Considerations on the Mechanism of Reaction between Xanthate and Sulphide Minerals

By

Shigeru MUKAI*, Takahide WAKAMATSU*, and Minoru ICHIDATE*

(Received March 30, 1964)

In order to study the mechanism of flotation, the phenomena of the collection and the depression were discussed, at first by means of thermodynamics, and then the reaction product on the mineral surface was confirmed by the infrared spectroscopic study.

In the thermodynamical discussion of the flotation phenomena, it was postulated that the adsorption of xanthate on the sulphide mineral depends on the chemical affinity. Consequently, the variation of free energy on the reaction between xanthate ion or hydroxyl ion and sulphide mineral was calculated as the function of pH value on the basis of thermodynamics. From the results, the pH range where xanthate ion or hydroxyl ion preferentially reacts on the sulphide mineral was determined. These ranges, respectively, coincided fairly well with those of the collection or the depression for the sulphide mineral flotation.

By the infrared spectroscopic study, it was confirmed that the metal xanthate should be produced on the surface of sulphide mineral.

Thus, it can be said that the chemical affinity between the sulphide mineral and the flotation reagent is an important factor in flotation.

1. Introduction

The reaction between the collector and the mineral surface in flotation is most important in order to clarify the principle of flotation. Accordingly, much research has been presented by investigators, for instance, the solubility theory by Taggart[1], the ion adsorption theory by Wark[2], the acid molecule adsorption theory by Cook[3], and so forth. However, the mechanism of the collection has not been fully understood, because the collection phenomena are due to the formation of mono-molecular film which may be produced at the surface of the mineral through the reaction between the collector and the mineral surface, and that the reaction amount of the mono-molecular film is too little to measure and to confirm the products.

The authors have investigated the reactions between the flotation reagents

---

and the sulphide mineral surface by the electrochemical procedures for several years and have pointed out that these reactions should depend on the chemical affinity between the reagent ion and the mineral surface.

In this research the reaction of the xanthate ion on the sulphide mineral surface is considered from the chemical affinity on the basis of the thermodynamical constants.

2. Chemical Affinities between the Sulphide Mineral and the Xanthate Ion or the Hydroxyl Ion

Taggart reported on the solubility theory of the flotation reaction, in 1930, in which he says "Sulphide minerals should be generally oxidized to produce the compounds of metal sulphate or metal carbonate on the mineral surface through the comminution process. These products are soluble in water containing the xanthate ion, and the ion-exchange reaction according to the difference of the solubility may occur with the production of a film of the metal xanthate compound on the mineral surface, thus the mineral becomes hydrophobic and floatable."

The reason why Taggart could postulate the oxidation of the mineral surface is probably that the solubility of sulphide minerals is generally too small to explain the production of the metal xanthate on the mineral surface without assuming the oxidation of the mineral surface.

Recently, du Rietz[4] considered the importance of chemical reaction in flotation. He estimated the solubilities of metal xanthate, metal soap and metal hydroxide in the solution of various pH value. Thus he attempted to investigate the flotation condition of minerals on the basis of the difference of the solubility.

The flotation reaction in the solubility theory by Taggart was considered only on the basis of the solubility products in the reaction products. And in the study by du Rietz, the flotation reaction was considered through the variation of solubility in the solution of various pH values.
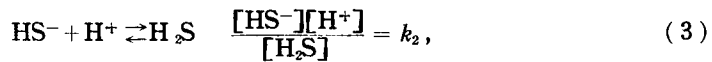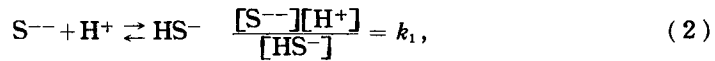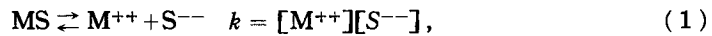
However, in these two works, the solubilities of products in the flotation reaction were only considered and the concentrations of reactants in the reaction system were not considered. It is well known that the floatability of minerals is considerably influenced by the amounts of the collectors or the depressants in pulp. Accordingly, the work by du Rietz as well as by Taggart may still be unsatisfactory for explaining the actual flotation.

