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The Collector Mechanism in Flotation

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Summary

This is a critical review of the research on the collector mechanism carried out during the last ten years. The work has been reviewed in three parts. The first part is concerned with the studies on the collector mechanism in sulfide minerals. The discussion centers on the collector action of xanthates and dixanthogens. The nature of the adsorbed film is discussed in the light of recent studies by infrared spectroscopy, electron diffraction, adsorption and calorimetric measurements. The influence of oxygen on the adsorption of xanthate on sulfide minerals is discussed and a critical evaluation made of the evidence for and against the theory that the presence of oxygen is crucial to the formation of a hydrophobic film at the sulfide mineral surface conditioned with xanthate. Recent studies on the stability of the adsorbed collector film are reviewed and correlated with the theories of the collector action of xanthates. The influence of modulating agents, activators, and depressants on the collector action of xanthates on pyrite, pyrrhotite, and marmatite are discussed. Finally, the collector action of xanthates on oxidized lead and zinc minerals has been reviewed and the known basic differences between the nature of the adsorbed species on these minerals and that on sulfide minerals is discussed. The collector mechanism in nonsulfide minerals is reviewed for the following groups of minerals: oxides, silicates, and aluminosilicates, polar salt-type minerals containing alkaline earth metal cations and soluble salts. The collector mechanism of anionic as well as cationic reagents is reviewed in conjunction with the action of modifying agents. The possibilities of employing chelating agents as mineral collectors for nonsulfide minerals are examined. The recent electrokinetic studies on nonsulfide systems in relation to the electrical double layer and nature of the adsorbed species is discussed in detail. In the third part certain new aspects of the collector mechanism, namely the role of impurities and nonstoichiometry of the mineral samples, are discussed. The possibility of controlling the floatabilities of minerals by incorporating impurity centers is examined. Finally, the kinetic factors affecting the collector mechanism are discussed.

I. INTRODUCTION

Mineral collectors are that class of reagents which by some mechanism create a hydrophobic film on the mineral surface and thereby bring about the attachment of mineral particles with the air bubbles produced in the froth. This is the basis of the froth flotation process for the selective separation of minerals. The mechanism of the action of mineral collectors has been the subject of many physicochemical investigations and much speculation during the past four decades. Most of the published information is scattered in chemical, metallurgical, and mineral technology literature. The monographs of flotation by Gaudin (*1*), Sutherland and Wark (*2*), and Klassen and Mokrousov (*3*) discuss the subject of collector action together with other phenomena in flotation. Some parts of the earlier work have also been reviewed in the AIME's *Froth Flotation, 50th Anniversary Volume* in 1962 (*4–6*) and by Joy and Robinson (*7*). The object of the present review is to summarize to date the various fundamental studies carried out during the last decade with a view to explaining the collector action in different mineral systems; to critically evaluate the published results in the light of the existing theories of adsorption and surface phenomena; and to attempt to draw correlations between the results obtained in different systems.

Investigations on the collector mechanism fall under two broad categories; the first is concerned with the collector mechanism in sulfide minerals and the second with the collector mechanism in nonsulfide and nonmetallic minerals. Although there is no fundamental reason to classify the available literature in this manner, it serves a useful purpose in the present state of knowledge, for the collector mechanism in sulfide minerals is concerned with a set of ideas and theories that are not relevant to the nonsulfide systems. Mention may be made of the fact that sulfide minerals are floated by collectors of the sulfhydryl type, the well-known xanthates being the most prominent example. These reagents possess strong chemical reactivity and are known to form strong chemisorbed bonds with the mineral surface. In contrast, the collectors used in the flotation of nonsulfide minerals such as oxides, silicates, and halides are comparatively inert and their collector action is mainly due to weaker physical forces. This will be seen in detail in the following discussion.

The experimental techniques employed in recent years are also dependent on the mineral systems. The investigators in sulfide minerals have employed thermochemical and electrochemical techniques, whereas in the studies of nonsulfide systems electrokinetic measurements have been found to have great utility. A notable advancement in recent years has been due to the application of infrared spectroscopy in the study of adsorbate films on mineral surfaces. This has been used with substantial success for minerals in both categories. Similarly, adsorption measurements using radio tracers have been continued on various mineral systems.

In the first part of the present review, the collector mechanism in sulfide minerals will be discussed in the light of the most recent studies on the subject. The earlier work, which has already been reviewed (see references), will not be discussed except where necessary to correlate with the recent developments. The special role of oxygen in the adsorption process, which has been a topic of intensive study during the last ten years, will be discussed in detail. Recent studies on the modulation of collector action by modifying agents such as activators and depressants will be reviewed in brief.

Collector mechanism studies on nonsulfide mineral systems will be reviewed by classifying minerals in the following order: oxides, silicates and aluminosilicates, polar salt-type minerals containing alkaline earth metal cations, and soluble salts. Electrokinetic studies will be discussed separately.

Finally, certain new aspects of the collector mechanism, namely the role of impurities, nonstoichiometry of the mineral samples, and the kinetic factors affecting the collector mechanism, will be discussed.

II. THE COLLECTOR MECHANISM IN SULFIDE MINERAL FLOTATION

Nature of the Adsorbed Film

The earlier investigations on the collector mechanism in sulfide mineral flotation centered around two rival theories, the solubility theory or chemical compound formation theory and the ion adsorption theory. According to the solubility theory, which originated from Taggart (*8*), the hydrophobic film was formed as a result of the formation of a chemical compound by simple double decomposition between the collector and the salts present at the mineral surface. The ion adsorption theory postulated the adsorption of collector ions by an ion exchange mechanism resulting in the displacement of an equivalent quantity of sulfoxylate ions present at the sulfide surface (*1*). This did not require the formation of a new phase. Much of the experimental evidence reviewed in earlier works (*1,2*) supported the ion exchange mechanism. A detailed analysis of the chemistry of the various reactions involved was recently made by Mellgren (*9*) and Mellgren and Rao (*10*). The technique used consisted of thermochemical measurements with an adiabatic calorimeter. The mineral system chosen was galena and ethyl xanthate and diethyl dithiocarbamate collectors were studied. The heats of reaction of the collector with lead salts such as sulfate, thiosulfate, basic thiosulfate, and carbonate were compared with the enthalpies of adsorption of the collector at the galena surface conditioned with the respective sulfoxylate ions. As revealed by some of the representative values shown in Table 1, there is an excellent agreement between the heats of reaction of the collector and lead salts and the heats of adsorption of the collector at galena treated with sulfoxylate ions.

The thermochemical data reveal the chemical nature of the collector action of xanthate and dithiocarbamate. But this cannot be taken as support for the chemical compound formation theory in view of two important findings. First, it has been observed that lead ethyl

TABLE 1

Heats of Reaction of Ethyl Xanthate with Lead Salts and Heats of Adsorption of Xanthate at Galena Surface[a]

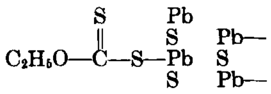
Reaction	$-\Delta H$, kcal per mole Pb^{++}
1. $PbSO_4 + 2KX \rightarrow PbX_2 + K_2SO_4$	22.0
$\boxed{\text{Galena}}SO_4 + 2KX \rightarrow \boxed{\text{Galena}}\begin{matrix}X\\X\end{matrix} + K_2SO_4$	21.4
2. $PbCO_3 + 2KX \rightarrow PbX_2 + K_2CO_3$	17.2
$\boxed{\text{Galena}}CO_3 + 2KX \rightarrow \boxed{\text{Galena}}\begin{matrix}X\\X\end{matrix} + K_2CO_3$	17.1
3. $PbS_2O_3 + 2KX \rightarrow PbX_2 + K_2S_2O_3$	19.6
$\boxed{\text{Galena}}S_2O_3 + 2KX \rightarrow \boxed{\text{Galena}}\begin{matrix}X\\X\end{matrix} + K_2S_2O_3$	19.7

[a] X stands for ethyl xanthate radical.

xanthate precipitated in a beaker does not show the same degree of floatability as galena treated with xanthate. Second, Mellgren and Rao (*10*) have found that the heat of adsorption (expressed per g mole Pb^{++}) measured does not alter even at very low collector concentrations. At such low concentrations the formation of lead dithiocarbamate precipitate is not expected if one considers the normal solubility of this compound. Furthermore, the galena surface does not consist of lead sulfate; it is only coated with a layer of sulfate ions with the counterions (potassium ions) diffused in bulk solution. These observations support the ion exchange mechanism in the creation of hydrophobic film.

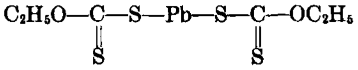
It must be recognized, however, from the magnitudes of the enthalpy values, that the bond energy of the collecter adsorbed at the galena surface is the same as the bond energy of lead xanthate or diethyl dithiocarbamate—although the two species are not identical. From a thermodynamic point of view one can infer that the difference lies in the difference in entropy between the two compounds or the difference in Gibbs free energies. This was in fact recognized by Taggart (*8*) when he mentioned that the solubility of the compound on the surface may not necessarily be identical with the same compound when it exists in bulk. Since the solubility product is related to Gibbs free energy, Taggart's statement can be supported on thermodynamic grounds; but the basic postulate of his theory is untenable.

The contention that chemisorbed xanthate is distinct from lead xanthate in bulk has been supported by the infrared studies of Greenler (*11*). He showed that when the mineral whose surface is superficially oxidized is treated with an excess of xanthate the infrared spectrum of the surface species corresponds to that of lead ethyl xanthate; but if this mineral sample is washed with acetone which dissolves lead xanthate the mineral still retains a film of xanthate, but the infrared spectrum of this is different from that of bulk lead xanthate and suggests a structure



$$\begin{array}{llll} & S & Pb & \\ & \| & S & Pb\text{—} \\ C_2H_5O\text{—} & C\text{—}S\text{—} & Pb & S \\ & & S & Pb\text{—} \end{array}$$

which is different from the bulk lead ethyl xanthate



$$\begin{array}{c} C_2H_5O\text{—}\underset{\underset{S}{\|}}{C}\text{—}S\text{—}Pb\text{—}S\text{—}\underset{\underset{S}{\|}}{C}\text{—}OC_2H_5 \end{array}$$

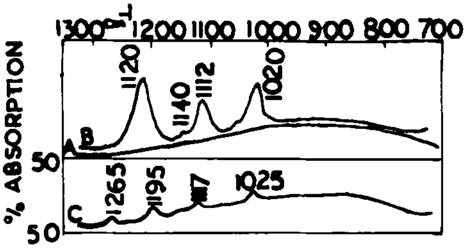
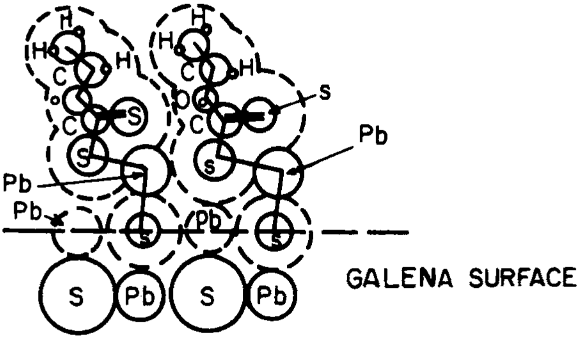


FIG. 1. Spectra of ethyl xanthate adsorbed on lead sulfide: A, freshly deposited PbS films; B, adsorbed multilayers of $Pb(EtX)_2$; C, same as B after 2 days under high vacuum. (After G. W. Poling and J. Leja, *J. Phys. Chem.*, **67**, 2121 (1963). Copyright 1963 by American Chemical Society. Reprinted by permission of the copyright owner.)

The infrared spectra of the two compounds would be expected to resemble each other but for a definite shift in the high-frequency C—O—C band from 1210 to 1195 cm^{-1}, as may be noted in Fig. 1, which shows typical infrared spectra. This has been confirmed by Leja and co-workers (*12,13*), who have shown that when galena treated with xanthate is subjected to the action of high vacuum the multilayers of xanthate are removed. The remaining xanthate present in monolayer thickness showed characteristic spectral frequencies similar to those observed by Greenler with the sample washed with acetone.

No attempt has so far been made to arrive at entropy values of the bulk species and surface species. This could well be the next and perhaps the most crucial step in the elucidation of the collector mechanism. It would be of great interest to compare the entropy values calculated from statistical thermodynamic principles employing the infrared spectroscopic data available in literature with the entropy of the surface species that may be determined experimentally. This would possibly lead to a clear identification of the surface species.

The chemisorbed monomolecular film of xanthate that is not removed by solvents such as acetone or by evacuating the sample has been represented by Hagihara (*14*) on the basis of results of his electron diffraction and crystal structure studies. The picture visualized by Hagihara given below essentially agrees with the molecular formula of Greenler. It postulates the existence of a lead xanthate molecule in which the lead atom shows a monovalent character in the vicinity of crystal surface. This forms under conditions of such low concentration of xanthate in solution as would prevent the formation of lead xanthate precipitate. The lead atom of the Pb SSCOR molecule



is said to interact and combine with the sulfur atom of the galena lattice regaining its divalent character. Hagihara also states that the atmosphere of xanthate solution in the vicinity of the galena surface is a reducing one, xanthate ions being oxidized to dixanthogen releasing electrons to lead ions. This seems rather doubtful because galena is generally considered an electron donor and the release of electrons to lead ions is not a necessary condition for the formation of the monolayer film formulated by Hagihara. The monolayer adsorption can be explained simply on the basis of the well-known ion exchange mechanism. The surface lead ions are originally bound with hydroxyl or an equivalent number of oxysulfur ions and the latter are exchanged for xanthate ions. This is also satisfied by the enthalpy data of Mellgren (*9*) discussed earlier.

