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N. P. Finkelstein[a]
[a] NATIONAL INSTITUTE FOR METALLURGY, JOHANNESBURG, SOUTH AFRICA

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Quantitative Aspects of the Role of Oxygen in the Interaction between Xanthate and Galena

N. P. FINKELSTEIN

NATIONAL INSTITUTE FOR METALLURGY
JOHANNESBURG, SOUTH AFRICA

Summary

The reaction between potassium ethyl xanthate, oxygen, and galena over periods of 20 to 30 hr has been studied. Quantitative results are presented for the reaction at pH 10, but it is shown that the general features of the behavior are the same within the range pH 8 to 11. Two types of reaction are observed. The first involves adsorption of the xanthate and takes place at a rate, dq/dt, that decreases exponentially with the quantity of reagent adsorbed. The second is thought to involve reaction between the xanthate and the oxygen catalyzed by the surface. Its rate increases with time until it reaches a constant value, R_f. A product of reaction may be ethyl monothiocarbonate.

The parameters of the adsorption rate equation, and, therefore, the rate and extent of adsorption at any time, vary directly with the square root of partial pressure of oxygen (p) for $p \leqslant 131$ torr. R_f varies with $p^{1/2}$ for values of p up to the maximum used (313 torr).

Possible mechanisms of reaction are discussed in the light of these findings.

INTRODUCTION

Plaksin and his school opened a new phase in the study of the chemistry of xanthate interaction with sulfide minerals when they showed that the participation of oxygen is essential (*1*, *2*). This finding has been amply confirmed in independent studies (*3–6*) and is now generally accepted. In this new phase, much attention has been devoted to the role of dixanthogen, which has been shown to occur at the surface (*3*, *4*, *5*, *7–9*) and is thought by some investigators (*4*, *8–13*) to be the species solely responsible for the hydrophobic properties. The latter theory is not undisputed (*14–17*). It has also been demonstrated that the distribution of xanthate species at the surface is unhomogeneous (*2*, *18–22*). Several mechanisms have been proposed to account for the action of oxygen and the other observations (*1*, *2*, *5*, *12*, *13*, *15*, *16*). However, with few exceptions (*16*, *23*) the work on the participation of oxygen is entirely qualitative. The stoichiometry of the reaction is not known, nor is there any understanding of the way in which the concentration of oxygen in solution affects the rate and extent of reaction.

At the National Institute for Metallurgy it was considered that further understanding of the system was being seriously hampered by the lack of quantitative data. A preliminary investigation (*6*) showed that the severe experimental problems involved might be soluble, and revealed an unsuspected complication in the fact that the system obeys a logarithmic rate law. The present paper describes the results of subsequent testwork.

EXPERIMENTAL METHODS

Basically, the same experimental methods were used in this work as were developed during the preliminary investigation (*6*). The modifications were aimed at providing an apparatus that would work reliably with minimum attention over the long runs necessary, and a suitable method of controlling the partial pressure of oxygen in solution. The methods used have been described very fully elsewhere (*24*).

Materials

Galena. A sample of natural galena (Ward's Natural Science Establishment, Inc.) was crushed to about 10 mesh and, after being freed from obvious impurities by handpicking, was ground further. The fraction between 150 and 325 mesh was selected and stored under water. A suitable sample (5 to 25 g) was selected immediately before use and transferred to the reaction column (Fig. 1) to which a conical glass elutriator was attached. Oxygen-free sulfide solution of pH 8 to 8.5 was driven through at about 5 ml/min for at least 1½ hr to ensure the removal of all oxidized compounds from the surface. The flowrate was then increased to the value chosen for the elutriation and was maintained at that level until all overflow of fines had ceased. Samples produced by this procedure had an average surface area of 425 $cm^2 g^{-1}$, with a standard deviation of 35 $cm^2 g^{-1}$. They showed no significant reaction with oxygen-free xanthate solutions.

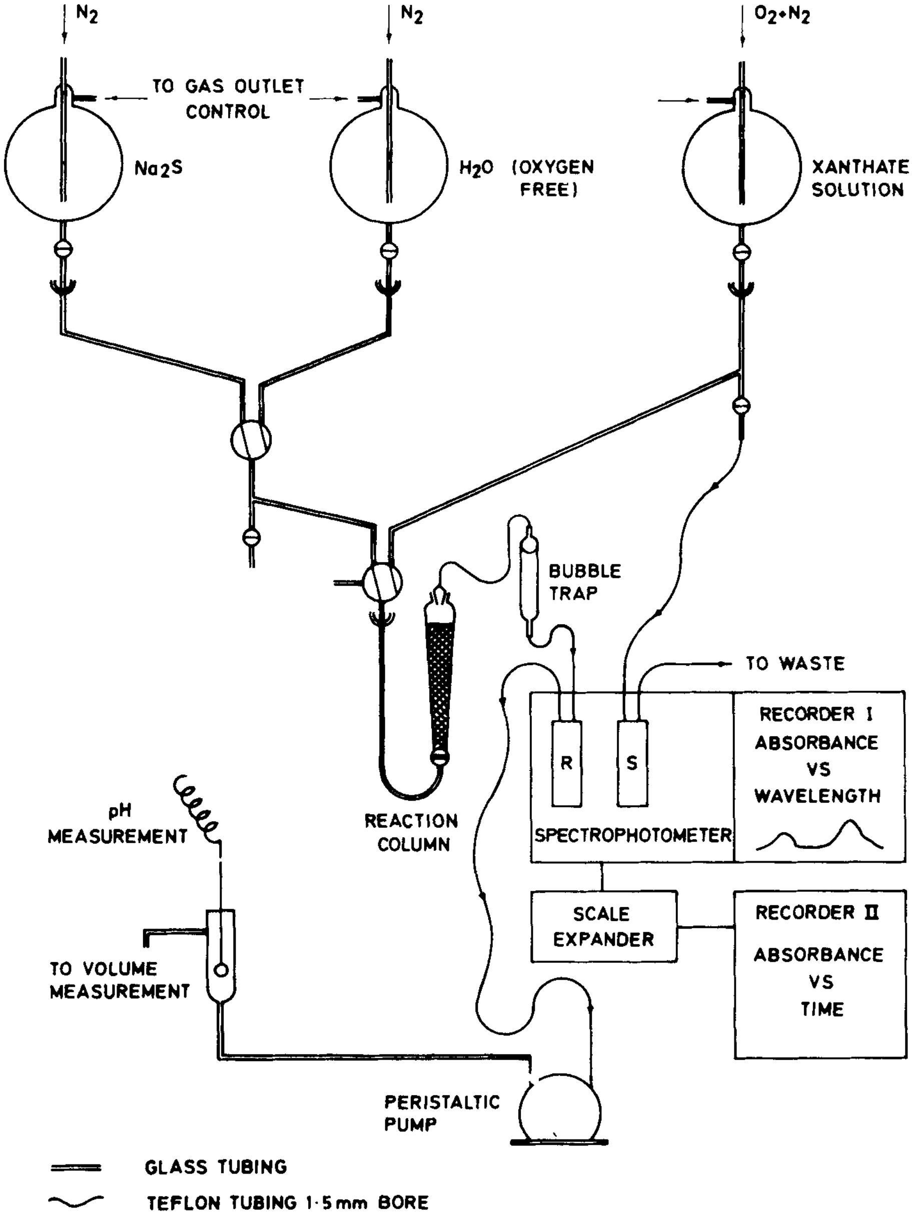

FIG. 1. The apparatus.

Xanthate. Potassium ethyl xanthate (British Drug Houses) was purified by multiple recrystallization from acetone and stored in a vacuum desiccator over silica gel, activated charcoal, and flakes of paraffin wax.

