THE SURFACE CHEMISTRY AND FLOTATION OF GALENA

by

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It is indeed a pleasure to express my gratitude to Dr. Ure, under whose general guidance this work was performed, for his many excellent discussions and to my wife for her assistance in the laboratory.
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THE SURFACE CHEMISTRY AND FLOTATION OF GALENA

INTRODUCTION

In a theoretical study of the flotation of galena, there arise two questions of prime importance. These are:-(1) Will galena float in the absence of collectors, that is, does galena possess a high degree of "inherent flotability"? and (2) What chemical action, if any, has a collector such as potassium ethyl xanthate on the surface of the mineral? The purpose of the research described here is to supply answers to both of these questions. The work divides itself naturally into two parts—the first part—preliminary tests in which analytical details were worked out and in which practically all aspects of the work were touched on, studied approximately and 'pioneered' so to speak; the second part—a planned series of experiments to prove or disprove ideas developed in the earlier studies.

Descriptions of the experiments performed are presented in considerable detail so that any or all parts of the work can be repeated critically. This is thought advisable in view of the fact that conclusions drawn by others from tests similar to some of those given here have been disputed. For this reason also all tests that were deemed necessary were performed without regard to precedent or priority in the hope that a complete and self-consistent set of data from one laboratory would afford a sure foundation for future work.
Where tests that are described are the same as or similar to those of other workers, the fact will be noted in the context, otherwise the reader is referred to Bennett's thesis\(^1\) and the books of Wark\(^2\) and Gaudin\(^3\), for authoritative and complete surveys of the literature concerning flotation.
MATERIALS

Galena

In the preliminary experiments, bright crystalline samples of several specimens of galena were used. These are designated Galena #2, #3, #4 and #5. For the second part of the work a lump of the mineral weighing some 30-40 pounds was obtained from the Provincial Assay Office at Victoria, B.C. Analysis (Appendix A) showed it to contain 83.6% Pb, which corresponds to 96.8% PbS, the remainder being antimony sulfide with but traces of silver and the metals of the iron group. Several thin veins of PbSO₄ traversed the lump but in selecting samples these were avoided, bright crystalline portions being taken for all tests. This galena is designated #6.

Potassium Ethyl Xanthate. (KETX)

This reagent was made in the usual way from KOH, C₃H₅OH and CS₂. 14g of KOH were dissolved in 70g C₃H₅OH and the solution filtered. To this was added 26g CS₂, cooling in an ice bath. The KETX which precipitated was filtered on a Buchner funnel, washed by shaking in 500cc of ether, dissolved in 250cc acetone, filtered and precipitated by the addition of a litre of benzene. The material was purified by reprecipitating with petroleum ether three times from 125cc of acetone. The product was finally filtered, dried in the oven at 35⁰ and stored in vacuum over concentrated sulfuric acid. It was white with but a slight yellow tint.
Grinding

The comparatively small samples of galena prepared for the preliminary experiments were ground under water by hand in an agate mortar. This procedure was not only too laborious for the preparation of large samples but also was open to the objection that contamination by small amounts of grease was possible and hence it was abandoned in the second part of the work and all grinding was carried out in a laboratory model ball mill with flint pebbles. The ore was first crushed to coarse lumps in a porcelain mortar and then transferred to the mill with water. Large lumps of the ore and the flint pebbles were handled with brass tongs and the ground material was transferred to the elutriator in a stream of water so that the galena was never touched by hand. The mill was generally charged with 100-200g of coarse galena and allowed to run for one hour. Residue left in the elutriator from the previous grinding lot was returned to the mill with the fresh charge to reduce sampling error. As noticed by Gaudin, it was observed that a slight vacuum develops in the ball mill during grinding, presumably due to the oxidation of the sulfide.

Sizing

Small samples of ground galena were sized in the elutriator described in Bennett's Thesis. For larger quantities of material a larger elutriator was constructed from a glass cylinder 7.5cm in diameter and 72cm high, set in a 30cm porcelain evaporating dish (Fig. 1). Water was supplied at a
constant head of 70cm, being injected through a glass tube ex­
tending to the bottom of the large cylinder. Overflow with
the mineral in suspension was taken off through a glass siphon
discharging into a beaker in the porcelain dish. The beaker
served as a baffle to slow down the current of water so the
mineral would settle in the dish, while the water was run off
slowly and discharged into the sink. Velocity of water up
the column was calculated from the dimensions of the column
and the time required to collect 500cc overflow. Particles
with settling rates from zero to 30cm/min could be segregated
with this instrument.

The standard procedure adopted for the operation of the
elutriator was substantially the following:—The contents of
the ball mill were thrown into a large porcelain casserole and
the ground mineral was washed away from the flint balls and
into a beaker with a strong stream of water. After settling
for several minutes the excess water and extremely fine min­
eral in suspension was decanted off and rejected. The remain­
ing body of the galena was washed into the elutriator column
and the feed water turned on at a rate sufficient to give the
water in the column an upward velocity of 8.6cm/min. The
position of the injecting tube at the bottom of the column
was frequently changed to ensure thorough stirring of the ore
to separate all the fine material. After several hours of
such treatment the column became practically clear when all
the ore particles with settling rates of less than 8.6cm/min
had been stripped off. The content: of the porcelain collect-
Figure 2

Fritted Glass Plate

Flotation Cell

8.2 cm

4 cm

365 cm
ing dish was now rejected and feed water turned on until the rate in the column was 28.3 cm/min. The mineral coming over into the lower dish from this time until the column again cleared was collected in water in a beaker or jar filled to a depth of 8-10 cm, allowed to settle for 5 minutes and the water then decanted. Several such 5 minute settling and decantation treatments were usually given to be sure that all extremely fine particles were removed. The sized galena was then stored under water in glass stoppered bottles until needed for tests.

The size of the particles segregated by this treatment can be estimated from Stokes' Law. This estimate was verified by direct measurement of a sufficient number of particles with the aid of a microscope (Appendix B).

**Flotation Tests**

The laboratory model flotation cell used in all flotation tests was constructed by Bennett and described in his thesis. Figure 2 is reproduced from his work. To secure best operation of the cell, air was supplied at 33-38 cm of mercury pressure and 5 cc of 250 mg/litre terpineol solution was added to the cell pulp to obtain a froth zone 3-5 cm thick. Feed water supplied from an overhead reservoir, was made up to contain the same concentration of terpineol as the liquid in the cell. After use the cell was washed thoroughly with concentrated HNO₃ followed by plenty of water and was usually allowed to stand with water slowly running through the plate.
Decantation Flask

Fig. 3
Procedure in using the cell varied somewhat in the early tests but was soon standardized to the following:- The mineral to be tested was placed in the cell with 250cc of water and 5cc of terpineol added. Air was turned on to 33-38cm of mercury and blown for a measured time, generally 2-5min from the first over-flow of froth. Heads and tails were collected on weighed crucibles, dried at 105° for at least two hours and weighed.

Potentiometric Titrations and $P_H$ Measurements

$P_H$ measurements were made with a Beckman $P_H$ meter using glass and calomel electrodes. The instrument was standardized frequently against known buffer solutions. Titrations of $K_{2}S_{2}O_{3}$ with iodine, amounting to some hundreds in number during the course of the work, were made with the same instrument using platinum and calomel electrodes. In all titrations the xanthate mixture was continually stirred mechanically.

Decantation Flask

Operations in nitrogen in the final experiments were carried out in a 250cc Erlenmeyer flask to which were blown suitable side tubes for admitting nitrogen and reagents and for ejecting the contents. This flask (Fig. 3) was connected to the reagent reservoirs by interchangeable ground glass joints. Absorption bottles (Fig. 9), for use in the nitrogen train were constructed from 500cc flasks since the ordinary laboratory absorbing bottles burst under the nitrogen pressure used in some of the experiments.
PRELIMINARY EXPERIMENTS

1. Presence of Oxidized Layer

While galena in bulk has the properties of lead sulfide, the readiness with which lead sulfide is oxidized by air to the sulfate makes it highly improbable that a freshly prepared surface of this mineral could long remain lead sulfide. The presence of an oxidized layer on the natural ore surface can be demonstrated easily and it will be expected to exert a profound influence upon the action which collecting agents may have upon the mineral.

Samples of galena were ground under distilled water in an agate mortar and portions with settling rates of 9-25 cm/min were taken from the elutriator. These were extracted with boiling solutions of ammonium acetate or sodium chloride both in air and under nitrogen. Extracts obtained in this way from many samples were tested for Pb^{2+} and SO_{4}^{2-} and both were invariably detected. Upon repeated extraction under nitrogen Pb^{2+} and SO_{4}^{2-} became progressively less until the extract gives only a slight darkening when tested for lead with hydrogen sulfide and sulfate cannot be detected with barium acetate.

2. Sulfate Layer and Flotation—Experiments with Ammonium Acetate

In the following experiments the flotation of untreated galena was compared with that of galena which was first washed by boiling with ammonium acetate.