The collector mechanism of xanthate at zinc sulfide surfaces has been recently studied by Yamasaki and Usui (*15*) by infrared spectroscopic examination. The results show striking similarity with the collector mechanism at galena. The infrared spectra have revealed that the nature of the adsorbed species is dependent on the extent of oxidation of the zinc sulfide sample. On an unoxidized sample, the amount of adsorbed xanthate does not exceed the amount of xanthate calculated for unimolecular adsorption. The infrared bands indicate that the xanthate adsorbed on the unoxidized sample is subject to an inhomogeneous electric field of the lattice. On the other hand, a sample of zinc sulfide that is subjected to superficial oxidation by hydrogen peroxide and then treated with xanthate shows infrared absorption bands that are similar to those of zinc dodecyl xanthate. The analysis of products in the suspension remaining after adsorption of xanthate has revealed that xanthate ions are adsorbed by the ion exchange mechanism, an equivalent quantity of an anion such as sulfate being released in the process. In the case of an oxidized sample other than the monolayer of xanthate, zinc dodecyl xanthate is formed by reaction between potassium dodecyl xanthate and the oxidation product of the mineral.

Yamasaki and Usui have further attempted to identify the nature of the adsorbed species by leaching it in pyridine and recording the infrared spectrum of the product obtained on adding water to the pyridine extract. The spectrum so obtained with the oxidized sample is identical with that of zinc dodecyl xanthate, as is to be expected. The pyridine extract with the unoxidized sample did not give any precipitate on adding water. The infrared spectrum of the pyridine extract indicates an absorption band that corresponds to the presence of carbon disulfide. This is further confirmed by adding potassium ethylate to the pyridine extract when potassium ethyl xanthate is formed and is identified by its characteristic absorption peak at 3010 Å. From this it is concluded that the monolayer consists of dodecyl xanthic acid or an ion pair consisting of dodecyl xanthate ions adsorbed on the zinc atoms and hydrogen ions adsorbed on the sulfur atoms of the zinc sulfide surface. This is also in accordance with the instability of the adsorbed film on the unoxidized sample, since on exposure to the atmosphere the H^+ ions and xanthate ions would unite forming unstable xanthic acid. This "ion pair" adsorption mechanism tends to support the theory of Cook and Nixon published in 1950 (*16*). This theory had been supported by a few investigators only (*17*,*18*) in the early 1950s; in recent years it has been virtually forgotten except for occasional references. The recent evidence in favor of this theory is therefore of special significance.

Recently, Steininger (*19*) has produced further support in favor of Cook and Nixon's theory. It is significant that his analysis also concerns the collector mechanism on sphalerite. His experimental results indicate that flotation is prevented when about 95% of the collector is ionized. This has been interpreted on the basis of the neutral molecule adsorption mechanism. This is represented in two steps:

$$—Zn^+ + H_2O \rightleftharpoons —ZnOH + H^+ \qquad (1)$$

where $—Zn^+$ represents zinc surface sites;

$$—ZnOH + RSH \rightleftharpoons —ZnSR + H_2O \qquad (2)$$

where R stands for an alkyl group and —ZnSR represents the collector adsorbed on the mineral surface. It has been shown that the upper pH limit of flotation is directly and closely related to the pK*a* of the neutral molecule (that is, for example, xanthic acid formed by the hydrolysis of xanthate) collector. Also,

$$\mathrm{pH} = \mathrm{p}Ka + \log \frac{[\mathrm{RS}^-]}{[\mathrm{RSH}]} \tag{3}$$

and at constant collector addition, *c*, and for low flotation recoveries when the amount of collector adsorbed on the mineral is small compared to *c*,

$$[\mathrm{RS}^-] \simeq c - [\mathrm{RSH}] \tag{4}$$

It follows, therefore,

$$\mathrm{pH} \simeq \mathrm{p}Ka + \log \left\{\frac{c}{[\mathrm{RSH}]} - 1\right\} \tag{5}$$

According to the mechanism proposed, the surface density of adsorbed collector varies with [RSH] and with the density of hydroxylated surface sites [—ZnOH]. Hence,

$$[\text{—ZnSR}] = Ks[\mathrm{RSH}][\text{—ZnOH}] \tag{6}$$

where *Ks* is a constant or

$$[\mathrm{RSH}] = \frac{[\text{—ZnSR}]}{Ks[\text{—ZnOH}]} \tag{7}$$

It can be assumed that the flotation recovery ρ is determined by the surface density of adsorbed collector [—ZnSR] at low surface coverage. This is expressed as $\rho = f([\text{—ZnSR}])$ or $[\text{—ZnSH}] = g(\rho)$, and hence it follows that

$$[\mathrm{RSH}] = \frac{g(\rho)}{Ks[\text{—ZnOH}]} \tag{8}$$

and

$$\mathrm{pH} \simeq \mathrm{p}Ka + \log \left\{\frac{c \cdot Ks[\text{—ZnOH}]}{g(\rho)} - 1\right\} \tag{9}$$

From the last expression it follows that for a constant density of hydroxylated surface sites and at constant flotation recovery, there is a linear relationship between pH and pK*a* if *Ks* is the same for different collectors. For constant zero recovery pH becomes the upper critical pH, pH*c*. This has been confirmed by flotation tests. The expected linear relation between pH*c* and pK*a* has been shown over the pH range 6–12 for five different sulfhydryl collectors.

The mechanism suggested above explains the well-known fact that sphalerite is not effectively floated by short-chain xanthates such as potassium ethyl xanthate. Since the pK*a* value decreases with decreasing hydrocarbon chain, the lower hydrocarbon chain xanthates are strongly ionized, and since the zinc salts of these xanthates are relatively soluble, hydrophobic film is not formed on the sphalerite surface. With un-ionized collectors, the formation of water also contributes to the free energy of the reaction and represents a supplementary driving force for the replacement of OH groups by collector entities.

The analysis of Steininger does not take into consideration the stability of the collector film at the sphalerite surface in relation to the stability of the neutral molecule in solution. It is well known that xanthic acids are unstable in water, their half-life being of the order of a few minutes. If this has to apply to the collector film at the mineral surface also, the flotation by neutral molecule adsorption would be rather untenable. It is possible, however, to explain the mechanism by postulating that the adsorbed state of the collector is not identical with the bulk state. Also, Yamasaki and Usui (*15*) have preferred to suggest the ion pair adsorption rather than neutral molecular adsorption. But in a recent publication Cook (*20*) has pointed out that while the "ion pair" adsorption mechanism and neutral molecule adsorption mechanism are superficially alike, free energy considerations favor the "ion pair" mechanism. This would necessitate the adsorption of xanthate ions together with H^+ ions. Thus the collector mechanism with regard to sphalerite is still rather ambiguous. Thermochemical study on the system might well reveal more in this direction.

Role of Oxygen in Adsorption of Xanthate at Sulfide Mineral Surfaces

One of the interesting and often controversial features that has attracted much attention has been the role of oxygen in the adsorption of xanthate. The studies on the adsorption of xanthate by Mellgren and Subba Rau (*21*) have revealed that a galena sample oxidized with hydrogen peroxide shows a large increase in the uptake of xanthate.

In a deoxygenated system the maximum uptake corresponds to nearly a monolayer. The data do not fit a Langmuir adsorption isotherm and there is no simple relationship between adsorption density, xanthate concentration, and pH. This finding appears to contradict the observations of earlier workers who found the adsorption of xanthate in multilayers (*22*). The discrepancy has been reconsidered by Gaudin and Finkelstein (*23*), who have pointed out that it is due to the considerably higher flow rates (100–200 ml/min) used in Mellgren's work. This difference in the flow rates makes a two-hundredfold difference in the residence time, and hence the sensitivity of detection of reaction is very much reduced. On the other hand, when low flow rates (0.3–1.5 ml/min) are employed the effluent concentration remains significantly different from that of the head solution even when the flow of the xanthate solution is continued for several days, which confirms the multilayer adsorption of xanthate. Furthermore, the mineral-xanthate interaction is greatly enhanced by contact with oxygen, as shown in Fig. 2. This effect of oxygen had previously been reported by several investigators. As far back as 1934 Gaudin and co-workers (*24*) recognized that oxidation of xanthate in solution giving rise to the neutral molecule dixanthogen as represented

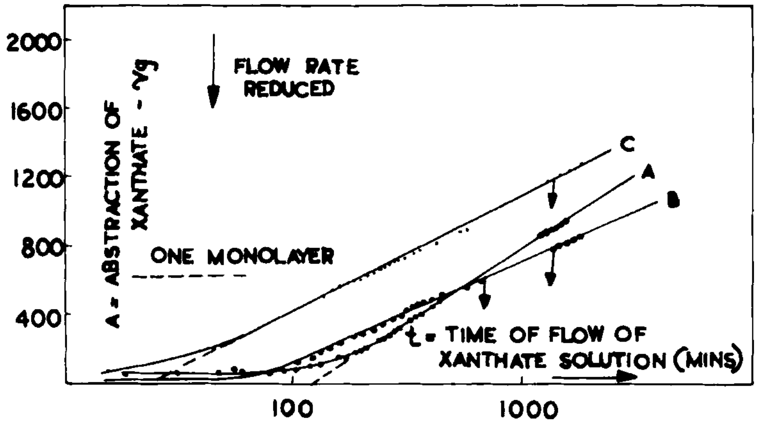
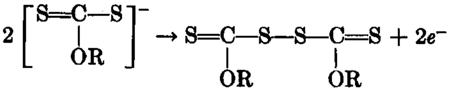


FIG. 2. Relationship between the quantity of xanthate abstracted from solution, *A*, and the time of contact with galena, *t*: A, 0.6 ppm oxygen in xanthate solution only; B, 0.3 ppm oxygen in both rinse and xanthate solutions; C, 0.6 ppm oxygen in both rinse and xanthate solutions. (After A. M. Gaudin and N. P. Finkelstein, *Nature*, **207**, No. 4995, pp. 389–391 (July 24, 1965), by permission of the Editor.)

by Eq. (10) may play a crucial role in the creation of the hydrophobic film:



$$2\left[\begin{matrix}S{=}C{-}S\\ |\\ OR\end{matrix}\right]^{-} \rightarrow \begin{matrix}S{=}C{-}S{-}S{-}C{=}S\\ \quad | \qquad\qquad | \\ \quad OR \qquad\quad OR\end{matrix} + 2e^{-} \qquad (10)$$

It was suggested that dixanthogen formed by the oxidation of xanthate is the effective adsorbate species. Again in 1952 Schulman (*25*) expressed this opinion at the International Mineral Dressing Congress in London. Since then much experimental evidence has accumulated in support of this view, although the exact role of oxygen and more particularly the mechanism of xanthate-dixanthogen adsorption are still not settled. According to Plaksin and his school (*26,27*) oxygen promotes the dehydration of the mineral surface, thus facilitating the penetration of xanthate and its consequent fixation. Another function of oxygen is to mop up the free electrons present in the conduction band of galena, which is known to be a semiconductor of *n*-type, and thus facilitate the adsorption of anionic xanthate. Oxygen functions as an electron acceptor and converts galena from *n*-type to *p*-type semiconductor. This has been experimentally shown by electrical conductivity measurements.

The results of electrochemical studies on the galena-xanthate system by Tolun and Kitchener (*28*) have given strong support to the essential role of oxygen. The effect of xanthate on the electrochemical potential of a galena electrode (against a saturated calomel electrode) has revealed that although the potential falls when xanthate is adsorbed, no bubble contact takes place. There is no interaction with the xanthate under relatively reducing conditions, for example, a freshly crushed galena, or a surface treated with a sulfide solution. On exposure to aerated water, galena develops a very thin film of thiosulfate and the potential at this surface falls when it is brought in contact with the xanthate. But the presence of lead xanthate film alone does not render the surface hydrophobic as tested by lack of contact with a nitrogen bubble. The bubble contact takes place only when the potential is raised to —0.13 by anodic current. This potential corresponds to the redox potential of the xanthate-dixanthogen system. Oxygen thus plays a dual role in the collector mechanism of xanthate. First, it superficially oxidizes galena, creating a film of basic thiosulfate which interacts with xanthate forming lead xanthate film on the surface. Second, it raises the electrochemical potential of galena until the xanthate begins to be oxidized to dixanthogen. Thus a mixed film of xanthate and dixanthogen renders the mineral surface hydrophobic.

It is now appropriate to examine the contact angle data of Wark and Cox (*29*) and others in the light of the above discussion on the role of oxygen in the adsorption of xanthate at the galena surface. It is known that a galena surface treated with ethyl xanthate samples that were kept in the atmosphere for a considerable length of time shows a contact angle of 80°, while the magnitude of the angle when xanthate is pure is 60°. The angle of 80° is identified with the formation of dixanthogen film at the galena surface. Longer chain xanthates also form the films of the corresponding dixanthogens in the presence of oxygen as revealed by the rise in the contact angle. The contact angle values for a series of xanthates and dixanthogens formed under oxidizing conditions were reported by Rao and Patel (*30*), who found that in the absence of air or oxygen the mineral conditioned with ethyl xanthate shows an angle of 60°, thus confirming the observations of Wark and Cox (*29*). The fact that ethyl xanthate alone gives rise to a contact angle of 60° while with diethyl dixanthogen the angle rises to 80° appears to indicate that xanthate alone could form a hydrophobic film at sulfide mineral surface. This apparent disagreement between the classical work and the results discussed above can be explained by suggesting that the value of 60° is probably the characteristic contact angle of a mixed film of xanthate and dixanthogen while the value of 80° is due to pure dixanthogen film. Although no direct confirmation of this view is so far available, it is appropriate to admit that in the contact angle studies reported previously no special precautions were taken to exclude oxygen from the system, and the presence of small quantities of dissolved oxygen could well give rise to a mixed xanthate-dixanthogen film. In support of this, in a recent study at the galena surface Beebe and Westley (*31*) have shown that appreciable time is required for the interaction of galena with oxygen either before or during its contact with xanthate solution to yield reproducible contact angles.

