



HOKKAIDO UNIVERSITY

Title	HYDROGEN ELECTRODE REACTION IN ALKALINE SOLUTIONS : I : Codeposition of sodium with hydrogen on mercury cathode
Author(s)	KITA, Hideaki; KURISU, Takao
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 18(1), 1-18
Issue Date	1970-04
Doc URL	https://hdl.handle.net/2115/24901
Type	departmental bulletin paper
File Information	18(1)_P1-18.pdf



HYDROGEN ELECTRODE REACTION IN ALKALINE SOLUTIONS

I: Codeposition of sodium with hydrogen on mercury cathode

By

Hideaki KITA^{*)} and Takao KURISU^{*)}

(Received January 16, 1970)

Abstract

Codeposition of sodium with hydrogen evolution on mercury was studied as a function of pH and Na^+ concentration in $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 + \text{NaOH}$ and NaOH solutions at $25 \pm 0.05^\circ\text{C}$ by the galvanostatic pulse and potential sweep methods.

Analysis of the results leads to the following conclusions:

- (1) Sodium deposition becomes detectable at *ca.* -1.6 v (N.H.E.).
- (2) The amount of sodium deposited, Q , is represented by $Q = k[\text{Na}^+] \exp(-0.44 FV/RT)$ in the range of $-1.9 < V < -1.7$ v (N.H.E.) and independent of the pH of solution.
- (3) Tafel relation for the discharge of sodium ion is $-V(\text{N.H.E. in volt}) = 1.76 + 0.133 \log i$ at $[\text{Na}^+] = 1$ N.
- (4) The discharge of sodium ion is the first step of hydrogen evolution reaction in sodium hydroxide solution and the rate-determining step is in the following steps, resulting in the formation of hydrogen molecule by the interaction of the deposited sodium with water molecule.
- (5) In acidic solutions, the hydrogen evolution reaction is much faster than the discharge of sodium ion.
- (6) The rest potential of mercury electrode is determined by the presence of HgO on the surface in alkaline solutions and by Hg_2SO_4 in the acidic solution containing SO_4^- ion.

One of the present authors reviewed^{1,2)} the works on the hydrogen electrode reaction reported in literature. He established the periodic change of activity of the electrode metal with its atomic number, where the activity was defined as the exchange current density of the hydrogen electrode reaction. Experimental results in alkaline solutions, however, are very few and show a considerable deviation of the activity from the periodic change.

Main object in the present series of papers is to obtain the reliable

^{*)} Res. Inst. for Catalysis, Hokkaido University, Sapporo, Japan.

values for the activity in the alkaline solution, so that one can check its periodic variation in the alkaline solution, which may give rise to a useful information for the elucidation of the reaction mechanism.

Part I dealt with the hydrogen evolution reaction on mercury in sodium hydroxide solution. In this system, the discharge of sodium ion is very possible to occur as a parallel process to or as one of elementary steps of the hydrogen electrode reaction. BOCKRIS and WATSON³⁾ have shown from the current efficiency of hydrogen evolution being 100% and the effects of alkali metal ion as well as of valency of metal ion on the hydrogen evolution, that a true hydrogen overvoltage is observed, though the alkali metal atom deposited is taken as an essential intermediate in the mechanism of the hydrogen evolution. They concluded the rapid deposition of alkali metal atoms which react irreversibly with water molecules to produce hydrogen and alkali metal hydroxide. MATSUDA *et al.* reported similar conclusion for the hydrogen electrode reaction on Pt⁴⁾ and Ni⁵⁾ in alkali metal hydroxide solutions. In the present paper, much emphasis was placed in detection of the contribution of sodium ion-discharge to the overall potential-current relationship.

§ 1 Experimental

The cell used was an all-glass vessel consisting of two compartments (Fig. 1). The main compartment with jacket for circulating thermostated water, contained the test electrode, the counter electrode (cylindrical platinized platinum net), the reference electrode (platinized platinum wire) and the cathode for pre-electrolysis (platinized platinum wire), all sealed into sliding ground glass tubes fitted to the cell cap by means of sleeve joints. Capillary for dropping mercury and small spoon were also set in the main compartment by means of sleeve joints. The anode for pre-electrolysis (platinized platinum foil) was set in another compartment, which was connected to the main compartment by a sintered glass disk and a closed tap.

The test electrode was a hanging drop of mercury (99.9999%) or dropping mercury. The hanging electrode was prepared by SHAIN's method.⁶⁾ The surface area was calculated from the weight per drop and the density, assuming its spherical shape.