Sized samples of Galena #5 ground under water in an agate
mortar were placed in the flotation cell and heads and tails collected and measured by weighing. Results of this test are given in Table I.

```
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Reagent</th>
<th>pH</th>
<th>Sample (g)</th>
<th>Heads (g)</th>
<th>Tails (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>------</td>
<td>6.6</td>
<td>2.63</td>
<td>.19</td>
<td>2.45</td>
<td>7.2</td>
</tr>
<tr>
<td>14</td>
<td>------</td>
<td>7.2</td>
<td>4.28</td>
<td>.11</td>
<td>4.18</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>HCl</td>
<td>3.0</td>
<td>5.06</td>
<td>.15</td>
<td>4.91</td>
<td>3.0</td>
</tr>
</tbody>
</table>
```

Flotation of the untreated mineral was now compared with that of galena which was first washed with ammonium acetate. Sized samples of Galena #5 were withdrawn from the elutriator. One part was transferred to the flotation cell with 250cc of water and 5cc of 250mg/litre terpineol and the yield measured. A second portion was boiled with 25cc of near saturated ammonium acetate solution, washed five times with boiling distilled water and transferred in suspension in water to the flotation cell with the minimum exposure to air. The flotation yield was measured under the same conditions as before. Another sized sample was divided into four parts each of which was extracted with a more concentrated ammonium acetate solution than the preceding. Flotation yield was again measured and was observed to parallel the vigor of the extraction treatment. The results of the test, which are in agreement with the work of Taggart, Taylor and Knoll are summarized in Table II.
**TABLE II**

*Ammonium Acetate Treatment-Galena #5*

<table>
<thead>
<tr>
<th>NH₄Ac</th>
<th>Wt. of Sample g</th>
<th>pH in Cell</th>
<th>Flotation Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.620</td>
<td>6.5</td>
<td>5.82</td>
</tr>
<tr>
<td>Sat. Sol'n</td>
<td>2.354</td>
<td>7.0</td>
<td>91.5</td>
</tr>
</tbody>
</table>

**Freshly reground sample:**

<table>
<thead>
<tr>
<th></th>
<th>Wt. of Sample g</th>
<th>pH in Cell</th>
<th>Flotation Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.175</td>
<td>6.78</td>
<td>21.8</td>
</tr>
<tr>
<td>Sat. Sol'n</td>
<td>2.345</td>
<td>6.92</td>
<td>82.3</td>
</tr>
</tbody>
</table>

**Graduated extraction treatment:**

<table>
<thead>
<tr>
<th></th>
<th>Wt. of Sample g</th>
<th>pH in Cell</th>
<th>Flotation Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.614</td>
<td>6.45</td>
<td>6.3</td>
</tr>
<tr>
<td>1g</td>
<td>2.923</td>
<td>---</td>
<td>25.5</td>
</tr>
<tr>
<td>2g</td>
<td>2.686</td>
<td>6.58</td>
<td>55.5</td>
</tr>
<tr>
<td>Twice with 2g</td>
<td>3.924</td>
<td>---</td>
<td>91.5</td>
</tr>
</tbody>
</table>

3. **Function of the Ammonium Acetate**

A test was undertaken showing that ammonium acetate solutions remove Pb⁺⁺ from the surface of the ore in proportion to the vigor of the wash and relating the increase in flotation observed to the lead removed.

Approximately equal samples of ground sized Galena #5 were treated with ammonium acetate in 50cc of boiling water on a hot plate, then washed by decantation through a filter, the solution passing into volumetric flasks. The ammonium acetate extract and washings were collected together and the lead in solution in these was determined by color-
imetric comparison with standard PbS colloids, a photo-electric colorimeter being used. The results of the first of these experiments are summarized in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>NH₄Ac g</th>
<th>Wt. of Sample g</th>
<th>Yield (heads) %</th>
<th>mgPb/g of Sample g</th>
</tr>
</thead>
<tbody>
<tr>
<td>.5</td>
<td>5.34</td>
<td>54.3</td>
<td>.064</td>
</tr>
<tr>
<td>1.5</td>
<td>4.742</td>
<td>61.6</td>
<td>.097</td>
</tr>
<tr>
<td>3.5</td>
<td>7.719</td>
<td>70</td>
<td>.077</td>
</tr>
<tr>
<td>Twice with 2g in 25cc</td>
<td>5.019</td>
<td>75.5</td>
<td>.15</td>
</tr>
</tbody>
</table>

These comparatively discordant results led to a more thorough investigation of the analytical technique and changes were made which were essentially in the direction of more rigorous standardization of procedure (Appendix C). After these changes the following results were obtained.

**TABLE IV**

<table>
<thead>
<tr>
<th>NH₄Ac g</th>
<th>Wt. of Sample g</th>
<th>Yield (heads) %</th>
<th>mgPb/g of Galena g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.393</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>.5</td>
<td>3.472</td>
<td>22.1</td>
<td>.19</td>
</tr>
<tr>
<td>1</td>
<td>2.126</td>
<td>41.3</td>
<td>.28</td>
</tr>
<tr>
<td>2</td>
<td>2.598</td>
<td>50.7</td>
<td>.29</td>
</tr>
<tr>
<td>Twice with 2g</td>
<td>2.606</td>
<td>84.2</td>
<td>.38</td>
</tr>
</tbody>
</table>
It should follow from the above results that if the action of the KEtX is on lead compounds more soluble than the sulfide, especially the sulfate, which has been shown to exist on the galena surface, then if these compounds are first removed less KEtX should be needed to cause complete flotation. Less KEtX should certainly be used if all or part of that added as a collector to natural galena is used up in forming the white turbidity presumed to be due to Pb(EtX)$_2$ usually observed in the flotation cell when unwashed ore is floated with this collector. The following experiment was devised to study the effect of a preliminary partial washing with ammonium acetate on the quantity of xanthate necessary to cause flotation.

4. The Effect of NH$_4$Ac Washing on Xanthate Consumption

For the first test 25mg of KEtX (prepared by Mr. Lips) was dissolved in cold boiled distilled water and made up to 500cc. For subsequent tests the KEtX concentration was increased. Galena samples were treated with various volumes of this solution and the corresponding degree of flotation was measured. Similar samples were then washed by boiling with NH$_4$Ac followed by distilled water, treated with the KEtX solution and flotation again measured. The results of these tests are compared in Tables V and VI.
### TABLE V

Ammonium Acetate Washing, Xanthate Consumption And Flotation Yield

<table>
<thead>
<tr>
<th>Run #1</th>
<th>Wt. of Sample</th>
<th>Yield</th>
<th>mgKETX/g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>KEtX(0.05mg/cc) Wt. of Sample Yield mgKETX/g Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.300</td>
<td>14</td>
<td>.019</td>
</tr>
<tr>
<td>1</td>
<td>1.627</td>
<td>31</td>
<td>.031</td>
</tr>
<tr>
<td>2</td>
<td>1.560</td>
<td>41.8</td>
<td>.071</td>
</tr>
<tr>
<td>4</td>
<td>1.570</td>
<td>83.5</td>
<td>.127</td>
</tr>
<tr>
<td>6</td>
<td>1.592</td>
<td>78.2</td>
<td>.188</td>
</tr>
<tr>
<td>10</td>
<td>1.220</td>
<td>88.5</td>
<td>.410</td>
</tr>
</tbody>
</table>

Sample first washed with NH₄Ac:

<table>
<thead>
<tr>
<th>Run #2</th>
<th>Wt. of Sample</th>
<th>Yield</th>
<th>mgKETX/g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>KEtX(0.2mg/cc) Wt. of Sample Yield mgKETX/g Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.371</td>
<td>44.8</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.455</td>
<td>72.8</td>
<td>.017</td>
</tr>
<tr>
<td>1.5</td>
<td>1.346</td>
<td>91</td>
<td>.056</td>
</tr>
<tr>
<td>5</td>
<td>1.117</td>
<td>89</td>
<td>.211</td>
</tr>
</tbody>
</table>

### TABLE VI

Ammonium Acetate Washing, Xanthate Consumption And Flotation Yield

<table>
<thead>
<tr>
<th>Run #2</th>
<th>Wt. of Sample</th>
<th>Yield</th>
<th>mgKETX/g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>KEtX(0.2mg/cc) Wt. of Sample Yield mgKETX/g Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9.64</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>10.69</td>
<td>19.7</td>
<td>.09</td>
</tr>
<tr>
<td>10</td>
<td>6.02</td>
<td>62</td>
<td>.34</td>
</tr>
<tr>
<td>20</td>
<td>4.98</td>
<td>74.5</td>
<td>.80</td>
</tr>
<tr>
<td>30</td>
<td>4.23</td>
<td>86.7</td>
<td>1.42</td>
</tr>
<tr>
<td>50</td>
<td>4.48</td>
<td>93.3</td>
<td>2.23</td>
</tr>
</tbody>
</table>
Figure 4: Xanthate Consumption vs. Flotation

(a) Unwashed Sample
(b) Washed with NH₄Ac
Figure 5

**Xanthate Consumption vs. Flotation**

(a) Unwashed

(b) Washed with $NH_4Ac$

$MgKEtX/g$ Galena #4
Ammonium Acetate Washing, Xanthate Consumption
And Flotation Yield

<table>
<thead>
<tr>
<th>Run #2</th>
<th>Washed four times with NH$_4$Ac</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KEtX (0.2 mg/cc)</td>
<td>Wt. of Sample g</td>
<td>Yield %</td>
</tr>
<tr>
<td>0</td>
<td>7.27</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.41</td>
<td>91.2</td>
<td>.021</td>
</tr>
<tr>
<td>5</td>
<td>5.59</td>
<td>99.1</td>
<td>.18</td>
</tr>
<tr>
<td>10</td>
<td>5.53</td>
<td>100</td>
<td>.36</td>
</tr>
<tr>
<td>0</td>
<td>8.41</td>
<td>30.4</td>
<td></td>
</tr>
</tbody>
</table>

Washed five times with NH$_4$Ac:—

<table>
<thead>
<tr>
<th></th>
<th>KEtX (0.2 mg/cc)</th>
<th>Wt. of Sample g</th>
<th>Yield %</th>
<th>mg KEtX/g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.80</td>
<td>11.2</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>9.60</td>
<td>57.1</td>
<td>.021</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8.47</td>
<td>98.2</td>
<td>.095</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.21</td>
<td>98.9</td>
<td>.23</td>
<td></td>
</tr>
</tbody>
</table>

In Figs. 4 and 5 the xanthate consumption in mg/g of sample is plotted against flotation yield. Gaudin and co-workers have reported curves of the type 4(a) and 5(a).