Sodium Sulfide. Solutions were prepared immediately before use. Hydrogen sulfide was passed into a 0.1 *M* sodium hydroxide solution, which had been freed of oxygen by nitrogen bubbling, until pH 8 was reached.

Apparatus and Procedure

Oxygen Concentration in Solution. The solution was brought to equilibrium with a nitrogen–oxygen mixture having the required partial pressure of oxygen. Under the conditions used, about 1½ to 2 hr were required for equilibrium. In practice, equilibration times of at least 6 hr were allowed, and the flow of gas was maintained as long as the solution was in use. The gas mixtures were prepared from high-grade compressed oxygen and nitrogen further purified to remove the last traces of oxygen (from the nitrogen) and carbon dioxide. The composition of the gas mixture was maintained to within ±1% of the set value by a double peristaltic pump. The mixtures were monitored continuously by a magnetic susceptibility oxygen gas analyzer (Beckman Model E2). The response of this instrument was linear to within ±1% of the reading. It was standardized with pure nitrogen and pure oxygen.

Spectrophotometry. A Beckman DK 2A double-beam recording spectrophotometer was used to monitor the reaction. The instrument was modified to allow the difference in absorbance at a fixed wavelength between the solutions in its S (sample) and R (reference) cells to be expanded up to ten times, and to be recorded against time on an external recorder. During the course of a run, the effluent solution from the reaction column flowed through the R cell, and the head xanthate solution through the S cell, and the wavelength was set at 301 nm. Thus the readout represented the difference in concentration of xanthate in the effluent solution due to its passage through the column. It was found that serious errors (of the order of 100%) could be introduced by cells that had bad flow characteristics, i.e., that allowed by-pass and hold-up of the solution. The cells used (Beckman 97290; path length = 10 mm; volume = 0.1 ml) showed plug-flow characteristics at the flowrates used and introduced an error of less than 1% when they were used to estimate the quantity of xanthate in a sharp pulse of the solution.

Differential spectra of the flowing solutions could be drawn by using the internal recorder of the spectrophotometer. Clearer indications of the presence of absorbing impurities in the effluent solution were obtained by recording the differential spectrum of a sample of the effluent against a pure xanthate solution of concentration exactly equal to that in the effluent.

Temperature Control. All experiments were carried out in a room maintained at a temperature of 25 ± 0.5°C.

Apparatus. The apparatus used to follow the reaction is shown in Fig. 1. Any of the three solutions stored in the reservoirs could be directed through the reaction column where its flow fluidized the galena sample. From the column, the solution passed successively through a bubble trap, the reference cell of the spectrophotometer, a peristaltic pump that maintained the flowrate constant to ±1% of the set value, and a pH cell, before passing to waste. A second stream, drawn from sampling points below either the water or the xanthate reservoir, flowed under gravity through the sample cell of the spectrophotometer.

Parts of the apparatus with which solutions came into contact before reaction and analysis were constructed entirely of Teflon and glass. The volume between the manifold and the S cell ("dead volume") was kept as low as possible (approximately 15 ml). Effects due to changes in the level of illumination were avoided by having the reaction column enclosed in a dark box.

The following procedure was used. The reservoirs were filled with their respective solutions: sodium sulfide (0.05 M, pH 8 to 8.5), water (pH 10), and xanthate (3.12×10^{-5} M, pH 10). The second of these solutions was equilibrated with N_2, and the third with O_2–N_2 of the requisite concentration. The galena sample had been left at the end of the pretreatment and sizing (see above) with Na_2S solution flowing through it. This solution was replaced by the water solution, which was allowed to flow at about 5 ml/min until all traces of sulfide had been eliminated. During this period, flow of the head solution was started through the S cell. The spectrophotometer was standardized, and a spectrum of the head solution was drawn against the effluent from the column. If the ratio (absorbance at 226 nm)/(absorbance at 301 nm) lay outside the range 0.48 to 0.52, the run was abandoned. Otherwise, the flow of xanthate solution was started, and xanthation commenced. At the same time, the recording was started of the change in absorbance due to passage through the column. Flowrates of 1.0

ml/min were used, except in runs where it was desired to test the effects of flowrate. The reaction was followed for some 20 to 40 hr. During this time the pH value was noted at intervals. At the end of the reaction period the standardization of the spectrophotometer was checked. The galena sample was washed, dried, and weighed, and its surface area was determined by the BET method with krypton as the absorbate.

From the areas under the recorded plot of difference in absorbance against time, the quantities of xanthate abstracted from solution during different time intervals were calculated. Corrections were made for the dead volume and the dead time of the apparatus on the assumption of plug flow. The error involved in this assumption is appreciable only during the first 10 to 20 min of reaction.

Under the conditions most commonly used (20 g of galena, specific area 425 cm^2 g^{-1}, xanthate solution concentration 3.12×10^{-5} M), the sensitivity of the apparatus was such that a reaction involving 5×10^{-8} mol of xanthate, which is equivalent to less than 1% of a hypothetical monolayer, was readily detectable.

RESULTS AND DISCUSSION

General Characteristics

Figure 2 shows typical experimental plots of the variation of rate of reaction with time. In a flow experiment the ultimate maximum rate of abstraction of xanthate from solution is determined by the concentration of the reagent in solution. Curves (i) and (ii) represent cases in which for some time the system operated at this maximum rate, i.e., in which the rate of reaction was great enough to denude the solution completely of xanthate. Under such "starvation conditions" the observed rates are determined only by the rate at which xanthate is made available at the surface and therefore are valueless as indicators of the characteristics and mechanism of the surface reaction. In the absence of oxygen pretreatment of the sample, the reaction rate passes through a minimum in the first 25 min after the flow of xanthate solution has started. The depth of the minimum varies inversely with the oxygen concentration of the xanthate solution. It appears that a period of induction is necessary before the reaction attains its maximum value. The experimental technique employed in this work is not suitable for the study of the induction period. Because of the dead volume of the apparatus and the fact that all parts of the sample are not brought

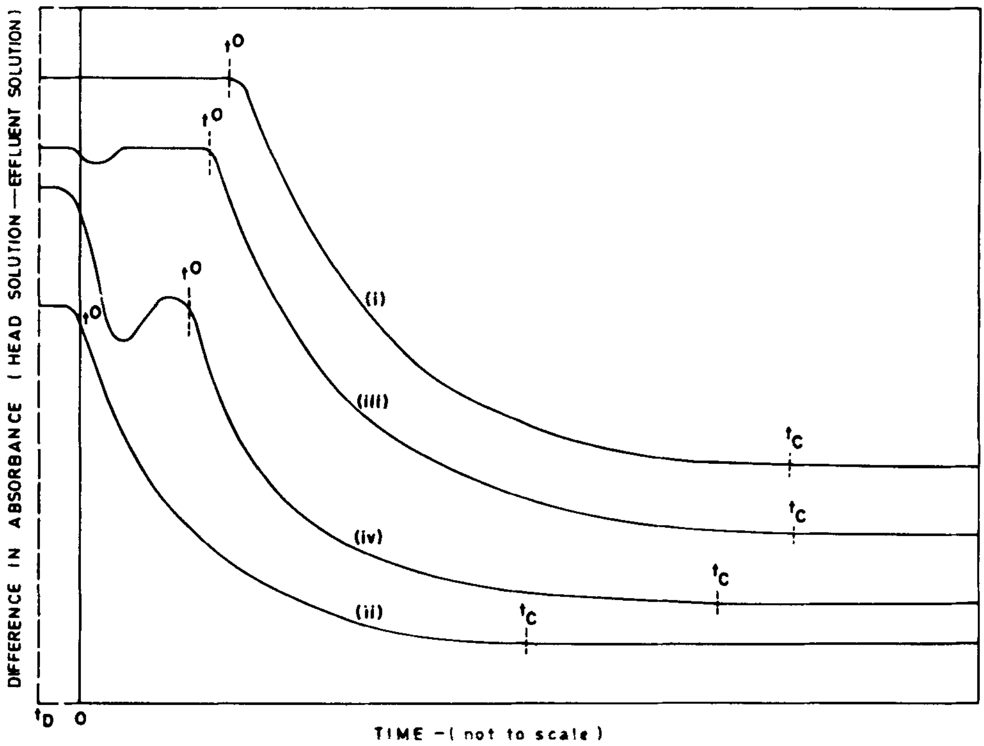

FIG. 2. Change in the difference between the absorbance of head solution and the absorbance of effluent solution with time. The time scale has been distorted to emphasize the earlier stages. (i) and (ii): Sample pretreated with oxygen-containing solution. (iii) and (iv): no oxygen pretreatment. (i) and (iii): High oxygen concentration; (ii) and (iv): lower oxygen concentration.

into contact with the reagent at precisely the same time, the observations recorded during this period lack definition. Therefore, in the quantitative interpretation of results, it was necessary to exclude from consideration the reaction occurring within the period, t°, in which the observed rate is influenced by either induction effects or reagent starvation, or both.