From the preceding discussion and the observation of Tolun and Kitchener (*28*), one is tempted to infer that the contact angle would be zero if pure xanthate is adsorbed at the sulfide surface. Although this has been reported to have been observed, it raises a basic question regarding the mechanism of hydrophobic film formation as distinct from an adsorbed film that it not hydrophobic. Xanthate ions alone are known to possess the well-known heteropolar structure required for the creation of a hydrophobic film, and as such if pure xanthate alone is adsorbed one would expect the formation of hydrophobic film (as was firmly believed until recently). It is hard to explain why this should not happen and in what way the presence of dixanthogen alongside xanthate alters the nature of the film, making it hydrophobic. No attempt has been made to assign a definite structure for the mixed xanthate-dixanthogen film. Furthermore, the thermochemical data of Mellgren (*9*) discussed before fail to show any evidence of the formation of a mixed xanthate-dixanthogen film. Last, if the hydrophobic film is attributed to a mixed xanthate-dixanthogen film, it is necessary to find out whether it holds good for sulfide minerals other than galena as well. Not enough work has been done in this direction, with the exception of electrochemical studies on pyrite to be mentioned later. However, in the case of cerussite ($PbCO_3$), Fleming (*32*) observed bubble pickup even in an inert atmosphere, and it is known that lead carbonate does not oxidize xanthate to dixanthogen.

Although the formation of mixed-xanthate dixanthogen film is still disputed, the role of oxygen in the adsorption process is well recognized. With reference to galena that is surrounded by a negatively charged electrical double layer (*3*, p. 31), the penetration of negatively charged xanthate ions is facilitated by oxygen, which serves as an electron acceptor. The process of penetration of xanthate can also be accounted for in the presence of nonionic dixanthogen molecule. Once penetrated through the double layer, dixanthogen molecules may remain coadsorbed along with xanthate or diffuse back into solution. The latter mechanism is supported by the study of the adsorption of xanthate in the presence of long-chain quaternary ammonium salts by Leja and co-workers (*33–35*). When the adsorption of equimolecular solutions of xanthate and alkyl trimethyl ammonium bromide are measured on copper, nickel, and sphalerite powders, there is a strong interaction between xanthate and quaternary ammonium bromide. The X-ray diffraction pattern has indicated the formation of a new compound. The rate of uptake of ethyl xanthate is greatly enhanced by the presence of alkyl trimethyl ammonium bromide, as shown in Fig. 3. But the surface species formed consists of only xanthate, and it is inferred that the 1:1 complex between xanthate and quaternary ammonium salt is not permanently adsorbed on the surface although it plays a major role in the adsorption of

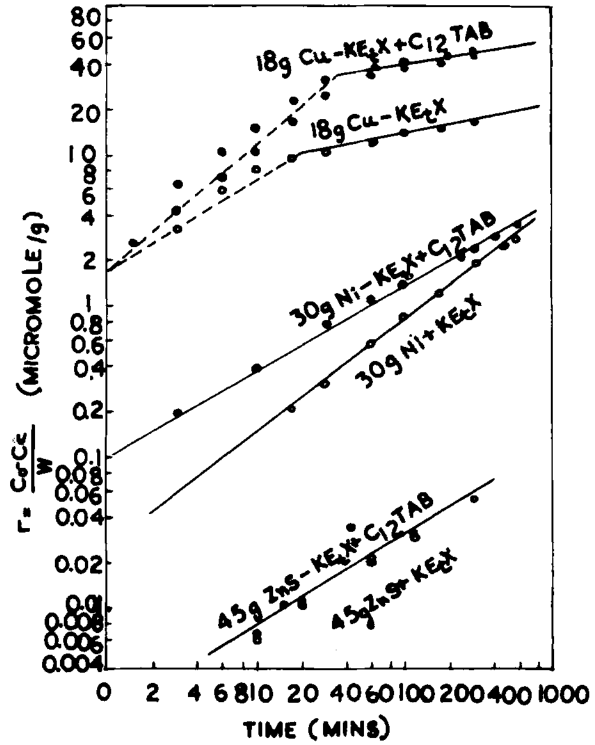


FIG. 3. Kinetics of ethyl xanthate ion abstraction by copper, nickel, and sphalerite powders. (After A. Pomianowski and J. Leja, *Trans. AIME*, **229**, 310 (1964), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

xanthate. After diffusing through the electrical double layer at the solid-liquid surface, it is readily decomposed and the quaternary ammonium ions either diffuse back into the bulk solution or act as a link in the transfer of a further amount of xanthate anion by serving as proton donors or electron acceptors. The role of dixanthogen could be similar, but the mechanism would be different since it is a nonionic molecule. So far, it has not been possible to compare the two situations. The principal difficulty has been to distinguish between xanthate and dixanthogen in the adsorbed state by any known experimental technique.

The collector mechanism of dixanthogens as such has been studied from time to time. The most recent work, reported by Kakovsky and

Arashkevich (*36*), has established the chemical nature of the adsorption of dixanthogens and other similar compounds such as thiouram disulfide (oxidation product of diethyl dithiocarbamate) at sulfide mineral surfaces. It was shown that dixanthogen film is removed by treatment of the mineral with sodium sulfide in the same way as xanthate ions are desorbed by this depressant. This indicates that the action of dixanthogen at the sulfide surface results in the formation of a chemically fixed layer of xanthate of the corresponding heavy metal. This confirms the infrared spectroscopic evidence of Leja and co-workers (*12*), who found the reduction of dixanthogen by accepting electrons from the galena lattice. However, it is further mentioned by Kakovsky and Arashkevich (*36*) that though both the anionic collector and its disulfide (oxidation product) are fixed chemically, they show different degrees of resistance to the action of depressants of intermediate activity such as a soluble chromate. In the presence of such depressants the dixanthogen is a weaker collector than xanthate, since with dixanthogen there is insufficient concentration of collector ions that would counteract the depressant. If a xanthate is used as a collector, the concentration of the ion in the pulp may be sufficient to ensure the fixation of the collector ions on the mineral surface. If, however, dixanthogen is added to the pulp or formed by the oxidation of xanthate in the pulp, the xanthate ions in the solution would appear only as a result of the following reactions:

$$PbS + X_2 = PbX_2 + S^0 \tag{11}$$

$$PbX_2 + 2OH^- = Pb(OH)_2 + 2X^- \tag{12}$$

Hence to obtain the same ion concentration in the latter case, a complete reduction of disulfide is necessary, which requires a very long and practically impossible contact time between the mineral and the reagents. Therefore, the ionic form of the collector resists the action of depressants better than the molecular one, that is, dixanthogen.

It follows from this work that in the end, xanthate ions are the adsorbed species bound to the galena lattice. This rules out the speculated mixed film of xanthate-dixanthogen. Also, it further supports the simple ion exchange mechanism. But a serious question arises in connection with the contact angle measurements of Wark and Cox (*29*). As mentioned already, an angle of 80° was recognized as characteristic of diethyl dixanthogen film as distinct from that of xanthate film, which gives an angle of 60°. The mechanism suggested by Kakovsky and Arashkevich (*36*), however, requires that the sulfide mineral treated with dixanthogen should also give the same contact angle as the one treated with xanthate. The discrepancy remains to be satisfactorily explained. The possibility of multilayers of dixanthogens giving rise to the higher contact angle appears to be worth considering.

The most recent work on the correlation between the adsorption of collectors and electrochemical properties of minerals by Mitrofanov and Ryskin (*37*) also supports the viewpoint of Tolun and Kitchener. Additional experimental evidence is presented by the measurement of the double layer capacity on an electrode of pyrite single crystal as a function of potential value. The pyrite electrode in a solution of K_2SO_4 has a characteristic capacity minimum at the potential of 0.15 V (with respect to the saturated calomel electrode). In a solution of K_2SO_4 containing $10^{-4}\,M$ of butyl xanthate the capacity minimum shifts to 2.0 V, and butyl xanthate is adsorbed on the surface of the pyrite at a potential exceeding —0.4 V as indicated by the sharp drop in the capacity value in this region. As this is close to the oxidation potential of xanthate (though not identical with it), it was inferred that dixanthogen is the adsorbed species at the pyrite surface. In the cathode region, dixanthogen is reduced to xanthate which is desorbed from the surface of pyrite at potential values of —0.5 to —0.55 V. This is indicated by a well-defined maximum in the capacity of the pyrite electrode.

Fuerstenau and co-workers (*38*) have made EMF measurements on pyrite-xanthate systems and concluded that the species responsible for the formation of hydrophobic film when xanthate is added as collector is dixanthogen. Measured oxidation potentials of this system show that xanthate should be oxidized to dixanthogen. The presence of dixanthogen on the pyrite surface is confirmed by infrared absorption. The authors also have calculated the concentration ratio $[\text{dixanthogen}]/[\text{xanthate ion}]^2$ at various pH values. The values so obtained show that at pH 9 and below, almost all of the added xanthate exists in the form of dixanthogen, and that at pH 11 and above, the amount of dixanthogen is exceedingly small. The depression of pyrite at pH 11 and above is attributed to the lack of dixanthogen. The depression at low pH values is due to the decomposition of xanthic acid. But the depression of pyrite around pH 6 cannot be due to a lack of dixanthogen. No satisfactory explanation has been given for this anomaly. The adsorption of dixanthogen has been explained by suggesting the resonance bonding of the pyrite sulfur with the sulfur of the dixanthogen molecule. But this has not been confirmed by independent structural evidence and the mechanism of dixanthogen adsorption at the pyrite-water interface is still open to further studies.

It is of interest to compare the collector mechanism at the pyrite surface with that at galena. For a long time it was believed that the collector mechanism would be similar in the two cases because both are known to be sulfide minerals of polar character. But it is now obvious from the results quoted above that at iron pyrite surface the adsorption of neutral molecule dixanthogen supersedes that of anionic xanthate. Thus the ion exchange mechanism does not prevail at pyrite surface. This could be related to the crystal structure of pyrite. It is known that in pyrite, the iron atom is sandwiched between a pair of sulfur atoms and in such a structure xanthate ions cannot find a favorable fit with the metal atom. This indicates that crystal structure or the arrangement of atoms in the mineral lattice is another important factor determining the collector mechanism. It would be of special interest to compare the collector mechanism of xanthate with minerals having a structure similar to pyrite possessing a disulfide group. Results of such a study are likely to be of considerable interest in flotation practice since the flotation characteristics of a number of such minerals as marcasite (FeS_2, but belonging to orthorhombic system), hauerite (MnS_2), arsenoferrite ($FeAs_2$), and arsenopyrite ($FeS_2 \cdot FeAs_2$) are not sufficiently known.

Role of Gases in Mineral-Collector Interaction

A series of investigations on the role of gases in the flotation of minerals has been conducted by the Russian school led by Plaksin during the last two decades (*3*). The two gases that influence the floatability are oxygen and carbon dioxide. The oxygen dissolved in water is adsorbed on the mineral surface preferentially to other gases such as nitrogen and carbon dioxide due to chemical forces. In the absence of oxygen the mineral surface is hydrophilic. When oxygen comes in contact it gets fixed on the surface by a process of activated adsorption followed by oxidation of the surface with oxygen diffusion in the surface layer. The dual role of oxygen in collector fixation has already been mentioned. Different quantities of oxygen in solution are necessary for the flotation of various sulfides. The rate of floatability increases for various sulfides depending on their activity in relation to oxygen. In the order of the increase in the amount of oxygen necessary for complete flotation with a collector, the following activity series has been given (*26*): galena, pyrite, sphalerite, chalcopyrite, pyrrhotite, and arsenopyrite.

In this work it is difficult to give an exact interpretation of the activity of the mineral in relation to oxygen. The chemical activity of minerals as reflected in their susceptibility to oxidation follows a different series according to Plante and Sutherland (*2*). In this series pyrrhotite is most susceptible to oxidation and sphalerite least. The activity of oxygen related to floatability as given by Plaksin and Bessonov (*26*) is probaby concerned with the creation of charge carriers by accepting electrons from the mineral lattice. As mentioned earlier this has been shown in the case of galena by electrical conductivity measurements. Other minerals need to be examined from this viewpoint. At present serious ambiguity occurs in the case of pyrrhotite, which is a mineral of nonstoichiometric composition with excess of sulfur over iron required by the stoichiometric formula FeS. This mineral has been shown to be very susceptible to oxidation, its floatability deteriorating in the presence of an appreciable amount of oxygen. The role of oxygen in the collector fixation on a mineral of this kind is highly questionable and it appears that the generalization for all the sulfide minerals as suggested by Plaksin and collaborators cannot be easily accepted in the light of the contradictions mentioned above, until further detailed analysis is carried out.