Hydrogen from cylinder was purified by passing through the hydrogen diffusion purifier (Japan Pure Hydrogen Co., Ind., type, LW-06SC) and liquid nitrogen trap. All chemicals used, NaOH, Na₂SO₄·10H₂O and conc. H₂SO₄ are of special grade of Wako Pure Chemical Industries Ltd., (Osaka, Japan). Solutions were prepared at a desired concentration using the purified water

Hydrogen Electrode Reaction in Alkaline Solutions, I

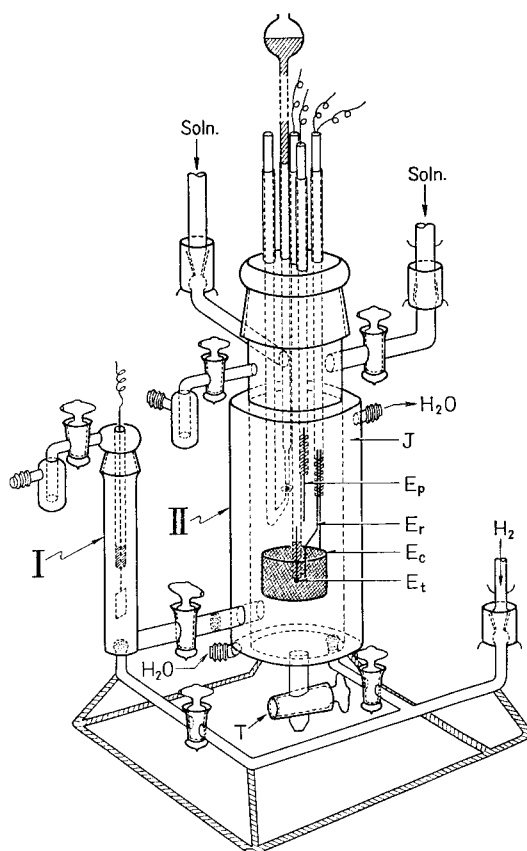


Fig. 1. Cell diagram. I, Anode compartment; II, Main compartment; E_r , Reference electrode; E_c , Counter electrode; E_t , Test electrode; E_p , Cathode for pre-electrolysis; T, Tap for sampling of solution; J, Water jacket.

(distilled thrice, conductivity, $\leq 10^{-6}$ mho/cm). All solutions except those with pH between 3 and 10 were subjected to the pre-electrolysis for a few days with current of $3\text{mA}/\text{cm}^2$ under bubbling of the purified hydrogen. The pre-electrolysis was terminated by pulling up the cathode for pre-electrolysis out of solution.

The open circuit potential of the test electrode (rest potential) was first observed and then the measurements were followed by the galvanostatic pulse, potential sweep and polarographic methods. In the case of the galvanostatic pulse method, single pulse of a constant current ranging from 10^{-4} to 10^{-1} A/cm² was applied to the test electrode of hanging drop, which was centered

inside the cylindrical counter electrode (Fig. 1). Resultant potential change of the test electrode with time (the galvanostatic transient) was observed against the reversible hydrogen electrode in the same solution by an oscilloscope (IWASAKI Communication Apparatus Ltd., Tokyo, Type 5302, 30 MC). A series of the galvanostatic transients with different constant currents was photographed. Triangular sweep of potential against the reference electrode was applied from the potentiostat (YANAGIMOTO MFG., Co., Ltd., Type, V8-2010; Input resistance, >500 Mohm) to the test electrode of hanging drop or dropping mercury. Sweep rate covers the range from 0.5v/10 hr to 4v/1.1 min. Resultant current-potential curves (I - V curves) were recorded (YANAGIMOTO MFG. Co., Ltd.; Type, V8-YR-101) as a function of the sweep rate and the potential range covered.

After the measurements described above at a given composition of the electrolyte solution (run), several other runs were followed by changing pH of solution by successive additions of a desired quantity of concentrated sodium hydroxide or sulfuric acid from the storage flask attached to the cell by application of the pressure of the purified hydrogen. Small quantity of solution was sampled from the bottom of the main compartment (tap T in Fig. 1) before and after each run for the determination of pH (pH meter, HITACHI-HORIBA, MG 5).

All measurements were carried out at $25 \pm 0.05^\circ\text{C}$ under the bubbling of the purified hydrogen.

§ 2 Results

2-1 The Tafel relation

Representative Tafel relations obtained by the galvanostatic pulse method are illustrated in Fig. 2. In sodium hydroxide solution (curve, 2), the potential, V^* , seems to approach the constant value of -1.7 v, while in sulfuric acid solution (curve, 1), the potential changes in usual manner, *i. e.*, linearly with the logarithm of current density with the slope of 0.10 v as observed previously⁷. Such a contrast in the Tafel relation gives rise to the question about the role of sodium deposition during the cathodic hydrogen evolution, though the potential range concerned is much more positive than the standard potential, -2.714 v⁸, of the sodium electrode reaction, $\text{Na}^+ + e^- \longrightarrow \text{Na}$.