In most respects the behavior observed confirmed the observations of the preliminary investigation (*6*). When galena freed from surface oxidation products came into contact with oxygen-free xanthate solution, no reaction could be detected at any pH value within the range tested. This means oxygen is an essential participant of any reaction that can take place between xanthate and galena between pH 7 and 11. When unoxidized galena was exposed to xanthate solutions containing dissolved oxygen, there was an initial induction period of a zero or a relatively low rate of reaction, as evidenced by the minima in curves (iii) and (iv) of Fig. 2. Thereafter, a reaction rate was established that declined regularly with time until it became more or less constant at some finite value. When the galena was pretreated with oxygen-containing solutions before being exposed to xanthate, the observed behavior differed qualitatively only in that it showed no induction effects. In this respect this work differs from the preliminary investigation in which pronounced induction effects were observed both when the mineral was pretreated with oxygen and when it was not. These observations are consistent with the conclusions that, for reaction between xanthate and galena to occur, oxidized surface species as well as dissolved oxygen must be present, and that the reaction, once it starts, continues as long as the three reactants are kept in contact.

The reaction rate was independent of the rate of flow of solution, at least within the range of flowrates studied (0.5 to 5 ml/min). This independence indicates that the rate of abstraction of xanthate from solution is reaction-controlled and is not dependent on the concentration of xanthate in solution.

A major finding of the preliminary investigation was that, at pH 8, the reaction between xanthate, oxygen, and galena continues as long as they are maintained in contact. The results of the present work are in agreement with this finding in that they show that significant reaction occurs even after some days of contact at all the pH values tested. Similarly, the present work confirms that the quantity of xanthate abstracted increases exponentially with time. However, as is evident from the plot shown in Fig. 3, the exponential behavior obtains only for a limited period. In all cases, the plots of q against log t given in Fig. 3 show a linear portion that changes into a region of positive curvature at some particular time, t_e. Careful testwork established that the curvature could not be attributed to some deficiency in the experimental method, and that it reflected the inherent chemistry of the system.

The length of time during which the rate followed a logarithmic law was found to be completely independent of the concentration of oxygen in solution. However, it varied markedly with pH value. For instance, at pH 10, the period was about 120 min, and at pH 8, it was some five to ten times greater.

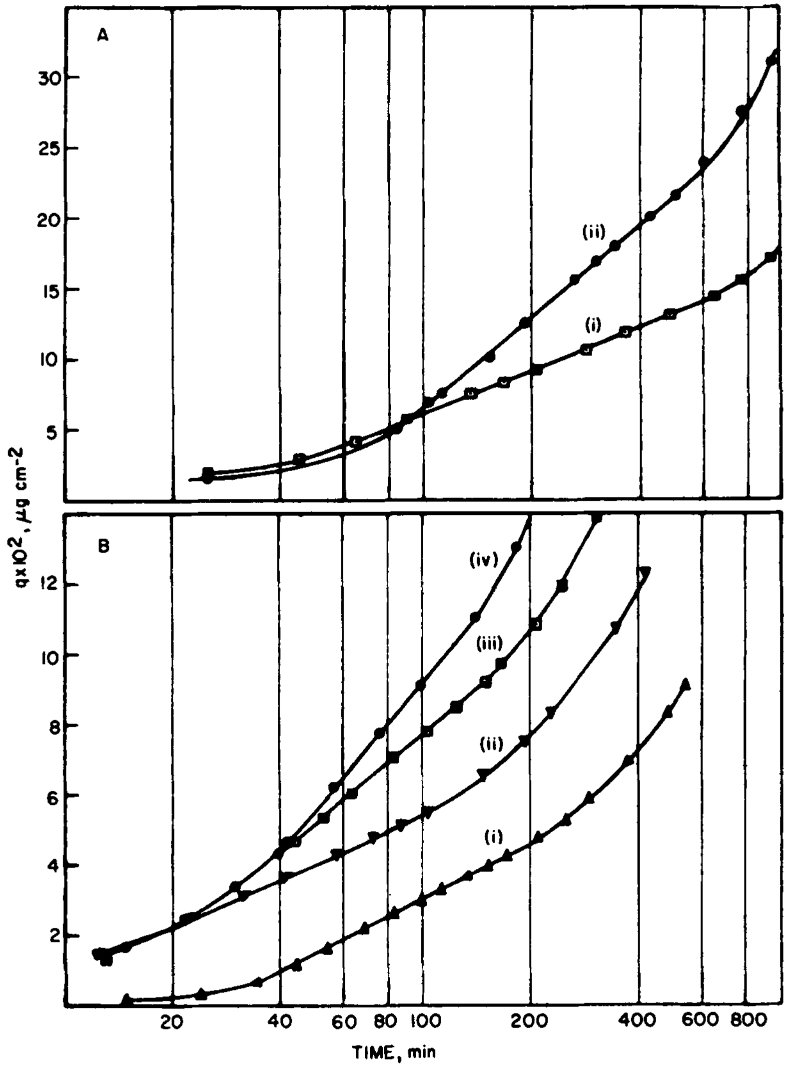

FIG. 3. Variation of the quantity of xanthate abstracted from solution with the logarithm of the time of contact. (A) pH 8.3; (i) $p = 36$ torr; (ii) $p = 131$ torr. (B) pH 10.0; (i) $p = 12.5$ torr; (ii) $p = 31.8$ torr; (iii) $p = 62.5$ torr; (iv) $p = 131$ torr.

In the preliminary investigation, experiments were carried out only at pH 8. Failure to observe the onset of nonlinearity of the semilogarithmic plot is thought to be due to the fact that the length of experimental runs was limited by the manually operated experimental apparatus.

The deterioration in the linearity of the semilogarithmic plot is associated with the fact that, after a relatively long time of contact, t_c, the rate of reaction becomes constant. t_c does not coincide with t_e but invariably occurs several hundreds of minutes later. The rate of reaction after t_c is dependent on the concentration of oxygen in solution (see below) and on the surface area of the galena sample. It is independent of the concentration of xanthate as long as this is greater than the "starvation" concentration.

To account for these observations, the following theory is proposed:

(a) Two distinct types of reaction are responsible for the abstraction of xanthate from solutions in contact with galena in the presence of oxygen.

(b) The first of these predominates until t_e. This is a chemisorption reaction whose rate is dependent on the concentration of active sites, and therefore it decreases as the reaction proceeds.

(c) The second type of reaction predominates after t_c. It involves reactions between xanthate and oxygen at the surface to form products that are returned to the solution and therefore do not reduce the number of reaction sites and, thereby, the rate of reaction.

(d) In the interval between t_e and t_c both types of reaction make a significant contribution to the overall rate of removal of xanthate from solution.

