on chromate adsorption on galena. Ten grams of galena (- 325 + 400 mesh) was put in one hundred milliliters of 1.0×10^{-2} M/L potassium chromate solutions which had various initial pH values. After gentle agitation for ten minutes at 25°C, the solutions separated from solid particles were used for spectrophotometric determinations and pH measurements. In Figure 11, the amount of chromate ions consumed are given in terms of both initial and final pH values. At pH below 9 chromate adsorption decreased linearly with pH, and above pH 9 it remained constant.

G. Desorption of Xanthate Ions or Chromate Ions From Galena Surface

As mentioned before, the adsorption and desorption experiments were carried out in order to understand the adsorbed states of xanthate and chromate on galena. Table III and Table IV show the results obtained for the desorption tests of chromate ions and xanthate ions, respectively.

Ten grams of galena (- 325 + 400 mesh), which was pre-treated with 4.0×10^{-4} M/L potassium chromate for forty minutes, was taken into twenty-five milliliters of 1.6×10^{-4} M/L potassium ethyl xanthate and agitated for thirty minutes at 25°C. The amount of xanthate ions adsorbed

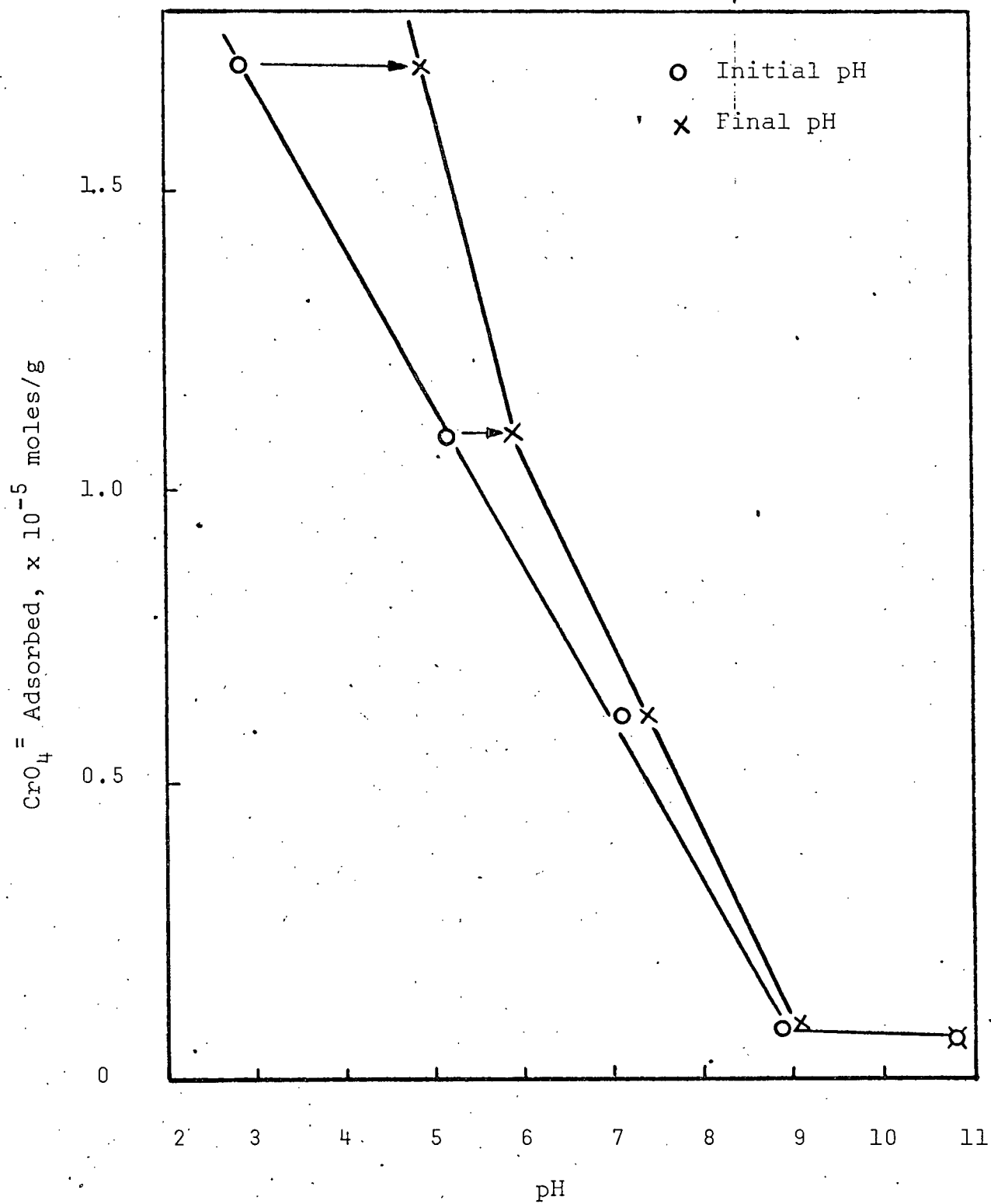


Figure 11 Effect of pH on Chromate Adsorption on Galena

on galena was 3.56×10^{-7} moles per gram of galena. This value was less than half of the amount adsorbed on untreated galena. In this experiment, no detectable amount of chromate ions from galena surface was desorbed counterbalancing the xanthate adsorption. This is true for all the other xanthate adsorption tests.

Then, ten grams of galena pretreated with 8×10^{-5} M/L xanthate solution were put in twenty-five milliliters of 4.0×10^{-4} M/L potassium chromate solution and agitated for thirty minutes at 25°C . The value of pH of the solution moved from 7.32 to 7.93 during the agitation. The amount of chromate ions adsorbed on xanthate-treated galena was 0.96×10^{-6} moles per gram of galena and was about 77 per cent of that adsorbed on the fresh galena. No xanthate ions were detected in the resulting solution. However, 1.12×10^{-7} xanthate moles per gram of galena were detected, when ten grams of galena pretreated with 1.6×10^{-4} M/L xanthate solution were immersed in a 1.0×10^{-2} M/L chromate solution for thirty minutes. Other experiments with more concentrated solutions were performed. The results obtained were similar to the above, and the results are also shown in Tables III and IV.

It is expected that dixanthogen is involved in this galena, chromate and xanthate system. In fact, Table V shows that about 40 per cent of total xanthate ions consumed stays as dixanthogen on the surface and in a bulk solution.

TABLE III
Desorption of Chromate Ion from Galena
Surface Due to Xanthate Adsorption

Galena: -325+400 mesh 10.0 grams

Potassium Ethyl Xanthate: 25 mls.

Retention Time: 30 minutes

Temperature: 25°C.

Initial pH of Xanthate Solutions: 6.3-7.8

Conc. of $\text{CrO}_4^{=}$ (M/L)	$\text{CrO}_4^{=}$ Ads. (moles/g)	Initial Conc. of EtX^- (M/L)	$\text{CrO}_4^{=}$ Des. (moles/g)	EtX^- Ads. (moles/g)
4.0×10^{-4}	1.2×10^{-6}	1.0×10^{-2}	N.D.	3.6×10^{-7}
4.0×10^{-4}	1.1×10^{-6}	1.0×10^{-2}	N.D.	1.4×10^{-6}
1.0×10^{-2}	-	1.6×10^{-4}	N.D.	3.5×10^{-7}
1.0×10^{-1}	-	3.2×10^{-4}	N.D.	6.6×10^{-7}

N.D. = Not Detectable

Ads. = Adsorbed

Des. = Desorbed

Conc. = Concentration

TABLE IV
Desorption of Xanthate Ion from Galena Surface
Due to Chromate Adsorption (1)

Galena: -325+400 mesh 10.0 grams

Potassium Chromate Solution: 25 mls.

Retention Time: 30 minutes

Temperature: 25°C.

Initial pH of Chromate Solutions: 5.3-7.4

Conc. of EtX ⁻ (M/L)	EtX ⁻ Ads. (moles/g)	Initial Conc. of CrO ₄ ⁼ (M/L)	EtX ⁻ Des. (moles/g)	CrO ₄ ⁼ Ads (moles/g)
8.0×10^{-5}	3.5×10^{-7}	4.0×10^{-4}	N.D.	1.0×10^{-6}
1.6×10^{-4}	7.6×10^{-7}	1.0×10^{-2}	1.1×10^{-7}	1.4×10^{-6}
1.0×10^{-2}	-	0	N.D.	0
1.0×10^{-2}	-	8.0×10^{-4}	2.4×10^{-7}	1.2×10^{-6}

N.D. = Not Detectable

Ads. = Adsorbed

Des. = Desorbed

Conc. = Concentration

This experiment for xanthate desorption was made using twenty grams of galena (- 270 + 325 mesh), one hundred milliliters of 1.0×10^{-4} M/L potassium xanthate. After separating solids from the solution, dixanthogen was extracted with fifty milliliters of hexane, and subjected to a spectrophotometric determination. The amount of xanthate ions staying as lead xanthate was calculated from the difference between total xanthate ions consumed and dixanthogen on galena surface. Initial pH of potassium ethyl xanthate was 5.92 and that of potassium chromate solution was 7.60. These results show that 66 per cent of lead xanthate and 40 per cent of dixanthogen initially present were desorbed from galena surface due to adding potassium chromate.

It is seen from these simple experiments that the adsorption of xanthate on chromate-treated galena was much more affected than that of chromate onto xanthate-treated galena. It is also seen that xanthate desorption from galena surface is possible when the mineral is treated with a concentrated solution of chromate, while no desorption of chromate ion is observed due to xanthate adsorption. These results agree with those obtained in the competitive adsorption tests of chromate and xanthate ions on galena and with the results obtained from the adsorption experiment of xanthate ions on lead chromate.