This experiment indicates that considerably less KEtX is needed to float washed than unwashed galena and the increase in flotation brought about by a small amount of xanthate is greater when the ore is first washed partially than when it is untreated.

The best that can be said of this experiment is that it points the way. It is not particularly practical for accuracy since the flotation tests were not capable of the precision expected from a more direct analytical method and the experiment itself does not furnish a direct approach to the
problem of xanthate absorption. Hence a new series of experiments was devised whereby the loss, if any, of xanthate from solutions in contact with galena could be measured by estimating the amount of xanthate left in solution after treatment with the mineral.

5. Absorption of Xanthate

Experiments were performed to ascertain if galena abstracted xanthate from dilute solutions. The method was substantially as follows:-

Samples of galena were treated with a measured volume of \( \text{KEtX} \) and after a time the solution decanted and titrated with iodine using starch as indicator. Various modifications were made to try to improve the poor end-points observed in these titrations. The results of a number of these tests are summarized briefly.

(a) 11.2g of Galena #3 were ground, the extreme fines removed by decantation and the sample divided into two parts. Part (A) was boiled with \( \text{NH}_4\text{Ac} \), washed and 10cc of .01mg/cc \( \text{KEtX} \) added. To the other part (B) without acetate treatment, was added 10cc \( \text{KEtX} \). The xanthate solutions were decanted off and titrated with \( \text{I}_2 \), 9.3cc of which was equivalent to 10cc of \( \text{KEtX} \) solution, 0.5cc of 2.5% starch solution containing 2cc of 50% \( \text{NH}_4\text{Ac} \) and 1cc of 1:10 HAc being used as indicator. Solution (A) required 5.5cc of \( \text{I}_2 \) compared to 2.75cc for (B).

(b) 30g of Galena #3 was ground, the fines removed by
Decantation Flask

Fig. 6
decantation, and the sample divided into four approximately equal parts which were treated with 5, 10, 20, and 30cc of .01mg/cc KEtX (equivalent to 10cc I₂). The xanthate solutions were decanted off through filters, the samples washed with 50cc H₂O and the solutions and washings titrated with I₂ using the starch indicator as before. Results were as follows:

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>vol. KEtX cc</th>
<th>vol. I₂ cc</th>
<th>KEtX abstracted cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>4.5</td>
<td>.5</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>24.4</td>
<td>5.6</td>
</tr>
</tbody>
</table>

(c) A similar sample of Galena #2 was treated with 20cc of .05mg/cc KEtX and absorption compared with that shown by one first washed by boiling with 50cc of 50% NH₄Ac under nitrogen. The xanthate from the washed sample required 21.5cc of iodine solution while that from the unwashed sample required only 12cc. 20cc of the stock xanthate solution was equivalent to 22.3cc iodine in the blank.

(d) The decantation flask shown in Fig.6 was constructed from a 250cc Erlenmeyer flask. Nitrogen was injected through tube 1; tube 2 could be raised and lowered by sliding through the rubber stopper. When raised it served as a vent for nitrogen and steam, when lowered it enabled the liquid contents of the flask to be blown out by N₂ pressure. Water and reagents were drawn in through tube 2 by applying suction.
Nitrogen was purified by bubbling through an oxygen absorbent mixture of 40g NaOH, 250cc H₂O, 33g NaHSO₄ and 10g sodium anthraquinone-4-sulfonate.

Starch indicator solution was made up by boiling 3g of starch in 500cc saturated KCl containing 80cc glacial acetic acid.

K₂EtX solution was made up to contain 0.05mg/cc and was equivalent to 24.9cc of iodine solution used.

Approximately 30g of Galena #5 was ground and the extreme fines removed in the elutriator. Half of this was boiled four times with 50cc portions of 50% NH₄Ac in the decantation flask under nitrogen bubbled through the oxygen absorbent, CaCl₂ and cotton traps. The galena was finally washed with distilled water and 20cc of K₂EtX drawn into the flask and the mixture shaken for five minutes. The K₂EtX solution was blown out, the mineral rinsed with water and solution and washings titrated. 23cc iodine solution were required.

To the remaining half of the sample 20cc K₂EtX was added stirred 15 minutes, decanted, washed and solution and washings titrated with iodine. Only 8-9cc were required showing that the washed galena abstracted considerably less xanthate than the unwashed.

(e) To see if the abstraction detected in the above tests was a true surface effect approximately 30g of Galena #5 were crushed and ground only to coarse powder to reduce the
Figure 7

Titration of 25cc M/160 KEtX

after Exposure to Galena

Clean Galena
46.27g

Unwashed Galena
37.13g

Volume of M/160 Iodine
Figure 8
Slope Curves for Fig. 7

Unwashed Galena

Washed Galena

$\frac{\Delta P.D.}{\Delta V}$

Volume of M/160 Iodine
surface area, and the fines rejected. Half the sample was washed three times under nitrogen as before with 10cc portions of 50% NH₄Ac followed by plenty of distilled water. 20cc KEtX was added to each part as before and after 15 minutes xanthate solution and washings were titrated with iodine. The solution from the washed sample required 21.5cc while that from the unwashed used only 19cc, while 20cc of the stock xanthate 0.05mg/cc was equivalent to 22.5cc of iodine solution. As before the washed sample abstracted less but this time it is also seen that the coarse mineral particles having a smaller total surface abstract less than the more thoroughly ground ore.

(f) Test 5(d) was repeated using potentiometric titration instead of the starch method. A sample of Galena #2 was divided into two parts, one of which was washed thoroughly with ammonium acetate as usual, treated for 7 minutes with 25cc of 1mg/cc KEtX and the solution decanted and titrated. The second part was treated with 25cc KEtX alone for 7 minutes, decanted and the solution titrated. The galena in each case was collected dried and weighed, the washed sample amounting to 46.27g and the unwashed portion 37.13g. The titration curves and the slope curves for these tests are given in Fig. 7 and 8 respectively. The first maxima in the slope curves are explained in later studies of this titration. The results of this test are in qualitative agreement with those using the starch indicator method.

Tests 5(a) and 5(f) are to be regarded as only qualitative
tests because the technique had not yet been completely worked out and standardized, the potentiometric titration had not yet been thoroughly studied. However they show that natural galena abstracts xanthate from dilute solutions and that if comparatively soluble lead salts are first removed from the mineral surface, considerably less xanthate is abstracted. The phenomenon is shown to be a true surface effect and the way is prepared for a quantitative study of it.
FINAL EXPERIMENTS

Following the preliminary experiments outlined, more exact experiments were undertaken to supply answers to the two fundamental questions pointed out in the introduction.

A--INHERENT FLOTABILITY

1. NaCl Extraction

Wark has raised the objection to Ravitz' work with ammonium acetate that the increased flotation yield observed when galena is washed with this reagent may be due to the collecting action of traces of impurities or reaction products including acetamide. The question raised is readily decided by using sodium chloride instead of ammonium acetate as the cleansing agent. Such tests using NaCl were performed, extreme precautions being taken to avoid impurities and oxygen.

Large samples of Galena #6 were ground with water in the ball mill. The ore was sized as usual to settling rates of 8.6 to 28.3 cm/min in the large elutriator and washed under nitrogen with saturated NaCl solutions. Nitrogen was bubbled through two absorption bottles containing 250 cc each of an oxygen absorbent solution consisting of 160 g of NaOH, 132 g of sodium hydrosulfite and 40 g of sodium anthraquinone-sulfonate per litre and then through concentrated H₂SO₄, activated charcoal and cotton traps to avoid entrainment of the oxygen absorbent. After every second run the second oxygen absorbent bottle was interchanged with the first which was refilled. The new solution was put back into second place in the absorb-
Nitrogen Train

Figure 9

- Trap
- To Float Cell
- Cotton
- Charcoal
- Decantation Flask
- Mineral to Float Cell
- NaCl
- H₂O
- H₂SO₄
- O₂ absorbent
ing train and the concentrated $\text{H}_2\text{SO}_4$ was renewed. Reagent solutions were made up in water freshly distilled through block tin, saturated with nitrogen, stored under nitrogen and transferred from storage by means of nitrogen pressure. The washing and storage apparatus was constructed entirely of glass with suitable ground joints so that liquids were never in contact with rubber. However, rubber was permitted in the connections in the nitrogen scrubbing train and in the gas distribution manifold so that pinch-clamps could be used in place of greased stopcocks. The rubber for these connections was boiled for some hours in NaOH solutions followed by distilled water. The absorption and washing train is shown in Fig. 9, and the decantation flask in Fig. 4.