At low current densities (less than 10^{-4} A/cm²), however, BOCKRIS and WATSON³) found the linear Tafel relation with the slope of 0.10 v in 0.1N

*) The potential, V , is always referred to the normal hydrogen electrode (N.H.E.) unless stated.

Hydrogen Electrode Reaction in Alkaline Solutions, I

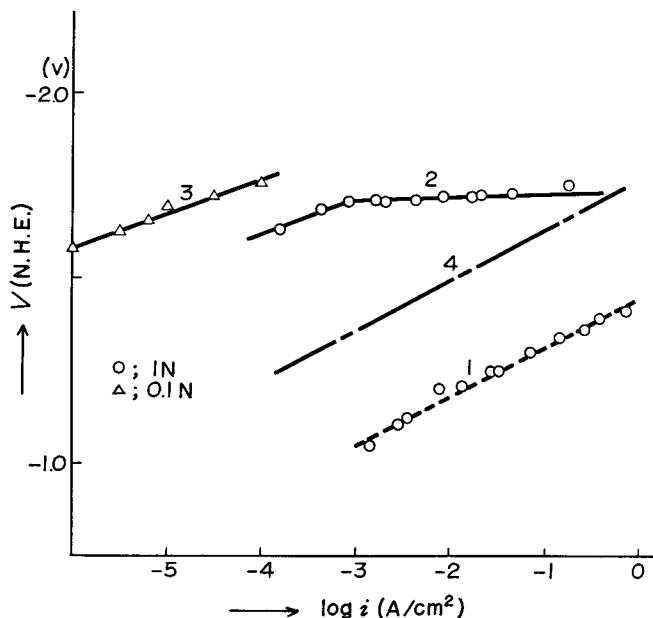


Fig. 2. Tafel relation on mercury in sodium hydroxide and sulfuric acid solutions at $25 \pm 0.05^\circ\text{C}$.

Potential, V , is referred to the normal hydrogen electrode. 1, 1N H_2SO_4 solution; 2, 1N NaOH solution; 3, BOCKRIS and WATSON³⁾ in 0.1N NaOH solution at 20°C ; 4, Tafel relation by Eq. (8) for the discharge of sodium ion.

NaOH solution (curve, 3 in Fig. 2). In the present case, such a linear relation is also observed at lower current densities than 1 mA/cm^2 , though the potential is more positive than that of curve 3.

2-2 Galvanostatic transient

Figure 3 shows typical charging-up and decay curves obtained in normal sulfuric acid (curve, a and c) and sodium hydroxide solutions (curve, b and d).

Comparison of charging-up curves, a and b, indicates that the potential reaches to the steady value within nearly the same time in both acidic and alkaline solutions. The differential capacity, C , was calculated from these curves by the equation, $C = i/(dV/dt)$, where i is the applied current density and t is the time. The capacities thus estimated are inserted in the figure. Its average values are 23.2 ± 5.7 and $13.9 \pm 3.4 \mu\text{F/cm}^2$ at lower and higher cathodic polarizations in 1N H_2SO_4 . In the alkaline solution, the charging-up curves do not show the break as in the acidic solution, giving smaller value of the differential capacity, *i. e.*, $12.2 \pm 0.4 \mu\text{F/cm}^2$. These values correspond