In this paper the two reactions are designated the "adsorption reaction" and the "oxygenation reaction," respectively.

The Effect of the Partial Pressure of Oxygen at a pH Value of 10

General. Solutions at pH 10 were used in the quantitative study of the effect of oxygen concentration on the reactions between galena, oxygen, and xanthate. A number of factors favored the choice of this pH value. First, at pH 7 or less, complications were found to arise because the rate of the hydrolytic decomposition of xanthate becomes appreciable. Second, it was felt that the region about pH 8 should be avoided because the work of Mellgren (*16*) indicated that a transition between two types of behavior might take place there. Third, it was important to work below the pH value at which the solubility of lead as the plumbite becomes appreciable. Finally, it was thought to be desirable that the one set of experiments should furnish information on both the oxygenation and the adsorption reaction. At pH 10 the relative lengths of the different stages were such as to allow both reactions to be studied conveniently.

The reproducibility of experiments in which the galena was pretreated with oxygen-containing solutions before the introduction of the xanthate–oxygen solutions was very much lower than those in which the pretreatment was omitted. A similar observation was made by Eadington (*25*), who found that the action of dissolved oxygen on freshly prepared samples of lead sulfide was very variable: not only were the initial rates of oxidation and the extent of oxidation irreproducible, but the induction period before sensible reaction occurred varied between 0.5 and 40 hr. Thus all experiments in the series were performed without an oxidizing pretreatment.

Table 1 shows the results of individual runs using solutions having oxygen partial pressures between 12.5 and 313 torr (1.67×10^3 to $4.18 \times 10^4\ N\ \mathrm{m}^{-2}$). Mean values and standard deviations of the various experimental parameters at each of the different levels of activity of oxygen are shown in Table 2.

The indifferent reproducibility of the experimental data can be ascribed only to some unrecognized variable or to the inadequacy of the sample preparation. It necessitated the use of statistical methods for the identification of the functional relationships between the experimental parameters and the partial pressure of oxygen. Table 3 gives the results of regression analysis of the experimental data by the method of least squares.

The Adsorption Reaction. As the graphs in Fig. 3 show, the plot of q, the quantity of xanthate abstracted from solution, against t, the time elapsed since contact started, is a straight line for a certain period. Thus, within this region

$$q = g \log kt \tag{1}$$

where g is the slope of the line and k is a constant.

The period before the start of semilogarithmic behavior is known to be one of relatively low or zero rate. In the absence of definite information regarding the reaction during this period, the simplest assumption is made, namely that the rate of reaction is a maximum at time t_i and zero at all times less than t_i, i.e., $q_{t_i} = 0$ and

$$\left(\frac{dq}{dt}\right)_{t_i} = \left(\frac{dq}{dt}\right)_{q=0} \tag{2}$$

TABLE 1

Experimentally Determined Reaction Parameters for Individual Runs

	Adsorption reaction					Oxygenation	
Partial pressure of O_2 (torr)	t^0 (min)	t_i (min)	g (μg cm^{-2} $\times 10^2$)	a (μg cm^{-2} min^{-1} $\times 10^3$)	q_c (μg cm^{-2} $\times 10^2$)	t_c (min)	R_f (μg cm^{-2} min^{-1} $\times 10^4$)
12.5	40	26	4.98	0.83	5.91	400	1.11
	40	28	3.90	0.61	4.60	148	1.03
	45	28	3.92	0.61	5.23	680	1.09
	20	13	3.01	1.02	4.49	400	1.08
	25	16	3.52	0.94			
31.8	17	8	4.83	2.58	8.95	581	1.81
	13	7	4.50	2.84	9.31	808	1.72
	17	10	4.63	2.01	8.52	695	1.41
	15	9	3.74	1.93	7.20	710	1.23
46.9	20	13	4.76	1.58			
	25	9	4.19	1.99	8.78	1140	2.51
	15	14	4.35	1.35	8.31	1140	1.84
	10	11	3.95	1.58	7.42	820	2.08
	20	10	3.77	1.64	7.54	1000	2.14
62.5	20	12	7.95	2.84			
	3	13	8.36	2.90	4.6	700	3.42
	25	10	6.11	2.78	12.4	1030	1.92
	10	7	4.87	3.77	9.49	500	1.98
	15	10	7.15	3.38	14.6	1020	2.02
	20	9	5.75	3.05			
	13	9	5.92	2.50	11.5	900	1.72
131	35	15	11.17	3.26	19.7	860	3.14
	11	19	10.64	2.38	19.1	1200	3.32
	3	19	11.31	2.80			
	13	18	11.20	2.69	18.8	860	3.56
	3	20	10.29	2.45			
	0	18	11.46	2.81	19.0	800	3.71
313	0	18	10.09	2.38			
	13	15	10.74	3.06			3.84
	0	10	10.64	4.59	21.4	1025	5.33
	14	15	10.06	2.92			3.40
	19	13	11.16	3.66			7.51
	24	19	11.77	2.72	20.0	940	4.39
	40	14	10.72	3.30			4.61

TABLE 2

Mean Values and Standard Deviations of Reaction Parameters at Different Levels of p

Parameter	p (mm)	Mean	Number of replicates	Standard deviation	Coefficient of variation (%)
g (μg cm^{-2} × 10^2)	12.5	3.87	5	0.65	16.8
	31.8	4.42	4	0.41	9.3
	46.9	4.20	5	0.34	8.1
	62.5	6.59	7	1.17	17.8
	131	11.01	6	0.41	3.7
	313	10.74	7	0.55	5.1
a (μg cm^{-2} min^{-1} × 10^3)	12.5	0.80	5	0.167	20.8
	31.8	2.34	4	0.38	16.4
	46.9	1.63	5	0.21	12.7
	62.5	3.03	7	0.39	12.9
	131	2.73	6	0.29	10.5
	313	3.23	7	0.67	20.7
q_c (μg cm^{-2} × 10^2)	12.5	5.06	4	0.57	11.3
	31.8	8.50	4	0.80	9.4
	46.9	8.01	4	0.56	7.0
	62.5	12.5	5	1.9	15.8
	131	19.1	4	0.3	1.8
	313	20.7	2	0.7	3.3
R_f (μg cm^{-2} min^{-1} × 10^4)	12.5	1.08	4	0.03	2.7
	31.8	1.54	4	0.23	15.0
	46.9	2.14	4	0.24	11.3
	62.5	2.21	5	0.62	27.8
	131	3.43	4	0.22	6.4
	313	4.85	6	1.34	27.6

is a maximum. Therefore

$$k = 1/t_i$$

i.e.,

$$q = g \log (t/t_i) \tag{3}$$

It is readily shown that

$$\frac{dq}{dt} = \frac{g}{2.303t_i} \exp\left(\frac{-2.303q}{g}\right) \tag{4}$$