Samples of ground sized ore in suspension in water were drawn into the decantation flask, washed twice with distilled water saturated with nitrogen and were then boiled with successive 50-100cc portions of saturated NaCl solution. After each NaCl extract was ejected the ore was washed with 50-100cc of distilled water and after the final NaCl treatment, water washings were continued until little or no $\text{Cl}^-$ could be detected with AgNO$_3$ or Pb$^{++}$ was negligible to $\text{Na}_2\text{S}$. Samples were given in this way from one to seven NaCl extraction treatments and then ejected by nitrogen pressure into the flotation cell, which was already filled with nitrogen-saturated water. The end of the ejection tube of the washing flask was kept under the water in the cell while the mineral was being transferred in order to avoid contact with air.
The cell was blown immediately with nitrogen for seven minutes using 5cc of 250mg/litre terpineol as frother. Heads were collected at 2 minutes and at 7 minutes. Tails and galena left in the washing flask were also collected separately and weighed. Lead in solution in the NaCl extracts and water washed was precipitated as \( \text{H}_2\text{S} \) and weighed. The results of these tests are shown in Table VIII. They indicate that a clean galena surface has a very high degree of flotability in the absence of collecting agents.

**TABLE VIII**

<table>
<thead>
<tr>
<th>NaCl Washes no.</th>
<th>Galena washed ( g )</th>
<th>Galena floated ( g )</th>
<th>Heads 2 min ( % )</th>
<th>Tails 7 min ( % )</th>
<th>mgPbS/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.0</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>19.40</td>
<td>17.86</td>
<td>nil</td>
<td>nil</td>
<td>6.6</td>
</tr>
<tr>
<td>2</td>
<td>21.8</td>
<td>10.85</td>
<td>12.2</td>
<td>15.2</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>15.39</td>
<td>9.69</td>
<td>65.8</td>
<td>72.8</td>
<td>11.3</td>
</tr>
<tr>
<td>4</td>
<td>-----</td>
<td>14.7</td>
<td>78.5</td>
<td>88</td>
<td>-----</td>
</tr>
<tr>
<td>4</td>
<td>20.64</td>
<td>10.56</td>
<td>82.8</td>
<td>86.6</td>
<td>12.5</td>
</tr>
<tr>
<td>5</td>
<td>17.92</td>
<td>16.68</td>
<td>79.9</td>
<td>89.0</td>
<td>11.8</td>
</tr>
</tbody>
</table>

New grinding lot:-

| 7               | 17.57                | 11.39                | 76.9              | 88.2              | 7.24    |
| 7               | 16.30                | 12.08                | 87.7              | 91.6              | 7.09    |

Ravitz\(^5\) has recently published the results of similar tests.

Since the measurements of lead extraction given in last column of Table VIII were not the prime purpose of the exp-
Figure 10

Flotation vs Washing
Figure 11

Lead Removal vs NaCl Washes

Mg of PbS/G Sample vs No. of NaCl Washes
periment they were not given the same attention as the rest of the work and so great accuracy is not claimed for them but it is interesting to notice how closely they parallel the flotation yield. In Fig. 10 (a) and (b) the 2 and 7 minute yields are plotted against the ordinal number of the wash and in Fig. 11, the amount of lead removed from the mineral in milligram per gram is plotted against the ordinal number of the wash. Apparently a considerable amount of PbSO₄ may be washed off the surface without affecting the flotation but as the lead removed approaches its upper limit, presumably all off the surface, the flotation yield approaches a maximum, that is when the surface becomes clean, excellent flotation ensues. It is interesting to note further that considerably less lead is removed from the freshly ground mineral than from older samples--the samples washed 7 times were treated within a few hours after grinding while the rest had been ground several days previously.

2. Effect of Oxidation

The following simple experiment demonstrates admirably the importance of an oxidized surface layer upon the flotation of galena.

Samples of Galena #6 were washed four times with NaCl under nitrogen, just as before but after thorough washing with H₂O, the decantation flask was connected to a stream of oxygen, warmed to 30⁰-40⁰C and shaken for not more than five minutes. The ore was driven over into the flotation cell and blown with nitrogen using 500 of 250mg/litre terpineol exactly as
usual in all respects save for the short exposure to oxygen. The flotation yield was now less than 10% in all the several tests tried and in one case was absolutely nil while in the absence of oxygen yields of better than 85% were obtained after four NaCl washes in the preceding tests on the same ore sample from the same grinding lot. A somewhat similar experiment was made during the preliminary tests in which galena was washed with ammonium acetate and found to give large flotation yields. Addition of a few drops of dilute H₂O₂ added to the ore in the cell completely suppressed flotation, and besides if heads from a washed sample were taken from the cell, treated with dilute H₂O₂ and returned to the cell and tested again for flotation, no yield was obtained from material which had necessarily floated 100% before treatment with H₂O₂. A number of such qualitative tests were performed, all of which agreed with the quantitative one outlined above.

3. Effect of Acetamide

The collecting action of acetamide was investigated to determine the weight to be attached to Wark's objection to its possible presence in ammonium acetate used in the preliminary tests. Sized samples of Galena #6 were treated when cold with 100cc portions of acetamide solutions of various concentrations and flotation measured. The flotation yield in every case using concentrations from 1g to 20g/litre was less than 10%. Hot acetamide solutions were not used because they like ammonium acetate have a solvent action on lead sulfate and hence their apparent collecting action could
be attributed to the same cause as that of the acetate or sodium chloride. Some results of these flotation tests are shown in Table IX.

**TABLE IX**

<table>
<thead>
<tr>
<th>Acetamide g/l</th>
<th>Total Galena g</th>
<th>Flotation Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.81</td>
<td>7.3</td>
</tr>
<tr>
<td>5</td>
<td>10.17</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>11.71</td>
<td>%&lt;1</td>
</tr>
<tr>
<td>20</td>
<td>10.88</td>
<td>%&lt;1</td>
</tr>
</tbody>
</table>

**REACTIONS OF POTASSIUM ETHYL XANTHATE**

1. Analytical

In order to study the action of potassium ethyl xanthate on galena a reliable method had to be developed for estimating $K\text{EtX}$ and $\text{Pb(EtX)}_2$ in dilute solutions, the usual method involving titration with iodine in the presence of starch indicator being found unsatisfactory because the results are distinctly erroneous when Pb is present in the solutions being titrated (Appendix D). Potentiometric titration of $K\text{EtX}$ which had already been applied in preliminary experiments was thoroughly tested and found suitable. Various oxidizing agents were tried but iodine was adopted as most satisfactory (Appendix E). By this method it was found possible to measure both $K\text{EtX}$ in solution and $\text{Pb(EtX)}_2$ in suspension at the same time if some care and patience is used.

Solutions were made up as follows:
Titration of KEtX and Pb(NO$_3$)$_2$

Figure 12

Slope: $\frac{\Delta \rho_d}{\Delta V}$
K\text{EtX} - 1g/litre; I_2 - 0.8g/litre containing 2g NaI/litre; Pb(NO_3)_2 - 1.00g/litre. 25cc portions of K\text{EtX} without the addition of Pb were measured from a pipette and titrated potentiometrically with iodine using platinum and calomel electrodes. Normal titration curves (Fig. 12(a)) were obtained with one sharp maximum corresponding to complete oxidation of the xanthate. Now, to 25cc portions of K\text{EtX} measured volumes of Pb(NO_3)_2 solution were added and solid Pb(\text{EtX})_2 appeared in near-colloidal form. These mixtures of Pb(\text{EtX})_2 and K\text{EtX} were titrated as usual but now two maxima were observed in the slope curves (Fig. 12(b)). It can be demonstrated that the first of these maxima occurs when all the K\text{EtX} has been oxidized and the second when the total xanthate is spent; for, assuming the difference on the volume axis (Fig. 12(b)) between the two maxima is a measure of the Pb(\text{EtX})_2 present in suspension, the volume of iodine solution corresponding to the Pb(NO_3)_2 added can be calculated and should be equivalent to the known amount of Pb(NO_3)_2 added. This agreement is indeed observed as shown in Table X.
TABLE X