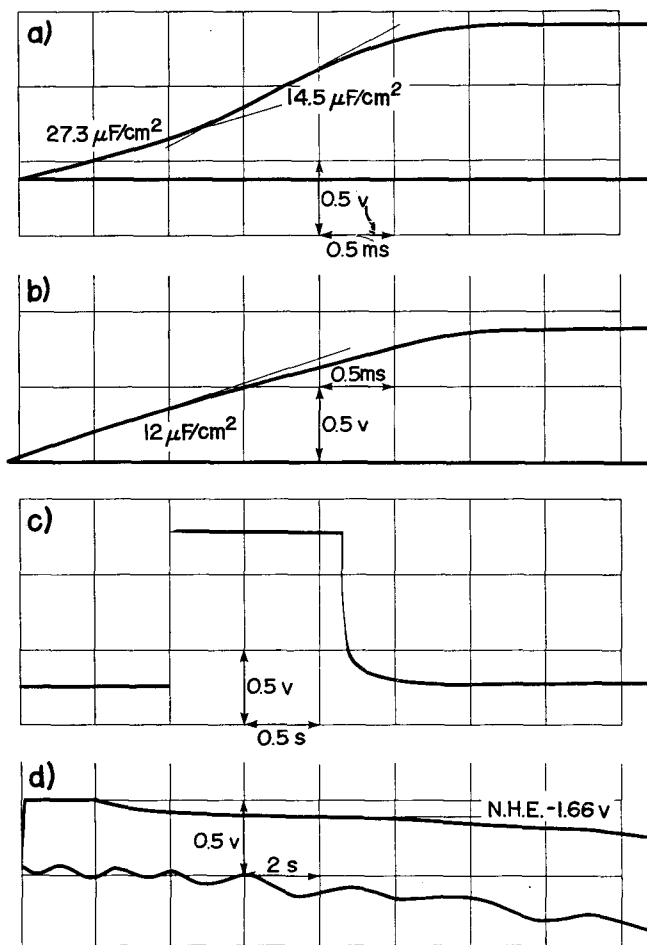


Fig. 3. Galvanostatic charging-up and decay curves at $25 \pm 0.05^\circ\text{C}$.
 Charging-up curves; a, 1N H_2SO_4 , $i = 7.5 \times 10^{-3} \text{ A/cm}^2$;
 b, 1N NaOH , $i = 4.0 \times 10^{-3} \text{ A/cm}^2$. Decay curves; c, 1N
 H_2SO_4 , $i = 7.5 \times 10^{-3} \text{ A/cm}^2$; d, 1N NaOH , $i = 4.0 \times 10^{-3} \text{ A/cm}^2$.

in order of magnitude to the capacity of the double layer, being much less than the pseudo-capacity, which is expected to be a few hundreds $\mu\text{F/cm}^2$ or more⁹). Thus, the absence of the pseudo-capacity, suggests no accumulation of substance deposited on the surface by discharge or ionization processes during the charging-up.

On the other hand, very abnormal behaviour of potential is observed on the decay curve obtained in sodium hydroxide solution (curve, d in Fig. 3).

Hydrogen Electrode Reaction in Alkaline Solutions, I

Namely, the potential slowly decays at first to a constant value (*ca.* -1.7 v) and then to the original potential with irregular fluctuation, in contrast to the monotonous, rapid decay in sulfuric acid solution (curve, c in Fig. 3). Such an abnormal decay was observed in the whole range of current density studied. Thus, in the alkaline solution, the accumulation of some substance is suggested to take place during the steady state of cathodic polarization. After the cessation of current, the substance disintegrates at the potential of

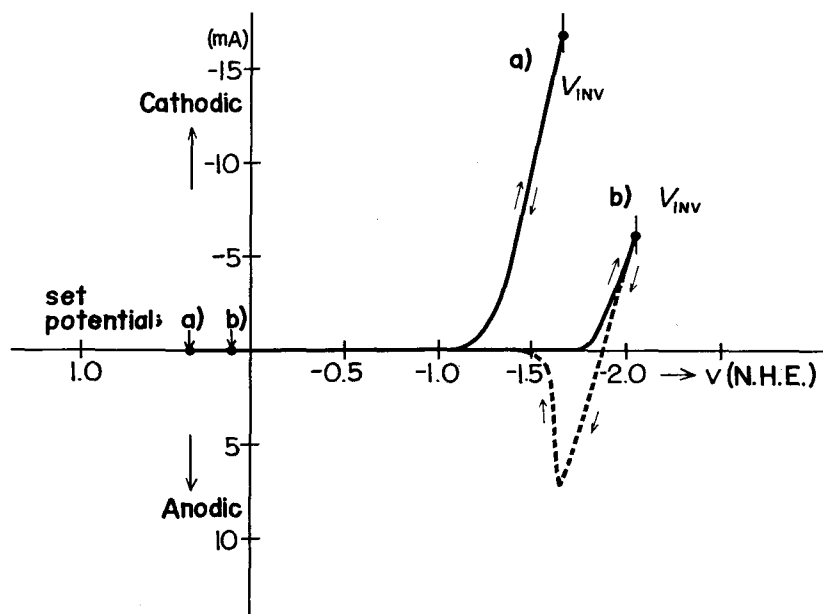


Fig. 4. $I-V$ curves by the potential sweep method ($25 \pm 0.05^\circ\text{C}$).
 a, 1N H₂SO₄; b, 1N NaOH; Sweep rate, $4\text{ v}/1.1\text{ min}$.
 Arrows indicate the sequence of the sweep.

plateau in the decay curve (*ca.* -1.7 v) or at more positive value.