It would have been very interesting to investigate the desorption of xanthate, which is less than mono-

TABLE V
Desorption of Xanthate from Galena Surface
Due to Chromate Adsorption (2)

Twenty grams of galena (-270+325 mesh) were treated with 100 mls. of 1.0×10^{-4} M/L potassium ethyl xanthate solution for ten minutes at 25°C.

	(as xanthate ion)
Xanthate adsorbed on galena	7.7×10^{-6} moles
as lead xanthate	4.1×10^{-6} moles
as dixanthogen	3.6×10^{-6} moles
Dixanthogen in an aqueous solution	1.2×10^{-6} moles

Then galena mentioned above was treated with 50 mls. of 1.0×10^{-3} M/L potassium chromate solution for ten minutes at 25°C.

Chromate adsorbed on galena	1.3×10^{-6} moles
Xanthate remained on galena	4.2×10^{-6} moles
as lead xanthate	2.7×10^{-6} moles
as dixanthogen	1.5×10^{-6} moles
Dixanthogen desorbed into solution	0.2×10^{-6} moles
Xanthate ion desorbed into solution	3.3×10^{-6} moles

layer coverage, from galena surface. However, the sensitivity of analytical technique used in this study was insufficient for such a purpose.

H. Adsorption of Xanthate Ions by Lead Chromate

In order to examine whether chromate ions are released or not to a solution from lead chromate when xanthate ions are adsorbed on it, adsorption tests of xanthate on lead chromate were conducted. One gram of precipitated fine lead chromate was placed in an Ehrenmyer flask which contained one hundred milliliters of xanthate solution and agitated mechanically for thirty minutes. The solution was then subjected to spectrophotometric determination of xanthate ions as well as chromate ions. This was done for solutions of different xanthate concentrations. The results obtained are shown in Table VI.

When the initial xanthate concentration was 1.0×10^{-2} M/L, the amount of xanthate ions adsorbed per one gram of lead chromate was 1.8×10^{-4} moles while the amount of chromate in the solution was found to be 3.9×10^{-5} moles after thirty minutes agitation. When 1.0×10^{-3} M/L xanthate solution was used 1.4×10^{-5} moles of xanthate ions were adsorbed per one gram of lead chromate. This is approximately one tenth of the amount adsorbed when $1.0 \times$

10^{-2} M/L xanthate solution was used. The amount of chromate ions released in the latter case was 4.7×10^{-5} moles. On the other hand, when no xanthate was added, 5.8×10^{-5} moles of chromate were found in the solution after thirty minute agitation. By using hexane as a solvent for dixanthogen, it was also found that more than 80 per cent of total xanthate consumption stayed as dixanthogen in this system.

These results show that the release of chromate ions from lead chromate was decreased slightly by xanthate adsorption on lead chromate.

I. Thermodynamic Considerations of the Reactions Involved In The System Pb-Cr-S-H₂O

In order to get information on the adsorbed species of chromate or dichromate salt on galena, it might be useful to investigate the system Pb-Cr-S-H₂O thermodynamically. For this purpose, the potential-pH diagram for the system Pb-Cr-S-H₂O at 25°C was constructed. Thermodynamic data used were cited from Latimer [20] and Pourbaix [21].

The potential-pH diagrams for the system Cr-H₂O and Pb-S-H₂O are shown in Figure 12 and 13 respectively. The expected reactions and their equilibrium conditions are given in Table VII. The potential-pH diagram for the system Pb-Cr-S-H₂O is shown in Figure 14. In these figures the solid lines represent the unit activity of the dissolved

TABLE VI
Adsorption of Xanthate Ion on
Precipitated Lead Chromate

Lead Chromate (precipitated): 1.00 gram

Potassium Ethyl Xanthate Solution: 100 mls.

Retention Time: 30 minutes

Temperature: 25°C.

Initial Conc. of Xanthate (M/L)	Adsorption of Xanthate (moles/g)	$\text{CrO}_4^{=}$ in Soln. (moles)	Pb^{++} in Soln.
1.0×10^{-2}	1.8×10^{-4}	3.9×10^{-5}	1 P.P.M.
1.0×10^{-3}	1.4×10^{-5}	4.7×10^{-5}	2 P.P.M.
0	0	5.8×10^{-5}	1 P.P.M.

ions and the broken lines an activity of 10^{-4} . The thermodynamic data for lead thiosulphate and basic lead thiosulphate were not available, therefore lead sulphate and basic lead sulphate were used instead.

It is seen from these figures that galena is oxidized to lead sulphate or basic lead sulphate, and that beyond that potential lead chromate is formed, ignoring the kinetic factors. Furthermore, lead chromate has a large stable domain. This indicates that even in the pH range where dichromate ion is stable, for example pH 1, the formation of lead chromate is favored and there is no lead dichromate stable domain. This is easily checked by mixing the dichromate solution and lead nitrate dissolved in a diluted nitric acid whose pH is 1. As mentioned above the formation of lead chromate in the bulk system is very much favored and lead chromate once formed has a very stable domain.

J. Identification of Reaction Products on the Surface of Galena Treated with Potassium Chromate or Potassium Dichromate

As mentioned previously, many investigators examined the surface products on galena treated with a chromate or dichromate solution by electron diffraction and reported that lead chromate was formed on galena surface. They used a single crystal of galena and treated it with a con-

