Electrochemical Study on Flotation

By

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For the purpose of studying the principle of mineral flotation, the mechanisms of both mercury-collector reaction and mercury-depressant reaction were investigated by means of electrochemistry; furthermore the mechanism of reaction between sulphide minerals and flotation reagents was discussed. From the electrochemical discussion on the mechanism of flotation reactions, it may be concluded that the floatability of the mineral in flotation using xanthate as a collector and NaCN, KCN, or Na_2S as a depressant is governed by the reaction accompanying the electron transfer, namely, the redox reaction. And it is confirmed that the change in electrode potential relates closely with the contact angle or floatability and consequently it plays an important role in flotation.

1. Introduction

It is important to make clear the condition of collection and depression in flotation for minerals, and many research works concerning it have been presented by investigators. However, the mechanism of collection or depression has not been fully understood, for the reasons that the flotation phenomena are due to the formation of mono-molecular film which may be produced at the surface of the mineral through the reaction between flotation reagent and mineral surface, and that the reaction amount of mono-molecular film is difficult to measure.

The authors have attempted to study the mechanism of collection and depression by means of electrochemistry.

Zeta-potential has been often measured for non-conductive substances such as oxide minerals. The Zeta-potential, however, varies in all cases where flotation reagents adsorb physically or react chemically to mineral surfaces, so that it may be difficult to determine the reaction in flotation from the Zeta-potential measurements.

In this study, the electrode potentials of mercury and sulphide minerals are

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measured to investigate the mechanism of reaction between mineral surface and collector or depressant reagent. Furthermore, the contact angle on mercury and the floatability of sulphide mineral are measured and then the mechanism of surface reaction of the mineral for the flotation reagents upon which flotation depends and the relation between surface reaction and the floatability are discussed.

2. Experimental

Mercury used in these experiments was purified by washing with dilute nitric acid and distilled twice at reduced pressure. Pyrite and galena were chosen for sulphide mineral testing samples. These samples were prepared to be cut and shaped in the form of a rectangular column whose surfaces were ground and polished with carborundum powder. The shaped samples were washed with pure water and stored up in a vacuum dryer until they were used. The small part of the mineral surface connected to a lead wire was plated with gold by the vacuum evaporation method to be more conductive.

The floatability of the sulphide mineral was measured by the bubble pick up method[1]. Samples used in this measurement were 35~48 mesh powders.

The measurement of contact angle on mercury was carried out by means of contacting a small air bubble on the surface of the mercury which was kept in a rectangular glass cell (10×20×28 mm) containing a solution. The magnitude of contact angles was measured with a travelling microscope fitted with an eyepiece containing cross-hairs.

In the measurement of electrode potential for the mercury, the mercury electrode and the standard calomel electrode were used, and the mineral electrode for the sulphide mineral and the standard calomel electrode were combined. The magnitude of the potential was measured by a vacuum tube voltmeter or potentiometer. The experiments were performed under conditions thermostatically controlled to $25\pm0.5°C$.

Three kinds of xanthate, potassium ethyl xanthate, potassium isopropyl xanthate and potassium amyl xanthate were prepared synthetically in the authors' laboratory and purified by dissolving with acetone and by precipitating with petroleum ether. The other reagents used in this experiment were chemicals of extra-pure grade. On adjusting pH in the alkaline solution, caustic soda was used throughout. Pure water of which conductivity is 1×10^{-6} mho·cm^{-1} or less was used in these measurements.

3. Results and Considerations

3.1. The Electrode Potential of Mercury and Sulphide Minerals in the Electrolyte Solution.

(a) For Mercury

The electrode potential of mercury in an electrolyte solution of NaCl, KCl, NaOH, Na₂S, NaCN or KCN was measured by varying the electrolyte concentration. The results are shown in Fig. 1.
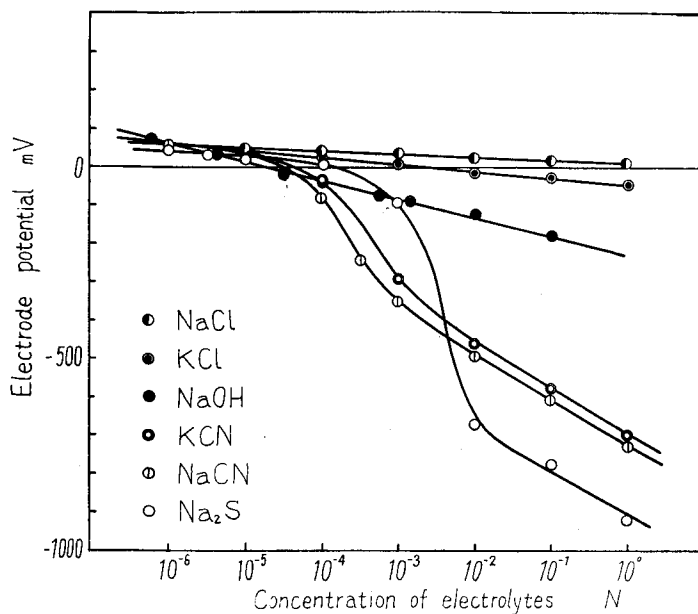

Fig. 1. Electrode potential of mercury in solutions of six different electrolytes.

As can be seen from Fig. 1, in a solution of NaCl or KCl the electrode potential of mercury hardly changes even though the electrolyte concentration is increased. Conversely, in a solution of NaCN, KCN or Na₂S as the electrolyte concentration is increased the value of the electrode potential decreased considerably. In a solution of NaOH, the electrode potential also decreases moderately with increase of the concentration of NaOH.

Assuming the electrode potentials as redox potentials of interface reaction accompanying the electron transfer, a following reaction is considered,
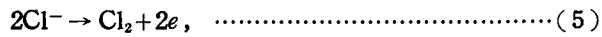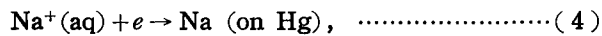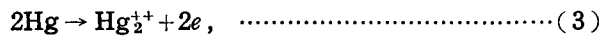
$$[\text{Red}] \rightleftharpoons [\text{Ox}] + ne, \qquad \cdots\cdots\cdots\cdots\cdots(1)$$

where [Red] is the concentration of reducing substance, [Ox] the concentration of oxidizing substance, and n the number of electron, e, taking part in the reac-

tion. The redox potential for reaction (1) is given as a following form,

$$E = E^0 + \frac{RT}{nF} \ln [\text{Ox}]/[\text{Red}], \qquad \cdots\cdots\cdots\cdots\cdots (2)$$

where E^0 is a standard electrode potential of the reaction system, R the gas constant, T the absolute temperature and F Faraday's number.

If the electron transfer occurs at the interface between mercury and NaCl solution, conceivable surface reactions which would occur at the interface are as follows:

$$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e, \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$
$$\text{Na}^+(\text{aq}) + e \rightarrow \text{Na (on Hg)}, \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$
$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e, \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$
and $\qquad 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-. \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$

Also in the case of mercury surface contacting the solution of the other electrolytes, similar reactions are conceivable.