which is of the same form as the Elovich equation,

$$\frac{dq}{dt} = ae^{-\alpha q} \tag{5}$$

TABLE 3

Results of Regression Analysis

Parameter Y	Variable x	p range (torr)	Regression equation $Y = Mx + C$			Coefficient of correlation
			M	C	Standard error	
$\log g$	$\log p$	12.5–131	0.453	−2.00	0.969×10^{-1}	0.895
		12.5–313	0.384	−1.89	0.914×10^{-1}	0.884
$\log a$	$\log p$	12.5–131	0.548	−3.62	0.127	0.820
		12.5–313	0.387	−3.37	0.134	0.791
$\log q_c$	$\log p$	12.5–131	0.560	−1.87	0.669×10^{-1}	0.941
		12.5–313	0.497	−1.84	0.721×10^{-1}	0.939
$\log R_f$	$\log p$	12.5–131	0.485	−4.51	0.731×10^{-1}	0.910
		12.5–313	0.468	−4.49	0.830×10^{-1}	0.933
$\log t_i$	$\log p$	12.5–131	-0.783×10^{-1}	1.24	0.172	−0.148
		12.5–313	0.197×10^{-2}	1.12	0.161	0.549×10^{-2}
$\log t_c$	$\log p$	12.5–131	0.420	2.16	0.152	0.669
		12.5–313	0.218	2.36	0.161	0.578
g	$\sqrt{p}$	0–131	0.905×10^{-2}	-0.286×10^{-2}	1.11×10^{-2}	0.946
		0–313	0.626×10^{-2}	1.12×10^{-2}	1.54×10^{-2}	0.913
a	$\sqrt{p}$	0–131	0.267×10^{-3}	-0.187×10^{-3}	0.589×10^{-3}	0.849
		0–313	0.172×10^{-3}	0.679×10^{-3}	0.714×10^{-3}	0.794
q_c	$\sqrt{p}$	0–131	1.62×10^{-2}	-0.671×10^{-2}	1.45×10^{-2}	0.971
		0–313	1.36×10^{-2}	0.572×10^{-2}	2.00×10^{-2}	0.953
R_f	$\sqrt{p}$	0–131	0.294×10^{-4}	-0.010×10^{-4}	0.336×10^{-4}	0.954
		0–313	0.275×10^{-4}	0.080×10^{-4}	0.658×10^{-4}	0.922

This empirical relationship has been found to apply very generally to the chemisorption kinetics of solid–gas systems and to describe gaseous oxidation of many metals (*26*). Despite this formal similarity, any extension of the analogy between the adsorption reaction observed here and the gas–solid chemisorption should be treated with caution. With gas–solid reactions, Elovich kinetics start immediately the reactants are brought into contact or after a very short period of very rapid reaction (*26*). Thus in the integration of Eq. (5), the lower limit used is either $q = 0$ at $t = 0$, or $q = q_0$ at $t = 0$ (where q_0 is the quantity of gas adsorbed instantaneously).

It should be noted that the adsorption of xanthate by galena in the presence of oxygen is fully described by two parameters, g and t_i. Thus the rate of reaction at any time, t, is given by

$$\left(\frac{dq}{dt}\right)_t = \frac{g}{2.303t}$$

and initial rate of reaction is

$$a = \left(\frac{dq}{dt}\right)_{ti} = \frac{g}{2.303t_i}$$

Some measure of the extent and duration of the adsorption reaction is provided by a consideration of t_c, the time at which adsorption becomes a negligible contributor to the abstraction of galena, and q_c, the corresponding adsorption.

The values of t_i shown in Table 1 vary from 6.5 to 28.3 min. Within this range no regularity can be discerned, and the correlation coefficients between log t_i and log p are close to zero. It may be concluded that the induction period is either independent of the oxygen concentration or is much more sensitive to other variables not controlled by the particular experimental technique used.

The results of the regression analyses (Table 3) show that there is a strong positive correlation between each of the parameters g, a, and q_c on the one hand, and the partial pressure of oxygen on the other. Furthermore, the magnitude of these parameters varies as the square root of the partial pressure. If the results of the analyses over the ranges $0 < p < 131$ torr are compared, it is seen that the introduction of data at 313 torr leads to a pronounced decrease in the slopes of the logarithmic regression equations. Reference to Table 2 shows that the parameters change little as p increases from 131 torr. A Student's t test indicated that the differences between the measured values of

g, a, and q_c at 313 torr and those predicted by extrapolation of the regression equation for $0 < p < 131$ torr were significant even at the 1% level. Table 3 also shows that the values of the constants, C, of the regression equations in $p^{1/2}$ do not differ significantly from zero.

Thus it may be concluded that the following relationships hold for $0 < p < 131$ torr at pH 10 and a temperature of 25°C:

$$g = 9.1 \times 10^{-3}p^{1/2}$$
$$q_c = 1.62 \times 10^{-2}p^{1/2}$$
$$a = 2.67 \times 10^{-4}p^{1/2}$$

By substitution of the first of these into Eq. (3),

$$q = 9.1 \times 10^{-3}p^{1/2} \log (t/t_i) \tag{6}$$

The Oxygenation Reaction. Observations of the oxygenation reaction were carried out over periods as long as 1500 min, and during this period the rate of reaction, R_f, per unit area of solid remained sensibly constant. There is no way of predicting what course the interaction would take at still longer times of contact. Discussion of the quantitative aspects of the reaction must, therefore, be confined to the parameters R_f and t_c.

The regression analysis of log t_c on log p shows that there is some direct relationship between the partial pressure of oxygen and the time at which the reaction rate becomes constant. However, because of the low value of the correlation coefficient and the extreme variability of the results that it reflects, it is not worth while pursuing the analysis any further.

Table 3 shows that the rate of the oxygenation reaction is directly dependent on the partial pressure of oxygen. Like the parameters defining the rate and extent of adsorption, R_f shows a high correlation with $p^{1/2}$, and the regression line passes through the origin. On the other hand, the correlation holds throughout the range of pressures considered: the measured value of R_f at 313 torr differs only at the 45% level of confidence from that predicted by the regression equation derived for $0 < p < 131$ torr.

Thus,

$$R_f = 2.75 \times 10^{-5}p^{1/2}$$

for $0 < p < 313$ torr at pH 10 and a temperature of 25°C.

Spectrophotometry of the Effluent Solutions

The presence of solutes other than potassium ethyl xanthate in the effluent solutions from the galena column was revealed by differential spectrophotometry. When the contribution of the xanthate was eliminated, spectra such as those shown in Fig. 4, curves (i) and (ii), were obtained. In no instance was any absorption at wavelengths greater than 240 nm detected. It is apparent that the absorption is due to the presence of some soluble product of the reaction between xanthate, oxygen, and the mineral surface.

Experimental difficulties and uncertainties made it impossible for the differential spectra to be used in a quantitative way. However, several qualitative observations are of interest.

No differential spectrum was detected during the initial stages of reaction. Significant absorptions were obtained only after a run had been in progress for some time. The times were of the order of hours and appeared to vary inversely with the concentration of oxygen in solution. The intensity of the absorption increased regularly with time after it was first detected until it reached a maximum value at which it became constant.

The spectra showed a single absorption maximum at 221 to 222 nm. The shape of the peak was not completely reproducible. As the examples in Fig. 4 show, the sharpness of the peak varied. This variation was mainly associated with a change in the rate of decline in absorption on the high-energy side of the maximum.

It was not found possible to identify positively the substance responsible for the observed spectrum. The ultraviolet spectra of several substances that were envisaged as possible products of reaction were determined. The positions of their absorption peaks are shown in Table 4. It is clear that all the possibilities but three (thiosulfate, sulfide, and monothiocarbonate) can be rejected without further discussion. Of these three, thiosulfate is the one whose presence in these reaction solutions is the most to be expected and the most easily accounted for. It has been shown that thiosulfate is one of the principal products of the oxidation of galena by aqueous solutions of oxygen (*25–27*), and that xanthate can adsorb at the galena surface by exchanging with adsorbed thiosulfate (*16*). However, there is no doubt that the absorption maximum observed in the effluent solutions is significantly different from 215 nm, the wavelength at which thiosulfate absorbs. Furthermore, if thiosulfate were being released into solution as a result of the ion-exchange adsorption of xanthate at the