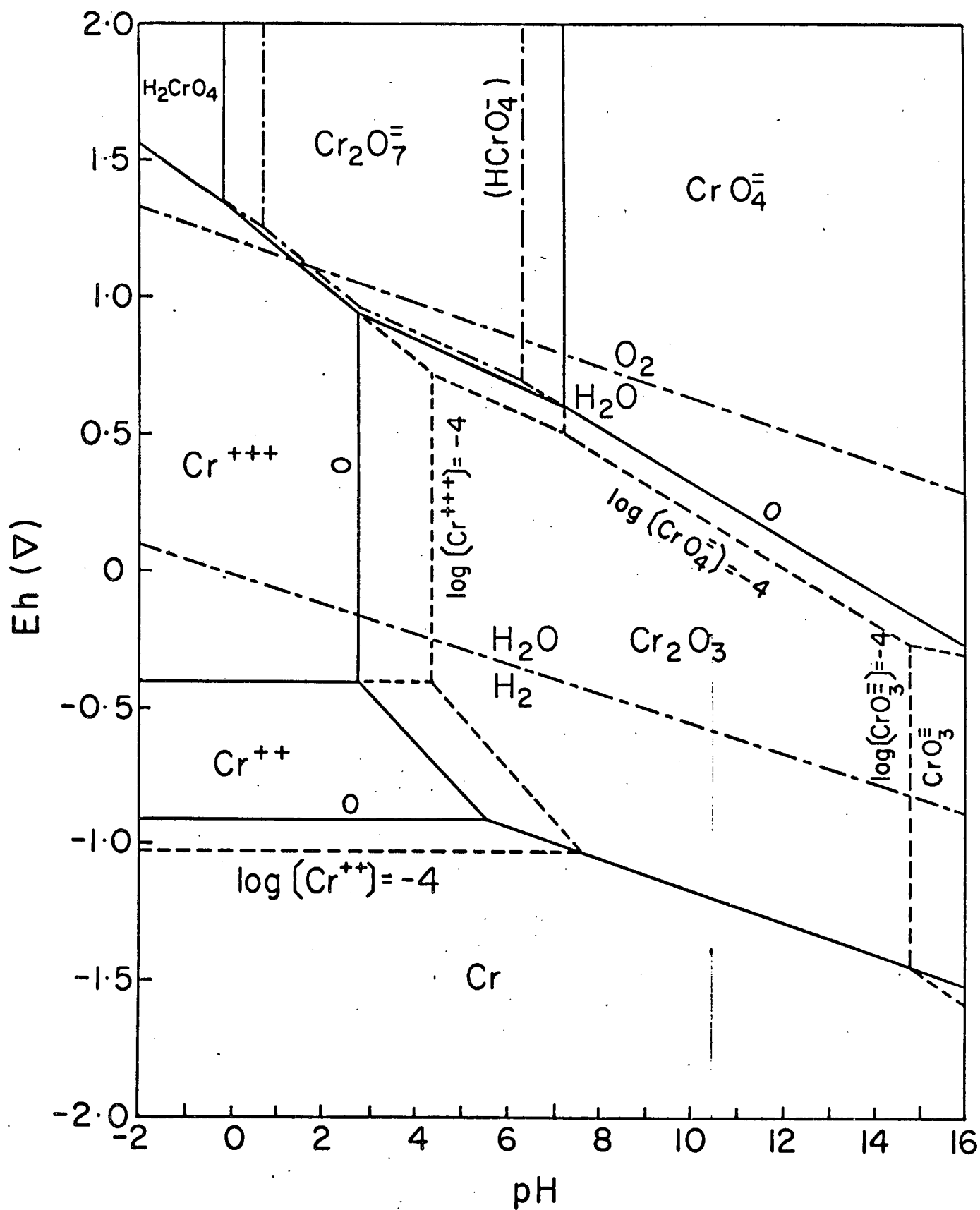


Figure 12 Potential-pH diagram for the system Cr-H₂O

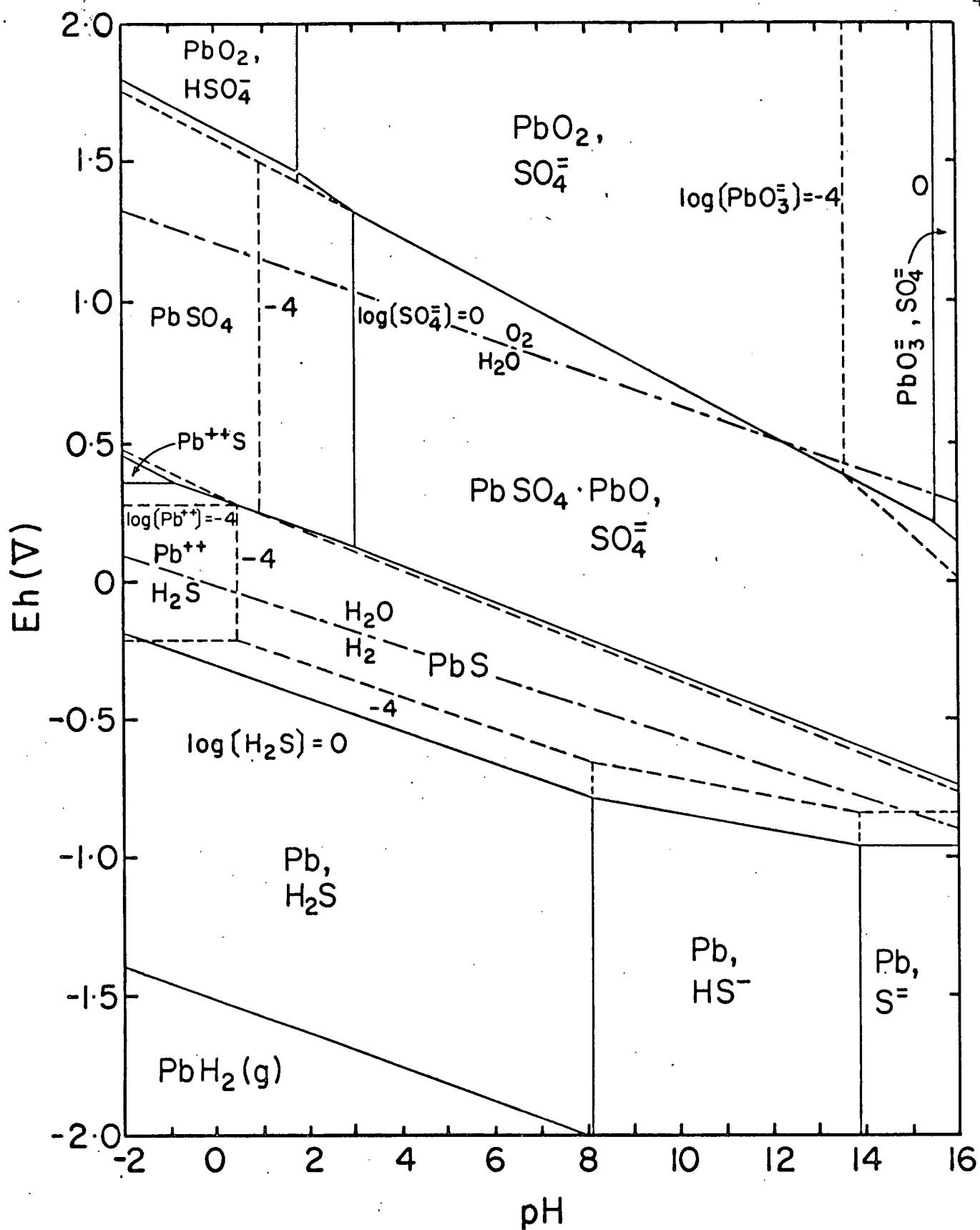
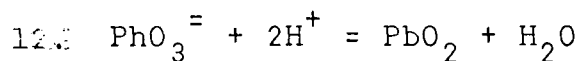


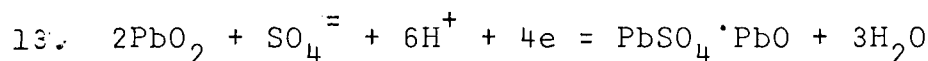
Figure 13 Potential-pH diagram for the system Pb-S-H₂O

TABLE VII
Reactions and Equilibrium Formulae For
The System Pb-Cr-S-H₂O

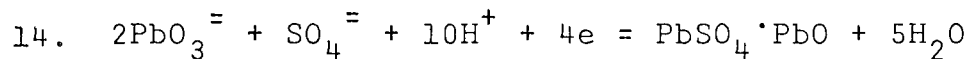
1. $\text{PbO}_2 + \text{CrO}_4^{=2} + 4\text{H}^+ + 2\text{e} = \text{PbCrO}_4 + 2\text{H}_2\text{O}$
 $E = 1.919 - 0.1182\text{pH} + 0.0295 \log [\text{CrO}_4^{=2}]$
2. $2\text{PbO}_2 + \text{Cr}_2\text{O}_7^{=2} + 6\text{H}^+ + 4\text{e} = 2\text{PbCrO}_4 + 3\text{H}_2\text{O}$
 $E = 1.704 - 0.0886 \text{pH} + 0.0148 \log [\text{Cr}_2\text{O}_7^{=2}]$
3. $\text{PbO}_2 + \text{H}_2\text{CrO}_4 + 2\text{H}^+ + 2\text{e} = \text{PbCrO}_4 + 2\text{H}_2\text{O}$
 $E = 1.706 - 0.0591\text{pH} + 0.0295 \log [\text{H}_2\text{CrO}_4]$
4. $\text{PbO}_2 + \text{HCrO}_4^{-} + 3\text{H}^+ + 2\text{e} = \text{PbCrO}_4 + 2\text{H}_2\text{O}$
 $E = 1.729 - 0.0886 \text{pH} + 0.0295 \log [\text{HCrO}_4^{-}]$
5. $\text{PbCrO}_4 + \text{SO}_4^{=2} + 8\text{H}^+ + 3\text{e} = \text{PbSO}_4 + \text{Cr}^{3+} + 4\text{H}_2\text{O}$
 $E = 1.318 - 0.1576 \text{pH} + 0.0197 \log [\text{SO}_4^{=2}] - 0.0197 \log [\text{Cr}^{3+}]$
6. $2\text{PbCrO}_4 + 2\text{SO}_4^{=2} + 10\text{H}^+ + 6\text{e} = \text{Cr}_2\text{O}_3 + 2\text{PbSO}_4 + 5\text{H}_2\text{O}$
 $E = 1.153 - 0.0985 \text{pH} + 0.0197 \log [\text{SO}_4^{=2}]$
7. $\text{PbSO}_4 \cdot \text{PbO} + 2\text{CrO}_4^{=2} + 2\text{H}^+ = 2\text{PbCrO}_4 + \text{SO}_4^{=2} + \text{H}_2\text{O}$
 $\text{pH} + \frac{1}{2} \log [\text{SO}_4^{=2}] - \frac{1}{2} \log [\text{CrO}_4^{=2}] = 11.053$
8. $2\text{PbCrO}_4 + \text{SO}_4^{=2} + 8\text{H}^+ + 6\text{e} = \text{Cr}_2\text{O}_3 + \text{PbSO}_4 \cdot \text{PbO} + 4\text{H}_2\text{O}$
 $E = 1.094 - 0.0788 \text{pH} + 0.0098 \log [\text{SO}_4^{=2}]$
9. $\text{PbO}_2 + \text{HSO}_4^{-} + 3\text{H}^+ + 2\text{e} = \text{PbSO}_4 + 2\text{H}_2\text{O}$
 $E = 1.626 - 0.0886 \text{pH} + 0.0295 \log [\text{HSO}_4^{-}]$
10. $\text{Cr}_2\text{O}_7^{=2} + \text{H}_2\text{O} + 2\text{H}^+ = 2\text{H}_2\text{CrO}_4$
 $\text{pH} + \log [\text{H}_2\text{CrO}_4] - \frac{1}{2} \log [\text{Cr}_2\text{O}_7^{=2}] = -0.091$
11. $2\text{CrO}_4^{=2} + 2\text{H}^+ = \text{Cr}_2\text{O}_7^{=2} + \text{H}_2\text{O}$
 $\text{pH} + \frac{1}{2} \log [\text{Cr}_2\text{O}_7^{=2}] - \log [\text{CrO}_4^{=2}] = 7.296$



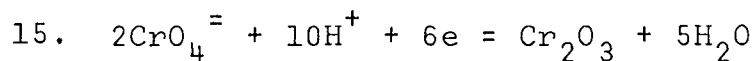
$$\text{pH} - \frac{1}{2} \log [\text{PbO}_3^{=}] = 15.660$$



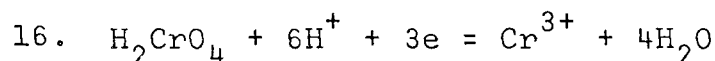
$$E = 1.593 - 0.0886 \text{ pH} + 0.0148 \log [\text{SO}_4^{=}]$$



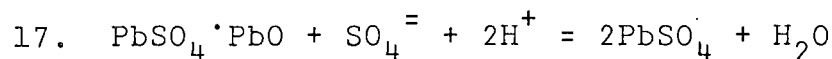
$$E = 2.518 - 0.1480 \text{ pH} + 0.0296 \log [\text{PbO}_3^{=}] + 0.0148 \log [\text{SO}_4^{=}]$$