2-3 Potential sweep transient

Figure 4 shows typical current-potential transients ($I-V$ curve) obtained in 1N H₂SO₄ and 1N NaOH solutions. Potential was first swept from a set potential in the negative direction and then inverted at a potential, designated as V_{INV} , towards the set value. The set potential was selected in the potential range where the current is negligible. No hysteresis is observed in sulfuric acid solution (curve, a), whereas in sodium hydroxide solution (curve, b), a large hysteresis occurs and the current becomes even positive in the backward sweep, though the potential is still in highly negative region against the

H. KITA and T. KURISU

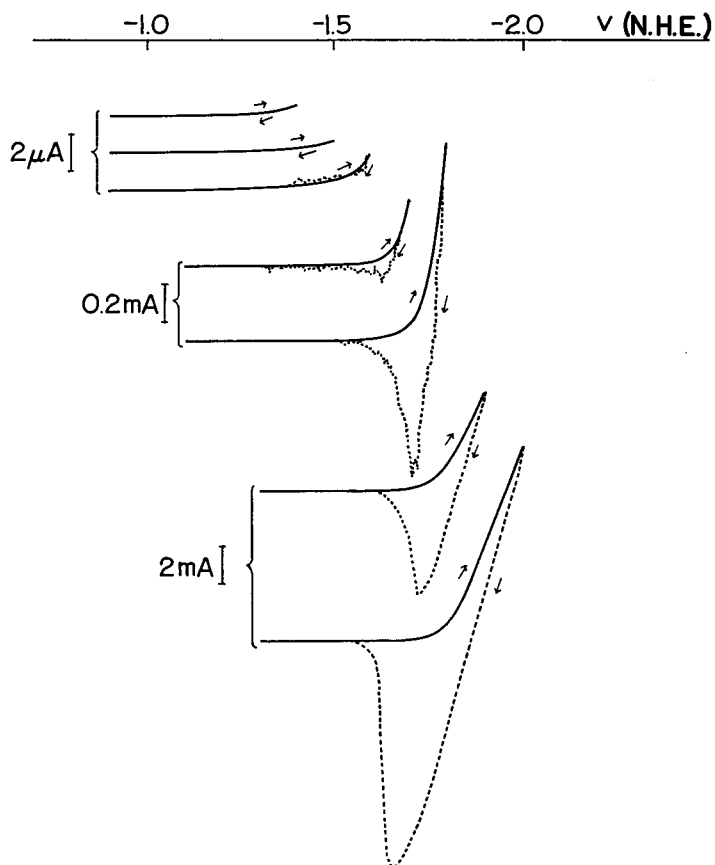


Fig. 5. I - V curves in 1N NaOH as a function of V_{INV} at the sweep rate of 2v/1.1 min and $25 \pm 0.05^\circ\text{C}$.

potential of the reversible hydrogen electrode. Such a hysteresis with anodic current suggests that the substance formed during the cathodic polarization is unstable and easily oxidized. We further studied the I - V curve as a function of V_{INV} , sweep rate, pH and sodium ion concentration.

(i) *Effect of V_{INV}*

Effect of V_{INV} on the I - V curve is studied to see from what potential of inversion the hysteresis commences. Results in 1N NaOH solution are shown in Fig. 5, where the sweep rate was kept constant at 2v/1.1 min. One can see from the figure that no hysteresis is observed at $V_{INV} \geq -1.5$ v, whereas the hysteresis commences at $V_{INV} = -1.6$ v and becomes increasingly large with decrease of V_{INV} .

Hydrogen Electrode Reaction in Alkaline Solutions, I

(ii) *Effect of the sweep rate*

A series of the I - V curves was taken as a function of the sweep rate in 0.1 and 1 N NaOH solutions, keeping the value of V_{INV} constant. The area surrounded by the hysteresis loop was treated as follows.

Denoting the electricities estimated graphically from the I - V curve before and after the inversion by Q_c and Q_a , the quantity, Q , was defined as follows;

$$Q \equiv (Q_c - Q_a)/2, \quad (1)$$

where Q_c and Q_a were taken positive for the negative electricity. The quantity, Q , represents the electricity used for the accumulation of the substance and is zero when there is no hysteresis as in the case of 1 N H_2SO_4