Measurement of \( \text{Pb(EtX)}_2 \) by Iodine Titration

<table>
<thead>
<tr>
<th>Pb added cc</th>
<th>( I_2 ) eq. of Pb measured cc</th>
<th>( I_2 ) eq. of Pb calculated cc</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>.97</td>
<td>+3</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.94</td>
<td>+3</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>2.90</td>
<td>+3</td>
</tr>
<tr>
<td>4</td>
<td>3.9</td>
<td>3.87</td>
<td>+1</td>
</tr>
<tr>
<td>5</td>
<td>4.9</td>
<td>4.84</td>
<td>+1.5</td>
</tr>
<tr>
<td>6</td>
<td>5.9</td>
<td>5.81</td>
<td>+2</td>
</tr>
<tr>
<td>7</td>
<td>6.8</td>
<td>6.76</td>
<td>+0.6</td>
</tr>
<tr>
<td>8</td>
<td>7.7</td>
<td>7.74</td>
<td>-0.6</td>
</tr>
<tr>
<td>10</td>
<td>9.7</td>
<td>9.68</td>
<td>+0.2</td>
</tr>
</tbody>
</table>

Column 1 of Table X gives the volume of \( \text{Pb(NO}_3\text{)}_2 \) solution (1.001g/l) added to 25cc K\( \text{EtX} \) (1g/l) before titration. Column 2 shows the \( \text{Pb(NO}_3\text{)}_2 \) that was actually recovered as measured by the volume of iodine between the maxima in the slope curves. Column 3 gives the iodine that should have been observed for the corresponding figures in Column 2. The average error over the range from 1 to 10cc, approximately that used in the practical application of the procedure, is about 1% high—being of course greatest when the difference in the volumes is small. Greater amounts of lead than would be equivalent to 2/5 of the xanthate present lead to an impractically slow analysis since the action of the iodine on the suspended \( \text{Pb(EtX)}_2 \) is slow, especially if the solutions are so concentrated that the \( \text{Pb(EtX)}_2 \) precipitates act-
Figure 13

25cc KEtX only

25cc KEtX after treatment with Galena (465g)

Slope \( \frac{\Delta P.D.}{\Delta V} \)

Volume of Iodine-cc-
ually settles out instead of remaining in fine suspension.
In making the measurements given in this table the reaction
was taken to be complete after each iodine addition if the
galvanometer needle of the P<sub>H</sub> meter showed no perceptible
movement in 15 seconds.

Since a great part of the work to be described now de­
pends for its validity on this analytical method the pro­
cedure was studied and the results verified in a very large
number of experiments. The data quoted above are the results
of only one good example from these studies. The results of
investigations of various factors related to this titration
are given in Appendix F.

2. Lead Xanthate Formed from Galena

As a result of the above investigation it becomes pos­
sible to estimate the amount of Pb(EtX)<sub>2</sub> formed when galena
samples are treated with dilute solutions of KEtX and this
turns out to be proportional to the area of the surface of
the mineral as the following experiment shows.

Samples of Galena #6 sized to settling rates of 8.6 to
28.3 cm/min, were treated with 25 cc of 1 mg/cc KEtX by stirring
with the solution for five minutes. The mixture was allowed
to settle for five minutes, and was then washed five times
at five minute intervals, with 5 cc portions of distilled
water. The solution with suspended Pb(EtX)<sub>2</sub> was titrated as
usual with iodine. The galena was collected on a weighed
crucible, dried in the oven at 105<sup>0</sup>C and weighed to the near­
est milligram. Figure 13 gives a typical titration curve and
Figure 14

(a) Pb(EtX)₂ formed vs Wt of Galena

(b) KEtX abstracted vs Wt of Galena

Wt of Galena - grams -
average slope curve for this titration. The scale units of potential are arbitrary but the same as for Fig. 12. By comparison of Figs. 12 and 13, it is seen that the changes of slope occur at the same potential for the galena extract as for the solution known to contain Pb(EtX)$_2$ formed by double decomposition with known amounts of Pb(NO$_3$)$_2$.

When samples of galena of various weights but ground to the same size are treated in this way with KEtX the amount of Pb(EtX)$_2$ formed is seen from Table XI to be roughly proportional to the surface of the mineral.

**TABLE XI**

<table>
<thead>
<tr>
<th>Wt. of Sample (g)</th>
<th>Pb(EtX)$_2$ (mg)</th>
<th>mgPb(EtX)$_2$/g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.84</td>
<td>16.7</td>
<td>.62</td>
</tr>
<tr>
<td>19.0</td>
<td>12.5</td>
<td>.66</td>
</tr>
<tr>
<td>13.46</td>
<td>9.0</td>
<td>.67</td>
</tr>
<tr>
<td>9.86</td>
<td>4.9</td>
<td>.49</td>
</tr>
<tr>
<td>9.73</td>
<td>6.6</td>
<td>.68</td>
</tr>
<tr>
<td>4.65</td>
<td>3.6</td>
<td>.75</td>
</tr>
<tr>
<td>2.46</td>
<td>2.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

In Fig. 14 (a), the amount of Pb(EtX)$_2$ formed is plotted against the weight of galena from which it was derived.

3. Abstraction of Xanthate

It was observed in the preceding experiment, as in the preliminary experiments, that all the xanthate added to the mineral was not recovered in the subsequent titration. That is, when KEtX solutions were exposed to ground and sized
galena, some $\text{K}_2\text{EtX}$ and some $\text{Pb}([\text{EtX}]_2$ were recovered and measured but some xanthate was apparently abstracted by the ore. Further, the amount of xanthate that was abstracted was closely proportional to the mass and hence to the surface of the ore to which it was exposed. The xanthate abstraction tabulated in Table 12 and abstraction against weight of sample is plotted in Fig. 14(b).

### TABLE XII

<table>
<thead>
<tr>
<th>Wt. of Galena (g)</th>
<th>Abstraction $\text{mgKEtX}$</th>
<th>Abstraction $\text{mgKEtX/g Sample}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.84</td>
<td>13.14</td>
<td>.490</td>
</tr>
<tr>
<td>19.0</td>
<td>4.25</td>
<td>.224</td>
</tr>
<tr>
<td>13.46</td>
<td>5.24</td>
<td>.390</td>
</tr>
<tr>
<td>9.86</td>
<td>3.76</td>
<td>.361</td>
</tr>
<tr>
<td>9.73</td>
<td>4.25</td>
<td>.437</td>
</tr>
<tr>
<td>4.65</td>
<td>1.77</td>
<td>.362</td>
</tr>
<tr>
<td>2.46</td>
<td>.79</td>
<td>.322</td>
</tr>
</tbody>
</table>

**Average** --- .375

Excluding one value, the proportionality factors in column 3 are fairly constant and even when the one low value is taken into consideration, the greatest deviation is two-fold while the weights of the samples vary tenfold.

This experiment was now repeated in every detail except that the samples of galena were made up of larger particles, the residue left in the elutriator from the preceding tests being used. This material had had all of the mineral particles with settling rates below 28.5cm/min stripped off while
Figure 15:

(a) $\text{Pb}(\text{EtX})_2$ formed vs Wt of Galena

(b) $\text{K EtX}$ abstracted vs Wt of Galena

Coarse Particles

Graph:

- $\text{Pb}(\text{EtX})_2$ formed - milligrams
- $\text{K EtX}$ abstracted - milligrams

Wt of Galena - grams
in the preceding tests only particles with settling rates between 8.6 and 28.3 cm/min were used. The Pb(\(\text{EtX}\))\(_2\) formed and the xanthate abstractions were measured exactly as before. The data from this experiment are given in Table 13.

**TABLE XIII**

<table>
<thead>
<tr>
<th>Wt. of Sample (g)</th>
<th>Abstraction mg (\text{K}\text{EtX})</th>
<th>(\text{Pb}(\text{EtX})_2) mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.63</td>
<td>slight</td>
<td>7.35</td>
</tr>
<tr>
<td>14.95</td>
<td>.5</td>
<td>8.0</td>
</tr>
<tr>
<td>19.50</td>
<td>1.3</td>
<td>9.0</td>
</tr>
<tr>
<td>24.75</td>
<td>1.8</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Average abstraction--------- 0.52 mg/g

The results are qualitatively the same as before but in this case the surface of the mineral is reduced by the use of coarser particles and so the abstraction observed is only about one-seventh as great. The abstraction and lead xanthate formed are plotted in Fig. 15 on the same scale as used in Fig. 14.

4. Non-abstraction of Potassium

When the abstraction or so-called adsorption of xanthate had been measured, it became of interest to see if potassium was also taken up by the ore surface.

40-50 g samples of Galena #6, sized to settling rates of 8.6 to 28.3 cm/min were treated with 50 cc of \(1 g/\text{litre K}\text{EtX}\) solution in the standard manner adopted throughout all previous tests. The galena was caught on a weighed crucible, dried and weighed and potassium assays by the chloroplatinate method.
were made on the filtrates, (Appendix G). These were compared with blanks in which no galena was used. The results of this experiment are given in Table 14.