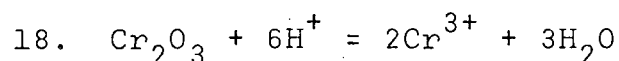
$$E = 1.310 - 0.0985 \text{ pH} + 0.0197 \log [\text{CrO}_4^{=}]$$



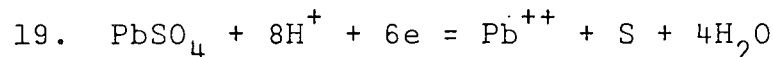
$$E = 1.330 - 0.1182 \text{ pH} - 0.0197 \log [\text{Cr}^{3+}] + 0.0197 \log [\text{H}_2\text{CrO}_4]$$



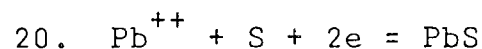
$$\text{pH} - \frac{1}{2} \log [\text{SO}_4^{=}] = 3.02$$



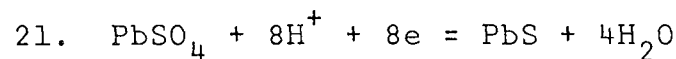
$$\text{pH} + \frac{1}{3} \log [\text{Cr}^{3+}] = 2.80$$



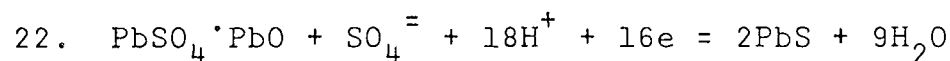
$$E = 0.280 - 0.0788 \text{ pH} - 0.0098 \log [\text{Pb}^{++}]$$



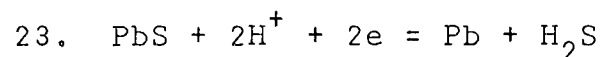
$$E = 0.354 + 0.0295 \log [\text{Pb}^{++}]$$



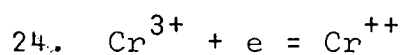
$$E = 0.299 - 0.0591 \text{ pH}$$



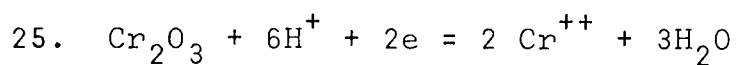
$$E = 0.321 - 0.0667 \text{ pH} + 0.0037 \log [\text{SO}_4^{=}]$$



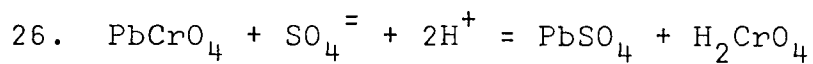
$$E = -0.301 - 0.0591 \text{ pH} - 0.0295 \log [\text{H}_2\text{S}]$$



$$E = -0.408 - \log [\text{Cr}^{++}] + \log [\text{Cr}^{3+}]$$



$$E = 0.088 - 0.1773 \text{ pH} - 0.0591 \log [\text{Cr}^{++}]$$



$$\text{pH} - \frac{1}{2} \log [\text{SO}_4^{=}] + \frac{1}{2} \log [\text{H}_2\text{CrO}_4] = -0.415$$

concentrated chromate or dichromate solution. In a flotation condition, the same product is expected to be formed on galena surface when a chromate or dichromate salt is used as a depressant; but to prove this, it is necessary to investigate whether the same reaction product is obtained when galena is treated with a dilute solution which contains the same level of chromate or dichromate per unit surface area. The author used a natural galena powder and also synthetic galena treated with a chromate or dichromate solution and tried to identify the products formed on galena surface by making pellets for use in a infrared spectrophotometer.

To make a pellet, an extremely fine galena powder was prepared according to the procedure mentioned before. Five hundred milligrams of the powder was immersed in fifty milliliters of 1.0×10^{-2} M/L dichromate solution whose pH was 4.2 and was mechanically stirred for one hour at room temperature. After filtering and drying the sample in a vacuum desiccator, the pellet was made with KBr. The same procedure was applied for lead sulphide which was treated in a dichromate and a chromate solution, and the pH values were 4.2 and 7.6 respectively. The spectra of these three pellets which were scanned on a Perkin-Elmer Model 521 against KBr blanks are shown in Figure 15 - (a), (b) and (c). As a comparison, a spectrum of lead chromate is shown in Figure 15 - (d). The spectrum of lead sulphide treated with a

chromate solution at pH 9.8 was the same as (c).

Spectra (a), (b) and (c) show the absorption bands at 848 cm^{-1} which indicates the formation of lead chromate on galena surface. The absorption bands for chromium oxide, chromium hydroxide, lead dioxide, or lead hydroxide were not found.

K. Identification of Adsorption Products of Xanthate on Lead Chromate

The same IR spectroscopic technique, which was employed for the identification of lead chromate on galena surface, was used in order to identify the adsorption products of xanthate on lead chromate. As the author mentioned before the spectra of powdered natural galena treated with a chromate or dichromate solution did not give a very clear absorption band. Therefore in this case, lead chromate precipitated and synthetic galena treated with potassium dichromate solution were used instead of natural galena treated with a chromate or dichromate solution.

In order to treat lead chromate with xanthate, one gram of lead chromate and synthetic galena pretreated with a potassium dichromate solution whose pH was 5.6 were placed in fifty milliliters of $1.0 \times 10^{-2}\text{ M/L}$ potassium ethyl xanthate whose pH was 6.8 respectively and stirred for one hour at room temperature; the materials were

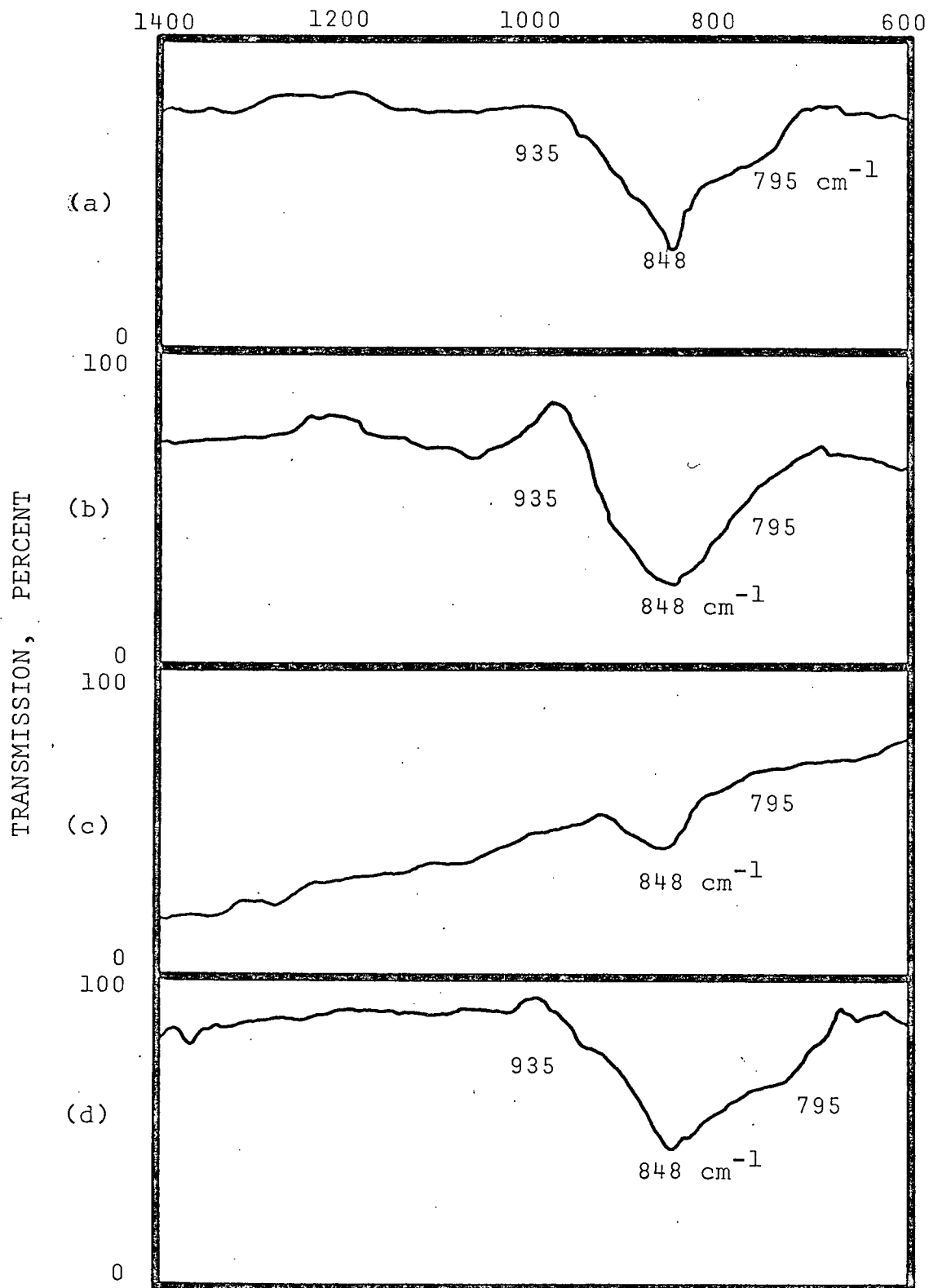


Figure 15 Infrared Spectra of (a) Synthetic PbS treated with K_2CrO_4 (pH 7.6), (b) Synthetic PbS treated with $\text{K}_2\text{Cr}_2\text{O}_7$ (pH 4.2), (c) Galena treated with $\text{K}_2\text{Cr}_2\text{O}_7$ (pH 4.3), (d) PbCrO_4 .

washed with distilled water and dried in vacuum. After making pellets with KBr, spectra were obtained. They are shown in Figure 16 - (a) and (b). Spectra of lead xanthate (c) and chromium oxide (e) are also shown in the same figure.