Stability of the Adsorbed Collector Film

Although the chemisorbed nature of the collector film at sulfide minerals is a well recognized fact, the bond strength differs for individual minerals. This results in variation of the physical stability of the collector film. Studies on the effect of thermal treatment on the xanthate film by Glembotskii (*39*) have shown that the xanthate adsorbed at the chalcopyrite surface is the easiest to destroy; treatment with water at 100°C for 2 min is enough to remove 99.5% of the adsorbed xanthate. Within the same time and by the same treatment, the percentages of the adsorbed xanthate removed from sphalerite and pyrite are 10% and 30%, respectively. This variation in the thermal stability of the collector film at different mineral surfaces has been applied for bringing out the selective destruction of adsorption layers of xanthates in order to facilitate the selective separation of the individual minerals. The thermal stability of the adsorption layers formed by amyl xanthate is lower than that of ethyl xanthate. The probable cause of this is the oxidation of the adsorbed film enhanced by the action of heat. The adsorbed amyl xanthate is more easily oxidized than adsorbed ethyl xanthate (*30*). It is likely that the bond strength of the resultant dixanthogen film is lower than that of the corresponding xanthate, although the nature of dixanthogen adsorption has not been sufficiently elucidated. In support of this it has been shown that the xanthate film adsorbed at the sphalerite surface does not undergo appreciable oxidation to dixanthogen as revealed by contact angle measurements (*40*). This agrees with Glembotskii's observation that the xanthate film at the sphalerite surface is most resistant to thermal effects. A thermochemical study on the bond strengths of the adsorbed xanthate and dixanthogen films is likely to prove fruitful.

Modulation of Collector Action at Sulfide Minerals

Floatability of a mineral is considerably altered by the action of certain modifying agents that play a very important role in flotation practice. Activators are that class of reagents which by their action at a mineral surface promote the adsorption of the collector and thus the flotation of the mineral. Depressants play the opposite role; their surface action prevents the adsorption of the collector and depresses the mineral. The mechanism of such modifying agents in conjunction with collectors is particularly important in the selective separation of sulfide minerals. In general, the results of the work obtained by the application of radioisotopes to follow the course of surface reactions support the view that the activation process involves an ion exchange mechanism between the metal ion in the mineral lattice and the activator ion. This has been corroborated by thermodynamic calculations. The earlier work on this has been reviewed by Rogers (*5*).

The activation mechanism with reference to pyrite (FeS_2), pyrrhotite (FeS), and marmatite (ZnS containing FeS in varying amounts) has been investigated by Bushell, Krauss, and Brown (*41,42*). Comparing the activation of sphalerite and pyrrhotite by Cu^{++} ions in accordance with the ion exchange mechanism, the following equilibrium expressions have been obtained:

$$[Fe^{++}]/[Cu^{++}] = 5 \times 10^{17} \quad (13)$$

$$[Zn^{++}]/[Cu^{++}] = 9 \times 10^{10} \quad (14)$$

From these one would expect preferential activation of pyrrhotite by cupric sulfate. In practice however this is not so; sphalerite is activated preferentially to pyrrhotite. This apparent discord is attributed to the protection of the pyrrhotite surface by a film of ferric hydroxide or oxide that shields the surface from Cu^{++} ions. The protective film is formed in the presence of oxygen and at a high enough value of pH (around 10). Pyrrhotite freely abstracts Cu^{++} ions in the absence of oxygen. But at pH exceeding 11.2 it releases sulfide ions following the reaction

$$FeS + 2OH^- \rightarrow Fe(OH)_2 + S^{-2} \tag{15}$$

The sulfide ions so liberated precipitate copper as cupric sulfide that occurs away from the mineral surface and is thus wasted. Sulfide ions that are not precipitated by copper exert a depressing action on the mineral surface and thus prevent flotation. This has been supported by the finding that in the activation of marmatite in the presence of oxygen and at high pH the total weight of Cu^{++} ions abstracted per unit surface area decreases with an increase in the iron content of marmatite.

The activation of pyrite by cupric sulfate has been discussed on the basis of the following mechanism:

$$FeS_2 \rightarrow Fe^{++} + S_2^{--} \tag{16}$$
$$S_2^{--} \rightarrow S^0 + S^{--} \tag{17}$$
$$Cu^{++} + S^{--} \rightarrow CuS \tag{18}$$
$$\overline{Cu^{++} + FeS_2 \rightarrow Fe^{++} + S^0 + CuS} \tag{19}$$

The equilibrium expression for the overall reaction is

$$\frac{[Fe^{++}]}{[Cu^{++}]} = K = 4.3 \times 10^5 \tag{20}$$

calculated from published thermodynamic data. If ferrous hydroxide is formed as a result of the oxidation of pyrite,

$$[Fe^{++}] = \frac{1.8 \times 10^{-5}}{[OH^-]^2} \tag{21}$$

where 1.8×10^{-15} is the solubility product of $Fe(OH)_2$

$$[Cu^{++}][OH^-]^2 = \frac{1.8 \times 10^{-15}}{4.3 \times 10^5} = 4.2 \times 10^{-21} \tag{22}$$

Significant Cu^{++} ion abstraction should therefore occur when the value of the product $[Cu^{++}][OH^-]^2$ is greater than 4.2×10^{-21}. This relationship holds good at different pH values. A limiting value of about three monolayers of CuS is deduced from the results of adsorption tests. The most striking feature of this study is that the activation of pyrite is not hindered by the presence of oxygen even at high pH, which shows that pyrite behaves differently from pyrrhotite; the activation of the latter is hindered by a protective film of ferric oxide or hydroxide. This difference between the two iron minerals has not been explained by the authors. It is probably due to the slower rate of oxidation of pyrite as shown by Plante and Sutherland (*2*).

Oxidized Lead and Zinc Minerals

The flotation of minerals under this category, namely, cerussite ($PbCO_3$), anglesite ($PbSO_4$), smithsonite ($ZnCO_3$), and wulfenite ($PbMoO_4$), is achieved by sulfhydryl collectors of the type of xanthates. The floatability of these minerals is not as impressive as those of sulfide minerals such as galena (PbS). Prior treatment with a soluble sulfide facilitates the action of xanthates. Furthermore, wide variations in flotation characteristics are noticed among the individual minerals in this group. This has been correlated with lattice energies of minerals (*43,44*). Lattice energies of the minerals increase and their reactivities with soluble sulfide and xanthate decrease in the following sequence: cerussite ($PbCO_3$), anglesite ($PbSO_4$), wulfenite ($PbMoO_4$), descloizite ($4Pb/ZnO \cdot V_2O_5\ H_2O$), vanadinite ($3Pb_3V_2O_8 \cdot PbCl_2$), pyromorphite ($3Pb_3P_2O_8–PbCl_2$), mimetite ($3Pb_3As_2O_8–PbCl_2$), beudantite ($2PbO \cdot 3Fe_2O_3 \cdot 2SO_3 \cdot As_2O_5–6H_2O$), plumbojarosite ($PbFe_6(OH)_{12}(SO_4)_4$), and calamine ($H_2O \cdot 2ZnO \cdot SiO_2$). The first three minerals have Pb^{++} cations with considerable uncompensated charges at the upper levels of the probable cleavage surface. The next four minerals are more refractory to flotation with the reagents mentioned. These are characterized by the absence of lead or zinc cations at the upper levels of the cleavage surfaces. The cations are situated relatively far beneath the surface, but they are not screened off by overlying ions and are relatively accessible for interaction with the ions of flotation reagents.

The last two minerals are totally refractory to flotation by sulfhydryl collectors with presulfidization by sodium sulfide. The lack of response to flotation agents is explained by the cations situated at the lower levels of the probable cleavage surfaces of the minerals completely screened off by overlying ions.

This discussion does not consider the collector mechanism of xanthates on these minerals. Evidence available with sulfide systems abundantly shows that it would be different in oxidized minerals. It is known that sulfoxy salts and carbonates of lead and zinc react with xanthates giving the corresponding metal xanthates which are different from the xanthate species adsorbed at sulfide surfaces as discussed above. It is reasonable to expect that the oxidized minerals of lead and zinc acquire hydrophobicity by the formation of xanthate precipitate and this is the cause of their less impressive floatability as compared to that of galena, since, as mentioned before, a precipitate of lead xanthate does not show the same degree of floatability as galena treated with xanthate. A detailed thermodynamic study of these mineral systems along with galena is likely to be of considerable theoretical interest.

III. COLLECTOR MECHANISM IN NONSULFIDE FLOTATION

Recent fundamental studies on the flotation of nonsulfide minerals are largely concerned with oxides, silicates, aluminosilicates, and halides. As in the studies on sulfide minerals the object of the investigations has been to identify the surface species responsible for the creation of hydrophobic film. The collector action on nonsulfide minerals is in most cases linked with the action of modulating agents, namely mineral activators, and hence a basic study on a nonsulfide system generally concerns the combined action of activators and collectors. The activating species play an important role in deciding the collector mechanism.

During the past decade, experimental techniques employed in studies on nonsulfide systems are generally an extension or refinement of methods known in the previous years, notably adsorption measurements, flotation tests, and electrokinetic measurements. The last-named is of special interest because of its application in a large number of complex minerals and the fact that it has provided deep insight into the nature of the potential determining ions on a mineral surface and its relation with the collector mechanism. In addition, the infrared spectroscopic studies are being increasingly applied in the identification of the collector species. No attempt has so far been made for obtaining thermochemical data; this is probably due to the fact that the magnitudes of heats of adsorption in nonsulfide systems would be generally of a lower order and to obtain reliable thermodynamic data it would be necessary to develop calorimetric assemblies of greater sensitivities than those found adequate for sulfide minerals. In the following discussion the adsorption, contact angle, infrared, and flotation studies will be reviewed for typical mineral systems; the electrokinetic studies will be discussed later in view of their special significance.

Quartz

No mineral among the oxides has been studied as thoroughly as quartz; for this reason the collector mechanism on quartz has been of considerable interest. The work done up to 1960 has been reviewed elsewhere (*1,2,4,6,7*), and these studies have been extended in recent years to get deeper insight into the collector mechanism in the pres-

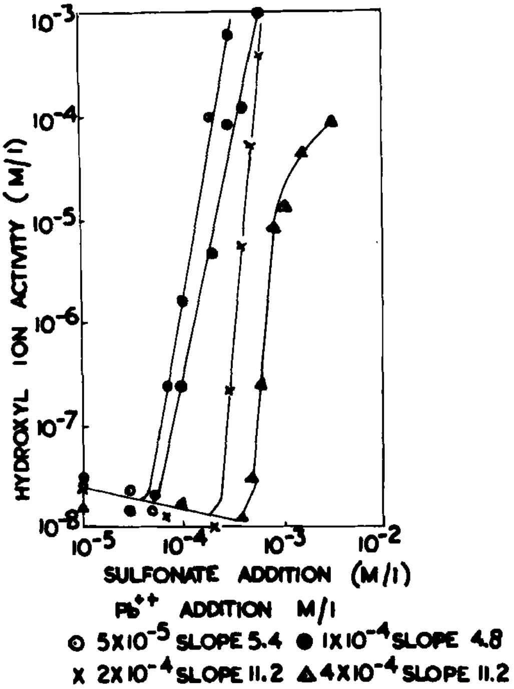


FIG. 4. Relationship between lowest value of pH for complete flotation and sulfonate addition at various constant Pb^{++} additions. (After M. C. Fuerstenau and S. Atak, *Trans. AIME*, **232**, 26 (1965), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

ence of a number of different variables of practical importance in flotation.

The collector mechanism of anionic collectors on quartz activated with metal ions has been extensively studied by Fuerstenau and coworkers. Fuerstenau and Atak (*45*), studying the lead activation in sulfonate flotation of quartz, found a linear relationship between the logarithm of the activity of hydroxyl ions and the logarithm of the sulfonate concentration in the range 10^{-5} to 10^{-2} mole per liter. The slope of the line varies for different concentrations of lead ions (see Fig. 4). As the lead ion concentration is increased the sulfonate ion concentration necessary for the maximum flotation recovery also rises. Furthermore, as shown in Fig. 5 with increase in lead ion concentration, the lowest value of pH for complete flotation is reduced. Conversely, as the sulfonate ion concentration is increased the pH value for the maximum flotation recovery is increased. These results have been explained by considering the concentration of different lead hydroxyl species present at different hydroxyl ion concentrations. The following equilibria are relevant in this system:

$$\mathrm{Pb(OH)_2(s)} \rightleftarrows \mathrm{Pb(OH)_2(aq)}; \quad K = 3.65 \times 10^{-4} \tag{23}$$

$$\mathrm{Pb(OH)_2(s)} \rightleftarrows \mathrm{Pb^{++}} + 2\mathrm{OH^-}; \quad K = 4.2 \times 10^{-15} \tag{24}$$

$$\mathrm{Pb(OH)_2(s)} \rightleftarrows \mathrm{Pb(OH)^+} + \mathrm{OH^-}; \quad K = 3 \times 10^{-7} \tag{25}$$

$$\mathrm{Pb(OH)_2(s)} + \mathrm{OH^-} \rightleftarrows \mathrm{HPbO_2^-} + \mathrm{H_2O}; \quad K = 4 \times 10^{-1} \tag{26}$$

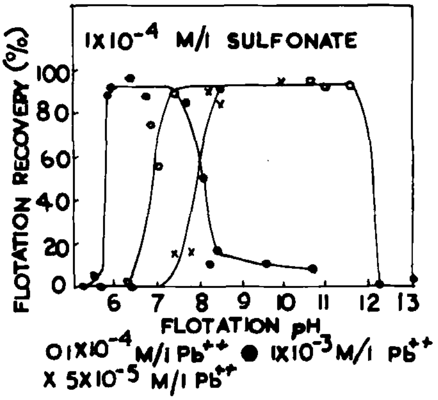


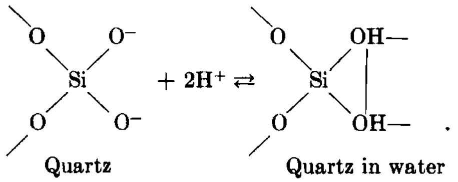
FIG. 5. Relationship between flotation recovery and pH at constant sulfonate addition with various Pb^{++} additions (separate experiments). (After M. C. Fuerstenau and S. Atak, *Trans. AIME*, **232**, 26 (1965), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

From these equilibrium data, it is shown that the $Pb(OH)^+$ is the dominant species that occur in the pH region (6 to 12) where flotation is possible. This indicates that some form of lead-hydroxy sulfonate is functioning as the collector. The adsorption mechanism of sulfonate in the presence of lead is expressed by the equation

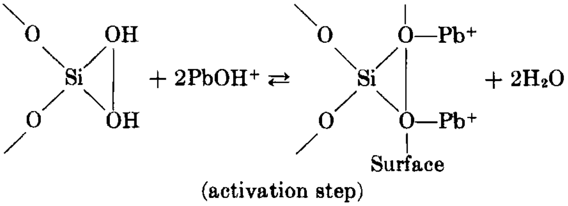
$$Pb_x(RSO_3)_y + OH^- \rightleftarrows Pb_x(OH)(RSO_3)_{y-1} + RSO_3^- \qquad (27)$$

According to this, $Pb_x(RSO_3)_y$, which occurs at high sulfonate concentration, is not the collector species and when this species dominates in the low pH region, the mineral is depressed, which explains the rise in flotation pH with increase in the sulfonate concentration.