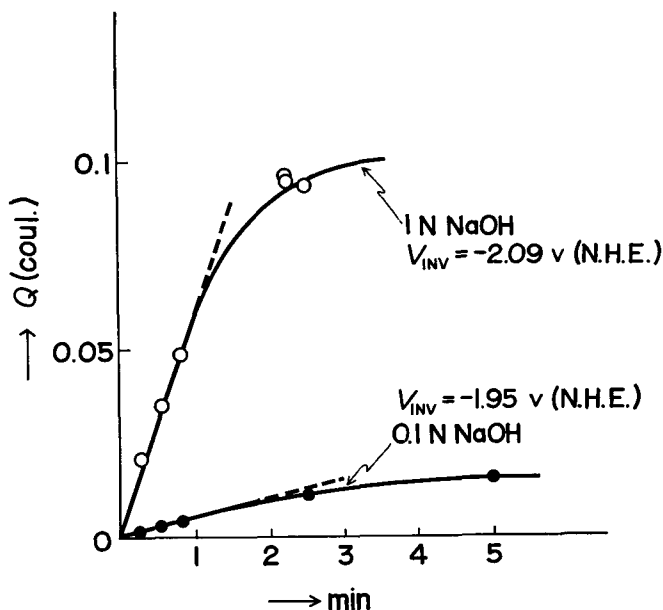


Fig. 6. Q as a function of the time required for the attainment of the potential change of one volt ($25 \pm 0.05^\circ C.$).

solution. The factor $1/2$ in Eq. (1) arises from the assumptions that the substance deposited during the forward sweep with an electron from the electrode, dissolves into the solution giving back the electron to the electrode during backward sweep, and that the contribution of the hydrogen evolution to the observed electricity is the same in the forward and backward sweeps.

In Fig. 6, Q is plotted against the time required for the attainment of

H. KITA and T. KURISU

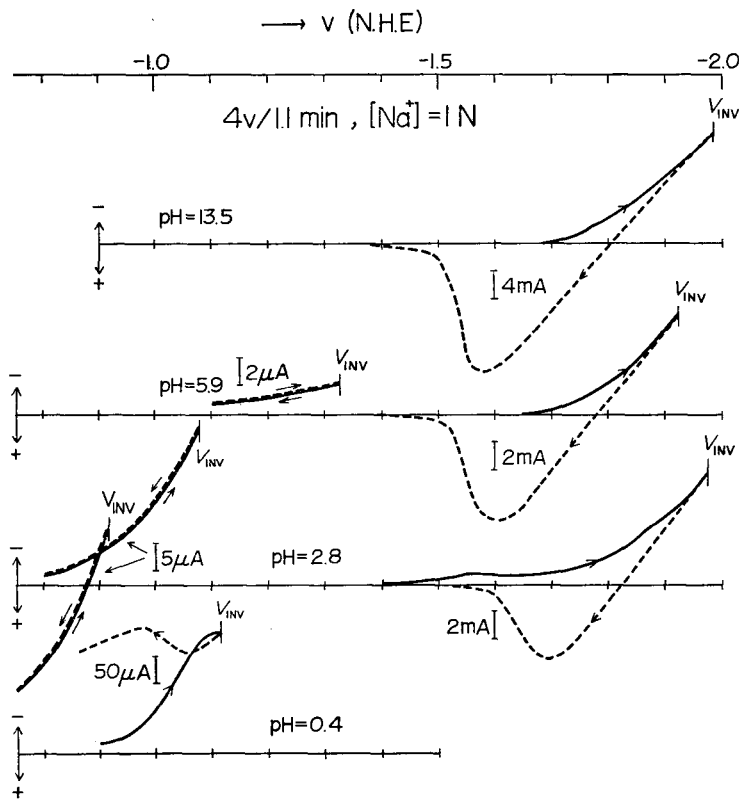


Fig. 7. I - V curves as a function of pH at the concentration of $[\text{Na}^+] = 1\text{N}$ and the sweep rate of $4\text{v}/1.1\text{ min}$ ($25 \pm 0.05^\circ\text{C}$).

the potential change of one volt. The Q increases proportionally to the time or inversely proportionally to the sweep rate at a rapid scanning of potential but seems to approach a constant value at slow rate of scanning in both 0.1 and 1N NaOH solutions. Difference of slopes of linear parts is attributed to the differences of V_{INV} and of sodium ion concentration.

(iii) *Effects of pH and the concentration of sodium ion, $[\text{Na}^+]$*

I - V curves obtained with the sweep rate of $4\text{v}/1.1\text{ min}$ at $[\text{Na}^+] = 1\text{N}$ are shown in Fig. 7 as a function of pH. Curves whose V_{INV} is around -1.95 v show the hysteresis of the similar dimension in order of magnitude, being roughly pH independent. The other I - V curves of V_{INV} being more positive than -1.3 v , however, strongly depend on pH and the current increases with decrease of pH. These curves further indicate no hysteresis and hence are considered as representing purely the potential dependence of