Applying equation (2) for the above reactions, the equilibrium concentration of reactant is calculated. For 1-N solution of NaCl, KCl, NaOH, NaCN or Na$_2$S, the results of the equilibrium concentration calculated for conceivable reactions are shown in Table I.

From Table I, it is found that the quantities of reactions at the mercury

Table 1. Equilibrium concentration calculated for conceivable reactions in mercury-electrolytes solution system.

System	Reaction	Equilibrium Concentration
Hg|$_{(N)}$NaCl|S.C.E	$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e$ $\text{Na}^+(\text{aq}) + e \rightarrow \text{Na(on Hg)}$ $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e$ $2\text{H}_2\text{O} + 2e \rightarrow 2\text{OH}^- + \text{H}_2$	$C_{\text{Hg}_2}^{++} \cong 10^{-35}$ mol/l $N_{\text{Na}} \cong 10^{-42}$ mol/l $P_{\text{Cl}_2} \cong 10^{-54}$ atm $P_{\text{H}_2} \cong 3.7 \times 10^{-7}$ atm
Hg|$_{(N)}$KCl|S.C.E	$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e$ $\text{K}^+(\text{aq}) + e \rightarrow \text{K(on Hg)}$ $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e$ $2\text{H}_2\text{O} + 2e \rightarrow 2\text{OH}^- + \text{H}_2$	$C_{\text{Hg}_2}^{++} \cong 10^{-34}$ mol/l $N_{\text{K}} \cong 10^{-46}$ mol/l $P_{\text{Cl}_2} \cong 10^{-54}$ atm $P_{\text{H}_2} \cong 5.4 \times 10^{-8}$ atm
Hg|$_{(N)}$NaOH|S.C.E	$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e$ $\text{Na}^+(\text{aq}) + e \rightarrow \text{Na (on Hg)}$	$C_{\text{Hg}_2}^{++} \cong 10^{-27}$ mol/l $N_{\text{Na}} \cong 10^{-46}$ mol/l
Hg|$_{(N)}$NaCN|S.C.E	$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e$ $\text{Na}^+(\text{aq}) + e \rightarrow \text{Na (on Hg)}$	$C_{\text{Hg}_2}^{++} \cong 10^{-12}$ mol/l $N_{\text{Na}} \cong 10^{-53}$ mol/l
Hg|$_{(N)}$Na$_2$S|S.C.E	$2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e$ $\text{S}^{--} \rightarrow \text{S} + 2e$ $\text{Na}(\text{aq}) + e \rightarrow \text{Na (on Hg)}$	$C_{\text{Hg}_2}^{++} \cong 10^{-4.3}$ mol/l $N_{\text{S}} \cong 10^{3.7}$ mol/l $N_{\text{Na}} \cong 10^{-68}$ mol/l

surface contacting the solution of NaCl or KCl are only negligible. On the other hand, for mercury contacting Na₂S or NaCN solution, the products at the surface reaction are appreciable in equilibrium.

When the quantities of the reaction products on the electrode surface contacting a solution are very small at equilibrium, Grahame[2] defined the electrode as an ideal polarized electrode which has a negligibly small amount of charge transfer. And he considered the electrode as a non-ideal polarized electrode which has an appreciable amount of the product of the surface reaction in equilibrium. Accordingly, from the above facts, it may be shown that there are no reactions accompanying the electron transfer at the mercury surface in KCl or NaCl aqueous solution, while there occur the reactions accompanying the electron transfer at mercury surfaces in NaCN, KCN or Na₂S aqueous solutions.

Thus, it is considered that the anions of electrolyte such as NaCN, KCN or Na₂S differ from the anion of NaCl or KCl in behavior of reaction at the interface between the mercury and the electrolyte solution. As a consequence, the interface reaction between the mercury and electrolyte solutions such as NaCN, KCN or Na₂S, a depressant in flotation, might be a reduction-oxidation reaction accompanying the electron transfer.

(b) For Sulphide Mineral

In galena or pyrite-electrolyte aqueous solution systems, the relation between electrode potential and electrolyte concentration is obtained, as shown in Figs. 2 and 3.

As can been seen from Figs. 2 and 3, the electrode potential of pyrite or galena contacting an aqueous solution of NaCl or KCl hardly changes when the electrolyte concentration is varied. In the solution of Na₂S, the electrode potential of pyrite or galena decreases considerably with increasing of the electrolyte concentration. The electrode potential of pyrite in the solution of KCN changes remarkably with the variation of concentration, while the electrode potential of galena in the solution of KCN does not change so remarkably as the electrode potential of pyrite. In the solution of NaOH, the electrode potential of both sulphide minerals changes moderately by varying the electrolyte concentration. Considering these results for two sulphide minerals in the same way as in the case of mercury, the electrolyte such as NaCl or KCl reacts more feebly with the surface of these sulphide minerals than electrolytes such as NaOH, NaCN or Na₂S. It can be considered that the interface reaction between the sulphide minerals and the electrolyte solution such as NaCN, Na₂S or NaOH might be a redox reaction accompanying the electron transfer.
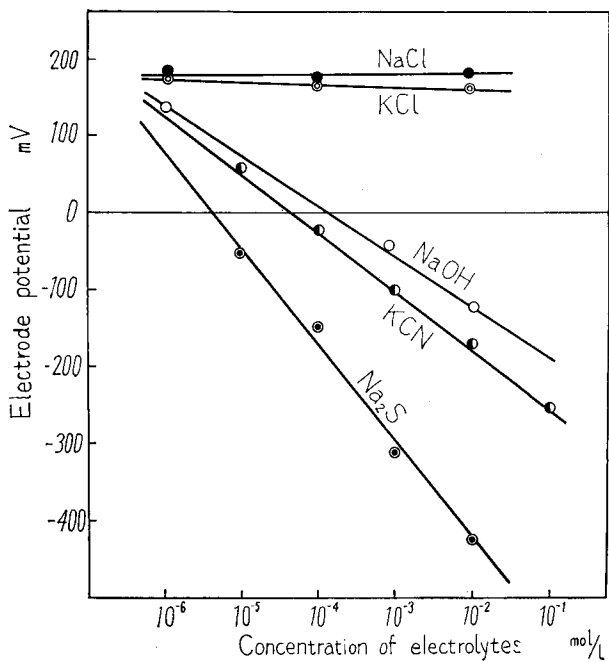
Fig. 2.   Electrode potential of pyrite in solution of five
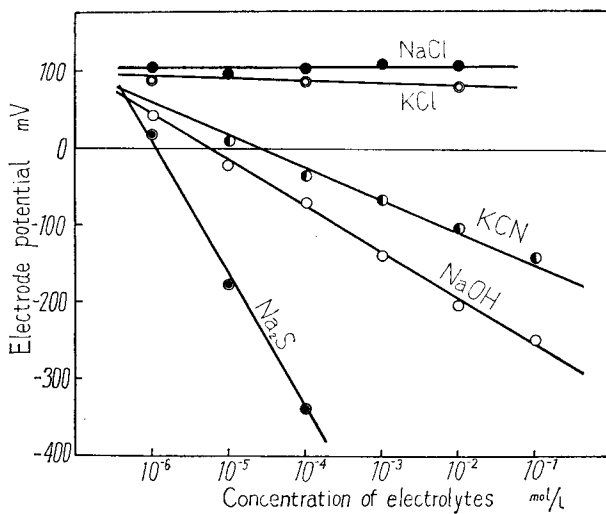   different electrolytes.