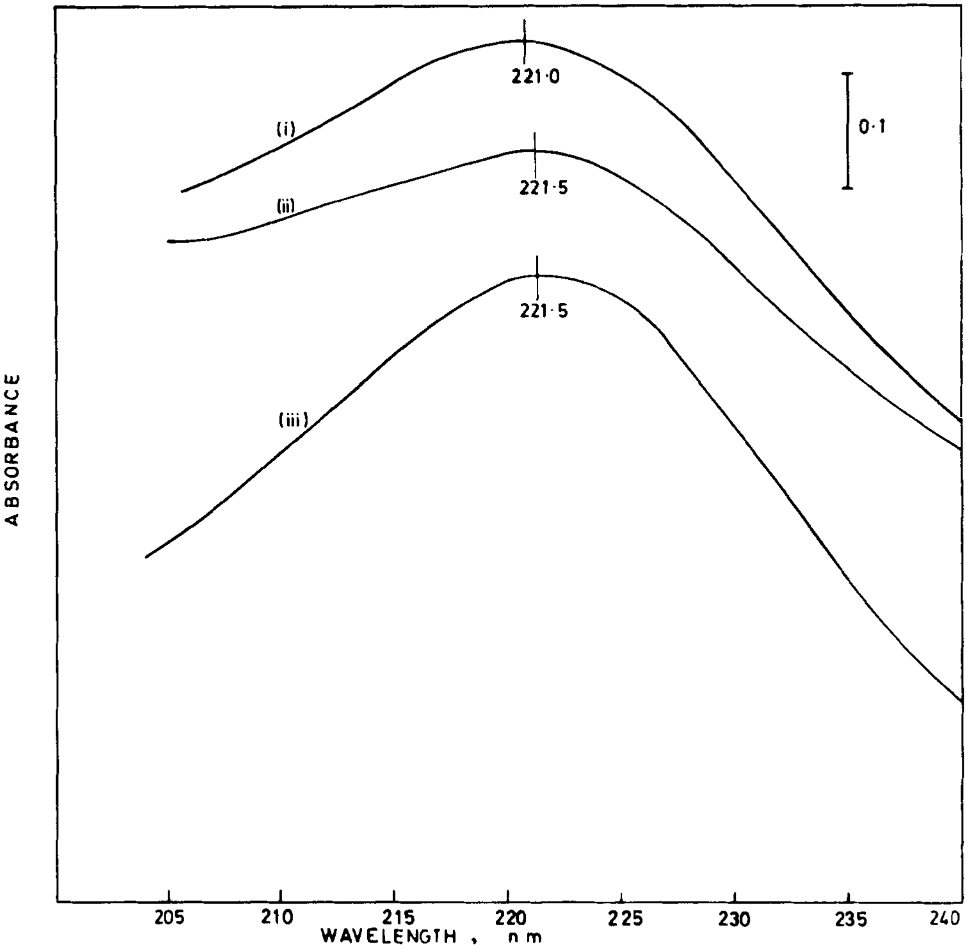

FIG. 4. Ultraviolet absorption spectra (i) and (ii): Differential spectra of effluent solutions at a pH value of 10, compensated for the absorption of the xanthate content. (iii) Potassium ethyl monothiocarbonate at a pH value of 10. The peak absorbances of these spectra are equal. Their base lines have been staggered for clarity.

surface, it would be found in the effluent solutions during the early stages of the reaction, when the adsorption reaction proceeds at its maximum rate, rather than at the later stages. The claims that sulfide is a possible reaction product are less strong than those of thiosulfate, for it has long been accepted that xanthate will not exchange with

TABLE 4

Ultraviolet Adsorption Maxima of Possible Products of the Oxygenation Reaction

	Absorption maxima (nm)
Sodium thiosulfate, pH 10	215
Sodium sulfide, pH 10	229
Potassium monothiocarbonate, pH 10	221
Potassium trithiocarbonate, pH 10	331, 301, 235 to 220, 206
Dixanthogen[a]	226, 285
Carbon disulfide[a]	206
Lead ethyl xanthate, pH 10[a]	None at wavelengths greater than 205 nm
Lead hydroxide, pH 10[a]	
Lead sulfate, pH 10[a]	

[a] Spectra refer to solutions obtained when insoluble materials were contacted with water at a pH value of 10.

sulfide at the surface of a mineral. In this instance, too, the difference between the observed absorption maximum and the characteristic absorption of the sulfide ion is significant.

The single absorption maximum of the spectrum of the ethyl monothiocarbonate ion occurs at 221.5 nm, which is identical with the maximum of the spectrum of the effluent solution. However, the spectra are not identical in other results. Even the sharper of the spectra of effluent solutions shown in Fig. 4 [spectrum (i)] is less sharp than the monothiocarbonate spectrum [Fig. 4, curve (iii)] and declines less steeply on the high-energy side. Therefore, it is not possible to ascribe the observed spectra solely to the presence of the monothiocarbonate ion. It is more likely that they are made up of the monothiocarbonate spectrum with minor contributions from other species such as thiosulfate and plumbite. The idea that there is more than one species contributing to the observed spectrum is favored by the observed irreproducibility and the pronounced asymmetry of peaks such as that in Fig. 4(ii). The presence of ethyl monothiocarbonate could be accounted for by the substitution reaction.

$$CH_3CH_2OCS_2^- + \tfrac{1}{2}O_2 \rightarrow CH_3CH_2O_2CS^- + S^\circ$$

The same reaction has been proposed recently (*28*) to account for a reaction between oxygen and xanthate in homogeneous aqueous solution. In that case, the reaction was promoted by the presence of alkyltrimethyl ammonium halides in solution; in the present case, the facts would suggest that the reaction is promoted by the presence of a xanthate–galena surface.

Plausible though this explanation may be, the evidence available by no means fully proves it. Many sulfur-containing compounds exhibit strong absorption maxima in the region 215 to 230 nm. Therefore, the mere matching of a spectrum with that of any particular compound hardly represents an unequivocal identification.

It is important to note that, even in the absence of a positive identification of the solutes responsible for the spectra of the effluent solutions, the spectrophotometric work does make one definite contribution to the understanding of the interactions between xanthate, galena, and oxygen. It provides positive proof that a reaction giving rise to a soluble rather than an adsorbed product can take place in this system—a proposition that can only be inferred from the studies of the kinetics of xanthate abstraction from solution. It agrees with the kinetic work that this "oxygenation reaction" is initiated only some time after the three components of the system are brought into contact.

The Effect of pH

Although no systematic study of the effect of pH was undertaken, a number of runs were performed at pH values other than 10, i.e., between 8 and 11. The rate of both the absorption and the oxygenation reaction at these pH values, are strongly dependent on the partial pressure of oxygen. The adsorption reaction obeys the Elovich equation, and its reaction parameters vary with a fractional power of p. Experimentation at pH 11 is complicated by the dissolution of lead in the plumbite form. An increase in the pH value results in a very marked decrease in the rate of adsorption. The effect of pH, if any, on the oxygenation reaction is much less pronounced.

Reaction Mechanism

In the absence of data on the stoichiometry of the reaction and on the quantitative effects of pH, it is impossible to deduce the detailed mechanisms of the reactions with any confidence. However, if this is borne in mind, it is instructive to consider a reaction scheme that embodies the available information, for in this way the broader implications of the experimental observations can be made clear.

The best-established conclusions of the experimental work are the following:

(a) Two types of reaction between xanthate and oxygen take place at the galena surface.

(b) The first of these results in the adsorption of xanthate; the second gives rise to soluble products.

(c) The adsorption reaction obeys an exponential rate law.

(d) Both reactions are zero order with respect to the concentration of xanthate.

(e) The rate of the oxygenation reaction and the parameters g, a, and q_c of the absorption reaction vary directly with the square root of the partial pressure of oxygen.