A similar mechanism is believed to hold good in the collector action of amyl xanthate on quartz activated by lead or zinc ions. The best flotation recovery is achieved in the pH range 5.8 and 8.5 in the presence of $1 \times 10^{-4}\,M$ xanthate. Under these concentrations, very little free xanthate would be present. The following mechanism has been suggested (*46*):

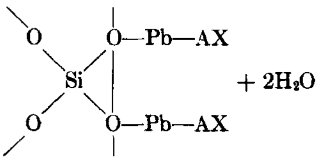


(28)



(29)

followed by the adsorption of xanthate ions:



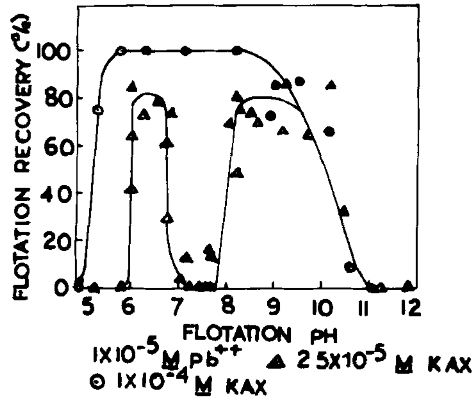
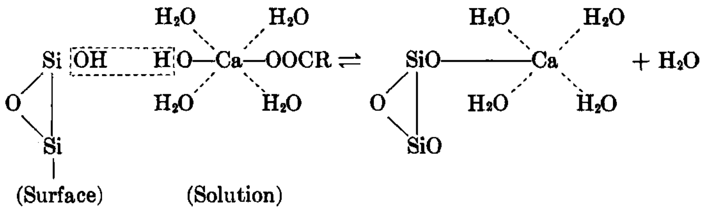


FIG. 6. Relationship between flotation recovery and pH with constant Pb^{++} and various amyl xanthate additions (separate experiments). (After M. C. Fuerstenau, J. D. Miller, R. E. Pray, and B. F. Perinne, *Trans. AIME*, **232**, 359 (1965), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

An interesting side result of this work is the observation that at the low concentration range of xanthate ($1 \times 10^{-5}\,M - 2 \times 10^{-5}\,M$ for $1 \times 10^{-4}\,M$ Pb^{++}) there is a flotation region followed by a depression region and again a flotation region all in the pH range 6–9. The intermediate depression region that separates the two flotation regions contracts with increase in the xanthate concentration and altogether vanishes when the collector concentration is raised to $1 \times 10^{-4}\,M$ (see Fig. 6). This result has not been explained and calls for further studies.

The role of basic aqueous complexes in the anionic flotation of quartz has been shown also for the calcium ion activation of quartz followed by sulfonate or fatty acid flotation. Considerations of the equilibria of the possible calcium hydroxy species show that the activity products of $Ca(OH^+)(RSO^-)$ and $Ca(OH^+)(Ol^-)$ determine the flotation of quartz by sulfonate and oleic acid respectively. But it is not certain whether the adsorbed species would be $(CaOH^+)(Ol^-)$ or the precipitated salt $Ca(OH)(Ol)$. An infrared spectroscopic study would be of interest to distinguish between the two species. With lauric acid as collector it has been shown (*47,48*) that flotation is not effected until calcium laurate is precipitated.

The mechanism of the collector action of fatty acid is expressed in the following equation:



(30)

This mechanism explains both the necessity of hydroxylating the mineral surface and the necessity of hydrolyzing the activating metal ion.

More experimental evidence in support of the role of basic metal complex ions has been provided by an electrokinetic study on the adsorption of ferric cations on quartz by Mackenzie (*49*) and adsorption studies by Daellanbach and Tiemann (*50*).

The mechanism of cationic collectors such as long-chain aminium salts has been extensively investigated in the past and reviewed in earlier works (*1,6*). There are several inconsistencies in the results reported by different investigators using different techniques. The important question of whether the collector species is aminium ion, neutral molecule amine, or a combination of the two has not been satisfactorily answered. The recent work of Smith (*51*) has provided additional data on the quartz-dodecylamine-nitrogen system. Contact angle measurements revealed that at pH 10 the magnitude of the angle was 80°, which corresponds to complete monolayer coverage. An angle of 38–40° was observed at pH 6 to 7 and about 36° at pH 4 to 5, both values corresponding to monolayer coverage. This suggests that both the dodecylamine ion and the dodecylamine molecule are active species. The concentrations of these species were calculated by the ionization constant of dodecylamine and the solubility of the dodecylamine molecule. The magnitude of the contact angle depends on the relative amount of amine ions and amine molecules. If the ion is the dominating species in the system the maximum contact angle is about 36°. The ions are adsorbed individually and because of the electrostatic repulsion no two ions would be adjacent to each other unless the charge is neutralized at the particular surface site. If, however, neutral amine molecules or a long-chain neutral molecule such as dodecyl alcohol are present along with amine ions, coadsorption of these neutral molecules by capture by dodecylamine ions serves to screen the repulsion between the neighboring like-charged ions. The contact angle rises to a value of about 86°

It should be noted, however, that the neutral molecules alone cannot be adsorbed on quartz; this is shown by the sharp drop in the contact angle at pH > 10 when the concentration of dodecylaminium ions is too small to be of any effect on the mineral surface.

Cassiterite

This is essentially stannic oxide, SnO_2. The crystal structure shows oxygen ions and tin (+4) ions in octahedral coordination, each tin ion being substantially equidistant from six oxygens. Thus it differs from quartz, SiO_2, which is built essentially on a tetrahedral lattice with four oxygen ions situated equidistant from one silicon ion. This dissemblance in crystal structure gives rise to a marked difference in floatabilities. Flotation of cassiterite has been studied using oleic acid and sodium cetyl sulfonate (*52*). Collins (*53*) has reviewed the earlier work. A new class of collectors, alkyl and aryl phosfonic acids and arsonic acids, has been introduced for the flotation of cassiterite. The collector mechanism is still obscure. Flotation tests with *p*-tolyl arsonic acid have shown satisfactory results. An interesting observation by Topfer (*54*) is that emulsification of the reagent with a hydrocarbon oil and an emulsifier such as alkyl sulfates or sulfonates serves to increase the speed and stability of the attachment of cassiterite particles to bubbles. This is explained by the hypothesis that when the reagent "edge" is at the three-phase contact, the contact angle increases and by decreasing the hydration of the mineral surface, the speed of attachment is increased.

Iron Minerals

The principal minerals of iron of both theoretical as well as technical importance are hematite (Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$). These are floatable by collectors of the long-chain fatty acid group, in particular, oleic acid. The adsorption of the collector is dependent on the accessibility of a maximum amount of surface area to the adsorbing ions and the number of ions capable of adsorbing on unit mineral surface area. This was assessed by Glembotskii (*55*) by counting for each of the probable cleavage planes of each mineral the possible number of iron cations per 1000 Å^2 accessible to carboxylate collectors. The average numbers so obtained are 96, 144, and 91 for hematite, magnetite, and siderite respectively and the average uncompensated charges of one ion cation are 0.67, 0.76, and 0.33, respectively. Hematite has large number of cations per unit surface area and more uniform distribution of uncompensated charges over its surface as compared to the other two minerals. This facilitates the adsorption of anionic collector and hematite floats more completely and readily than magnetite and siderite. In respect of floatability siderite is considerably inferior to magnetite because of the much smaller average uncompensated charge per cation. The floatability of all three minerals is greatly influenced by pH because H^+ and OH^- are the potential determining ions.

Joy and Watson (*56*) have investigated the adsorption of amine on negative sites of hematite surface. A titration technique involving potentiometric titrations of perchloric acid and potassium hydroxide in the presence of hematite was used to estimate the surface charge. It is shown that the total amine adsorbed is comparable with the change in surface charge density calculated from ζ-potential measurements only at low amine concentrations (below $10^{-5}\,M$). Above this region, more amine is adsorbed than can be accounted for by attachment of an aminium cation at negative sites. This can be explained by two additional modes of adsorption. Either the amine can be adsorbed as neutral molecules or aminium ions are adsorbed by exchange of H^+ ions at pH values distant from the zero point charge of the mineral. In the latter case however, the pH of the suspension would decrease with adsorption. This has not been checked. Physical adsorption of amine molecules seems to be a reasonable mechanism. Adsorption of aminium ions would be practically negligible under conditions of flotation since the hematite surface has been shown to possess a high density of uncompensated positive charge that would not attract cationic species.

An infrared study of the flotation of hematite with oleic acid and sodium oleate has been described by Peck, Raby, and Wadsworth (*57*). An attempt is made to characterize and interpret the adsorption processes involved. The infrared spectra are given in Figs. 7 and 8. The spectrum of hematite shows a broad band at 3420 cm^{-1} that corresponds to the surface hydroxyl group resulting from the chemisorbed and the physically adsorbed water. In the spectra of oleic acid and sodium oleate the bands at 2850 and 2920 cm^{-1} result from C—H stretching of CH_2 and CH_3 groups respectively. The —COOH group of oleic acid produces a band at 1705 cm^{-1} that shifts to higher wavelengths on ionization (in sodium oleate). The salts of oleic acid show a band at 1555 cm^{-1} due to the antisymmetrical C=O group. This

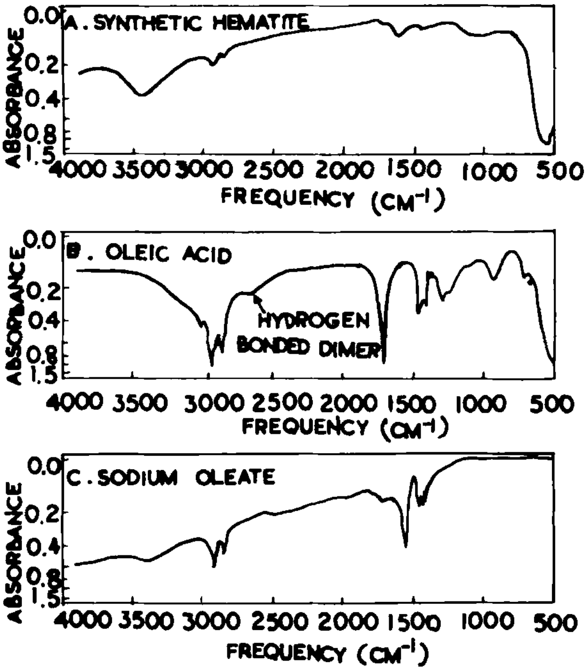


FIG. 7. Infrared spectra of hematite, oleic acid, and sodium oleate. (After A. S. Peck, L. H. Raby, and M. E. Wadsworth, *Trans. AIME*, **235**, 303 (1966), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

is the most characteristic band of oleates, as is revealed from the spectra of sodium and ferric oleates. Comparison of the spectrum of the latter with that of hematite in contact with oleic acid reveals that both of them show the band around 1520–1590 cm^{-1} due to the antisymmetrical C:O group. From this it is inferred that hematite chemisorbs oleate ions giving rise to a chemisorbed bond between ferric ions and oleate ions. The reverse band at 3400 cm^{-1} in the reaction for hematite at pH 9.4 is due to the displacement of surface —OH group by the reaction. Furthermore, the difference between the spectra of ferric oleate and chemisorbed oleate shows that the latter is not identical with the bulk salt and is a distinct entity characteristic of the surface adsorbed layer. It is of interest to compare this with the infrared spectroscopic study on the galena-xanthate system discussed earlier. In both cases the difference between the

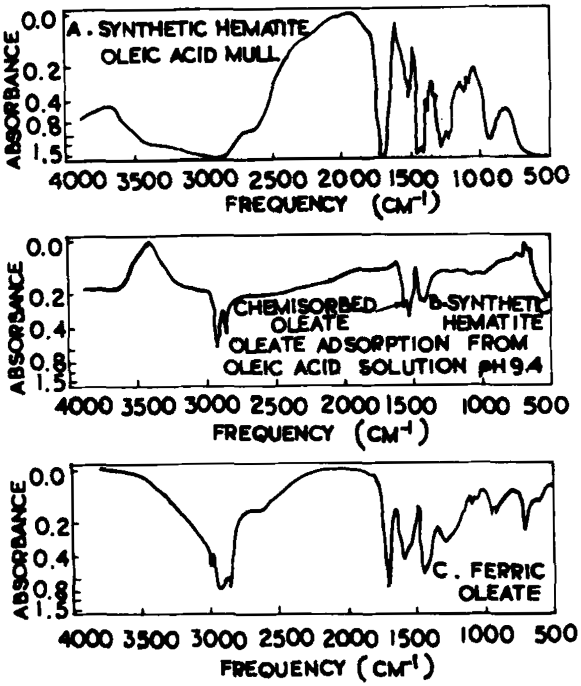


FIG. 8. *Infrared spectra of ferric oleate and hematite after reaction with* oleic acid. (After A. S. Peck, L. H. Raby, and M. E. Wadsworth, *Trans. AIME*, **235**, 304 (1966), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

chemisorbed surface species and the bulk compound is clearly shown by the infrared spectrum.