Hydrogen Electrode Reaction in Alkaline Solutions. I

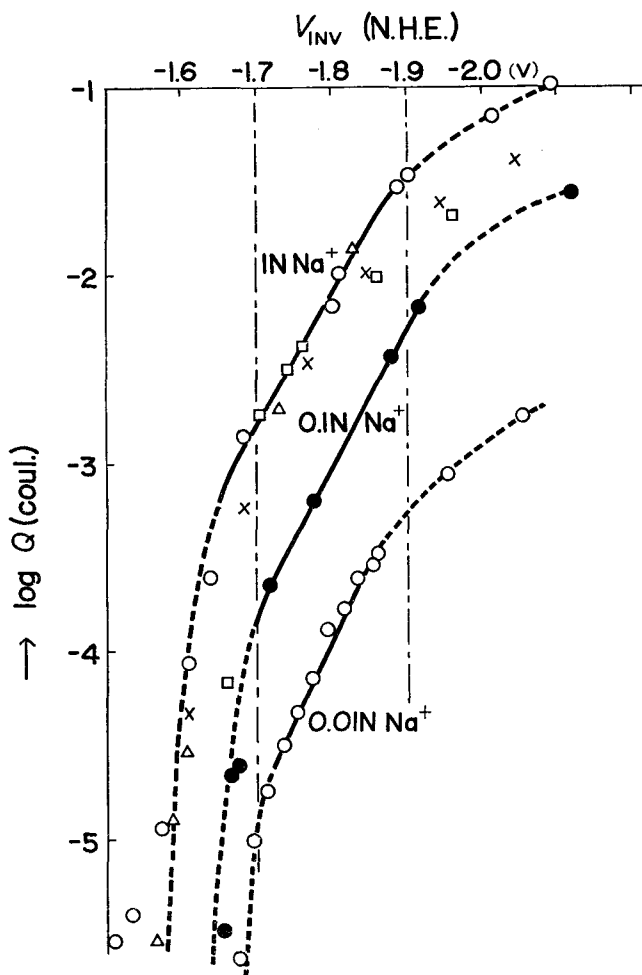


Fig. 8. $\log Q$ vs. V_{INV} curve as a function of pH and Na^+ concentration ($25 \pm 0.05^\circ\text{C}$). Sweep rate, $4\text{v}/1.1\text{ min}$. For the curve of 1N Na^+ ; \circ , pH=13.5; \times , pH=5.9; \triangle , pH=2.8; \square , pH=2.5 respectively.

hydrogen evolution, except for the one with $V_{INV} = -1.11\text{ v}$ at pH=0.4. In the latter case, the $I-V$ curve is very irregular, because of the strong formation of hydrogen bubble on the electrode surface.

Q -values obtained by Eq. (1) are summarized in Fig. 8 as a function of pH and $[\text{Na}^+]$. From the figure, one can see the following points:

(1) In the range of $V_{INV} < -1.9\text{ v}$, $\log Q$ approaches to the limiting value

with decrease of V_{INV} in all cases studied.

(2) In the range of $-1.9 < V_{INV} < -1.7$ v, $\log Q$ changes linearly with V_{INV} . The Q is proportional to $[Na^+]$ but independent of pH as exemplified in the case of 1 N Na^+ solution. Thus, we obtain in this potential range

$$Q = k[Na^+] \exp(-\alpha FV_{INV}/RT), \quad (2)$$

where k and α are the constants. The constant, k , is inversely proportional to the sweep rate at the rapid scanning of potential as seen from Fig. 6 where $[Na^+]$ and V_{INV} are kept constant. The other constant, α , was found at 0.44 on an average, being independent of the electrolyte composition. Further studies with different sweep rates show the absence of the sweep rate effect on α .

(3) In the range of $V_{INV} > -1.7$ v, the $\log Q$ deviates from the linear relation and sharply decreases at a certain potential, depending on $[Na^+]$, *e.g.*, *ca.* -1.6 v for 1 N Na^+ solutions. This characteristic value of potential is in fair agreement with the potential of plateau in the decay curve (Fig. 3) as well as the commencement potential of the hysteresis (Fig. 5). Figure 9 shows a polarogram taken in the solution of pH=0.4 and $[Na^+]=1$ N. Sharp change of current occurs also at the potential of -1.52 v, which is independent of pH and the direction of potential sweep. Such an abrupt change of current at a definite potential was not observed in the pure sulfuric acid solution. Analogous curve was reported with respect to the derivative curve of the galvanostatic transient on mercury in the solution containing Pb^{++} ion.¹⁰ The sharp cut-in in the curve was attributed to the deposition of Pb.

(iv) *Deposition of sodium*

The test electrode of hanging drop was subjected to the forward sweep of cathodic polarization, *i.e.*, from the set potential to V_{INV} in 1 N Na_2SO_4 solution (pH=6.0) and then the electrode was transferred into 5 cc of the conductivity water (pH=6.0). The pH change of the water was then followed. The pH increases from 6.0 to 10~11.