**TABLE XIV**

**Potassium Assays**

<table>
<thead>
<tr>
<th>Wt. of K₂PtCl₆</th>
<th>70.8mg</th>
<th>70.8mg</th>
<th>70.5mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>K recovered</td>
<td>11.35mg</td>
<td>11.35mg</td>
<td>11.25mg</td>
</tr>
<tr>
<td>Wt. of Galena</td>
<td>33.76g</td>
<td>43.00g</td>
<td>43.14g</td>
</tr>
</tbody>
</table>

**Blanks**

<table>
<thead>
<tr>
<th>Wt. of K₂PtCl₆</th>
<th>74.7mg</th>
<th>72.3mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>K recovery</td>
<td>12.1mg</td>
<td>11.63mg</td>
</tr>
</tbody>
</table>

Extrapolating the abstractions shown in Table 12, 40g of galena should abstract xanthate corresponding to about 17mg KETX if molecular KETX including the K is adsorbed. That is, more than 4mg of K should be lost. Taking the average of the blanks as recoverable K, losses of .5, .5 and 6mg of K were observed. This substantially no loss within the limits of error in the analysis attempting to recover 12mg of K from large mass of original material.

5. **Effect of Xanthate on Cleaned Galena**

It was observed in the preliminary experiments that galena abstracts less KETX when washed with NH₄Ac than when unwashed. This was studied now using NaCl as washing agent and taking extreme care to avoid oxidation and impurities.

The apparatus previously used for washing galena under nitrogen was modified by the addition of an opening with a ground glass plug through which KETX could be admitted. The
ore was ground and sized as usual, washed by boiling with saturated NaCl solution as before, 25cc of 1g/litre KEtX introduced, shaken for five minutes, the solution decanted off by nitrogen pressure and the ore washed under nitrogen with nitrogen-saturated distilled water. The solution and washings were titrated immediately in the usual fashion with the following results.

<table>
<thead>
<tr>
<th>No. of NaCl Washes</th>
<th>Wt. of Galena g</th>
<th>EtX abstraction mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>15.74</td>
<td>.62</td>
</tr>
<tr>
<td>5</td>
<td>28.45</td>
<td>.1</td>
</tr>
<tr>
<td>6</td>
<td>24.89</td>
<td>.3</td>
</tr>
</tbody>
</table>

Abstraction of xanthate by the washed galena is seen to be almost negligible. Also Pb(EtX)₂ could not be detected in the solutions. Comparison with an abstraction of 13mg of KEtX by an unwashed galena sample of mass comparable to the greatest of the above and ground to the same particle size indicates that an oxidized surface layer is necessary for the action of KEtX on this mineral to be possible.
DISCUSSION

1. The Nature of the Adsorbed Layer

The experiments that have been described show that when the surface of galena is thoroughly cleaned of comparatively soluble oxidation products, the mineral has a high degree of "inherent flotability", and they also lead to certain conclusions concerning the action of $\text{KEtX}$ on a natural galena surface. The presence of a comparatively soluble layer of lead salts has been shown to exist on the surface and $\text{Pb(EtX)}_2$ has been detected and measured in the solution after the ore is treated with $\text{KEtX}$. It has also been shown that the potassium content of the solution remains substantially constant. This constitutes positive evidence for a reaction of the simple type:

$$\text{Pb}^{2+} + 2\text{KEtX} \rightarrow 2\text{K}^+ + \text{Pb(EtX)}_2$$

taking place at the mineral-water interface. It is of little moment whether the compound supplying the lead ions is $\text{PbSO}_4$ or a basic sulfate or some intermediate oxidation product. It is presumed to be the sulfate, since $\text{SO}_4^{2-}$ can be detected easily when the mineral is extracted with suitable solvents. The sulfate is readily formed from the sulfide by oxidation and it satisfies the essential solubility condition, $\text{Pb(EtX)}_2$ being precipitated when $\text{KEtX}$ is added to saturate $\text{PbSO}_4$ solutions. Further—no significant amount of $\text{Pb(EtX)}_2$ forms when pure precipitated PbS is treated with $\text{KEtX}$ under conditions such that oxidation is avoided and $\text{Pb(EtX)}_2$ does not form when galena is thoroughly washed with NaCl under
nitrogen and then treated with KEtX. In short, there is no need to assume anything but the most elementary type of chemical reaction to explain the formation of Pb(EtX)$_2$ in the solution when galena is exposed to KEtX solution.

Besides explaining the formation of Pb(EtX)$_2$ in the solution the experiments described allow certain conclusions to be drawn concerning the fate of the xanthate that remains on the mineral surface. It has been pointed out that a galena surface will not abstract xanthate from solution when the mineral is first freed of comparatively soluble lead salts and yet when the oxidized layer is not removed by washing the abstraction is proportional to the surface area. That is, the same considerations may be applied to explain the xanthate abstraction as were used to explain the formation of Pb(EtX)$_2$ with the important difference that Pb(EtX)$_2$ on the surface has not been measured directly as it was measured in the solution. However, the magnitude of the abstraction itself supplies indirect evidence in support of the conclusion that the loss observed is due to the formation of Pb(EtX)$_2$ that remains on the surface; for, the extent of the surface layer can be calculated from the data of Table XII, and it turns out to be very close to what should be observed if exposure of the mineral to KEtX solution resulted in the formation of a unimolecular layer of Pb(EtX)$_2$ that remained on the surface of the mineral.

The mineral used for the tests in which the data given in Table XII was obtained was sized to a settling rate of
From Stokes' Law (Appendix B), the root mean square particle diameter is thus $1.475 \times 10^{-3} \text{cm}$ which corresponds to an area of $4070\text{cm}^2$ per cubic centimeter of galena. Taking the average abstraction (Table 12) as $0.375\text{mg/g}$, $2.70\text{mg}$ of KEtX are spread over $4070\text{cm}^2$ of surface per cubic centimeter of galena (density $7.5\text{g/cc}$). This gives an average of $4.02\text{A}^2$ per xanthate group, or slightly more than $8\text{A}^2$ for two xanthate groups. If the particle size is taken from the direct measurement of 100 particles under the microscope this value becomes about 10% higher, i.e. about $8.8\text{A}^2$ (Appendix B). Taking the molecular volume of PbS as slightly less than $32\text{cc}$ the area presented by a lead atom on the surface of the galena crystal should be of the order of $8.9\text{A}^2$ or $9\text{A}^2$ in round numbers. In view of the monovalent character of the xanthate group this indicates that the surface layer is essentially $\text{Pb(EtX)}_2$, the EtX chains undoubtedly being oriented out of the surface, so conferring on the mineral surface its paraffin-like character when treated with KEtX. Additional weight is lent this conclusion by Warks' work in which he shows that when various minerals are treated with solutions of the homologous xanthates, the contact angles with an air bubble are independent of the mineral and depend only on the number of carbon atoms on the paraffin chain in the xanthate. If by "adsorption" is meant a chemical reaction in which one of the products remains in the solid-liquid interface, the phenomenon whereby xanthate is abstracted from the solution can be called adsorption,
and emphasis is to be laid on the essentially chemical nature of the phenomenon observed here.
SUMMARY

The following experimental facts have been observed:-

1. PbSO₄ has been detected on the surface of natural galena.

2. When galena is washed with ammonium acetate or NaCl under conditions such that oxygen is excluded the flotation yield has been shown to rise with increasing removal of lead salts from the surface and when the surface is thoroughly cleansed virtually complete recoveries have been obtained without the aid of a collecting agent.

3. Reoxidation of the surface reduces flotation yield.

4. Less KE₄X is required to cause complete flotation of galena when the surface of the mineral is first partially freed of oxidation products than when the mineral is untreated.

5. When galena is treated with dilute KE₄X solutions, some Pb(EtX)₂ forms and appears in suspension. The amount formed is proportional to the surface area of the mineral.

6. When KE₄X solutions are treated with ground and sized galena xanthate ion is abstracted from the solution in proportion to the surface area of the mineral.

7. Cleaned galena does not abstract any significant amount of xanthate.

8. Natural galena which adsorbs xanthate ion does not take up potassium from the solution.

The following logical conclusions are drawn:-
1. A pure clean PbS surface is sufficient to cause galena to exhibit a high degree of inherent flotability. The natural mineral does not float without reagents because the surfaces of the particles are coated with comparatively soluble lead sulfate which is wet by water.

2. The action of xanthate is twofold. It forms some Pb(EtX)$_2$ which splits off and appears suspended in the solution and it also forms a layer of Pb(EtX)$_2$ on the mineral particles giving them a paraffin-like character. The particles are then less wet by water than the sulfate and so they can make contact with an air bubble and float. Adsorption measurements made with sized galena particles show the surface layer is unimolecular.
APPENDIX A

ANALYSIS OF GALENA


Samples were chipped from parts of the large lump and ground to fine powder in an agate mortar. Samples weighing .35g were taken with a steel spatula from a weighing bottle containing about 20g, placed in 500cc Erlenmeyer flasks with 10cc concentrated HCl and gently boiled for 15-20 minutes. Complete dissolution occurred. 18cc of conc. H₂SO₄ was added to each and evaporation carried out on the hot plate until the mixture fumed strongly. The flasks were cooled, the walls washed down with water and the mixture again evaporated to fumes. To each sample was added 300cc of water and the flasks allowed to stand for 3/4 hour in an ice bath before collecting the PbSO₄ on a weighed crucible. Precipitates were washed with 25-35cc of 3% H₂SO₄, dried slowly and ignited at barely red heat in an asbestos shield to protect from reducing gases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PbSO₄</th>
<th>% Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3509g</td>
<td>0.4301g</td>
<td>83.76</td>
</tr>
</tbody>
</table>

Calculated as PbS—96.75%

When filtrates from the above procedure were treated with HCl to test for Ag, scarcely enough AgCl formed to set-
tle out but when Ag was precipitated with NaI, the solution poured through filter paper and the paper exposed to bright sunlight, blackening was obtained. When the silver was removed from the combined filtrates from several lead analyses and the solution containing HCl was saturated with H₂S a clean orange precipitate was thrown down. This precipitate dissolved completely in Na₂S and when reprecipitated with HCl, it was dissolved again completely by conc. HCl saturated with H₂S. When diluted from 10cc to 40cc with water the orange precipitate again appeared indicating the presence of a considerable amount of antimony. A trace of the metals of the iron group was indicated by the formation of a small dark precipitate when the HCl-H₂S filtrate was treated with (NH₄)₂S and allowed to stand for some hours.