Based on the infrared data, the reactions of hematite with oleic acid are expressed by the equation,

$$\text{M—OH} + \text{HOl} \rightarrow \text{M—OH} \cdots \text{HOl} \qquad (31)$$

$$\text{M—OH} \cdots \text{HOl} \rightarrow \text{M—Ol} + \text{H}_2\text{O} \qquad (32)$$

where HOl denotes oleic acid, M—OH the mineral surface site with chemisorbed water, and M—Ol the mineral surface site with chemisorbed collector.

The maximum chemisorption of oleic acid occurs near the isoelectric point, which is located at pH 9.4, 7.9, and 8.8 respectively for synthetic, specular, and red hematite. As the pH value is removed appreciably from the isoelectric point chemisorption falls and there is only physical adsorption, which is not adequate for the formation of a stable hydrophobic surface. The observation that adsorption is maximum at the isoelectric point has led to the conclusion that adsorption of oleic acid is caused by a molecular mechanism.

The mechanism expressed above is in partial agreement with the surface charge calculations discussed before. The surface species M—OH results from the interaction of OH^- ions with the uncompensated mineral surface charge. But there is some doubt about the molecular mechanism because the bond represented between M—OH and HOl would not be expected to be a strong one. The displacement of the —OH group by Ol ions cannot be ruled out, even at the isoelectric point. This can be better elucidated by studying the solution chemistry of the system. Determination of bond energies by thermochemical studies should also be of interest.

The flotation of magnetite has been investigated with a new class of polymer complexes (*58*). Polyvinyl acetate (PVAc) in combination with a polyelectrolyte such as sodium lauryl sulfate (NaLS) or laurylamine hydrochloride (LAHCl) is shown to be a more effective collector system than either of the polyelectrolytes alone. A polymer complex LAHCl–PVAc or NaLS–PVAc is believed to be the active collector species and with this flotation is effective far beyond the isoelectric point of the mineral. This is explained by suggesting the formation of hemimicelles whose action on the surface is governed by factors other than simple electrostatic attraction. The selectivity of such polymer complexes has not been studied and at present the collector mechanism involved can be taken as a tentative guide for further studies on other oxide minerals and correlation with the crystallochemical factors.

Fluorite (CaF_2), Barite ($BaSO_4$), and Calcite ($CaCO_3$)

These three minerals closely resemble each other in flotation characteristics by virtue of the predominant ionic character of the bonds in their crystalline lattices. The ionic character results in active interaction between their cations with anions of the collector. The anionic collectors of importance are fatty acids and their sodium salts. Infrared study of these systems with sodium oleate as collector (at pH 9.5) has, however, shown that parts of the mineral surfaces are covered with chemisorbed oleate and some parts with physically adsorbed sodium oleate. The two are distinguished by the characteristic infrared absorption peaks of sodium oleate (at 6.40 μ) and surface barium oleate (at 6.48 μ) in the case of barite and surface calcium oleate (6.20 μ) in the case of fluorite and calcite. The relation between the amount of chemisorbed oleate θ_1 and physically adsorbed oleate θ_2 has been represented by Peck and Wadsworth (*59*) by an equilibrium expression

$$K = \frac{\theta_1}{\theta_2}(\text{NaX}) \tag{33}$$

where K is an empirical equilibrium constant and X represents the anion of the adsorbent mineral.

The chemisorbed oleate is susceptible to the action of anionic depressants. In the case of fluorite the magnitude of depression is of the order $F^- > SO_4^{-2} > Cl^-$ while for barite it is of the order $SO_4^{-2} > F^- > Cl^-$. Thus the anions characteristic of the adsorbent mineral have the greatest depressant action. The depression of chemisorbed oleate simultaneously permits the enhanced physical adsorption of sodium oleate on the mineral surfaces. The physically adsorbed sodium oleate is assumed to be weakly bonded to the mineral in the form of neutral molecules or submicelles. This does not, however, preclude the possibility of the formation of bimolecular or multimolecular films of sodium oleate bonded to the chemisorbed layer. A mineral surface coated with physically adsorbed collector film would be expected to show poor floatability because of the instability and random orientation of the collector films.

The chemisorption mechanism of fatty acids has been supported by the work of Fuerstenau and Miller (*60*) on the role of the hydrocarbon chain in the anionic flotation of calcite. These investigators have not shown evidence for the physically adsorbed film. However, their interpretation of the infrared spectra of the calcite-lauric acid system is admittedly subject to some uncertainties regarding the identification of the surface species, and further clarification seems desirable.

Silicates and Aluminosilicates

In this class are included a large number of complex minerals of considerable interest in the mineral industry as well as in mineralogy and crystallography. The basic structural unit of these minerals is the silica tetrahedra in which a silicon atom is located in the center of four tetrahedrally coordinating oxygen atoms. The linkage of silica tetrahedra, which occurs in a number of ways in the different minerals, determines the properties of these minerals. An excellent review of the crystal chemistry of these minerals has been given by Aplan and Fuerstenau (*6*), who have also discussed their flotation characteristics in the light of studies made prior to 1962.

An attempt has been made by Joy and co-workers (*61*) to classify the silicate minerals according to their flotation response. Two broad divisions are suggested. In the first, the framework structures consist of a network of $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-$ links extending in three dimensions. Quartz (SiO_2) and feldspar ($NaAlSi_3O_8$) belong to this class. In this structure, there is no way of cleaving the mineral particles without breaking Si—O bonds. When Si—O bonds are broken, active sites $\rangle$SiOH and $\rangle$Si—O^- are created which permit the adsorption of cationic collectors such as long-chain aminium salts. The surface sites will not respond to anionic reagents such as oleate. The minerals are depressed by fluoride ions which exchange for OH^- ions at the surface resulting in the suppression of ionization of $\rangle$SiOH to $\rangle$Si—O^-, thus effectively reducing the number of active sites for the adsorption of amines. The second division of minerals is represented by andalusite (Al_2OSiO_4 containing single SiO_4^- groups), beryl ($Be_3Al_2(SiO_3)_6$ containing rings with six silicon atoms in each ring), and spodumene ($LiAlSi_2O_6$ containing $(SiO_2)_n$ chains). When these minerals are ground they tend to break up in such a way as to preserve the polysilicate groups. The breakage of the crystals presents the surface cationic (Be^{++}, Al^{+++}, etc.) high-energy sites at which anionic collectors such as oleate could be adsorbed. The minerals in this division are readily depressed by the adsorption of fluoride ions which close the cationic sites by chemical interaction. The possibility of adsorption of neutral molecular oleic acid by hydrogen bonding cannot, however, be ruled out, as will be seen later.

Smith (*62*) has suggested a mechanism of activation of some of the silicate minerals by fluoride in cationic flotation. By contact angle tests, it is shown that adsorption of the collector is closely related to the molecular concentration of hydrogen fluoride. As the maximum molecular concentration of HF is approached closely for a particular concentration of NaF, the contact angle falls sharply (see Fig. 9). This indicates competition between H^+ ions and some other species in

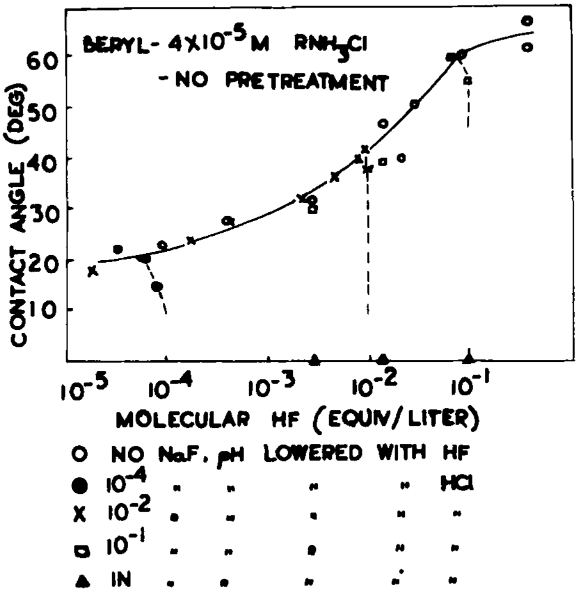
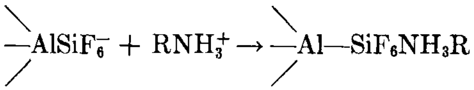


FIG. 9. Contact angle on beryl vs. molecular HF concentration for systems containing a fluoride. No pretreatment. (After R. W. Smith, *Trans. AIME*, 232, 160 (1965), by permission of the American Institute of Mining, Metallurgical, and Petroleum Engineers.)

solution. If, however, the pH is lowered by the addition of HF the contact angle continues to rise. The activator species is shown to be SiF_6^{-2} ion since large contact angles are obtained by treatment of the mineral with H_2SiF_6 at pH > 3.5. Below pH 3.5, the contact angle drops, again suggesting a competition with H^+ ions. The control of pH should be made by HF because when the mineral is pretreated with HCl, only small or zero contact angles are found. The difference between treatment with HF and that with HCl is due to the action of HF on surface silicic acid, thus creating additional active aluminum and possibly beryllium sites, while HCl decreases the number of aluminum and beryllium sites and exposes the surface silicic acid (which is not dissolved by HCl), thus hindering the adsorption of the collector. The following mechanism has been suggested:

$$\diagdown\!\!\!\!\diagup\!\!-\mathrm{Al{-}OH} + \mathrm{S_iF_6^{-2}} \rightarrow \diagdown\!\!\!\!\diagup\!\!-\mathrm{AlSiF_6^-} + \mathrm{OH^-} \qquad (34)$$

The cationic amine collector adsorbs on the negative sites:



$$\text{—AlSiF}_6^- + \text{RNH}_3^+ \rightarrow \text{—Al—SiF}_6\text{NH}_3\text{R} \qquad (35)$$

At low pH values, $HSiF_6^-$ may form, which could compete with SiF_6^{-2} ions for active surface sites on minerals. When $HSiF_6^-$ is adsorbed there would be no net negative charge on the surface and the mineral is depressed.

This mechanism has been further supported by Smith and Smolik (*63*) by infrared and X-ray diffraction study of the activation of beryl and feldspars in cationic collector systems. The infrared spectrum and X-ray diffraction pattern of the precipitate formed when the beryl specimen is placed in dodecylamine hydrochloride saturated with HF is similar to that of dodecylammonium fluosilicate.

Although the above mechanism appears reasonable, it is not in agreement with another set of observations of Joy and co-workers on beryl and feldspar systems (*64*). They found that when the mineral is treated with HF, the fluoride losses from the solution are so low as to preclude the formation of SiF_6^{-2} Second, an interesting observation has been made which demonstrates that although large amounts of collector may be adsorbed, that does not always ensure the floatability of the mineral. This happens when feldspar is washed with perchloric acid. The mineral adsorbs dodecylamine to the same extent as the mineral not treated with $HClO_4$, but it is strongly depressed. This is attributed to the high surface charge leading to a heavily hydrated surface which would require greater collector adsorption for equivalent floatability. Since $HClO_4$ removes aluminum atoms at the surface and yet the amine is adsorbed, it shows that aluminum atoms are not essential in the activation of feldspar and the adsorption of dodecylamine. An alternative mechanism has not been suggested. Moreover, the action of perchloric acid has not been explained. From the experimental technique described by Joy and co-workers, the quantity of $HClO_4$ retained on the mineral surface is not known. The consumption of dodecylamine as revealed by analysis might be due to simple chemical reaction of excess perchloric acid with amine. Further clarification appears desirable.

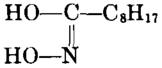
Peck and Wadsworth (*65*) have studied the flotation of beryl by oleic acid after preactivation with HF and HCl. The infrared examination of beryl treated with HCl and then with oleic acid did not show the characteristic absorption band of —COOH group indicating that oleic acid is not adsorbed. With the mineral pretreated with HF this band was found. The adsorption is mainly physical in nature because there was no evidence of the formation of surface carboxylic group. It is believed that oleic acid is bound to the beryl surface by hydrogen bonding through the strongly electronegative fluorine atom.

Anionic collectors such as long-chain alkyl or aryl sulfonates are chemisorbed on aluminosilicate minerals through direct linkage with free valence of aluminum ions. The presence of iron activates the surface and significantly enhances the adsorption of anionic reagents. The mechanism of iron activation and anionic flotation has been described by Fuerstenau and co-workers (*66,67*) and Matar and Rudolph (*68*). There is general agreement between the two groups of investigators. The activating species has been shown to be $FeOH^{++}$, which interacts with alkyl sulfonate ions giving a surface compound of the composition $Fe(OH)(RSO_3)_2$. At high concentration of Fe^{++} the minerals are depressed because the collector in solution is consumed with the formation of $Fe(RSO_3)_3$ which precipitates out. It is worth recalling that a similar activation mechanism has been described in the anionic flotation of quartz, lead hydroxy complexes being the predominant activating species. These results emphasize the need for careful pH control in the activation and flotation of quartz and silicate minerals.