In this research, it is attempted to investigate the reaction between the xanthate ion and the hydroxyl ion thermodynamically on the flotation of the

sulphide mineral without considering the surface oxidation according to Taggart's theory and without only on the basis of the solubility of chemical compounds as does du Rietz. Furthermore, both the ion concentration of the additional flotation reagent and the dependence of the original solubility of the minerals on pH in the solution are considered to discuss the flotation reactions.

(1) Solubility of the Sulphide Mineral with Varying pH in the Solution

The solubility of sulphide minerals varies remarkably with the varying pH value of the solution. When the metal sulphide represented as MS is immersed in pure water, the conceivable equilibria in water are as follows:

$$MS \rightleftarrows M^{++} + S^{--} \quad k = [M^{++}][S^{--}], \tag{1}$$

$$S^{--} + H^+ \rightleftarrows HS^- \quad \frac{[S^{--}][H^+]}{[HS^-]} = k_1, \tag{2}$$

$$HS^- + H^+ \rightleftarrows H_2S \quad \frac{[HS^-][H^+]}{[H_2S]} = k_2, \tag{3}$$

and

$$[M^{++}] = [S^{--}] + [HS^-] + [H_2S]. \tag{4}$$

If the solubility of the sulphide is represented as $[M^{++}]$, it becomes the equation (5):

$$[M^{++}] = \sqrt{k} \left\{ 1 + \frac{[H^+]}{k_1} + \frac{[H^+]^2}{k_1 k_2} \right\}^{1/2}. \tag{5}$$
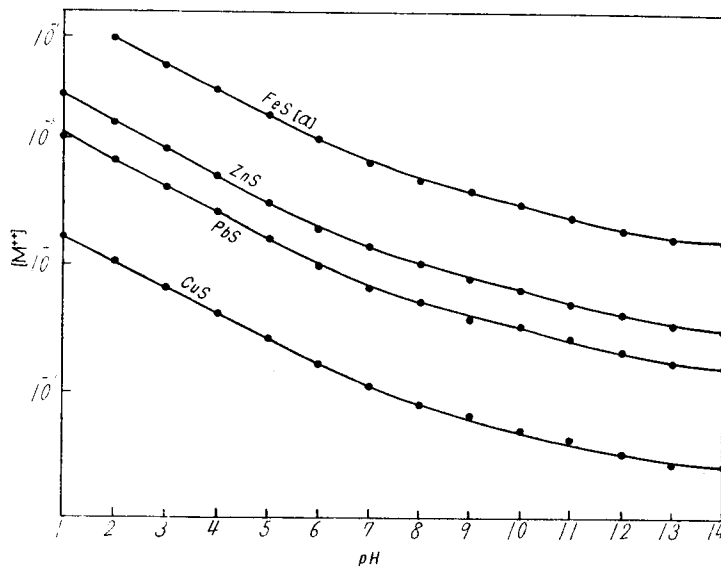

Fig. 1. The solubility of PbS, CuS, ZnS, and FeS as a function of pH value.

Equation (5) shows that the solubility of sulphide depends on the hydrogen ion concentration.

For some sulphides, the relations between the solubility and pH were calculated, where k, k_1 and k_2 were obtained by Latimer's thermodynamical data[5]. In Figure 1, the solubility of PbS, ZnS, CuS, and FeS is shown as a function of pH value

(2) Chemical affinities between the sulphide mineral and the xanthate ion or the hydroxyl ion

Paneth and Horovitz[6] concluded in their studies of adsorption that an electrolyte ion tends to be strongly adsorbed on a crystalline solid if it forms a difficultly soluble or weakly dissociated compound with the oppositely charged ion of the crystal lattice, that is, the adsorption depends on the solubility product of the reaction product, the chemical affinity.

Assuming that the adsorption of xanthate ion on the surface of sulphide mineral depends on the chemical affinity of the reaction between the cation due to mineral lattice and the xanthate ion;

$$M^{++} + 2X^- \rightleftarrows MX_2 . \qquad (6)$$

The abbreviation "X⁻" and "MX₂" are used for xanthate ion and metal xanthate.