APPENDIX B

Estimation of Particle Size

The well-known Stokes' Law formula gives the velocity of a spherical particle of radius 'a' and density 'd₁' falling through a liquid of density 'd₂' and viscosity 'v' as

\[ V = \frac{2ga^2(d_1 - d_2)}{9} \]

Since the galena particles are cubes, not spheres and the conditions in the elutriator are not strictly those for which this formula is valid, a test was made in which the particle size calculated from this formula was compared with
that obtained by direct measurement of 105 particles with the aid of a microscope and calibrated eye-piece.

In taking a sample of galena with settling rates between 9 and 25 cm/min from the elutriator, the upper and lower limits of the velocity were controlled as closely as possible and the average particle size calculated from Stokes' formula. The average velocity is 17 cm/min, density of galena in excess of that of water is 6.5 g/cc and the viscosity of water at 20°C 0.010 poise, whence \( a \), the root mean square particle size, is \( 1.42 \times 10^{-3} \) cm.

The galena was now dried and a sample smeared on a microscope slide. One dimension of 100 particles chosen at random was measured by comparison with an eye-piece scale previously calibrated against a standard slide, graduated in tenths and hundredths of a millimetre. Two dimensions of five more particles were measured. Squaring these measurements averaging over the 110 readings and extracting the square root gave \( 1.29 \times 10^{-3} \) cm for the root mean square particle size by measuring the individual particles. The agreement is fair. The distribution-in-size curve for the 105 particles is shown in Table 16.
Particle-size Distribution for Elutriator

9-25 cm/min

X - Particle-size
\bar{X} - R.M.S. Particle-size
ΔN = no. of Particles in Δx = 35 \times 10^{-3} cm

**Figure 16**
### TABLE XVI

**Distribution-in-size for Elutriated Galena Particles**

<table>
<thead>
<tr>
<th>Size Range cm x 10^{-3}</th>
<th>No. of Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - .35</td>
<td>14</td>
</tr>
<tr>
<td>.36 - .70</td>
<td>33</td>
</tr>
<tr>
<td>.71 - 1.05</td>
<td>27</td>
</tr>
<tr>
<td>1.06 - 1.40</td>
<td>15</td>
</tr>
<tr>
<td>1.41 - 1.75</td>
<td>11</td>
</tr>
<tr>
<td>1.76 - 2.10</td>
<td>3</td>
</tr>
<tr>
<td>2.11 - 2.45</td>
<td>4</td>
</tr>
<tr>
<td>2.46 - 2.80</td>
<td>1</td>
</tr>
<tr>
<td>2.81 - 3.15</td>
<td>1</td>
</tr>
<tr>
<td>3.16 - 3.50</td>
<td>1</td>
</tr>
</tbody>
</table>

This distribution is plotted in Fig. 16.

When the galena particles were examined under the microscope, they were seen to be very nearly cubical as the following data for measurements of two dimensions of 5 particles indicates. The units of size in Table 17 are those of the calibrated eye-piece scale used with the microscope (2.85 = 1/10mm).
TABLE XVII

Two Dimensions of Galena Particles

<table>
<thead>
<tr>
<th>Particle No.</th>
<th>Dimensions (Eye-piece Scale Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2 x 0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.4 x 0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.35 x 0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.35 x 0.3</td>
</tr>
<tr>
<td>5</td>
<td>0.25 x 0.25</td>
</tr>
</tbody>
</table>

APPENDIX C

Colorimetric Determination of Pb

The method depends on preparing dilute lead sulfide colloids and comparing opacities with those of a series of standard colloids made up in the same way and containing known amounts of lead. The standards and unknowns were compared by means of a photoelectric colorimeter. Zero for the instrument was based on distilled water in the absorption cells.

Solutions were made up as follows:-

Standard lead acetate—91.5mg of Pb(C₂H₃O₂)₂·3H₂O were weighed out and dissolved in water containing 1cc acetic acid and made up to 500cc.

Cane sugar—70g in 100cc H₂O.

Hydrogen sulfide—500cc of distilled water were saturated with washed H₂S gas. This solution was frequently renewed.
Preparation of Standards:

Standard lead acetate solution was measured from a burette into 100cc volumetric flasks, 5cc sugar solution and 2cc NH₄Ac solution and 1cc glacial acetic acid were added and the volume made up to about 80cc with water. 10cc of H₂S solution was added from a burette and the volume made up to 100cc. PbS is formed rapidly as a reasonably stable colloid or fine suspension if the total amount of lead acetate in 100cc does not exceed 1-2mg, some standards containing about 1mg or less showing not appreciable variation over a period of 12 hours. The upper limit of lead acetate used was about 3mg per 100cc and in this case precipitation corresponding to about 10% of the colorimeter scale reading was observed in 3-4 hours. To avoid change in the standards with time each one was made up separately, mixed and shaken thoroughly, the optical cell of the instrument rinsed three times with the solution and then filled, dried outside with filter paper and the opacity measurement made immediately and verified on a second sample, the whole process taking not more than 10 minutes. A standard curve of the type obtained is shown in Fig. 17, the ordinates being the arbitrary units of the colorimeter scale and the abscissae cc of standard lead solution. 1cc contained .183mg of Pb(Ac)₂·3H₂O. To indicate the reproducibility of the results obtained by this method two separate sets of standards made for different analyses are shown by the crosses and circles.
Since these standards were to be used for the analysis of lead solutions containing varying amounts of ammonium acetate they were tested for variation with ammonium acetate concentration. No appreciable difference in colorimeter reading was observed over a threefold variation in the ammonium acetate content of the solutions.

The Analysis

To the cooled ammonium acetate extracts washings prepared in I (3) were added sugar and ammonium acetate solutions, glacial acetic acid and H₂S solution in the same order and the same amount as for the standards. The optical cell was rinsed and filled as before, and the colorimeter scale reading compared with that given on the standards-curve to obtain the lead present. In the final experiment considerable attention was given to reducing every operation in the analysis to exactly the same conditions.

APPENDIX D

Titration of KEtX with Iodine Using Starch as Indicator

When xanthate in solutions more dilute than M/160 is titrated with iodine using starch as indicator, serious difficulties are encountered. The end-point is not at all sharp and although this defect can be overcome to some extent by colorimetric comparison the procedure is tedious and impossible if the mixture is at all turbid. If lead is present in the solution Pb(EtX)₂ precipitates and the end-point then fades badly since the iodine acts but slowly on
the Pb(EtX)$_2$ and the end-point will probably be reported somewhere between what should be obtained for the potassium xanthate and total xanthate. Further, the end-point depends on the amount of starch used, the $P_H$ of the solution and, if the ammonium acetate is added as a buffer, the volume of iodine used will depend to some extent on the acetate concentration. The following data is submitted illustrating these facts.

(a) Dependence on $P_H$

KEtX solution was made up to contain 0.01mg/cc. Iodine dissolved in NaI was made up so that 10cc of KEtX was equivalent to 11cc of this solution when titrated in the presence of 0.5cc of 2.5% starch solution only. To 10cc portions of KEtX containing 1/2cc of 2.5% starch were added HCl, NH$_4$Ac, HAc etc. and the resulting solutions titrated with iodine with the results shown in Table 18.
(b) Dependence on Starch

The effect of varying the starch concentration is shown by the following:-

<table>
<thead>
<tr>
<th>KEtX cc</th>
<th>30%NH$_4$Ac cc</th>
<th>Addition cc</th>
<th>Iodine cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>none</td>
<td>5cc 1:10 HCl</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>none</td>
<td>5cc 1:9 HCl</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>none</td>
<td>5cc 1:10 NH$_4$OH</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>none</td>
<td>10.75</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>5cc 1:10 HCl</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>1cc 1:9 HCl</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>2cc 1:9 HCl</td>
<td>10.75</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>5cc 1:9 HCl</td>
<td>10.75</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>1cc NaOH</td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>2</td>
<td>1cc 1:9 HAc, H$_2$O to 50cc</td>
<td>1.2</td>
</tr>
<tr>
<td>none</td>
<td>2</td>
<td>3cc 1:9 HAc, H$_2$O to 50cc</td>
<td>1.8</td>
</tr>
<tr>
<td>none</td>
<td>2</td>
<td>5cc 1:9 HAc, H$_2$O to 50cc</td>
<td>1.3</td>
</tr>
<tr>
<td>none</td>
<td>none</td>
<td>Starch only and H$_2$O to 50cc</td>
<td>4.5</td>
</tr>
</tbody>
</table>

As a result of these tests, when starch was used to
indicate the end-point in the K\textsuperscript{+}X-Iodine titration, .5cc starch, 2cc 30\% NH\textsubscript{4}Ac and 1cc of 1:9 HAc were added to the mixture.