Fig. 3.   Electrode potential of galena in solution of five
          different electrolytes.

(c) Effects of Electrolytes on Contact Angle of Mercury

The contact angle on mercury in the solution of NaCl, KCl, NaOH or Na₂S was measured under conditions of various concentrations of each electrolyte. The results of measurements are shown in Fig. 4.
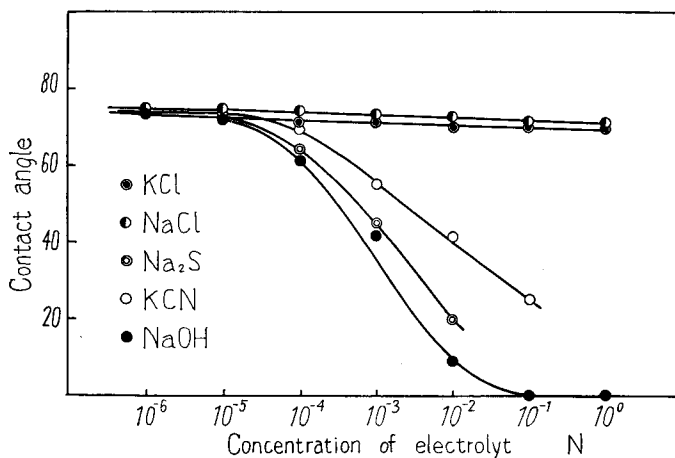

Fig. 4. Contact angle for mercury-electrolyte solution systems.

Fig. 4 shows that the magnitude of the contact angle is much affected decreasingly in the solution of NaOH, KCN or Na₂S with increasing of the electrolyte concentration. On the other hand, in the solution of NaCl or KCl, the increase in electrolyte concentration produces no effect on the contact angle.

From the above facts, it may be considered that the electrolytes such as NaOH, KCN and Na₂S which are used generally as depressants of flotation of sulphide minerals react on the surface of mercury or sulphide minerals as a redox reaction accompanying with electron transfer. As a consequence of the reaction, the surface of mercury or sulphide minerals changes into different conditions of floatability.

(d) The ε-Potential and the ζ-Potential

Generally there occurs an electrical double layer at the solid-liquid interface. The electrical potential in the double layer due to the distribution of the excess charges in the solution phase is shown in Fig. 5 as a function of the distance from the solid surface[3].
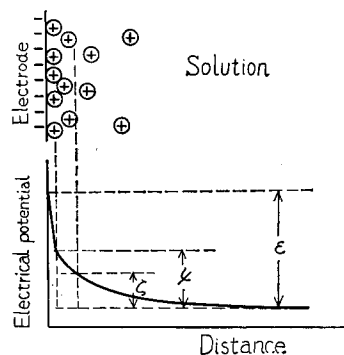
The electrical potential at the solid phase

Fig. 5. Schematic representation of the structure of the double layer and potential distribution in the double layer in electrolyte solutions.

with respect to a point far out in the bulk liquid is usually called the ε–potential (electrode potential). The potential drop across the diffuse part of the double layer—that is the potential difference between a point at a distance of one ion radius from the solid surface and the interior of the solution—is the ψ–potential.

The electrical potential at the slipping plane with respect to a point far out in the bulk liquid is called the ζ–potential (electro-kinetic potential).

At the ideal polarized interface at which there occurs no reaction accompanying the electron transfer across the solid-liquid interface, the electrical potential concerning the distribution of the excess charges in the solution phase as shown in Fig. 5 varies with the variation of electrolyte concentration, and as a result the ζ–potential also varies. Conversely, at the non-ideal polarized interface at which there occurs an electron transfer across the solid-liquid interface, the ε–potential varies with the variation of the concentration of the electrolyte which causes a redox-reaction to the solid surface. As a consequence, the counter ions in the electrical double layer rearrange at the interface. This rearrangement of ions causes the variation of electrical potential as a function of the distance from the solid surface, and thus it brings about the change in the ζ–potential. Accordingly, if the reaction between flotation reagent and mineral surface is governed by the physical adsorption without electron transfer, flotation phenomena, depressing or collecting, should not relate to the electrode potential, but correlate with the ζ–potential. If surface reaction is based on the reaction accompanying the electron transfer, flotation phenomena should be related to the electrode potential and the ζ–potential. Thus, the mechanism of reaction between flotation reagent and mineral surface cannot be corroborated from the results of the ζ–potential measurement alone.

In this study, the electrode potential of both mercury and sulphide minerals was measured. From the experimental results, it was recognized that electrolytes such as NaOH, NaCN, KCN or Na$_2$S which usually have effects on the floatability of sulphide minerals make a variation of electrode potential of mercury and sulphide minerals with the increase of electrolyte concentration.

It may be said from these facts that the reaction between flotation reagent and mineral surface is mainly based upon the reaction accompanying the electron transfer at the solid-liquid interface and that the electrode potential is closely correlative with the floatability of sulphide minerals.

3. 2. Electrode Potential and Concentration of Xanthate

(a) Mercury-Xanthate Solution System

The change of mercury electrode potential with the variation of concentration of various xanthates is shown in Fig. 6.
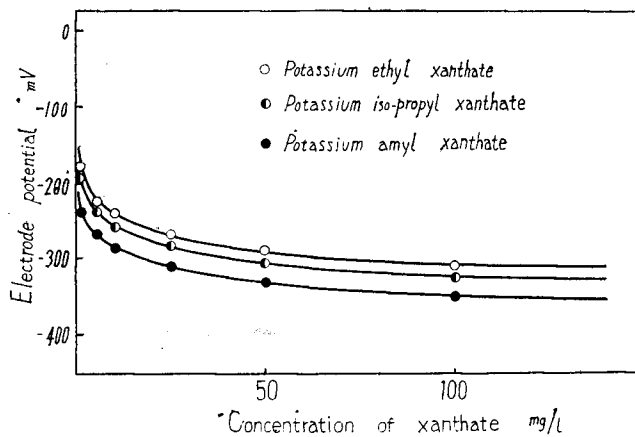
Fig. 6. Electrode potential of mercury in aqueous solutions of various xanthates.