Spectra (a) and (b) have four significant absorption bands respectively at 1200 cm^{-1} , 1106 cm^{-1} , 1016 cm^{-1} and 848 cm^{-1} . The absorption bands due to chromium oxide, dixanthogen, lead dioxide, or lead hydroxide could not be obtained. The band at 848 cm^{-1} is considered to represent lead chromate and others represent lead xanthate. However, these three absorption bands in spectra (a) and (b) do not agree exactly with those in spectrum (c). Poling and Leja studied the surface products on deposited lead sulphide treated with potassium ethyl xanthate by infrared spectrophotometer and suggested a 1:1 co-ordination between the surface metal atom and xanthate radical in the first monolayer. The deviation of absorption peak for xanthate adsorption products on lead chromate may indicate the possibility of 1:1 co-ordination between xanthate and lead in this system. However, this matter will be discussed later.

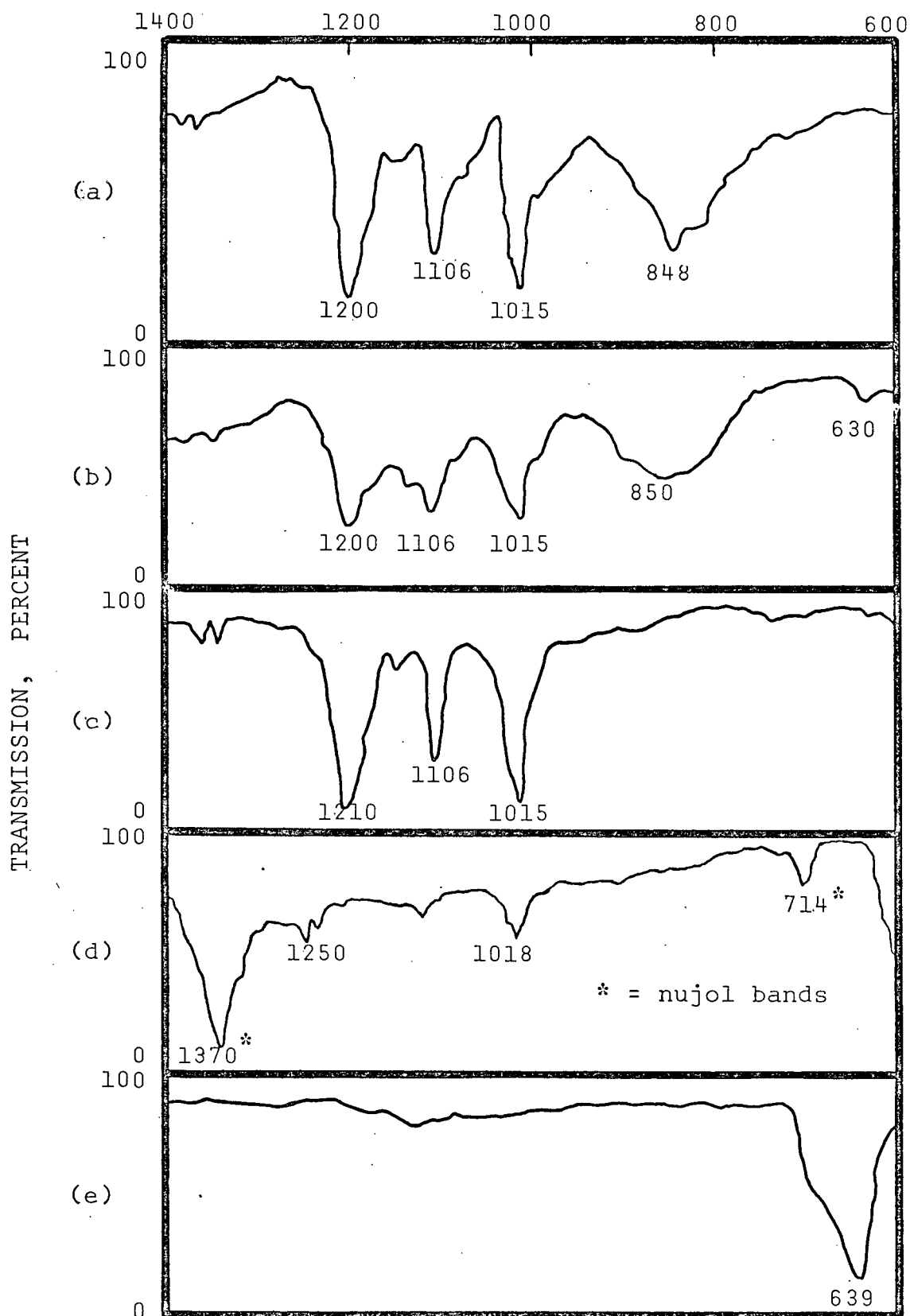
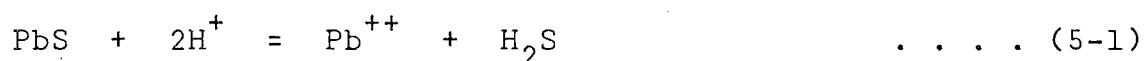


Figure 16 Infrared Spectra of (a) PbCrO_4 treated with K.Et.X. (pH 7.2); (b) PbS treated with $\text{K}_2\text{Cr}_2\text{O}_7$ (pH 6.3), then K.Et.X. (pH 7.2); (c) $\text{Pb}(\text{EtX})_2$; (d) X_2 ; and (e) Cr_2O_3

DISCUSSIONS

A. Changes in pH of the Solutions Containing Galena

As shown in Figures 4 and 5, the explanations for buffer action can be given in several ways. Firstly when oxygen was excluded, in alkaline solutions, no significant large shift in pH was observed, whereas the changes in pH were fairly large in acidic solutions. Neglecting the oxidation of galena by oxygen contained in nitrogen gas used in these experiments, the shift of pH to the acidic side might be due to a dissolution of galena in the perchloric acid used to adjust pH and the preferential adsorption of hydrogen on galena. The dissolution of galena is expressed by the next equation:



Secondly, when oxygen is present, the initial oxidized product of galena is thought to be lead thiosulphate or basic lead thiosulphate. A number of investigators studied the oxidation reaction of sulfide minerals in aqueous solutions in the connection with the flotation or hydrometallurgy of sulfide ores. Hagihara et al. [22] indicated the formation of lead sulphate. Leja, Little and Poling [23] suggested the formation of lead thiosulphate and, Eadington

and Prosser [24] reported the formation of basic lead thiosulphate. In the leaching of pentlandite or galena in ammonical solutions at elevated temperature, Forward et al. [25] found that the initial oxidized product was metallic salts of thiosulphate, and that the final product was metallic salts of sulphate. Therefore, if the conditions of flotation are considered, the results obtained by Leja et al., and Eadington et al. seem to be more reasonable than that by Hagihara et al. [22] and by Abramov [26]. As pH of a solution is increased, lead thiosulphate may convert to basic thiosulphate. When the dissolution of adsorbed species is discussed, solubility data of adsorbed species must be used. Solubility data, however, are not available for the adsorbed species of lead thiosulphate or basic lead thiosulphate on galena. The solubility of lead thiosulphate is reported to be 0.94×10^{-3} M/L, while no data is given on the solubility of basic lead thiosulphate. When the dissolution of those oxidized species proceeds in an acidic solution, hydrogen ion is consumed. Therefore, in the acidic side, hydrogen ion consumption by the dissolution of galena itself and the oxidized products of galena surface may cause the increase in pH, and at the same time, the preferential hydrogen ion adsorption [27] may cause the pH to increase.

In alkaline solutions, then, the shift of pH is explained by the formation of lead hydroxide adsorbed or

deposited on the galena surface as well as the precipitation of lead hydroxide in a bulk solution.* As bulk lead sulfide is less soluble in comparison to bulk lead hydroxide, and assuming this tendency is true for adsorbed species, the formation of lead hydroxide on fresh galena surface is not favored. This assumption seems reasonable because the shift of pH in the alkaline side was not large when oxygen was avoided. When an oxidized film is formed on galena surface, the film is dissolved by increasing pH, followed by the reaction of lead ions dissolved with hydroxyl ions. Thus, $\text{Pb}(\text{OH})_2$ is precipitated on the galena surface and in a bulk solution as well. This explanation can be supported by the fact that slightly oxidized galena, or at least when oxygen is present in the system, galena can be floated by sulphhydryl collectors, whereas no flotation is observed in a strong alkaline solution.

B. Chemisorption of Chromate or Dichromate Ions on Galena Surface

As mentioned in the previous section, from the thermodynamic point of view, the formation of lead chromate on galena surface is very much favored when galena is treated with chromate salt or dichromate salt. In acidic

*The solubility of lead hydroxide is $6.4 \times 10^{-4} \text{ M/L}$ and that of galena is $1.2 \times 10^{-6} \text{ M/L}$.

region, where dichromate ion is very stable, lead chromate is also very stable.

Furthermore, as seen from the infrared spectra given in Figure 15, all spectra have an absorption band at 848 cm^{-1} which is assigned to Cr-O symmetrical stretch [28]. However, the weak peaks at 795 and 935 cm^{-1} are also observed. Both peaks may be assigned to Cr-O-Cr asymmetric stretch, and may indicate the formation of lead dichromate on galena surface. Anyway it is obvious that the main product on galena surface is lead chromate when galena is treated with chromate or dichromate salt.