The change of free energy ΔF_I in this reaction (6) is

$$\Delta F_I = \Delta F_I^0 + RT ln \frac{[MX_2]}{[M^{++}][X^-]^2} \quad ,$$

where $[MX_2]$, $[M^{++}]$ and $[X^-]$ are activities for reactants. If the activity coefficients of the reactants equal to unit, $[MX_2]$, $[M^{++}]$ and $[X^-]$ are identified as concentrations.

Assuming that $[MX_2]$ is in solid phase for simplification

$$\Delta F_I = \Delta F_I^0 - RT ln [M^{++}][X^-]^2 \quad ,$$

where $\Delta F_I^0 = RT ln\, L_{MX_2}$ and L_{MX_2} represents the solubility product of the metal xanthate compound.

Thus,

$$\Delta F_I = RT ln\, L_{MX_2} - RT ln [M^{++}][X^-]^2 \qquad (7)$$

The values of L_{MX_2} are evaluated as 6.8×10^{-17} [7], 6.3×10^{-25} [8] and 5.3×10^{-9} [9] for lead xanthate, copper xanthate and zinc xanthate, respectively. And they are values obtained on a reaction in aqueous solution. Wark[10] pointed out that the adsorption solubility product in surface reaction should be less than in aqueous solution, and also Taggart[11] prophetically stated that the solubility

of the substance as a surface coating is less than that of the same substance independently put into solution.
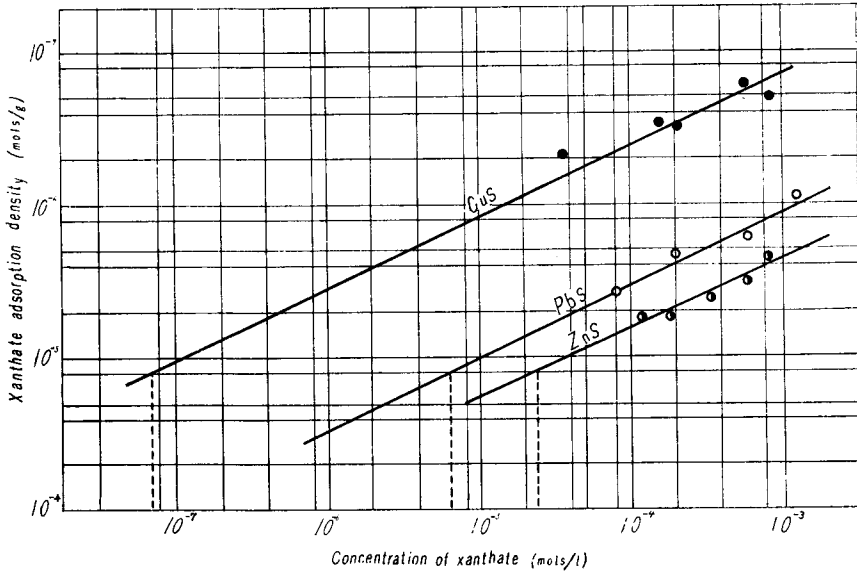

Fig. 2. Adsorption of xanthate on minerals with varying xanthate concentration;
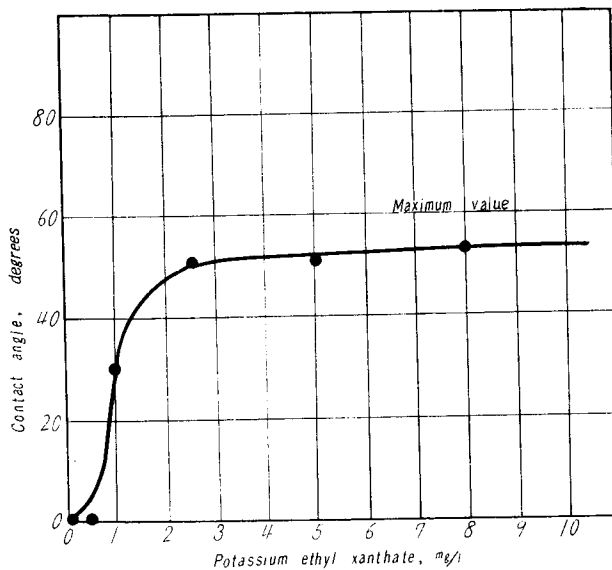CuS, PbS, and ZnS.