As can be seen in Fig. 6, the electrode potential of mercury changes usually with the variation of xanthate concentration and it decreases remarkably with increasing of the xanthete concentration. If the same consideration as taken in the case of the mercury-electrolyte solution system is carried out, it may be said that there occurs the electron transfer across the mercury-liquid interface and that the xanthate ion consequently combines with the mercury surface by redox reaction with the exception of the case of a fairly dilute xanthate solution. At concentrations less than 10 mg per litre, the change of electrode potential which is due to the variation of xanthate concentration is remarkable, while at concentrations more than about 10 mg per litre it is relatively small. The electrode potential of mercury in the xanthate solution shows some difference according to the kind of xanthate. At the same concentration, the higher the alkyl group of xanthate, the more negative is the electrode potential of mercury.

Generally, the Nernst equation is in existence for the relation between electrode potential and ion concentration. The Nernst equation is represented in the following form;

$$E = E^0 + \frac{RT}{nF} \ln a, \qquad \qquad \cdots\cdots\cdots\cdots\cdots (7)$$

where a is activity of ion.

Equation (7) is also expressed as the following form:

$$E = p + q \log C, \qquad \cdots\cdots\cdots\cdots\cdots(8)$$

where C is the concentration of xanthate, and p and q and constants.

With concentration of xanthate used in this experiment, the potential-concentration curves obtained by these measurement accord with the Nernst relation perfectly as shown in Fig. 7 and Fig. 8.
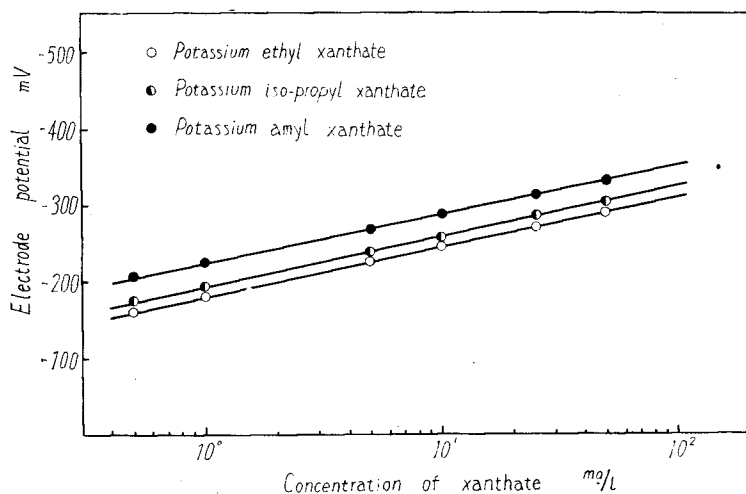
Fig. 7.   Relation between mercury electrode potential and concentration of xanthate.
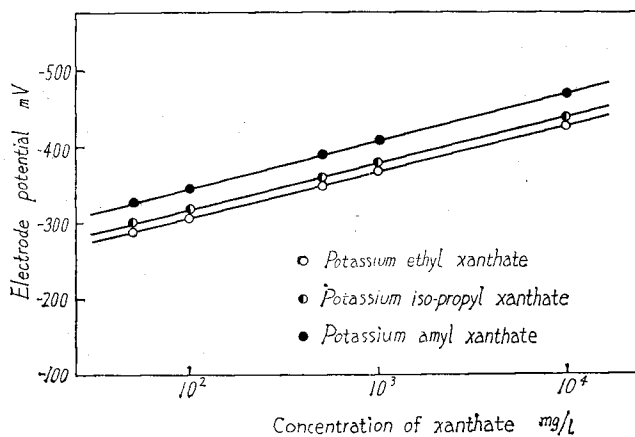
Fig. 8.   Electrode potential of mercury in aqueous solution of various xanthates at the concentrations more than 100 mg/l.

(b)   Sulphide Mineral-Xanthate Solution Systems

The electrode potentials of sulphide minerals vary with the lapse of time

after the immersion of an electrode piece into the xanthate solution and constant values were usually obtained about one and a half hours later. The electrode potentials on sulphide minerals were measured about one and a half hours later after immersion of the electrode piece into the xanthate solution.

Relations between electrode potentials of pyrite and concentrations of xanthate for potassium ethyl xanthate, potassium iso-propyl xanthate and potassium amyl xanthate are shown in Fig. 9.
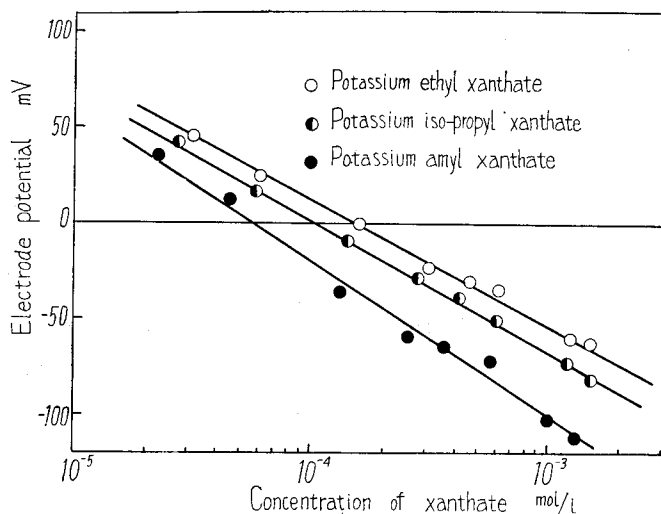
Fig. 9. Electtode¯'potential of pyrite in aqueous solutions of various xanthates.

Fig. 9 indicates that the electrode potential of pyrite decreases with increase of the xanthate concentration and that amyl xanthate gives the most negative potential among the xanthates used.

The relation between electrode potential, E, and the concentration of xanthate, C, is expressed as follows:

$$E = a + b \log C, \qquad \cdots\cdots\cdots\cdots\cdots\cdots (9)$$

where a and b are constants.

Fig. 10 shows the relation between the electrode potential of galena and the concentration of xanthate.

As can be seen from Fig. 10, the relation between the electrode potential and the concentration of xanthate for galena is similar to the results obtained for pyrite.
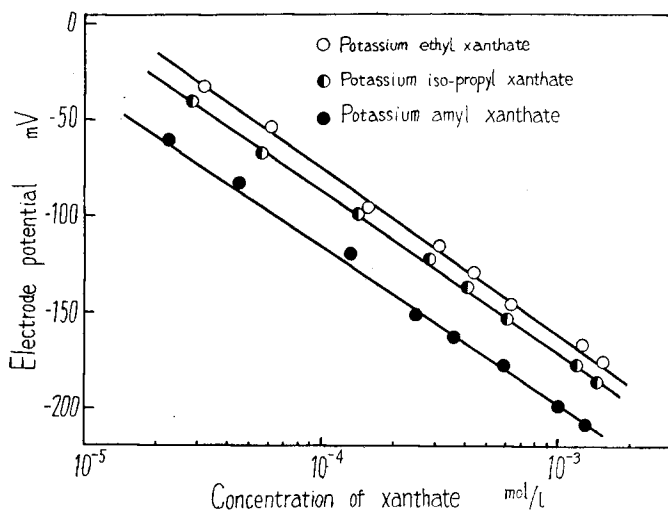
Fig. 10.   Electrode potential of galena in aqueous solutions of various xanthate.