On the other hand, as shown in Figure 11, the amount of chromate uptake on galena increased almost linearly with dichromate concentration. In acidic region, the amount of chromate adsorption was very large, and this indicates the hydrophilic property of galena surface. Therefore, it is very understandable that dichromate salt is a more efficient depressant than chromate salt in flotation.

C. Influence of Chromate on the Adsorption of Xanthate on Galena Surface

(1) Competitive Adsorption

It has been shown that lead chromate is formed on the galena surface when galena is treated with a chromate solution. Due to the hydrophilic property of this film, the floatability of galena is suppressed. However, Wark and

Cox [6] reported that crocoite, PbCrO_4 , was floated by xanthate, and Plaksin and his co-worker [4] suggested that the chemical attachment of xanthate ion and that of chromate ion took place in different areas.

In the present work, the adsorption rates of xanthate ions and chromate ions on galena, the competitive adsorption of these two species, the desorption of xanthate ions or chromate ions from galena surface due to chromate or xanthate treatment were completed. Furthermore the rest potential of galena electrode in a chromate solution, and the products on galena surface were examined to investigate the depression of galena with chromate or dichromate ion and the possibility of flotation of chromate-treated galena by xanthate.

Under the conditions described in Figure 10, xanthate is adsorbed more rapidly than chromate. Nevertheless, in competitive adsorption tests, as shown in Table I, xanthate adsorption is more suppressed than chromate adsorption. It might be possible to explain such a phenomenon in several ways. However, it is reasonable to consider that the adsorption rate of xanthate is retarded, even if its initial rate is fast, by the inhibition due to the hydrophilic film of chromate adsorbed species on galena.

Oxidation of xanthate by chromate ion in an aqueous solution is expected to be very slow from the fact that the U.V. spectrum of the mixture of chromate and

xanthate solutions is very stable as shown in Figure 1. Such a slow oxidation of xanthate in chromate solution is quite understandable from the electron transfer theory of chromium reduction [30]. However, if a semiconductor like galena is involved in the system, the enhanced oxidation rate of xanthate by a catalytic effect due to galena is predictable. Pomianowski and Pawlikowska [16] showed that the rest potential of galena was raised strongly by the chromate addition. This phenomenon indicates the possibility of oxidation of xanthate to dixanthogen by chromate ions in the presence of galena. In fact, the formation of dixanthogen amounted to about 80 per cent of the total xanthate adsorbed. This was detected by analyzing the resultant solution of xanthate adsorption test with the aids of U.V. spectrophotometry. The amount of dixanthogen formed in the presence of chromate in the system is much higher than that without chromate.

(2) Adsorption Products of Xanthate on Lead Chromate

It has been shown that lead xanthate and dixanthogen are formed when lead chromate is treated with a xanthate solution, as shown in Figure 13 and Table V. However, as shown in Figure 13, the one absorption band of lead xanthate is located at 1200 cm^{-1} and this indicates a certain shift from the absorption band at 1210 cm^{-1} for lead xanthate which can be formulated by $\text{Pb}(\text{EtX})_2$. Leja et al. [29] obtained an infrared spectrum of lead sulfide

treated with a xanthate solution and suggested a 1:1 co-ordination between the surface metal atom and the xanthate radical in the first monolayer from the shift in C-O-C band frequency from about 1210 to 1195. As the same type of shift in frequency was observed in this experiment, a 1:1 co-ordination between the surface lead atom and the xanthate radical may be suggested on lead chromate surface. As mentioned before, the formation of dixanthogen can be explained in terms of the high rest potential of lead chromate. (Cf. Figure A-1.)

CONCLUSIONS

In order to obtain a better understanding of the depressive action of chromate or dichromate salt on galena, some experimental work was performed and the thermodynamics were considered. The main results obtained under the conditions employed in this study are as follows:

- (1) Galena shows a buffer action in an aqueous solution. However in the absence of oxygen at alkaline range, no significant pH change was observed.
- (2) The adsorption amount of chromate on galena stays almost constant above pH 9 and it increases with the increase in dichromate concentration in solution.
- (3) When galena is treated with chromate salt or dichromate salt, lead chromate is formed on the galena surface as the main adsorbed species.
- (4) The potential-pH diagram of Pb-Cr-S-H₂O system at 25°C. was constructed. This indicates that lead chromate is a very stable substance whereas lead dichromate is very unstable.
- (5) Xanthate can adsorb on chromate-treated galena surface and also on lead chromate surface.

- (6) Xanthate adsorbed on chromate-treated galena or lead chromate appeared mostly as dixanthogen.
- (7) The desorption of chromate from galena surface due to xanthate addition is very slight.
- (8) The desorption of xanthate from galena surface which is covered with more than a monolayer thickness of xanthate, due to chromate addition is possible. However the desorbed amount of xanthate in such a case is only 10-20% of the amount of chromate adsorbed.
- (9) When xanthate-treated galena is subjected to desorption test by chromate, it is found that both xanthate ions and dixanthogen were desorbed.

SUGGESTIONS FOR FUTURE WORK

- (1) In this study, when much xanthate was adsorbed on galena surface, xanthate ions were desorbed by adding chromate salt. However, it may be very helpful to investigate the possibility of the desorption of xanthate when the amount of xanthate adsorption is much less. For this purpose, to use xanthate including radio active sulfur may be very useful.
- (2) The mechanism of depression of galena by chromate or dichromate salt is not clear enough. It may be very useful to study more about galena-chromate-xanthate system and to investigate the role of dixanthogen in this system.

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A P P E N D I X

ELECTROCHEMICAL STUDY

Electrochemical Measurements on Natural Galena Specimen

Electrochemical measurements were made on natural galena specimens, mounted in plastic and mechanically polished to expose a measured surface area to solutions, chromate, dichromate, and 1M HClO_4 . This acid, HClO_4 , was chosen because it is completely ionized at this dilution and the perchlorate ion is very stable and does not significantly complex metal cations.

Polarization studies were performed with a Beckman model TM30 Electroscan instrument equipped with a potentiostat. A three-electrode system was used involving a calomel electrode in a Luggin capillary with the point located very close to the specimen to eliminate as much as possible of the IR potential drop in the solution. The potential between the calomel electrode and the specimen was controlled and could be scanned with the potentiostat, while current passed only between the specimen and an auxiliary electrode.

The solution was usually kept almost oxygen-free by bubbling with helium in a covered cell. The helium from the cell could be passed through a gas train to absorb gases such as H_2S , which are given off under certain conditions by the specimen. The normal kind of experiment

that was performed consisted of determining the polarization curve. The potential between the specimen and the reference electrode was varied at a selected scan rate and the current was recorded. This curve could be divided into anodic and cathodic regions corresponding to the direction of current in the specimen, and the potential dividing the anodic and cathodic regions is known as the "rest" potential of the specimen.

The rest potential of galena electrode was measured in a chromate solution at pH 10.8, where chromate salt stays as chromate ion in a solution. The result is shown in Figure A-1. It increased by adding chromate salt and stayed almost constant at concentration 1.0×10^{-3} M/L.

It may be said that the rest potential increases while lead chromate is formed on galena specimen.

Figure A-2 shows pH dependence of the rest potential of galena electrode in 1.0×10^{-3} M/L chromate solution. As seen from the figure, pH dependence in acidic region is different from that in alkaline region. An inclination in acidic region was 46mV/pH and in alkaline region 66mV/pH. When 1.0×10^{-3} M/L $K_2Cr_2O_7$ solution was used, an inclination was 46mV/pH in alkaline and 70mV/pH in alkaline solution.

These results indicate that the ratio H^+/e^- is 4/5 in acidic region and 9/8 in alkaline region. However it must be emphasized that the rest potential of galena electrode in aqueous solutions of various pH values also changes.

Figure A-4 shows an example of anodic polarization curves of galena electrode in various solutions. The polarization curve of galena electrode in 1M HClO_4 was studied by Brodie [31]. When chromate or dichromate salt was added, the current density was suppressed significantly. This may indicate the formation of passive film on galena surface. Figure A-5 shows cathodic polarization curve of galena electrode.