The finding that the rates of reaction are independent of the concentration of xanthate indicates that xanthate does not participate in the rate-determining step of the reaction. Dependence on $p^{1/2}$ suggests that oxygen acts through the formation of atomic oxygen. It appears that the reactions take place in two distinct stages: first, oxygen reacts with the surface to produce an intermediate species, and then the intermediate reacts with xanthate to form the final products of the reaction. The first stage is very much slower than the second and is rate-determining. In addition, certain side reactions may take place that do not affect the rate-determining step. For instance, the only possible product of the oxidation of sulfide in the rate-determining step is elementary sulfur. However, it is quite possible that this is not a final product but is further oxidized in a subsequent fast reaction. The following reactions will be considered:

$$2\mathbf{B} + \mathrm{O}_2 \rightleftharpoons \mathbf{B}_2\text{—}\mathrm{O}_2 \qquad (7)$$

$$\tfrac{1}{2}\mathbf{B}_2\text{—}\mathrm{O}_2 + \mathbf{A} \rightleftharpoons \mathbf{A}\text{—}\mathrm{O} + \mathbf{B} \qquad (8)$$

$$\mathbf{A}\text{—}\mathrm{O} + \mathrm{H_2O} \rightarrow \left|\begin{matrix}\mathrm{Pb}^{2+}\\ \mathrm{S}^\circ\end{matrix}\right. + 2\mathrm{OH}^- \qquad (9)$$

$$\tfrac{1}{2}\mathbf{B}_2\text{—}\mathrm{O}_2 \rightarrow \mathbf{B}\text{—}\mathrm{O} \qquad (10)$$

$$\mathbf{A} + \mathbf{B}\text{—}\mathrm{O} \rightleftharpoons \mathbf{A}\text{—}\mathrm{O} + \mathbf{B} \qquad (11)$$

$$\left|\begin{matrix}\mathrm{Pb}^{2+}\\ \mathrm{S}^\circ\end{matrix}\right. + 2\mathrm{X}^- \rightleftharpoons \left|\begin{matrix}\mathrm{PbX}_2\\ \mathrm{S}^\circ\end{matrix}\right. \qquad (12)$$

$$\mathbf{B}\text{—}\mathrm{O} + \mathrm{X}^- \rightleftharpoons \mathbf{B}\text{—}\mathrm{S}^\circ + \mathrm{CH_3CH_2O_2CS}^- \qquad (13)$$

The symbol | is used to denote the surface of the solid. Square brackets denote the activity of a species, and X the xanthate radical. **A** and **B** denote two types of surface sites.

As part of this scheme, the following assumptions are made:

(a) There are two types of sites of differing reactivity at the surface.

(b) Sites **B** can take part in adsorption and dissociation of oxygen

[Reactions (7) and (10)], and their activity is not affected as reaction proceeds.

(c) Only at **A** sites is the electron-transfer reaction [Reaction (9)] completed after dissociation of oxygen.

(d) Reactions (9) and (10) are rate determining.

(e) $K_{11} \gg 1$, $k_{11} \gg k_{10}$, $k_{11} > k_{13}$.

There is considerable uncertainty as to the reactions that take place during the second, rapid stage of the oxygenation reaction. Several reactions may well be taking place simultaneously. The only restriction made by the experimental evidence is that at least one of these should lead to a soluble product that absorbs at 221 nm, such as ethyl monothiocarbonate. The formation of ethyl monothiocarbonate by substitution [Reaction (13)] is included in the scheme as a suggested component of the fast stage of oxygenation rather than as a unique or necessary part of it.

For the absorption reaction, because Reaction (9) is rate-determining,

$$
\begin{aligned}
-\frac{d[\mathrm{X}^-]}{dt} &= 2\,\frac{d\left[\begin{array}{|l}\mathrm{Pb}^{2+}\\ \mathrm{S}^\circ\end{array}\right]}{dt} \\
&= 2k_9K_7^{1/2}K_8p^{1/2}[\mathbf{A}] \qquad (14)
\end{aligned}
$$

At this juncture it is necessary to consider how the concentration of active sites, [**A**], varies with q, the extent of the reaction. Since chemisorption has been little studied in liquid–solid systems, reference must be made to the better established field of gas–solid chemisorption.

In physical adsorption it is found that the activity of the surface is proportional to the area that is not covered, and that the number of sites incapacitated per unit adsorption is constant and independent of Q, i.e.,

$$N = N_0 - Q \qquad \text{and} \qquad -dN/dQ = \text{constant} \qquad (15)$$

where N_0 is the initial concentration of sites, N is the concentration of sites remaining at any time, and Q is the concentration that has been filled at that time. The assumption that the same simple characteristics will apply to chemisorption is not permitted. Where chemisorption obeys a logarithmic rate law, the relationships found are (*26*):

$$N \neq N_0 - Q \qquad (16)$$

$$-dN/dQ = \alpha N \qquad (17)$$

This means that sites disappear in numbers exceeding occupancy.

On integration, Eq. (17) gives

$$N = N_0 e^{-\alpha Q}$$

The analogous equation for the PbS–xanthate–oxygen system is

$$[\mathbf{A}] = [\mathbf{A}]_{t_i} e^{-\alpha q} \tag{18}$$

Substitution in Eq. (14) gives

$$-\frac{d[\mathrm{X}^-]}{dt} = 2k_9 K_7^{1/2} K_8 p^{1/2} [\mathbf{A}]_{t_i} e^{-\alpha q}$$

If all the xanthate abstrated from solution adsorbed at the surface, this becomes

$$dq/dt = 2k_9 K_7^{1/2} K_8 p^{1/2} [\mathbf{A}]_{t_i} e^{-\alpha q} \tag{19}$$

which is of the same form as the Elovich equation [Eq. (5)] and which will integrate to the form of the relationship observed experimentally [Eq. (6)]. A comparison of Eqs. (19) and (5) shows that

$$a = 2k_9 K_7^{1/2} K_8 [\mathbf{A}]_{t_i} p^{1/2}$$

Thus the initial rate of reaction is determined by the condition of the surface and by the concentration of oxygen. This illustrates one of the features that has been observed in other systems obeying Elovich kinetics (*26*): ". . . the validity of the Elovich equation, particularly in systems where the pressure of the adsorbable gas varies considerably during the course of the adsorption, indicates that of the two reactants —gas and solid—it is only the mass action of the latter that determines the rate at each moment. The mass action of the gas determines the initial rate, *a*."

In the oxygenation reaction, it can be shown that

$$R_f = \frac{d[\mathbf{B}\text{—O}]}{dt} = k_{10} K_7^{1/2} [\mathbf{B}] p^{1/2} - k_{11} [\mathbf{B}\text{—O}][\mathbf{A}]_{t_i} e^{-\alpha q} \tag{20}$$

Since Reaction (10) is rate-determining, $k_{10} \ll k_{11}$. Thus the rate of this reaction becomes appreciable only when the influence of the second term begins to be reduced by the progress of the adsorption reaction (increase in q, shortage of **A**). At high values of q, R_f is independent of time and directly proportional to $p^{1/2}$.

A relationship can now be written to describe the rate of change in xanthate concentration over the whole course of the interaction at pH 10, and $0 < p < 131$ torr.

$$-\frac{d[\mathrm{X}^-]}{dt} = \frac{dq}{dt} + R_f$$
$$= 2k_9K_7^{1/2}K_8p^{1/2}[\mathbf{A}]_{t_i}e^{-\alpha q} + k_{10}K_7^{1/2}[\mathbf{B}]p^{1/2} - k_{11}[\mathbf{B}\text{—O}][\mathbf{A}]_{t_i}e^{-\alpha q} \tag{21}$$

At high values of q, $dq/dt \ll R_f$. $-d[X^-]/dt = R_f$, and does not vary with time.

Thus the proposed mechanism is successful in accounting for the observed variation of the rate of xanthate abstraction with time, and for the observed oxygen dependence. It leaves one important aspect of the interaction unexplained, viz., the induction period. As was mentioned above, the experiments undertaken in this investigation were unsuited to the study of the induction period. Thus there were no data on which to base an explanation for the occurrence of this phenomenon. One can only speculate that, during this period, active sites are generated by the action of oxygen on the surface.