3. 3.   Thermodynamical Considerations of Electrode Potential

The electrode potential of mercury in the mercury-xanthate solution system may be considered to be based on the reaction accompanying the electron transfer. This reaction, however, is not obvious in detail.
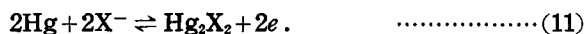
The reaction that the electrical potential of mercury contacting the xanthate solution is based upon will be elucidated on the results of the measurements of the potential difference for the electrochemical cell.   This cell is based upon the chemical reaction of the formation of the mercury xanthate compound.   For this purpose, the mercury xanthate compound was prepared synthetically and the above cell was constructed.

(a)   Electrochemical Cell due to the Chemical Reaction from Formation of Mercury Xanthate Compound

The electrode reaction at $Hg|Hg_2^{++}$ boundary is:

$$2Hg \rightleftharpoons Hg_2^{++} + 2e, \qquad \cdots\cdots\cdots\cdots\cdots(10)$$

while the reaction of the mercury-mercury xanthate electrode, $Hg|Hg_2X_2|X^-$, is:

$$2Hg + 2X^- \rightleftharpoons Hg_2X_2 + 2e. \qquad \cdots\cdots\cdots\cdots(11)$$

(The abbreviation 'X' is used for the xanthate.)

Thus, the reaction taking place in the following cell, $Hg|Hg_2X_2|X^-||Hg_2^{++}|$ Hg, is:

$$Hg_2^{++} + 2X^- \rightleftharpoons Hg_2X_2. \qquad \cdots\cdots\cdots\cdots(12)$$

Accordingly, the change in free energy due to the above reaction can be taken out as the electrical potential difference between both electrodes of the cell.

(b) Standard Potential, Equilibrium Constant and Reaction Heat

In the chemical reaction, $aA + bB \rightleftharpoons cC + dD$, the change in free energy, ΔF, is expressed in the following form:

$$\Delta F = \Delta F^0 - RT \ln \frac{\alpha_C^c \cdot \alpha_D^d}{\alpha_A^a \cdot \alpha_B^b}.$$

In equilibrium, $\Delta F = 0$, thus

$$\Delta F^0 = RT \ln \frac{\alpha_C'^c \cdot \alpha_D'^d}{\alpha_A'^a \cdot \alpha_B'^b} = RT \ln Kc,$$

where α_A', α_B', α_C' and α_D' are activities for reactants in equilibrium and Kc is the equilibrium constant. When the decrease of free energy due to the reaction can be taken out as the electrical energy, the following relation is obtained:
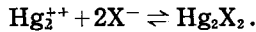
$$\Delta F = nFE.$$

Hence,
$$E = \frac{RT}{nF} \ln k - \frac{RT}{nF} \ln \frac{\alpha_C^c \cdot \alpha_D^d}{\alpha_A^a \cdot \alpha_B^b}. \qquad \cdots\cdots\cdots\cdots (13)$$

For the standard condition,

$$E^0 = \frac{RT}{nF} \ln Kc.$$

In the cell, $Hg | Hg_2X_2 | X^- \| Hg_2^{++} | Hg$, the reaction is:

$$Hg_2^{++} + 2X^- \rightleftharpoons Hg_2X_2.$$

Thus,
$$E^0 = \frac{RT}{nF} \ln \frac{[Hg_2^{++}]}{[Hg_2X_2][X^-]^2} = \frac{RT}{nF} \ln Kc, \qquad \cdots\cdots\cdots\cdots (14)$$

where $[Hg_2X_2]$, $[Hg_2^{++}]$ and $[X^-]$ are equilibrium concentrations for reactants. When Hg_2X_2 is in solid phase,

$$E^0 = -\frac{RT}{nF} \ln [Hg_2^{++}][X^-]^2$$

$$= -\frac{RT}{nF} \ln L, \qquad \cdots\cdots\cdots\cdots (15)$$

where L represents the solubility product of the mercury xanthate compound. Therefore, the solubility product of the mercury xanthate compound is calculated by determining E for the above cell.

The relation between free energy change and the heat of the reaction is exprssed by the following Gibbs-Helmholtz equation deduced by thermodynamic treatment.

$$\Delta F = \Delta H + T(\partial F / \partial T)_p, \qquad \cdots\cdots\cdots\cdots (16)$$

where ΔH is the heat of reaction and T the absolute temperature. Consequently the heat of reaction is calculated from the change of free energy, ΔF, and the

dependence of free energy on temperature at constant pressure.

When the change in free energy can be taken out as the electrical energy, the following relation is obtained.

$$\Delta H = -nF[E - T(\partial E/\partial T)_p].$$

If ΔH is represented in cal/mol and E in volt,

$$\Delta H = -23060n[E - T(\partial E/\partial T)_p]. \qquad \cdots\cdots\cdots\cdots\cdots (17)$$

Thus, the heat of reaction can be estimated by the determination of E and $\partial E/\partial T$.

(c) Experimental results

For the above cell, the standard potential was measured and then the solubility products of mercury xanthate were calculated by using the equation (15). From the results of the measurement of $\partial E/\partial T$, the heat of reaction was determined by using the equation (17). These numerical data are summarized in Table II.

Table II. Standard potential, equilibrium constant and reaction heat for mercury-xanthate reaction.

	$Hg_2^{++} + 2X^- \rightleftharpoons Hg_2X_2$ $E°$ (volt)	$L = [Hg_2^{++}][X^-]^2$	ΔH (cal/mol)
Mercury ethyl xanthate	1.066	1×10^{-36}	-5.45×10^4
Mercury iso-propyl xanthate	1.078	4×10^{-37}	-5.53×10^4
Mercury amyl xanthate	1.109	4×10^{-38}	-5.68×10^4

As can be seen in Table II, mercury-xanthate is extremely insoluble in water and it seems that the formation of the mercury-xanthate occurs easily. Furthermore, the heat of reaction for mercury-xanthate is a considerable amount.

(d) Consideration of the Reaction of Xanthate to the Mercury Surface

For the two cells, $Hg|Hg_2X_2|X^-||KCl|Hg_2Cl_2|Hg$, and $Hg|X^-||KCl|Hg_2Cl_2|Hg$, the electrode potential of mercury is measured by varying the xanthate concentration and the results are as shown in Fig. 11 and Fig. 12.