Fig. 3. Contact angle of galena in potassium ethyl xanthate
solution after 40 min to 1 hr contact.
(From the data of I. W. Wark and A. B. Cox)

One of the authors reported the experimental results of the xanthate adsorption on galena, covelline, and sphalerite as shown in Figure 2.

Previously, Wark and Cox[12] showed the relation between contact angle and the concentration of potassium ethyl xanthate as illustrated in Figure 3. From this results, the contact angle on galena is about 10° in the xanthate concentration of 0.7 mg/l, about 30° in 1 mg/l, and about 50° in 2 mg/l. Accordingly, it is considered that the effective adsorption of xanthate on galena may be performed in the xanthate solution of 1 mg/l. Thus, the xanthate concentration requiring the same quantity of the xanthate adsorption to sphalerite and covelline as to galena can be obtained from Figure 2, and evaluated as 2.2×10^{-5} mol/l for sphalerite and 5.6×10^{-8} mol/l for covelline. On the other hand, the cencentration of cations due to metal of mineral lattice can be calculated by the equation (5).

Assuming that the above determined xanthate concentrations are the least amount of xanthate required to adsorb on mineral, the solubility product of metal xanthate at mineral surface should be given as shown in Table 1.

Table I.　Solubility product of metal xanthate.

Sulphide	Solubility product of metal xanthate		A_{II}/A_I
	At mineral surface (A_I)	In a solution (A_{II})	
Gelena	$10^{-21.99}$	$10^{-16.17}$	$10^{5.82}$
Covelline	$10^{-30.04}$	$10^{-24.23}$	$10^{5.81}$
Sphalerite	$10^{-19.40}$	$10^{-8.28}$	$10^{11.12}$

Comparing A_I with A_{II}, it is recognized that the solubility product of metal xanthate in a solution is 10^6 to 10^{11} times as much as at mineral surface. Similarly, Wark[13] stated in his work that the solubility product in a solution is 10^3 to 10^9 times as much as at mineral surface.

From the above fact, it is considered that the solubility products of surface coating substance should be extremely smaller than the value of those obtained in a solution. Accordingly, as the first approximation, the coefficient of 10^{-9} was used in this study.

Thus, the equation (7) becomes

$$\Delta F_1 = RT \ln 10 \left\{ \log L_{MX_2} + \log 10^{-9} - \log [M^{++}] - 2 \log [X^-] \right\}, \qquad (8)$$

where $RT \ln 10 = 1364.282$ cal/mol.

In xanthate aqueous solution, the xanthate ion is in equilibrium with the hydrogen ion as follow ;

$$H^+ + X^- \rightleftarrows HX \qquad k_{HX} = \frac{[H^+][X^-]}{[HX]} . \qquad (9)$$

If the additional amount of xanthate represents C_X, then

$$C_X = [HX] + [X^-] . \qquad (10)$$

From the equation (10) and k_{HX}, the concentration of the xanthate ion is represented in the following formula:

$$[X^-] = C_X \Big/ \Big\{ 1 + \frac{[H^+]}{k_{HX}} \Big\} . \qquad (11)$$

Substituting the equation (5) and (11) into (8), the change of free energy in the formation reaction of the metal xanthate can be obtained.

As in the case of the reaction of the xanthate ion on the mineral surface, the reaction of the hydroxyl ion on the mineral surface can be considered.

$$M^{++} + 2OH^- \rightleftarrows M(OH)_2 . \qquad (12)$$

The change of free energy, ΔF_{II}, in this reaction (12) is

$$\Delta F_{II} = RT \ln 10 \Big\{ \log L_{M(OH)_2} + \log 10^{-9} - \log [M^{++}] - 2 \log [OH^-] \Big\} , \qquad (13)$$

where $L_{M(OH)_2}$ represents the solubility product of the metal hydroxide and $[M^{++}]$ is calculated by the equation (5).