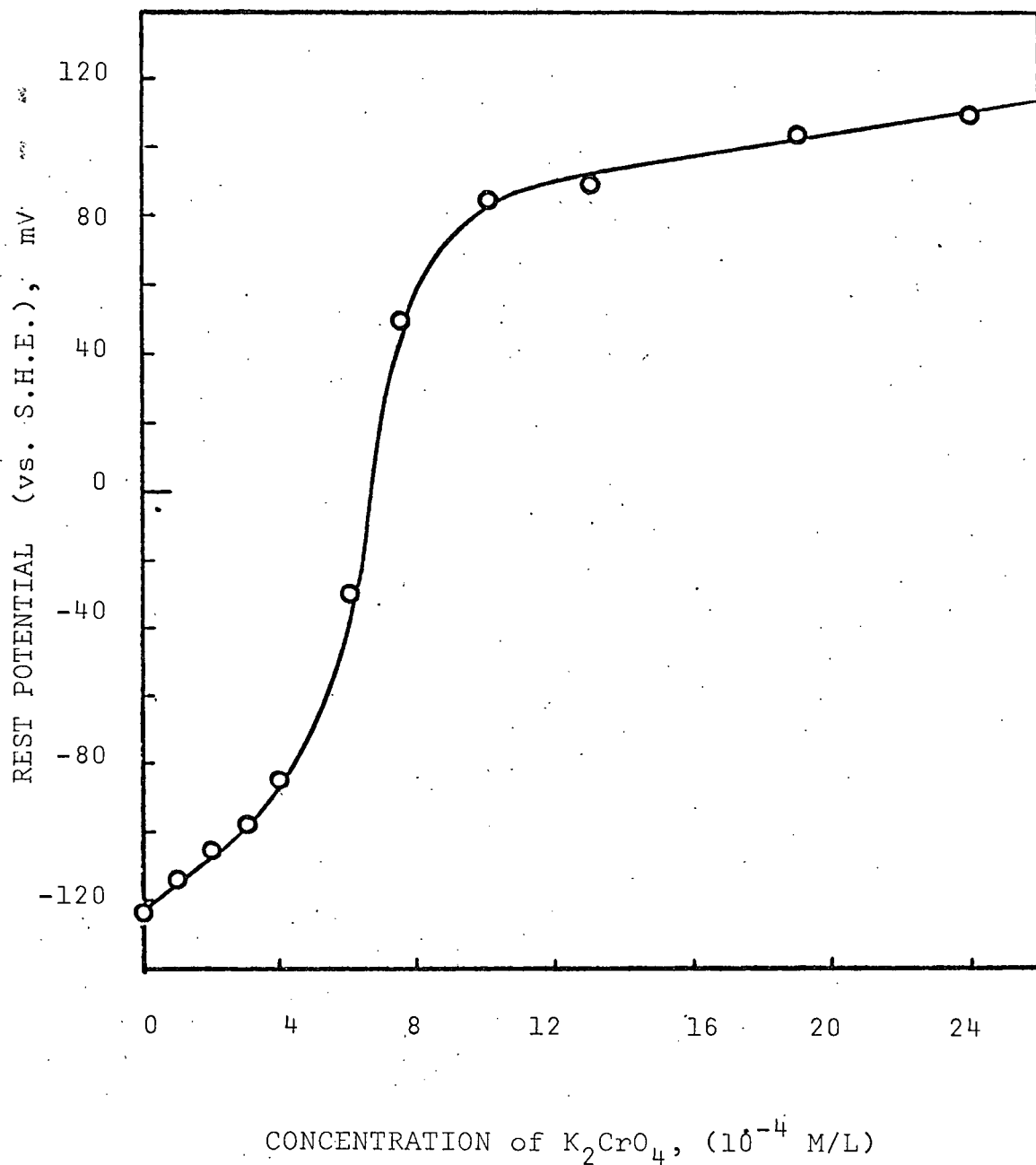


Figure A-1 Effect of the Concentration of Potassium Chromate on the Rest Potential of Galena Electrode
(Initial pH of the Solution: 10.8)

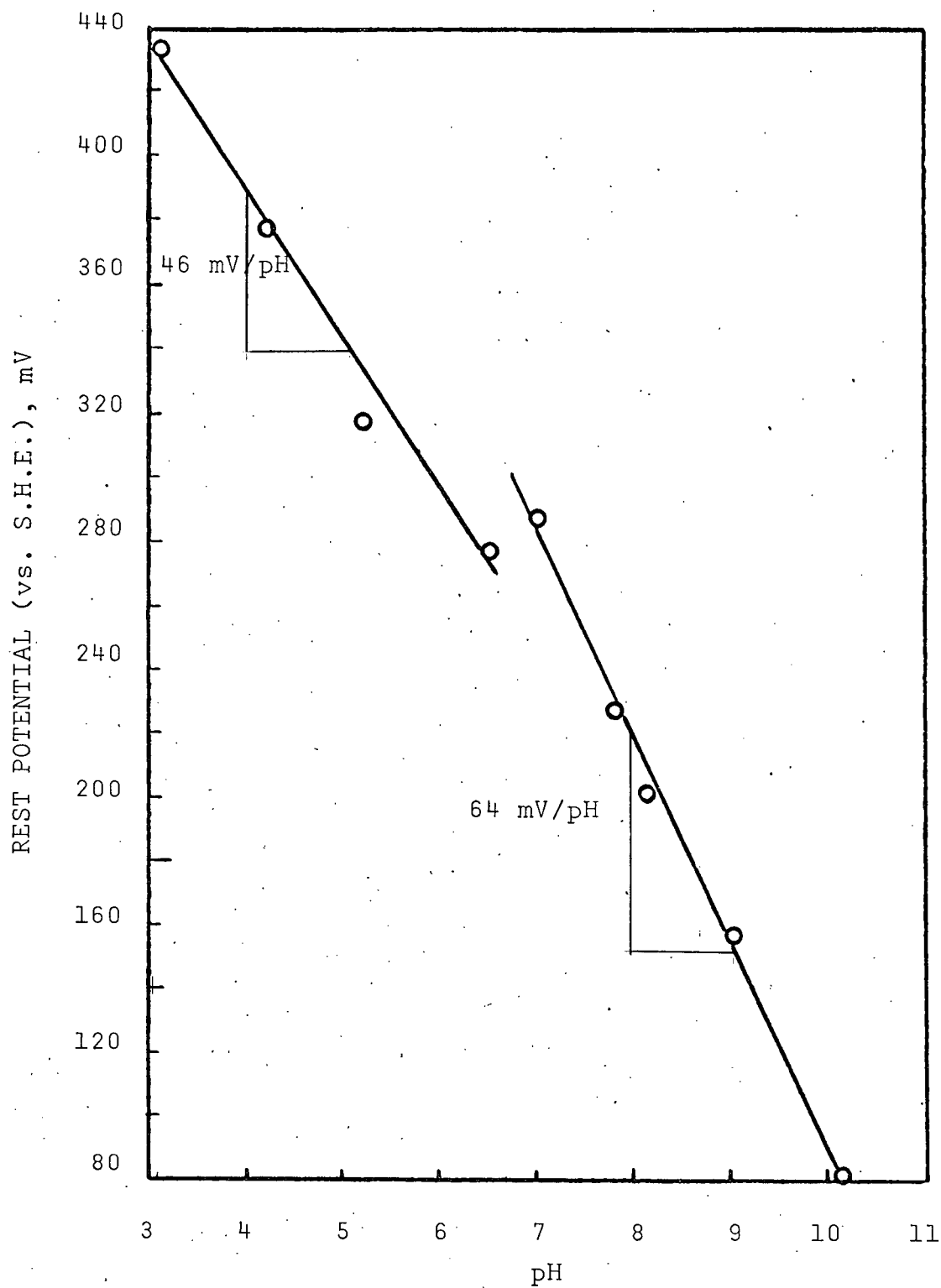


Figure A-2 Effect of pH on the Rest Potential of Galena Electrode in 1.0×10^{-3} M/L K_2CrO_4 Solution

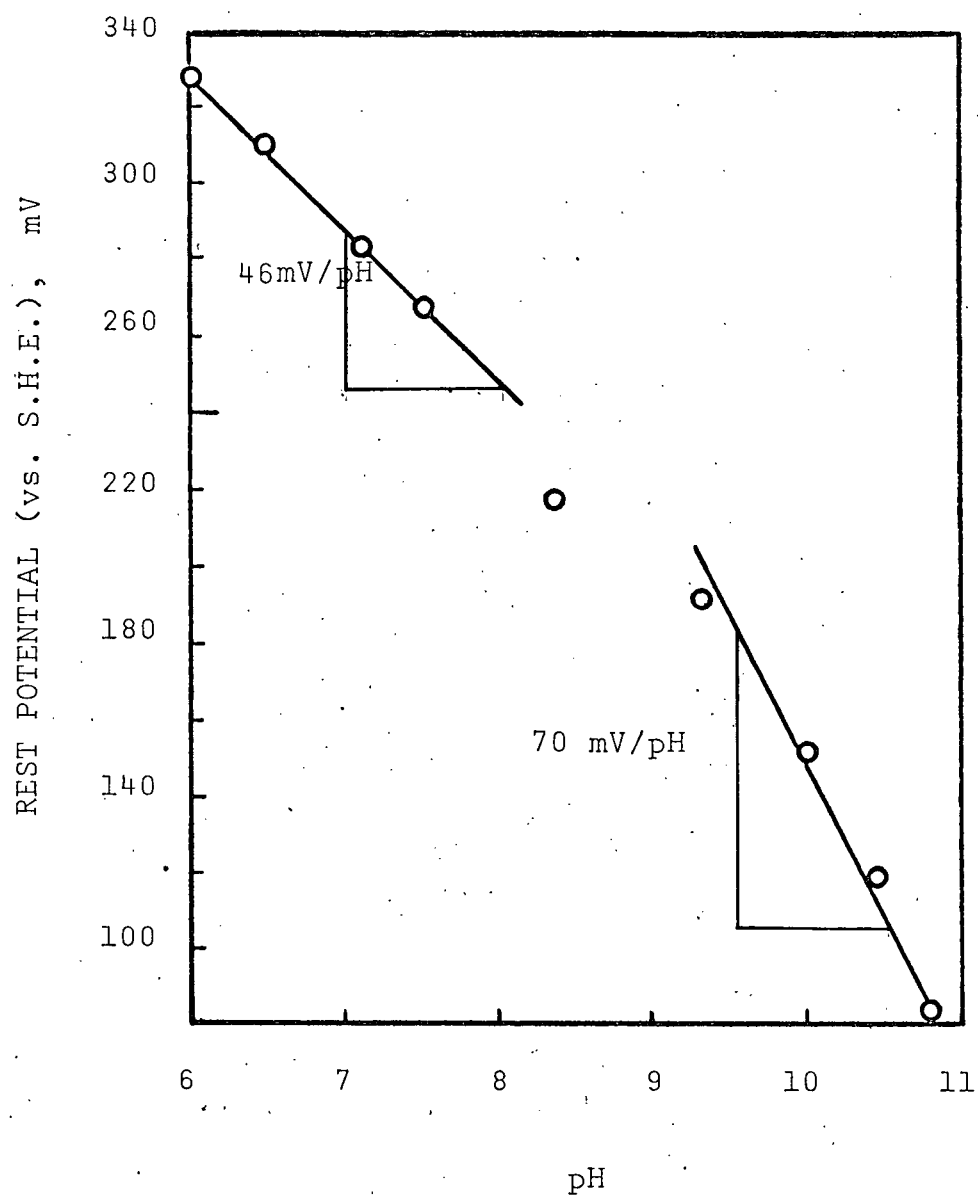


Figure A-3 Effect of pH on the Rest Potential of Galena Electrode in 1.0×10^{-3} M/L $K_2Cr_2O_7$ Solution