An interesting finding of Lai and Smith (*69*) has indicated the potentialities of mixed collector adsorption in the flotation of silicate minerals. While the flotation recovery of beryl is virtually negligible with dodecyl alcohol alone and only about 45% with sodium dodecyl sulfate, it rises to nearly 100% with a mixture of sodium dodecyl sulfate and dodecyl alcohol. This is a good example of interaction between an ionic surfactant and a nonionic one. The nonionic dodecyl alcohol dipoles fit in between the dodecyl sulfate ions and thus partially screen the mutual repulsion due to like charges of the heads of the dodecyl sulfate ions resulting in increased surface coverage. This is an interesting possibility and a further evidence in favor of the use of mixed collectors. A close similarity can be seen between this system and the xanthate-quaternary ammonium salt (or xanthate-dixanthogen) system for sulfide minerals discussed earlier.

Collector Action of Chelating Agents

In recent years a new class of collectors, chelating agents, are being introduced in mineral flotation. The chelating agents are compounds that possess hydrocarbon groups and that form coordination complexes with certain specific metal atoms and thereby have potential mineral collecting properties. Their action is essentially dependent upon the availability of metal ions in concentrations enough to form a sparingly soluble complex. This has so far limited their use to the collection of very few minerals. Notable studies have been reported on chrysocolla (*70*), a silicate of copper that is collected by potassium octyl hydroxamate. The effective collector species is believed to be the free hydroxamic acid formed by hydrolysis at low pH:



$$\begin{array}{l} HO{-}C{-}C_8H_{17} \\ \qquad \| \\ HO{-}N \end{array}$$

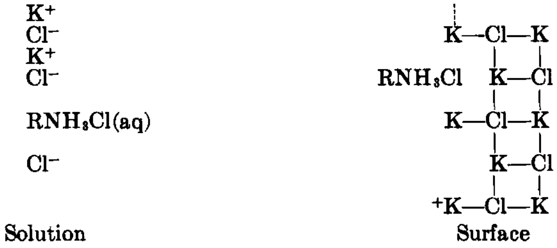
By virtue of their specificity and selectivity in forming metal ion complexes, the chelating agents should find much wider use in mineral flotation. It is rather surprising that even with the rapid progress of the chemistry of chelates in recent years, very little work has been done on the study of their potentialities as collectors. An economic factor—the chelating agents would be considerably more expensive than most conventional anionic and cationic collectors—seems to have hindered much progress in this direction.

Soluble Salts

The flotation of halite (NaCl) and sylvite (KCl) from their saturated solutions has acquired industrial utility in recent years. Sylvite is floatable by long chain-amine and sulfonate collectors and sylvite by potassium salts of long-chain fatty acids. The selective action of the collectors was first explained on the basis of ionic size (*72*). If the collector ion can fit into the crystal lattice at the surface in place of a constituent cation, the particular halide is floated. A slightly different explanation was given by Rogers and Schulman (*73*) based on the heats of solution of the salts. According to this, weakly hydrated salts can be floated with alkyl amines and sulfonates, while strongly hydrated salts are floatable by fatty acids. Excessively hydrated salts show poor or no floatability by any collector. However, it has been shown that the heat of hydration (L) which is the controlling factor is related to the ionic radius (r) by $Lr = 87.5$ for the alkali cations and $Lr = 167.5$ for the halide anions. Hence the collector mechanism would ultimately depend upon the ionic size.

A different approach to the problem has recently been made by Roman and co-workers (*74*). They have attempted to classify the floatabilities of halides on the basis of an electrical mechanism of adsorption. From the data of the free energies of hydration of the ions of these salts it has been shown that NaCl is negatively charged and KCl is positively charged. The flotation of positively charged halides by long-chain amines is explained by the van der Waals attraction of the negative end of its dipole by the positive surface of the salt. The collector mechanism of the amine is not dependent upon the adsorption of aminium ions which would have been expected to show selectivity toward the negatively charged sodium chloride surface. Similar considerations apply to the action of fatty acid salts on sodium chloride and other negatively charged halide surfaces. It is suggested that the collector species is an aqueous complex formed when the collector is dissolved in water. The mechanism of action of the amine on KCl is represented schematically as follows:

KCl Surface in Absence of Collector



KCl Surface after Adsorption of $RNH_3Cl(aq)$

Other forms of interaction are, however, not ruled out. Thus, while KCl is floated by lauryl sulfonate and NaCl is not, the situation is reversed in the presence of lead ions ($10^{-2}\,M$) when the effective collector species is believed to be a basic aqueous complex $Pb(OH)RSO_3$. According to Roman and co-workers this complex may get adsorbed by hydrogen bonding between the hydroxyls of the adsorbed water on the NaCl surface and the aqueous complex. In support of this it has been pointed out that the surface of NaCl is more strongly hydrated than that of KCl.

The structure of KCl shown in the above schematic representation of the collector mechanism is rather speculative, and no structural chemical evidence has been put forth in support of it. Furthermore, the bonding of amine with the halide would be expected to have a fairly low strength, whereas if the ion is adsorbed by electrostatic attraction a stronger bond would result. The bond strength and the nature of the adsorbed species in the halide systems have so far not been elucidated and it remains to compare the bond strengths in the case of species adsorbed by hydrogen bonding with those in the case of species adsorbed by dipole attraction. An electrokinetic study of the system together with thermochemical measurements to determine the bond energies involved is very desirable for further confirmation of the above mechanism.

Electrokinetic Studies on Collector Mechanism

The well-known electrokinetic phenomena arising out of asymmetric charge distribution at the mineral surface suspended in water have long been recognized in mineral flotation. Early work on the electrical double layer surrounding the mineral particle was reported by Gaudin and Sun (*75*). In recent years Fuerstenau and co-workers have conducted a series of studies involving the zeta potential measurement at the mineral particles suspended in flotation reagents. Extensive reviews of the work up to 1960 have been given in the AIME's *Froth Flotation, 50th Anniversary Volume* (*4,6*).

The basic explanation of electrokinetic phenomena is given on the basis of the Stern concept of double layer. The work W_i required to bring an ion of valency Z from the bulk of the liquid to a point in the double layer at potential ζ is given by

$$W_i = Ze(\zeta + \phi + \phi') \tag{36}$$

where e is the electronic charge, $Ze\phi'$ denotes contribution of the chemical work, and $Ze\phi$ is an additional work term to account for the van der Waals association between hydrocarbon chains of adsorbed ions. The term $Ze\phi'$ is zero in most of the systems studied because there is no chemical interaction between the collector species and the mineral surface.

The adsorption density of the ions in the Stern layer is given by

$$\Gamma = 2rc \exp\left[-\frac{W_i}{kT}\right] = 2rc \exp\left[\frac{-Ze\zeta - nZe\phi}{kT}\right] \qquad (37)$$

where c is the ion concentration in mole cm^{-3} in bulk solution, k the Boltzmann constant, n the average number of CH_2 groups per hydrocarbon chain, and r the radius of the adsorbing ion.

If there are two ions a and b competing for the surface, the ratio of their adsorption densities can be given by

$$\frac{\Gamma_a}{\Gamma_b} = \frac{r_a c_a}{r_b c_b} \exp\left\{\frac{-Z_a e\zeta + Z_b e\zeta}{kT}\right\} \exp\left\{\frac{-Z_a e\phi_a + Z_b e\phi_b}{kT}\right\} \qquad (38)$$

where the terms ϕ_a and ϕ_b denote specific adsorption potentials of the two ions. In the case of surface active ions with hydrocarbon chains this term will, as mentioned before, denote the cohesive energy of CH_2 groups and with other surface active ions their contribution will depend upon electrostatic attraction or chemical interaction. The magnitude of the specific adsorption potential can be evaluated in a number of ways; one method is based on the consideration of the double layer as a molecular condenser when ζ is zero (*76*).

The concentration of the ion is thus dependent on its adsorption potential. If one of the ions is specifically adsorbed, its concentration in the double layer is greatly favored. This enables the floatability of a mineral by a collector to be determined and the possibility of its depression by an inorganic ion. Onoda and Fuerstenau (*77*) have shown that at low concentrations of dodecyl ammonium acetate, sodium and barium ions reduce the ζ potential of quartz because they are coadsorbed with the aminimum ions. As the concentration of inorganic salt is increased while the collector concentration is below about $5 \times 10^{-4}\,M$, the ζ is reduced indicating that the inorganic ions are adsorbed in preference to the collector ions. But as the collector concentration is increased above $5 \times 10^{-4}\,M$, the specific adsorption potential of the collector species becomes effective since the dodecylammonium acetate ions have associated through van der Waals interaction of hydrocarbon chains. Above collector concentration of $8 \times 10^{-4}\,M$ only collector ions are adsorbed to the exclusion of inorganic cations and the mineral is not depressed.

Dependence of the mechanism of surfactant adsorption on chain

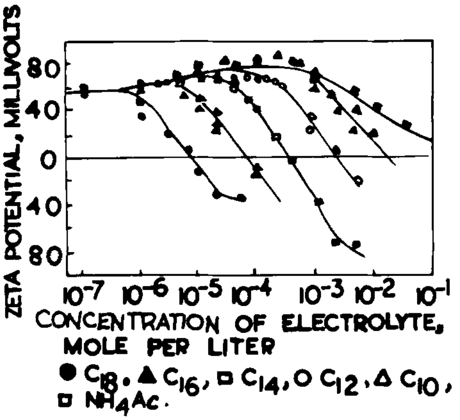


FIG. 10. Effect of hydrocarbon chain length on the zeta-potential of quartz in solutions of alkyl-ammonium acetates and in solutions of ammonium acetate. (After P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, 68, 3562 (1964). Copyright 1964 by the American Chemical Society. Reprinted by permission of the copyright owner.)

length has been studied with special reference to the quartz-alkyl ammonium acetate system by Somasundaran, Healy, and Fuerstenau (*78,79*). At low concentrations alkyl ammonium ions affect the ζ potential of quartz in nearly the same way as do sodium ions; at a certain concentration of alkyl ammonium ions there is a sudden change in the ζ potential (see Fig. 10). This critical concentration varies with the number of carbon atoms in the alkyl group. It has been shown for different alkyl chains that the critical concentrations at which the ζ potential is reduced to zero are far below the respective critical micelle concentrations for the various alkyl groups. This is explained by postulating the formation of hemimicelles resulting from the patches of ions associated by the van der Waals interaction. The critical concentration at which the association is observed is referred to as the hemimicelle concentration. This is shown to be a linear function of the number of carbon atoms in the alkyl chain of ammonium acetate. This is in accord with the Stern model of the double layer and Eq. (37), which reduces to the following expression when ζ is zero after association of the alkyl chains.

$$\ln C_0 = \frac{nZe\phi}{kT} + \ln (\Gamma)_0 - \ln 2r \qquad (39)$$

The van der Waals cohesive energy calculated from the linear relationship between C_0 and n is found to be 580 cal mole^{-1}. This value is in excellent agreement with values of $Ze\phi$ determined from solubility data or from the studies of micelle formation as a function of alkyl chain length of monofunctional surfactants. This is a substantial evidence in favor of hemimicelle hypothesis.

Further confirmation of the hemimicelle hypothesis has been advanced by the excellent correlation shown (*79*) between the different interfacial parameters for the system quartz-dodecylammonium acetate at critical hemimicelle concentration. The expected marked increase in adsorption density at this concentration is accompanied by the concomitant rapid change in the ζ potential. Contact angle and flotation recovery also increase abruptly at the hemimicelle concentration showing that these phenomena depend primarily on the formation of aggregates of long chain ions at the solid-liquid interface. The formation of hemimicelles and the subsequent association between the hydrocarbon groups has also been shown with the alumina-dodecylsulfonate system (*80*) and the beryl-hexadecyl sulfonate system (*68*).

Polkin and Berger (*81*) have studied the forms of fixation and mechanism of action of a large number of long-chain collectors by ζ potentials measurements. The collector is adsorbed by the ion exchange mechanism at low concentrations. But as the concentration is increased the ζ potential comes to a steady value (referred to as "stopping") or its sign is reversed at a definite concentration. This is explained by the formation of hemimicelles when any ion exchange practically ceases and the collector is adsorbed in molecular form.

While the hemimicelle hypothesis satisfactorily correlates collector adsorption and hydrocarbon chain length in the concentration region above critical hemimicelle concentration, a dependence of flotation on the chain length is also observed at concentrations below that required for hemimicelle association; this cannot be explained by the above mechanism, which postulates hydrocarbon chain interaction only at the solid-liquid interface. An explanation for the collector mechanism under such incipient flotation conditions has recently been put forward by Somasundaran and Fuerstenau (*82,83*) and supported by a few sets of observations. According to this view, the collector species are adsorbed both at the solid-liquid interface and the liquid-gas interface. The collector adsorbed at the liquid-gas interface, that is, at the interface of the gas bubble, facilitates reduction of the time necessary for the formation of the solid-gas interface, since the collector ions are now carried to the solid surface by the bubble. It has been shown by the surface tension, adhesion tension, and adsorption data that the collector that could be transferred to the solid-gas interface from the bubble surface upon contact is significantly higher than that which could be transferred from the solid-liquid interface. This suggests that for better flotation conditions, one should consider the conditions of adsorption at the liquid-gas interface and solid-gas interface rather than just at the solid-liquid interface as is usually done. Transfer of the collector to the solid-gas interface is energetically more favorable in the gas-phase adsorption process than in the liquid-phase adsorption process. This may be seen from the thermodynamic condition for solid-bubble attachment. According to Young's equatiton, $\gamma_{lg} > \gamma_{sg} - \gamma_{sl}$ for a large contact angle. (γ_{lg}, γ_{sg}, and γ_{sl} stand for interfacial tensions at the liquid-gas, solid-gas, and solid-liquid interfaces respectively.) There is little control on γ_{lg} in a mineral flotation system. By gas-phase adsorption γ_{sl} is kept as large as possible and γ_{sg} is simultaneously reduced, while by the conventional conditioning techniques γ_{sl} is reduced since positive adsorption (at the solid-liquid interface) tends to decrease the surface tension.