3. Considerations on the Collection by Xanthate and the Depression by the Hydroxyl Ion

It has been investigated from the chemical affinity to see which ion, the xanthate ion or the hydroxyl ion, preferentially reacts with the mineral surface, by comparing the variation of free energy.

The change of free energy in the reaction between CuS, PbS or ZnS and the xanthate ion or the hydroxyl ion was calculated from the equation (8) and (13), and is shown in Figure 4, 5, and 6.

Now, the change of free energy in the reaction between the xanthate ion and the mineral is ΔF_I. The change of free energy in the reaction between the hydroxyl ion and the mineral is ΔF_{II}. Comparing the absolute value of ΔF_I with that of ΔF_{II}, at a constant concentration of xanthate, it is recognized that $\Delta F_I > \Delta F_{II}$ at low pH values and $\Delta F_I < \Delta F_{II}$ at high pH values.

Considering this from the chemical affinity, if $\Delta F_I > \Delta F_{II}$, the xanthate ion should react preferentially on the mineral surface. On the other hand, if $\Delta F_I < \Delta F_{II}$, the reaction of the hydroxyl ion on the mineral surface should
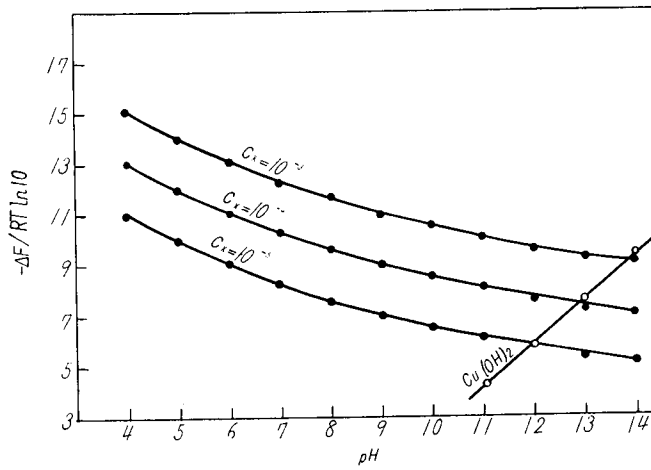
Fig. 4.   Change of free energy in the reaction between CuS and
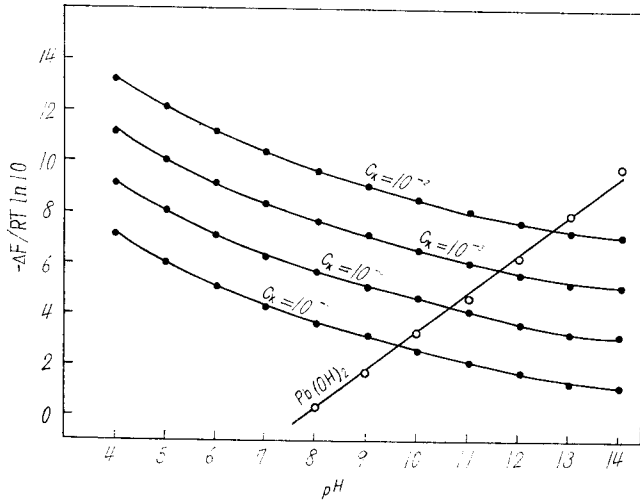xanthate ion or hydroxyl ion with variation of pH value.

Fig. 5.   Change of free energy in the reaction between PbS and
xanthate ion or hydroxyl ion with variation of pH value.

follow.   And in the case of $\Delta F_I = \Delta F_{II}$, either the xanthate ion or the hydroxyl ion might be react on the mineral surface, namely, the critical point.