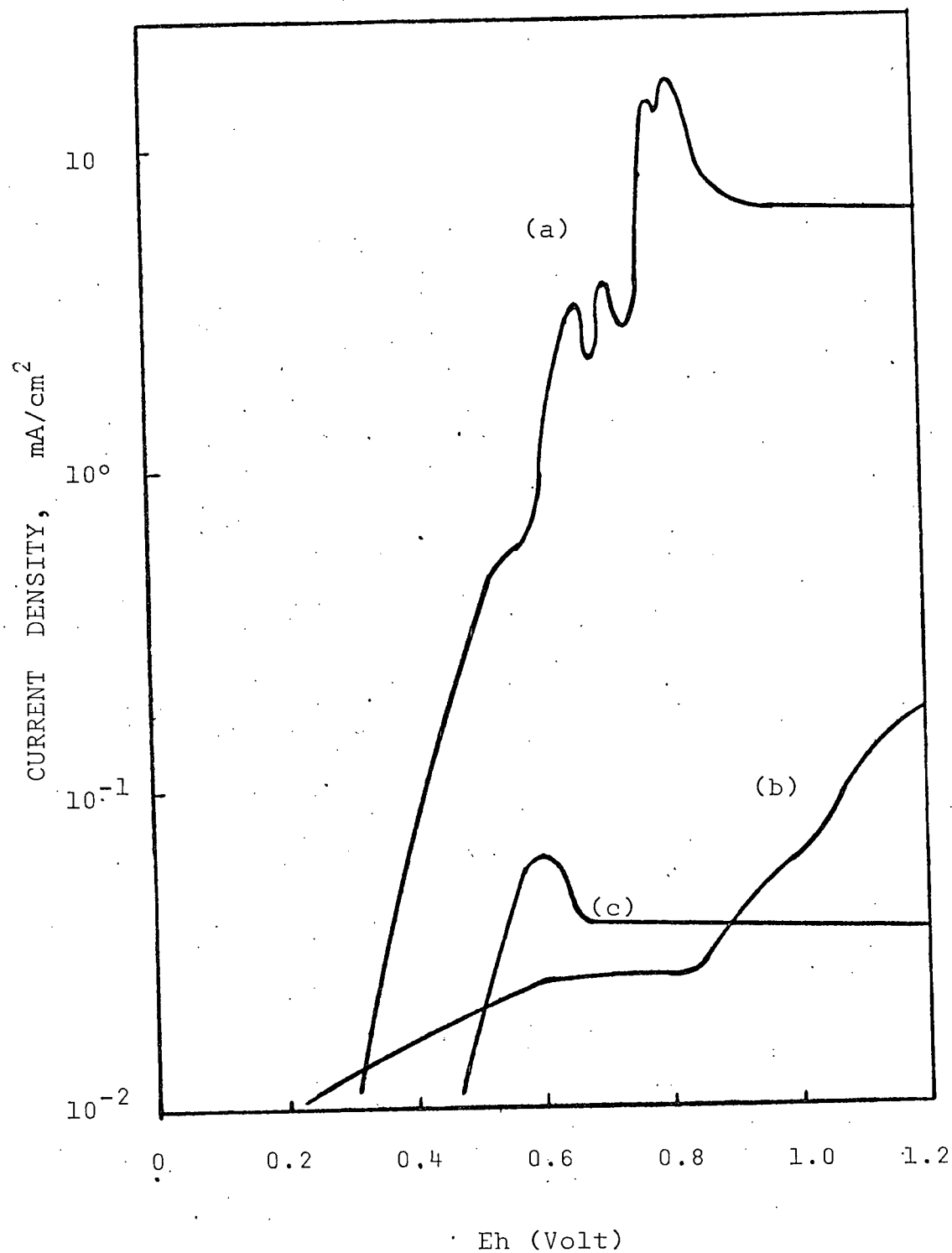


Figure A-4 Anodic Polarization Curves for Galena Electrode in (a) 1M HClO₄ (b) 4.0 x 10⁻⁴ M/L K₂CrO₄ (pH 10.0) (c) 4.0 x 10⁻⁴ M/L K₂CrO₄ (pH 2.9) scan rate 2.8 mV/sec. He bubbled

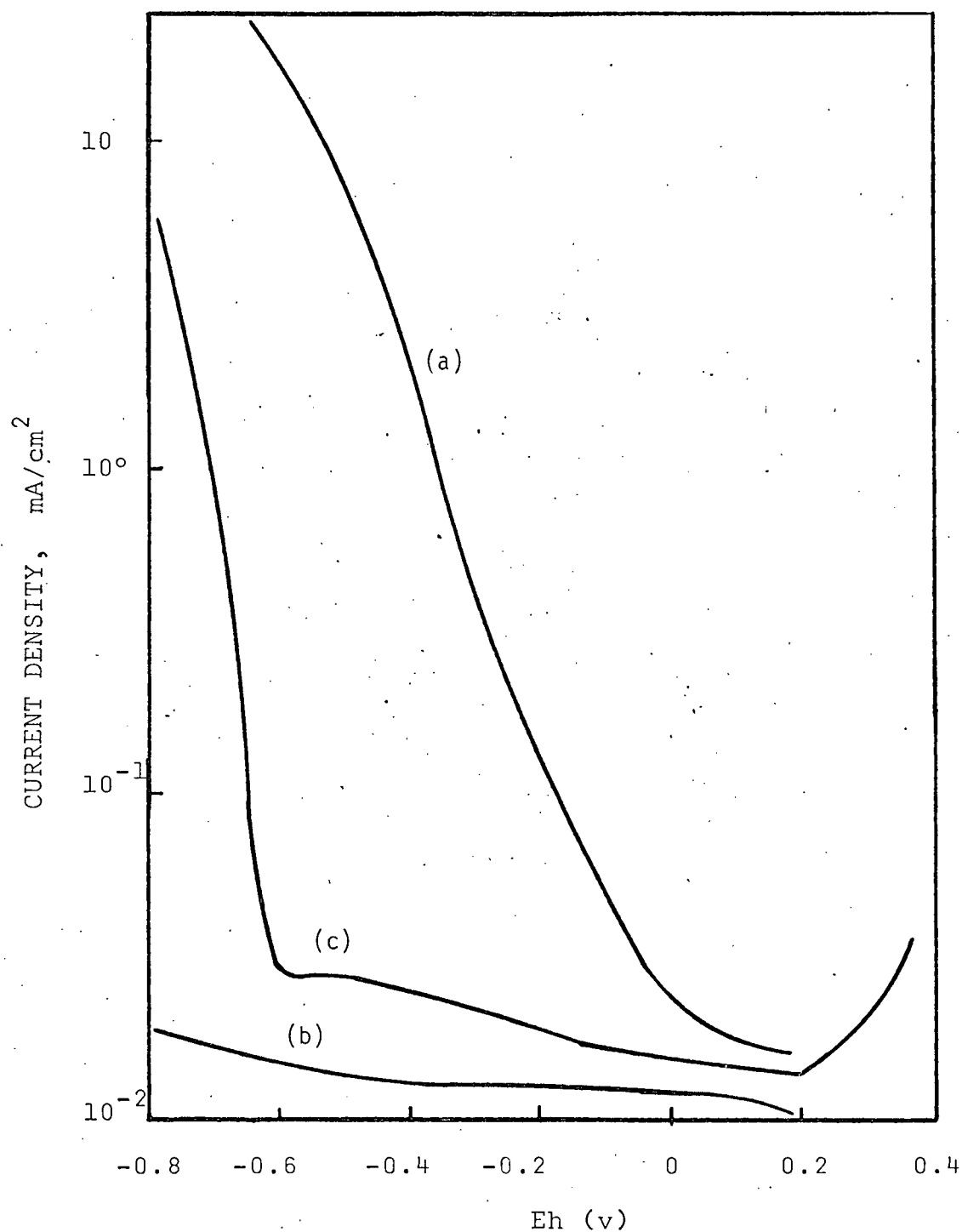


Figure A-5 Cathodic Polarization Curves for Galena Electrode in (a) 1M HClO₄ (b) 4.0 x 10⁻⁴ M/L K₂CrO₄ (pH 10.0) (c) 4.0 x 10⁻⁴ M/L K₂Cr₂O₇ (pH 2.9) scan rate: 2.8 mV/sec. He bubbled