By comparing the results shown in Fig. 11 with those of Fig. 12, it is observed that the electrode potential of mercury contacting the xanthate solution perfectly accords with the potential of the electrode constructed by the mercury-xanthate compound which is prepared synthetically. As a consequence, it should be recognized that the electrode potential of mercury contacting the xanthate solution is based on the reactions of the formation of mercury-xanthate.

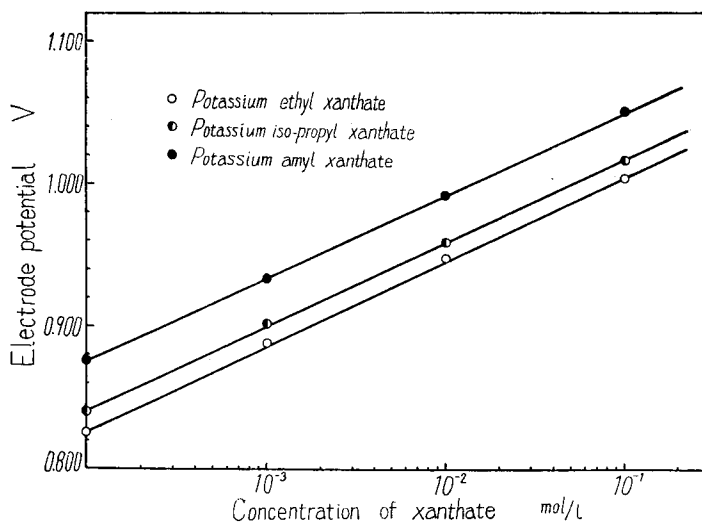In the case of the formation of mercury xanthate at the mercury surface, the electrode reaction is:

Fig. 11. Electrode potential difference of the cell, $Hg|Hg_2X_2|X^-\parallel Hg_2^{++}|Hg$, with varying the concentration of xanthate (Hg_2^{++}, $a=1$).
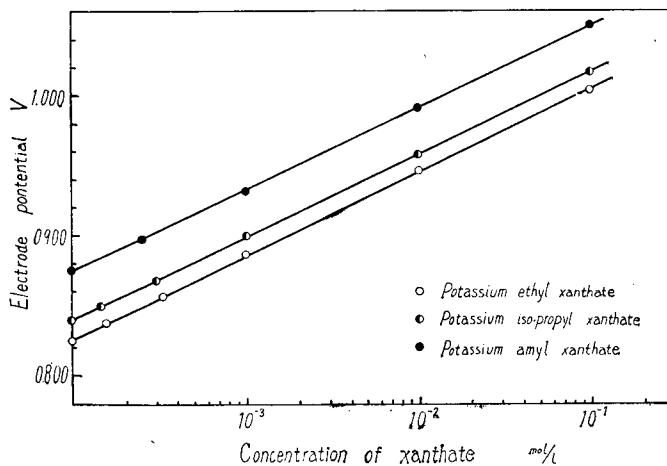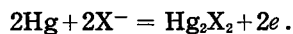

Fig. 12. Electrode potential difference of the cell, $Hg|X^-\parallel Hg_2^{++}|Hg$, with varying the concentration of xanthate (Hg_2^{++}, $a=1$).

$$2Hg+2X^- = Hg_2X_2+2e\,.$$

Thus, the potential is expressed in the following form:

$$E = E^0+\frac{RT}{2F}\ln[Hg_2X_2]-\frac{RT}{F}\ln[X^-]\,.$$

In the above equations, if it is considered that Hg_2X_2 is in a stable state and $[Hg_2X_2]$ is constant, the electrode potential of mercury depends only on the xanthate concentration, $[X^-]$. This means that $E-\ln[X^-]$ curve indicates a linear

relationship. The linear relationship holds even in a fairly dilute aqueous solution of xanthate, as can be seen in Figs. 12, 7, and 8.

These results may be due to the fact that the formation of the mercury xanthate at the mercury surface contacting a xanthate solution would be performed.

3.4. Electrode Potential with Solutions of Varying pH Value

The change of mercury electrode potential with varying pH value in a mercury-NaOH solution system is shown in Fig. 13.
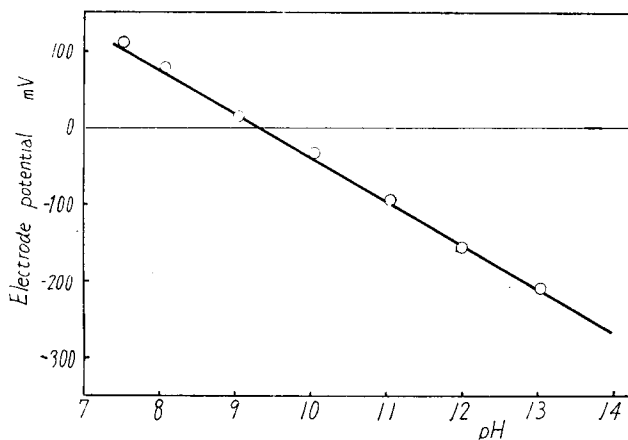

Fig. 13. Electrode potential of mercury in function of pH for the mercury–NaOH solution system.

As shown in Fig. 13, it is recognized that the electrode potential of mercury varies in linear relation with the change of pH value.

The mercury electrode potential with varying pH value in a solution of various concentrations of potassium ethyl xanthate is shown in Fig. 14.
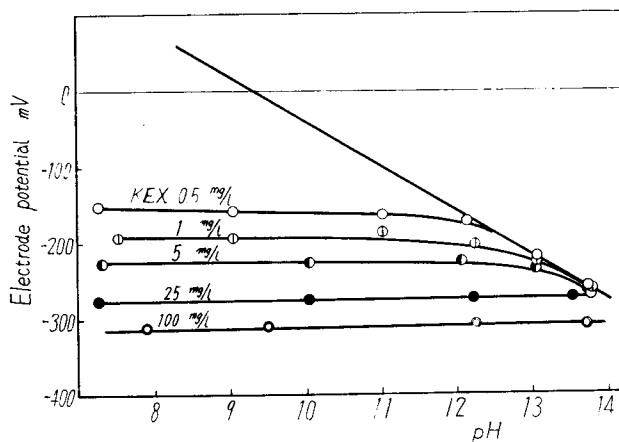

Fig. 14. Relation between mercury electrode potential and pH at various concentration of potassium ethyl xanthate (KEX)

In Fig. 14, for instance, at 0.5 mg per liter of xanthate solution the value of the mercury electrode hardly changes until the pH value becomes about 12 and if the pH value of the solution exceeds 12, the value of the mercury electrode potential changes to that of the potential governed by the hydroxyl ion. At 25 mg/l of xanthate solution, the mercury electrode potential does not change in magnitude in spite of the increasing of the pH value.

That is, the electrode potential of mercury in the xanthate solution changes from the potential governed by the xanthate ions to the potential governed by the hydroxyl ions at the pH value prescribed by the xanthate concentration. These above results are based upon the fact that xanthate ions and the hydroxyl ions react to the mercury surface competitively.