This finding has some interesting implications. The adsorption density of the collector on the mineral is shown to be dependent on the mode of transfer of the collector to the solid-gas interface. This would suggest a possible factor of improving the flotation efficiency, that is, by injecting the collector with the gas stream. But the point that should be examined is whether this holds good for all collector systems. According to the thermodynamic reasoning given above it should. But it is difficult to conceive the transfer of strongly ionic collectors such as xanthates through the liquid-gas interface because the concentration of ionized species at the liquid-gas interface would be expected to be insignificant. This aspect deserves to be examined.

An attempt has been made to elucidate the collector mechanism on monazite and zircon in relation to electrochemical changes on their surfaces (*84*). Zircon has an ionic crystal lattice made up of complex $[SiO_4]^{-4}$ and Zr^{4+} ions. Because of their smaller size Zr^{4+} ions would be placed in the interspace between the $[SiO_4]^{-4}$ ions that are present on the surface and edges of the minerals. The structure of the mineral, however, shows that Zr^{4+} is found on the surface and particularly on the corners of the crystal lattice; this is of special importance in the flotation of zircon, which is achieved by preactivation with sulfuric acid followed by collector action of amyl xanthate. The bisulfate ions derived from the dissociation of sulfuric acid activate the mineral surface according to the reaction

$$Zr^{4+} + HSO_4^- \rightleftarrows ZrSO_4^{2+} + H^+ \tag{40}$$

When amyl xanthate ions are adsorbed at the activated surface the following surface reaction is believed to occur:

$$Zr^{4+}SO_4^{2-} + nK^+nAX^- \rightleftharpoons [ZrAX_n]^{(n-4)-} + K_2SO_4 + (n-2)K^+ \tag{41}$$

The mechanism is supported by the reversal of the sign of zeta potential from the positive to the negative side on addition of xanthate.

The reagents mentioned above do not serve to bring out the flotation of monazite, although this has a crystalline lattice similar to that of zircon. In this case the positive sign of the zeta potential is not reversed in the presence of xanthate. No explanation is offered for the difference in the response to the collector between the two minerals having similar crystal structures. This seems to indicate that electrokinetic studies alone which are based primarily on surface charge considerations are not adequate to explain the collector mechanism. The bond energies involved in the collector adsorption should also be determined before arriving at a resonable mechanism of collector action. This again emphasizes the need for thermochemical studies on oxide and silicate mineral systems.

IV. ROLE OF IMPURITIES AND DEFECTS IN THE COLLECTOR ACTION

In the discussion on sulfide minerals mention was made of the relationship between the collector adsorption and the semiconductivity of the mineral arising out of the nonstoichiometry of the mineral sample and impurity centers. This aspect has attracted considerable attention in recent years largely due to the influence of solid-state chemistry and the realization that microdefects and impurities present in small quantities can have a significant effect on the floatability of a mineral. This could be one of the reasons for the wide discrepancy in flotation characteristics that is often noticed between two samples of the same mineral obtained from two different ore bodies.

Plaksin and Shafeyev (*85*) have measured the adsorption of the collector at different spots on the mineral surface by the microradiographic technique, which involves treatment of the mineral with the collector sample containing a radioisotope and obtaining a radiogram of the mineral. The radiogram so obtained shows unequal distribution of xanthate on sulfide minerals with certain sections of the surface unaffected by the collector and certain other regions acquiring several monolayers of reagent. The higher adsorption density has been attributed to the existence of anodic potential regions, and it has been shown that if a crystal of galena is kept under voltage there is a rapid uptake of xanthate when the potential rises to positive values. This conforms with the findings of Tolun and Kitchener (*28*) mentioned earlier. But the major inference of Plaksin and Shafeyev regarding the nonuniform adsorption has not been adequately supported by studies on other mineral systems. The adsorption studies do indeed reveal multilayer adsorption, and this has been shown to be due to chemical interaction between the surface oxidation product and the collector. But Plaksin's work deserves further attention because the possibility of nonuniform distribution due to microscopic defects in mineral crystals cannot be ruled out. This has indeed been observed, at least in the case of stibnite, by contact angle measurements.

To understand the role of impurities in the collector mechanism, it is desirable to have a knowledge of the structure of the electron bands in a solid (*86*). The presence of impurities in the mineral lattice serves either to donate electrons to the conduction band, thus increasing the n-type conductivity, or to accept electrons from the valence band, thereby increasing the p-type characteristic of the semiconductor. This can be illustrated with reference to zinc oxide, which has been studied in detail by Mular (*87*). Natural zinc oxide is known to be an n-type semiconductor. The cause of this n-type characteristic could be, in some samples, due to the defect state. If the sample shows slight deviation from stoichiometry resulting in deficiency of oxygen or excess zinc, this serves as impurity centers donating electrons to the conduction band (instead of donating electrons to oxygen as in the stoichiometric sample). This can be represented as follows:

$$\underset{\text{(excess)}}{\text{Zn}} \rightleftarrows \text{Zn}^{+}\,\text{(interstitial)} + e^{-} \tag{42}$$

The usual collector for zinc oxide is an anionic species such as oleate. It is expected that the adsorption of this will be facilitated if the mineral is transformed from an n-type to a p-type state and will be hindered if the n-type characteristic is increased. This was demonstrated by Mular by investigating the flotation characteristic of ZnO samples doped with Al_2O_3 and Cu_2O separately. When doped with Al_2O_3 the Al^{+3} ions replace some of the Zn^{++} ions in the lattice. In this process electrons are released into the conduction band in accordance with the equation

$$2Zn^{++} \text{ (in lattice)} + Al_2O_3 \rightarrow 2Al^{+3} \text{ (substituted for } Zn^{++}) + 2ZnO + \tfrac{1}{2}O_2 + 2e^- \quad (43)$$

On the other hand if it is doped with Cu_2O, the mineral is rendered less *n*-type or more *p*-type because when Cu^{++} ions replace some of the Zn^{+2} ions they accept some electrons from the valence band:

$$2Zn^{++} \text{ (in lattice)} + Cu_2O \rightarrow 2Cu^{+} \text{ (substituted for } Zn^{++}) + 2ZnO - \tfrac{1}{2}O_2 - 2e^- \quad (44)$$

When this is done the floatability of zinc oxide by oleate is greatly enhanced.

This work clearly shows that collector action is significantly influenced by the presence of impurities to deserve attention in elucidating the collector mechanism. This realization has given rise to new methods of altering the floatability of minerals by introducing impurities. In a recent paper Plaksin and collaborators (*88*) have presented results that establish the importance of the concentration of free electrons and holes in the interaction of reagents. Measurements of electrical conductivities of a large number of sulfide and nonsulfide minerals and simultaneous adsorption studies have shown that an increase of the concentration of electron vacancies in the body of the mineral results in an increase of the adsorption activity of the mineral surface in respect of the anionic collector and in an increase of the yield of the mineral in the concentrate. The adsorption activity of a mineral is a function of the ratio of the number of free electrons and holes: $\Gamma = f\ (n_e/n_p)$. The ratio of free charge carriers in the surface layer of a mineral can be varied by adjusting the oxidation reduction potential of the liquid phase, addition of oxidizing agents such as H_2O_2, $KMnO_4$, and O_2 to the liquid phase, or addition of reducing agents such as H_2S, Na_2S, or pyrogallol. The irradiation of minerals by γ-rays has also been employed to alter the ratio of charge carriers, thereby affecting the adsorption activity of the mineral. The floatability can thus be varied or controlled.

V. KINETIC ASPECTS IN COLLECTION MECHANISM

In addition to the action of the collector at the mineral surface with the formation of a hydrophobic film, a second important factor that determines the success of froth flotation is the attachment of a mineral particle with the air bubble. It was recognized early that in every system a certain minimum time known as the induction period is required to establish adhesion between a gas bubble and a mineral particle. The earlier work up to 1955, which has been reviewed by Sutherland and Wark (*2*), concerned only the various mechanical factors and was not related to collector action. The dependence of the induction period on collector action was first studied by Eigeles and co-workers (*89–91*). According to these studies small quantities of collectors, insufficient even for flotation, reduce the induction time. The higher the collector concentration, the shorter the induction period. The interesting implication of these findings is that adhesion of minerals to an air bubble in water occurs even in the absence of a surface-active agent. This has been demonstrated experimentally and induction times ranging from about 60 to 9600 sec have been recorded for a wide variety of minerals from sulfide as well as nonsulfide groups.

The effect of solution temperature on induction time has indicated a basis for the mechanism of bubble-mineral attachment. The experimental dependence of the induction time τ on the solution temperature is represented by the equation

$$\log \tau = (A/T) + B \tag{45}$$

where A and B are constants, A being the tangent of the slope of the straight line. This can be expressed in the form of the familiar Arrhenius type equation, thus:

$$\tau = \tau_0 \exp(W/kT) \tag{46}$$

where k is Boltzmann constant and τ_0 and W are constants that are interpreted by the following mechanism.

The change in the kinetics of attachment of solids can be regarded as a change in the surface state of the adhering particles, primarily of their boundary layers. Raising the temperature of the solution changes the state of the double layer and changes the chemical composition of the surface compound. As a consequence, the boundary layers pass into a labile state that promotes the growth of the attraction forces responsible for the mineral bubble attachment. According to this the constant τ_0 is characteristic of the boundary layer and W is the apparent activation energy in ergs per boundary layer molecule. This apparent activation energy depends on the nature of the mineral, the specific features of its genesis, and other factors that influence the surface structure. The introduction of a collector into the mineral suspension greatly lowers the value of W. The higher the collector concentration, the lower the activation energy. At a certain concentration it approaches zero. The adsorption of the collector on the mineral surface results in a drastic disturbance of the structure of the wetting film and hence in the labilization of the boundary layers. The work done in this process can be characterized by the difference between the apparent activation energy before introduction of the collector and its value after the addition of the collector. Some of the values are shown in Table 2.

The foregoing discussion implies that according to the mechanism suggested above the apparent activation energy should be equal in magnitude to the enthalpy of adsorption of the collector at the mineral surface if the value of W is 0 in presence of the collector. Thermochemical data are at present available only for galena. The value of W for galena shown in Table 2 is 0.92×10^{-12} erg per molecule, which amounts to 13.2 kcal mole^{-1}. The enthalpies of adsorption of xanthate and diethyl dithiocarbomate given by Mellgren and Rao (*9,10*) vary from 9.9 to 13.4 kcal per mole of xanthate, depending upon the surface treatment of the galena sample. If the value of W for galena treated with these collectors is taken as nearly 0, the close agreement between the enthalpy of adsorption and the value of W in the absence of the collector is significant. It should be of great interest to determine similar thermochemical data for quartz and other minerals to test the validity of the mechanism of bubble-mineral attachment.

Adhesion of minerals to an air bubble without surface active agents tends to revive the belief that most minerals have inherent floatability.

TABLE 2

Apparent Activation Energy for Passage of Boundary Layers into Labile State

Mineral	Conditions of surface preparation	Medium	W, erg $\text{molecule}^{-1} \times 10^{12}$
Quartz	Dry ground in steel mill	Distilled water	4.75
Barite	Dry ground in steel mill	Distilled water	1.8
Galena	Dry ground in porcelain mill	Distilled water	0.92
Quartz	Dry ground in steel mill	Dodecylamine, 1.4×10^{-5} M	0.78
Quartz	Dry ground in steel mill	Dodecylamine 2.8×10^{-5} M	0

Although defended by a group of investigators in the 1920s and 1930s, it was long discarded, particularly after it was demonstrated that a polished mineral surface showed no contact with the air bubble in the absence of a collector. It is now argued that the discrepancy is due to the fact that the contact angle tests were carried with a large air bubble and a polished surface where the attraction force required for bubble attachment would be three to five times higher than that needed to balance the weight of a small mineral particle. Although qualitatively reasonable, this has not been supported by quantitative energy calculations. Moreover, the bubble-mineral attachment in the absence of reagent does not consider the wetting of the solid. Native floatability has been correlated with crystal structure (*92*), and it has been shown that native floatability results when at least some fracture or clevage surfaces form without rupture of interatomic bonds other than residual bonds. When all natural fracture or cleavage surfaces offer ionic bonds to the surrounding liquid in greater density than some threshold value, there will be no native floatability. It is not easy to find out what the "threshold value" should be and whether it is dependent on the nature of the mineral. The situation with regard to sulfide minerals and most nonsulfide has not been analyzed. Further work involving surface chemical and energy calculations will be useful to clarify the phenomenon.

The kinetics of adsorption of collectors and modulating agents has been examined by Bogdanov and co-workers (*93*). The rate of interaction of xanthate with galena, and copper ions with sphalerite, are in a linear relation with concentration of the respective ions in solution provided the density of the sorption layer constitutes only a fraction of a monolayer. This is taken as supporting the theory that with slightly oxidized galena, when xanthate sorption is limited to a fraction of a monolayer, one lead ion on the mineral surface binds only one xanthate ion and hence the compound formed by reagent sorption on the mineral surface differs from the compound formed by reaction in bulk. This constitutes additional evidence in favor of the adsorption mechanism previously discussed in detail.

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