In the formulation of the proposed reaction mechanism it was not essential to consider the possibility of the formation of dixanthogen as no evidence for its formation was obtained during the course of the work. It will be recalled that the differential spectra of effluent solutions showed no sign of the presence of dixanthogen at the surface. However, the possibility of the formation of the compound cannot be entirely discounted because of previous findings that it can be co-adsorbed with xanthate. It can be accounted for quite satisfactorily by the proposed mechanism as long as the assumption can be made that it would result from fast reactions involving the intermediates, **A**—O and **B**—O.

It is of interest to consider what the mechanism is that gives rise to the exponential decrease in rate of adsorption with quantity adsorbed. In the field of gas–solid chemisorption the Elovich equation has been found to be so widely applicable that it is considered futile to attempt to explain it in terms of a unique mechanism (*26*). Mechanisms such as surface and bulk diffusion, activation and deactivation of catalysis, and semiconductor barrier effect have all been shown to be consistent with a logarithmic law. The adsorption reaction encountered here is more complex than many of those dealt with in gas–solid studies in that there are two adsorbing species, oxygen and xanthate. Nevertheless, it is possible, at least qualitatively, to show that the observations made can be explained by a surface barrier theory. The net effect of the adsorption reaction is the replacement of one sulfide ion in the surface lattice by two xanthate ions and, perhaps, a sulfur atom. Xanthate and sulfur are both better electron acceptors than the sulfide ion is. Thus, one would expect the surface to become more *p*-type as a result of the reaction, and therefore the energy barrier to the chemisorption of oxygen to be raised.

Comparison with Other Work

Although the results of the present investigation confirm the finding of Gaudin and Finkelstein (*6*) that the interaction between galena, xanthate, and oxygen is a continuing one that does not reach equilibrium or a limit with the progress of time, they come into conflict with a large body of previous work. In a recent publication, Mellgren (*29*) suggests that the disagreement with his adsorption work (*30*) may be ascribed to differences between the two investigations in the nature of the oxidized species present at the surfaces. There is little doubt that this is an important factor, and that a knowledge of the oxidized species present is necessary to any complete understanding of the system. Indeed, it is likely that certain of the observed differences may be explained on this basis. However, it is not thought that the failure of the reaction to reach finality is one of these. Wottgen (*31*) has obtained this type of behavior in batch xanthating tests in which no special precautions were taken to remove the naturally occurring oxidized layers of the galena sample. As no attempt was made to eliminate carbon dioxide from the solutions or the air bubbled through them, it can be assumed that carbonates predominated among the oxidized species, and therefore that the galena surface was similar to that employed by Mellgren. Wottgen's tests were conducted at a pH value of about 6. This indicates that the continuing nature of the interaction is not associated with the use of alkaline conditions as has also been suggested (*29, 30*).

The present work shows that the adsorption of xanthate at unoxidized or sparingly oxidized galena surfaces involves the participation of oxygen in a reaction at the surface. This conclusion is inescapable because the observed kinetics are Elovichian and are governed by the square root of the activity of oxygen. These findings do not appear reconcilable with the theory (*5*) that oxygen acts on xanthate in solution to give dixanthogen, which then adsorbs both as lead xanthate and as dixanthogen. This theory is based on the finding that xanthate does not adsorb at lead sulfide and copper surfaces on which a monolayer of oxygen has been chemisorbed. Viewed in the light of present knowledge that adsorption on such relatively clean surfaces requires the presence of significant concentrations of oxygen in solution, this evidence is insufficient to eliminate the possibility that oxygen acts at the surface.

On the other hand, it cannot be claimed that the type of mechanism proposed here, in which oxygen and xanthate interact more or less simultaneously at the surface, represents the only way in which xanthate can adsorb. The thermochemical work of Mellgren (*16*) leaves no room for doubt that xanthate can adsorb by a metathetical reaction when there are substantial quantities of oxidation products at the surface. Unless they are freshly ground, galena surfaces will always have accumulated such products; thus the metathetical reaction must be regarded as an important mechanism under industrial flotation conditions.

The results of the present work do nothing to resolve the controversy regarding the necessity for dixanthogen to be present before a surface becomes hydrophobic. Whereas no positive evidence was obtained to show that this compound was formed under the conditions of the experiments, its formation would in no way be inconsistent with the observations made.

One of the features of the mechanism proposed to account for the experimental observations is the proposition that elementary sulfur is one of the products of the rate-determining step of the adsorption reaction. This agrees with mechanisms proposed by Kitchener (*32*) and Bushell (*15*). It is also in harmony with the suggestion (*25*) that sulfur is always one of the products of the oxidation of PbS by dissolved oxygen. The suggestion that xanthate reacts at galena/lead–xanthate surfaces with the formation of ethyl monothiocarbonate has also been made previously. Fleming (*33*) observed that lead xanthate decomposes in solutions more alkaline than pH 9.8, and that lead sulfide is one of the products. He suggested the reaction

$$PbX_2 + 2KOH \rightarrow PbS + 2CH_3CH_2O_2CSK$$

but did not obtain direct evidence for the formation of the monothiocarbonate. Given a mechanism for regenerating lead xanthate from the lead sulfide product, this equation would be consistent with the mechanism proposed here for the oxygenation reaction. However, in other respects, Fleming's work accords less well with the present work, particularly in his finding that the threshold for this reaction is pH

9.8 and in his suggestion that all adsorbed xanthate is unstable under such conditions.

CONCLUSIONS

(a) Two types of reaction take place between xanthate and oxygen at a galena surface at pH values in excess of 8. The first reaction results in the adsorption of xanthate; the second gives rise to soluble products.

(b) When an initially oxidation-free surface is brought into contact with oxygen-containing solutions of xanthate, no reaction of xanthate is observed until after an induction period.

(c) The adsorption reaction obeys a logarithmic rate law, analogous to the Elovich equation, which applies to many gas–solid chemisorption reactions. The rate and extent of adsorption at any time are governed by the square root of the partial pressure of oxygen for $0 < p < 131$ torr. Within this range of partial pressures, at pH 10 and 25°C, the extent of adsorption at any time is given by

$$q = 9.1 \times 10^{-3} p^{1/2} \log (t/t_i)$$

(d) Once the adsorption reaction has been established, the rate of reaction is determined by the mass action of active sites. The activity of oxygen determines the initial mass action of the surface and hence the initial rate of reaction.

(e) The second type of reaction ("oxygenation") is responsible for the constant rate of reaction observed after several hours of contact between the surface and the reagents. One of the reaction products gives rise to an adsorption peak at 221 nm and may be ethyl monothiocarbonate.

(f) The rate of oxygenation varies with the square root of the partial pressures of oxygen in solution. At pH 10, 25°C, and $0 < p < 313$ torr,

$$R_f = 2.75 \times 10^{-5} p^{1/2}$$

(g) The rate-determining stages of both reactions involve atomic oxygen.

NOTATION

a	rate of reaction at time $t_i = g/2.303t_i$ (μg cm^{-2} min^{-1})
g	gradient of the linear region of the plot of q against $\log t$ (μg cm^{-2})
K_n	equilibrium constant for reaction number n
k_n	specific rate of reaction number n in forward direction

p	partial pressure of oxygen (torr)
q_t	quantity of xanthate that has been abstracted from solution in time t (μg cm^{-2})
R_f	final, constant rate of abstraction of xanthate from solution (μg cm^{-2} min^{-1})
q_c	extent of the adsorption reaction at time t_c (μg cm^{-2})
t^0	time during which the rate of abstraction of xanthate is governed by xanthate-starvation and induction effects (min)
t_c	time at which the observed reaction rate becomes constant (min)
t_i	induction time (min)
t_e	time after which the overall reaction no longer follows a logarithmic rate law (min)
X	ethyl xanthate radical

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