The contact angle on mercury in the solution of xanthate with the increasing pH value was measured. The results are shown in Fig. 15.
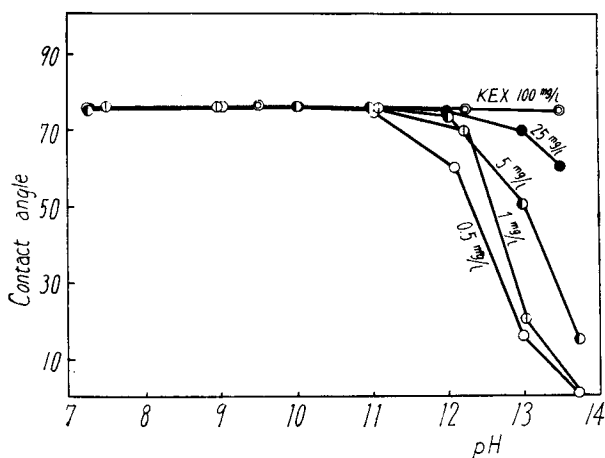

Fig. 15. Effect of pH on contact angle of mercury at various
concentrations of potassium ethyl xanthate (KEX).

It can be seen in Fig. 15 that the contact angle on mercury is affected at relatively low pH values in the dilute aqueous solution of xanthate, while in the strong solution of xanthate it is affected at extremely high pH value.

Comparing the result of Fig. 15 with that of Fig. 14, it is recognized that the contact angle on mercury decreases in magnitude at pH values where the mercury electrode potential changes from the value governed by xanthate ions to the value governed by hydroxyl ions.

Similar results were obtained in the other xanthate-mercury systems as the results for potassium ethyl xanthate.

The above facts coincide with the flotation phenomena that the mineral particles are depressed at low pH value in a dilute soultion of xanthate, while they are depressed at high pH value in a higher concentration of xanthate.

For the exemplification of natural sulphide minerals, pyrite and galena were used instead of mercury in the experiment. The electrode potential of pyrite in the xanthate solution with varying pH values was measured in the same way as stated in the preceding section. The results of the measurements are shown in Fig. 16.
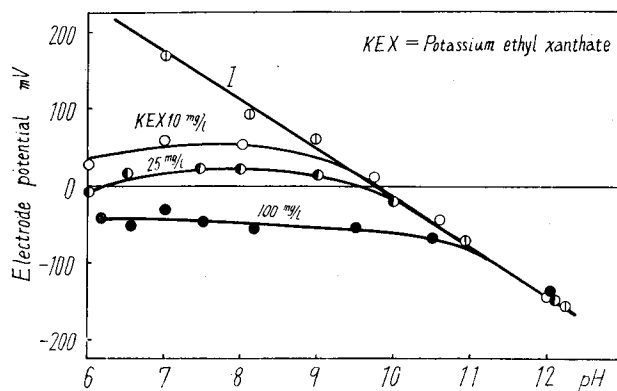

Fig. 16.   Relation between electrode potential of pyrite and pH at various concentration of potassium ethyl xanthate (KEX).

Line I is the curve without addition of xanthate. As can be seen in Fig. 16, the electrode potentials of pyrite in the solution containing hydroxyl ions and xanthate ions have a strong resemblance to the potentials obtained with mercury.

The floatability of pyrite in potassium ethyl xanthate solutions with varying pH values is shown in Fig. 17.
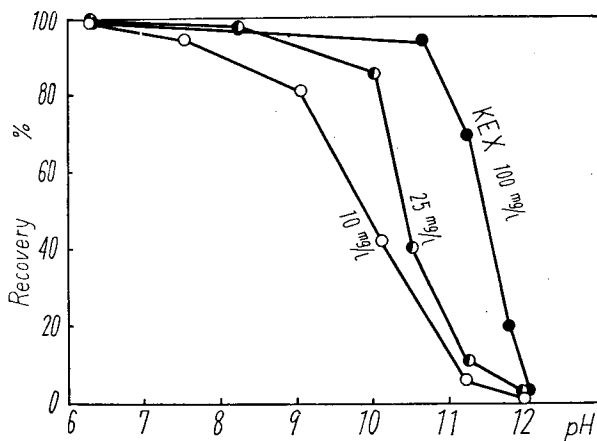

Fig. 17.   Relation between recovery of pyrite and pH at various concentrations of potassium ethyl xanthate (KEX).

From comparing the floatability of pyrite revealed in Fig. 17 with the results of its electrode potential shown in Fig. 16, it can be recognized that flotation or non-flotation of pyrite is closely related to the electrode potential of pyrite. That is, the decrease of floatability arises at the pH value where the value of the electrode potential of pyrite changes from a value of the potential governed by xanthate ions, almost independent of pH value, to that of the potential governed by hydroxyl ions, notably dependent on pH value. These above results show that the xanthate ions and hydroxyl ions react to pyrite surfaces competitively.

3. 5. Considerations on the Relations between Concentrations of Xanthate and Critical pH Value

The relationship between the concentrations of xanthate and the critical pH value is obtained for mercury from the experimental results of the electrode potential and contact angle measurements. Fig. 18 illustrates the two lines determined by the experimental results of the electrode potentials and contact angles respectively. These two lines coincide with each other.

In Fig. 19, the critical lines for potassium amyl xanthate, potassium iso-propyl xanthate and potassium ethyl xanthate are shown comparatively.

The critical curve for potassium amyl xanthate locates itself in the extreme right hand.
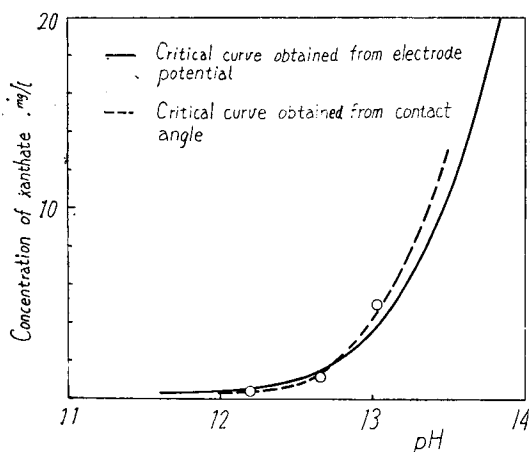

Fig. 18.   Critical curves for mercuty obtained by the measurement of electrode potential and contact angle using potassium ethyl xanthate.
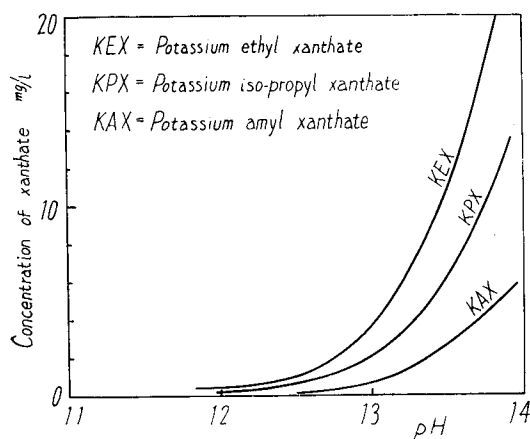

Fig. 19.   Critical curves for mercury-xanthate systems.