The critical points for ZnS, PbS and CuS are shown in Figure 7.   Figure 8 shows the comparison of the critical condition obtained from the measurement of the floatability for sphalerite, galena and covelline with that shown in Figure 7.
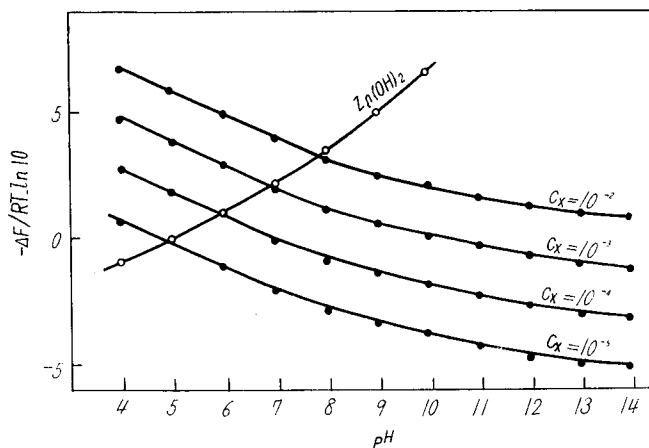
Fig. 6. Change of free energy in the reaction between ZnS and xanthate ion or hydroxyl ion with variation of pH value.
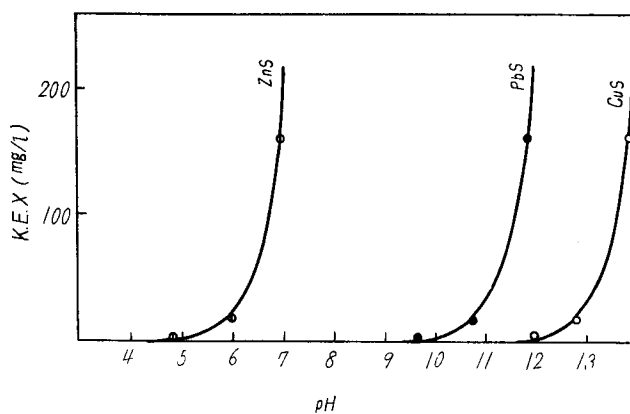

Fig. 7. Critical conditions obtained thermodynamically for ZnS, PbS, and CuS.

It is recognized from Figure 8, that the critical conditions obtained by the measurement of floatability coincide fairly well with those of the above considerations on the chemical affinity.

At the mineral-solution interface, the concentration of the xanthate ion or the hydroxyl ion becomes generally higher than in the bulk because of the adsorption of ions on the mineral surface.

Considering that the concentration of xanthate ion or the hydroxyl ion might distribute from the interface to the bulk solution according to the Maxwell-Boltmann's law, the ion density ρ_+ or ρ_- at interface is
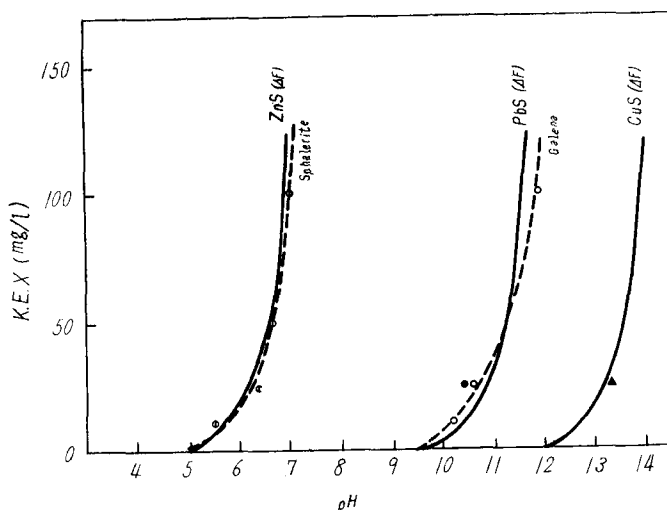
Fig. 8. Comparison of the critical conditions obtained ther-
modynamically for ZnS, PbS, and CuS with those by the
measurement of floatability for sphalerite, galena, and
covelline.
(▲, ● from the data of I. W. Wark and A. B. Cox)

$$\rho_+ = \rho_{+\infty} e^{-\varepsilon + \varphi/kT} , \qquad \rho_- = \rho_- e^{-\varepsilon - \varphi/kT} \tag{14}$$

where $\rho_{+\infty}$ and $\rho_{-\infty}$ are the ion density at the point of infinity of the bulk
solution. ᵢ and   are signs of positive charge and negative charge,
respectively.

If the equation (14) is expressed in terms of concentration,

$$C_+ = C_{+\infty} e^{-E_+/kT} , \qquad C_- = C_{-\infty} e^{-E_-/kT} \tag{15}$$

where E_+ and E_- are the adsorption energy for the positive ion and the nega-
tive ion.