APPENDIX E

Titration of K\textsuperscript{+}X with Various Reagents

1g K\textsuperscript{+}X was dissolved in 1000cc of distilled water to make M/160 solution. This was titrated potentiometrically with solutions of approximately the same concentration of Iodine, AgNO\textsubscript{3}, CuSO\textsubscript{4}, KMnO\textsubscript{4} and Ce(SO\textsubscript{4})\textsubscript{2}. Titration curves of the type shown in Fig. 18 were obtained for the first three of these; the last two were useless. Iodine was adopted for all work. Iodine was tested at various dilutions and about M/160 was found most satisfactory, although considerably more dilute solutions could be used if necessary.

APPENDIX F

Miscellaneous Studies Concerning the Xanthate Titration

(a) Comparison of Starch and Potentiometric Methods:- To 25cc of 0.2mg/cc K\textsuperscript{+}X was added sufficient dilute Pb(NO\textsubscript{3})\textsubscript{2} to precipitate nearly all the xanthate. Starch indicator was added and the solution titrated potentiometrically with iodine. The starch began to turn blue after about 9cc of iodine had been added but the color slowly faded on standing. After about 20cc of iodine had been added the blue color became permanent although all the xanthate was not spent until 25cc of iodine had been added. The results of
Figure 19

Titration of KEtX-Pb(EtX)₂-Starch

Mixture of Iodine

Volume of Iodine - cc

End Pt Fades

Blue
this test are represented in Fig. 19.

(b) The Effect of Time on the Titration:

Since the action of iodine on suspended Pb(EtX)₂ is slow it becomes of interest to see if any significant error is introduced if time is not allowed for the reaction to entirely complete itself after the addition of each portion of iodine.

To 25cc of 1mg/cc KEtX was added 2cc of 2mg/cc Pb(NO₃)₂ and the mixture titrated with iodine, allowing not more than one minute between additions of iodine and then the test was repeated allowing for the galvanometer needle to become completely steady after the addition of iodine. The end-point was not sensibly changed in the second case but the slope was more than twice as great. In other words, economy of time is gained at the expense of sharpness in the break in the titration curve.

(c) Effect of Galena on the End-point:

25cc portions of KEtX to which were added various amounts of galena, from a few milligrams to 10grams, were titrated potentiometrically with iodine. The end-points were indefinite when large amounts of finely divided galena were present but small amounts from a few milligrams to about 500mg did not make any sensible difference. Iodine does react with galena but the reaction is extremely slow and takes place at a considerably lower potential than that for KEtX and even lower than that for Pb(EtX)₂, as would be expected from ion concentrations in equilibrium with solid
Figure 20

Titration of 10cc N/160 KETX
Solid Lead Salts added

Solid PbCrO₄
Solid PbI₂

Volume of Iodine
PbS and Pb(EtX)$_2$. In applying the titration to tests where xanthate solutions were treated with galena the solution was always freed of galena as far as possible by careful decantation, floating galena being retained in the beaker from which the solution was being decanted by placing a glass rod across the lip of the beaker. If the operation is carried out carefully and the galena has been properly sized to eliminate extremely fine particles, the mixture can be nearly freed of the mineral.

(d) Effect of Excess Solid Lead Compounds:

Measured volumes of KEtX were potentiometrically titrated with iodine after the addition of a gram or two of precipitated lead salts including PbS, PbCrO$_4$, PbI$_2$ and PbSO$_4$. Times between iodine additions were limited to about 1 minute. Titration curves for the first three of these when approximately equal amounts of solids were present are shown in Fig. 20. It is observed that the titration can be carried out successfully in the presence of the comparatively insoluble sulfide and chromate but in the case of an excess of salt more soluble than Pb(EtX)$_2$ it is impossible in a finite time.

APPENDIX G

Potassium Assays


The filtrates containing potassium and 100 conc. HCl were evaporated to about 200cc in 250cc Erlenmeyer flasks,
cooled, saturated with H₂S, filtered, made alkaline with NH₄OH, saturated with H₂S, filtered evaporated with 3cc HCl and 1cc HNO₃ and ignited to remove NH₄. The residue was taken up in dilute HCl and transferred to small porcelain crucibles, evaporated, ignited and weighed, dissolved in 1% HCl and treated with 74 drops 10% PtCl₄ solution from a calibrated dropper delivering 54 drops to the cc. The solution was evaporated until crystals formed, cooled, filtered in a weighed crucible, washed with 80% ethyl alcohol saturated with K₂PtCl₆, dried and weighed as K₂PtCl₆. Blanks were run on KEtX solution untreated with galena.

APPENDIX H

Calculation of the Extent of the Surface Layer

The data of Table 12 give an average abstraction of .375mg of KEtX per gram of galena. This amounts to 2.70mg of KEtX spread over 7.5g or 1cc of the mineral. From Stokes' law the root mean square particle size is 1.475 x 10⁻³ cm and hence the original 6cm² area of a centimetre cube of galena is increased to 4070cm². From these figures the area available for one xanthate group is:

\[
\frac{4070 \times 160,000}{2.70 \times 6.03 \times 10^{23}} \text{ cm}^2
\]

where 160,000 is the molecular weight of KEtX in milligrams. This works out to 4.02Å².

If the direct microscope measurement of particle size is accepted as a better value than that obtainable from
Stokes' law, this area should be increased in approximately the ratio of 1.42:1.29 (Appendix B). The result is $4.4A^2$ per single xanthate group. The direct measurement rests only in the assumption that the sample taken for measurement with the microscope was representative while the first value relies on the validity of Stokes' law applied under conditions where it can be expected to be but an approximation.

The area of a lead atom on the surface of the crystal lattice is obtained from $\left(\frac{V}{N}\right)^{2/3}$ where $V$ and $N$ are the average atomic volume and the Avogadro number respectively. The atomic volume of lead calculated from the atomic weight and density of the metal is about 18cc, that of sulfur 16cc, the molecular volume of PbS from the molecular weight and density of galena is 31.9cc; whence the atomic volume of Pb in galena can be estimated to be between 16 and 18cc, probably nearer to 16cc. These figures give 8.9 to 9.6$A^2$ for the limits of the area of a lead atom in the surface.

It should perhaps be pointed out that the area of a cube circumscribing a sphere is greater than that of the sphere in the ratio $\frac{6}{\pi}$. The area to which the 6cm$^2$ per cubic centimetre of original galena is increased on grinding is estimated by imagining each centimetre cube to be subdivided into smaller cubes of width 'd'. Their total area is $6/d$ and this is taken to be equal to $\frac{6 \times 3}{\pi}$, the area of the cubes circumscribing the small spheres if an original loc were reduced to
spheres of radius 'a' instead of cubes. In effect \( d = \frac{\pi}{3} a \), and so if the sphere radius obtained from Stokes' law is taken to equal the cube width, the error is that of taking \( \frac{\pi}{3} = 1 \), and the area will be about 5% high. The justification for this application of Stokes' law to cubes is seen in the fair agreement between the elutriator and microscope values for the particle size. In all calculations of the area of a xanthate group, the width of a cubical particle has been taken equal to Stokes' 'a' and the 5% correction neglected as being within the experimental error. The terms particle size and Stokes' radius have been used interchangeably.
SUGGESTIONS FOR FURTHER WORK

The work described suggests certain extensions that could be undertaken profitably. In order to generalize the results obtained, the adsorption experiments with both cleaned and uncleaned surfaces should be repeated not only on samples of galena from a number of sources but also on other minerals if possible. No difficulty is to be expected in repeating the work on galena but the application of the method to minerals which do not possess the beautifully regular cubic cleavage of galena will require some ingenuity on the part of the investigator to estimate the total surface. Also it is important that various other pure collectors be prepared—for example, the homologous xanthates and the adsorption experiments be repeated with them. A priori, it is reasonable to expect the higher xanthates will act similarly to KEtX. Will they? Since it has been shown that EtX⁻ is taken up by the galena surface only when it is coated with a layer of the sulfate which is more soluble than Pb(EtX)₂, it becomes of interest to learn what are the exact conditions under which such adsorption can occur. It would be anticipated that most solid lead salts more soluble than Pb(EtX)₂ would adsorb EtX⁻ from solution. Do they? Would xanthates more insoluble than PbS be adsorbed on a PbS surface? In other words is the observed adsorption to be controlled by solubility considerations and if so does it follow the usual solubility product rule with a normal solution solubility product or is the con-
cept of a "surface solubility product" necessary?

In view of the ease with which the reactions of the xanthates can be studied and the surface of galena particles measured, these substances constitute rather ideal reagents not only for the study of collector action but also for work on the general theory of surface reactions.
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