(a) Critical Contact Curve for Mercury

The change in the electrode potential of mercury which is due to the variation of the pH value of the solution is represented as a following general equation, referring to Fig. 13.

$$E = K_1 \cdot (\text{pH}) + C_1 , \qquad \cdots\cdots\cdots\cdots\cdots (18)$$

while the variation of the mercury electrode potential by varying the xanthate concentration is expressed in the following form for dilute aqueous solutions of xanthate:

$$E = p + q \log [\text{X}] . \qquad \cdots\cdots\cdots\cdots\cdots (19)$$

The electrode potential obtained from the equation (18) and (19) respectively are considered to be equal in the critical condition, thus

$$p + q \log [\text{X}] = K_1 \cdot (\text{pH}) + C_1 . \qquad \cdots\cdots\cdots\cdots\cdots (20)$$

Assuming $[\text{X}] = K_3 \cdot [\text{X}^-]$, and representing pH in terms of $[\text{OH}^-]$,

$$p + q' \log [\text{X}^-] = K_1 (\log [\text{OH}^-] - \log K_w) + C_1$$
$$= K_1 \log [\text{OH}^-] + C_2 , \qquad \cdots\cdots\cdots\cdots\cdots (21)$$

where $C_2 = C_1 - K_1 \cdot \log K_w$, K_w is the dissociation constant of water. The above relation can also be represented by the following expression:

$$[\text{X}^-]/[\text{OH}^-]^m = \text{constant} , \quad m = K_1/q . \qquad \cdots\cdots\cdots\cdots\cdots (22)$$

Equation (22) is the critical condition for mercury flotation obtained from the measurement of electrode potentials and contact angles in the mercury-xanthate solution system.

(b) Critical Contact Curve for Sulphide Minerals

For pyrite, a sulphide mineral, the two critical curves obtained from the measurement of electrode potentials and floatability are illustrated in Fig. 20. These two curves coincide with each other.

The change in electrode potential of pyrite by varying the pH value in which no xanthate is added is represented as a linear function
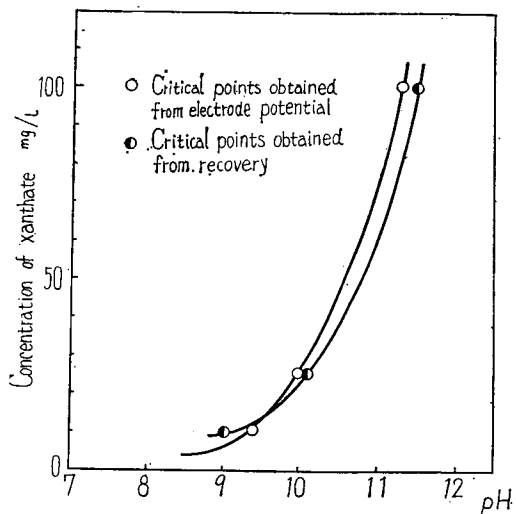

Fig. 20. Critical curves for pyrite obtained by the measurement of electrode potential and recovery using potassium ethyl xanthate.

with pH, as shown in Fig. 16.

$$E = b_1(\text{pH}) + a_1. \qquad \cdots\cdots\cdots\cdots (23)$$

While the relation between the electrode potential of pyrite and the concentration of xanthate is expressed by the following equation:

$$E = a + b \cdot \log [X^-]. \qquad \cdots\cdots\cdots\cdots (24)$$

The critical condition for pyrite is obtained by combining the equation (23) with equation (24):

$$b_1(\text{pH}) + a_1 = a + b \log [X^-],$$
$$b_1(\log [OH^-] - \log K_w) + a_1 = a + b \log [X^-],$$
$$a_1 - a - b_1 \log K_w = b \log [X^-] - b_1 \log [OH^-]$$
$$= b \{\log [X^-] - (b_1/b) \times \log [OH^-]\},$$
$$\frac{a_1 - a - b_1 \log K_w}{b} = \log [X^-]/[OH^-]^{b_1/b}.$$

Putting
$$A = (a_1 - a - b_1 \log K_w)/b,$$
$$\log [X^-]/[OH^-]^{b_1/b} = A.$$

Thus,
$$[X^-]/[OH^-]^n = \text{constant}, \qquad \cdots\cdots\cdots\cdots (25)$$
where $n = b_1/b$.

If the equations, (23) and (24) coincide with the Nernst equation perfectly, n takes the ratio of the valency of the ions taking part in the surface reactions. If the xanthate ions and the hydroxyl ions take part in the reaction to the mineral surface, $(b_1/b) = n = 1$, accordingly, equation (25) is perfectly in accord with the Barsky relation, $[X^-]/[OH^-] = $ constant.

4. Conclusions

For the purpose of studying the principle of mineral flotation, the mechanisms of both mercury-collector reactions and mercury-depressant reactions were investigated by means of electrochemistry, furthermore the mechanism of the reaction between sulphide minerals and flotation reagents was discussed.

From the comparison of the floatability measurement with the results of the electrode potential, it is revealed that the change in electrode potential relates closely with the contact angle or floatability and consequently it plays an important role in flotation.

The reaction causing the electrode potential of mercury in the xanthate solution was ascertained by means of an electrochemical cell, $Hg|Hg_2X_2|X^-||Hg_2^{2+}|Hg$. On a mercury surface in contact with a xanthate solution, a stable formation of metal xanthate would be performed even in a fairly dilute aqueous solution of xanthate. And it may be concluded that the reaction between the mercury and

xanthate solutions may be a redox reaction accompanying the electron transfer. From the experimental results of the electrode potential, the reaction between mercury and electrolytes such as NaCN, KCN, or Na_2S also may be considered to be based on a redox reaction. Similarly the same considerations for the reaction between sulphide minerals and xanthate solutions or depressing agents can be adopted. From the above discussion, it may be concluded that the floatability of the mineral in flotation using xanthate as a collector and NaCN, KCN, or Na_2S as a depressant is governed by the reaction accompanying the electron transfer, namely, a redox reaction.

From the electrochemical discussion of the critical conditions in flotation it may be said that the reactions on a mercury surface contacting a xanthate solution in any pH value prescribed by a xanthate concentration are based on the competition between xanthate and hydroxyl ions. Thus, the following relation between xanthate ion concentration and pH value is derived:

$$[X^-]/[OH^-]^m = \text{constant.}$$

Furthemore, discussing electrochemically the critical curve for sulphide minerals, the relation between xanthate ion concentrations and pH value is expressed in the following form:

$$[X^-]/[OH^-]^n = \text{constant.}$$

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