When the concentration of the ion increases at the interface according to
the equation (14) and (15), the possibility in the reaction between the xanthate
ion or the hydroxyl ion and the mineral surface could be increased to combine
each other chemically.

If the adsorption energy of the xanthate ion to the mineral surface is
equal to that of the hydroxyl ion under the critical condition, the critical point
coincides with the results shown in Figure 7, though the increase in concen-
tration at the interface occurs.

Thus, it can be said that the phenomema of the collection and the depre-
ssion in flotation is based on the chemical affinity between the xanthate ion

or the hydroxyl ion and the mineral surface.

4. Infrared Study on the Xanthate-Mineral Reaction

As mentioned above it may be considered by thermodynamical studies that the xanthate ion or the hydroxyl ion reacts chemically on the mineral surface. Then it was attempted to confirm the reaction product on the mineral surface by the infrared spectroscopy.

The infrared studies on metal xanthate compounds were reported by J. Leja and G. W. Poling[14]. They found the variation of specific bond, $C=S$ and $C-O-C$, which is characteristic in the xanthate polar group of the metal xanthate. R. G. Greenler[15] confirmed the lead xanthate on PbS by the infrared spectroscopy. This PbS was synthetically prepared by precipitation and immersed in the xanthate solution.

In the author's investigation, the natural galena was used. After the pure galena was ground, the ground galena was purified in 0.01 N NH_4OH solution and then washed in distilled water to store up in a vaccum dryer. 500 mg of dried sample was immersed in 50 cc of 10^{-2} mol potassium ethyl xanthate and stirred for 1 hr. at 25°C. Then, 2 mg of the xanthate treated sample was made into a KBr pellet with 200 mg of KBr. The KBr pellet was used in the experiment of the infrared spectroscopy.

Thus, the infrared adsorption spectrum of the reaction compound on the natural galena was obtained. The result is shown in Figure 9. For comparison, the infrared adsorption spectrum of the lead xanthate precipitated synthetically was taken. This spectrum is shown in Figure 10.
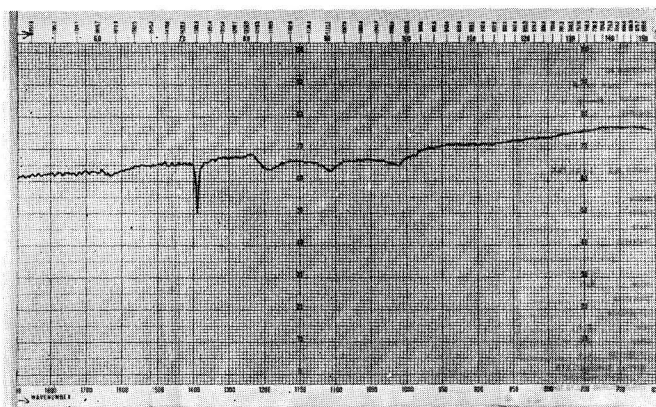

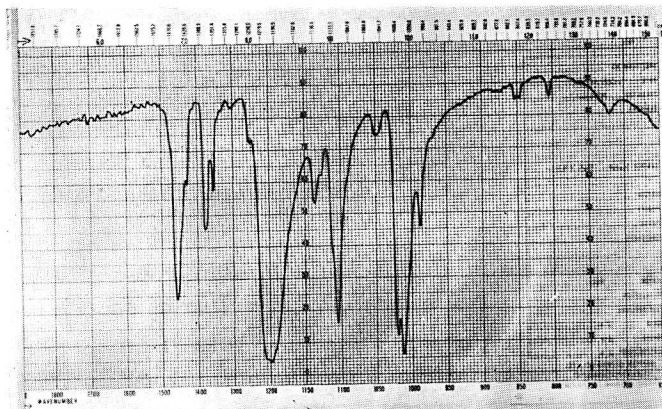Fig. 9. Infrared spectrum of galena treated with xanthate solution.

Fig. 10.   Infrared spectrum of lead xanthate compound.

From Figure 10 the lead xanthate obtained by precipitation was assigned in the stretching vibrations for C=S bond and C−O−C bond as follows:

(ⅰ) C=S stretching vibration at 1010 cm⁻¹

(ⅱ) C−O−C stretching mode at 1105 cm⁻¹ and 1200 cm⁻¹

On the other hand, as can be seen in Figure 10, the infrared spectrum of the natural galena treated with the xanthate solution recorded the specific bands at 1015 cm⁻¹, 1108 cm⁻¹ and 1198 cm⁻¹.

Consequently, it can be confirmed that lead xanthate should be produced on the surface of the galena.

5. Conclusion

In order to study the mechanism of flotation, the phenomena of the collection and the depression were discussed, at first by means of thermodynamics, and then the reaction product on the mineral surface was confirmed by the infrared spectroscopic study.

In the thermodynamical discussion of the flotation phenomena, it was postulated that the adsorption of xanthate on the sulphide mineral depends on the chemical affinity.   Then, the variation of free energy on the reaction between xanthate ion or hydroxyl ion and sulphide mineral was calculated as the function of pH value on the basis of thermodynamics.   From the results, the pH range where xanthate ion or hydoxyl ion preferentially reacts was determined by the chemical affinity.   These ranges respectively coincided fairly well with those of the collection and the depression of the sulphide minerals. Thus, it can be said that the chemical affinity between the sulphide mineral and the flotation reagent is an important factor in the flotation reaction.   And

this consideration is not inconsistent with the flotation phenomena, even if the concentration of the ion in the liquid phase adjacent to the mineral surface increases.

Comparing the infrared spectrum of galena treated with the xanthate solution with that of lead xanthate prepared synthetically, the reaction produced on the galena surface was studied and it was confirmed that the formation of lead xanthate on galena should follow.

References

1) Taggart, A. F., Taylor, T. C. and Knoll, A. F. Chemical Reactions in Flotation, *Transactions of the American Institute of Mining and Metallurgical Engineers* (1930) 87 : 285–315.

2) Wark, I. W., *Principle of Flotation*, Melbourne : Australian Institute of Mining and Metallurgy 1938, 142.

3) Cook, M. A. and Last, G. A., Collector Depressant Equilibria in Flotation, *Journal of Physical Chemistry* (1952) 56 : 637.

4) Du Rietz, C. Fatty Acid in Flotation, *International Mineral Dressing Congress*, Stockholm (1957), 417–433.

5) Latimer, W. M., *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd ed.

6) Paneth, K. and Horovitz, F., Über Adsorptionsversuche mit Radioelementen, *Zeitschrift für Physikalische Chemie*, (1915) 89 : 513.

7) Gaudin, A. M., *Flotation*, New York : McGraw-Hill Book Company Inc., 1957, 202.

8) Du Rietz, C., Xanthate Analysis by Means of Potentiometric Titration Some Chemical Properties of the Xanthate (Abstract) *Chemical Abstract*, (1958) 52, 7033–d.

9) Gaudin, A. M. *Flotation*, New York : McGraw-Hill Book Company Inc., 1957, 202–203.

10) Wark, I. W., *Principles of Flotation*, Melbourne : Australian Institute of Mining and Metallurgy, 1938, 138–144.

11) Taggart, A. F., Taylor, T. F. and Knoll, A. F., Chemical Reactions in Flotation, *Transactions of the American Institute of Mining Metallurgical Engineers* (1930) 87 : 285–315.

12) Wark, I. W. and Cox, A. B., Principles of Flotation, 1, *Transactions of the American Institute of Mining and Metallurgical Engineers*, 112, 189–244, especially 209.

13) Sutherland, K. L. and Wark, I. W., *Principle of Flotation*, 2nd ed., Melbourne : Australian Institute of Mining and Metallurgy.

14) Leja, J. and Poling, G. W., Infrared Spectra of Xanthate Compounds Assignment of Vibration Frequencies, *Canadian Journal of Chemistry*, (1961) 39 : 745–754.

15) Greenler, R. G., An Infrared Investigation of Xanthate Adsorption by Lead Sulphide, *Journal of Physical Chemistry*, (1962) 66 : 879–883.