The experimental results described hitherto, *i.e.*, 1) the abnormal Tafel relation in the alkaline solution, 2) the abnormal decay curve in the alkaline solution, 3) the hysteresis in the $I-V$ curve, 4) no effect of pH on Q , 5) the proportionality of Q to $[Na^+]$ and 6) the pH change of water, confirm the deposition of sodium.

2-4 Rest potential

Open-circuit potential of the test electrode in a given electrolyte solution (rest potential, V_r) was measured as a function of pH and the concentration

Hydrogen Electrode Reaction in Alkaline Solutions. I

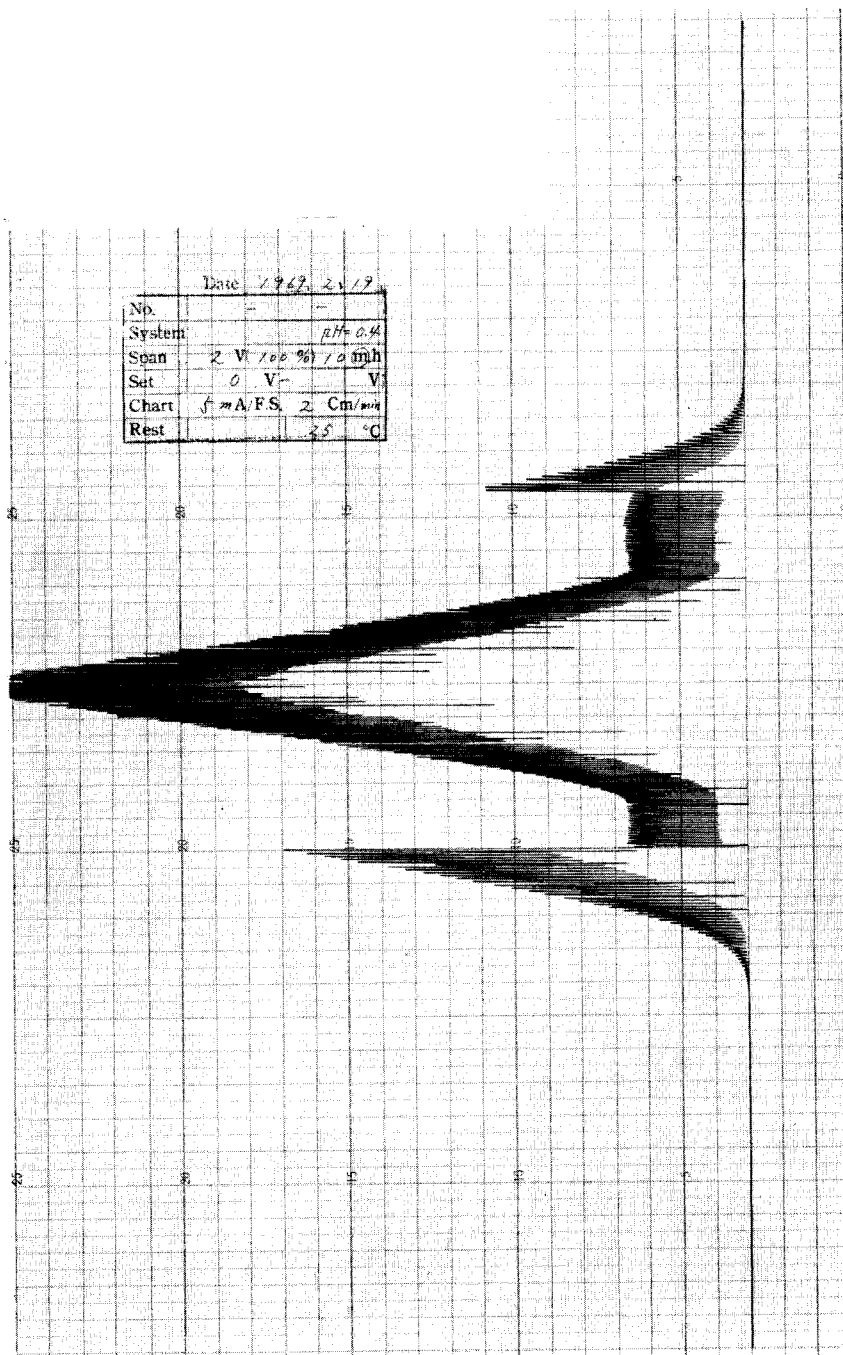


Fig. 9. Polarogram taken in the solution of pH = 0.4 and $[\text{Na}^+] = 1\text{N}$ with the sweep rate of $2\text{v}/1.1\text{min}$ ($25 \pm 0.05^\circ\text{C}$).

H. KITA and T. KURISU

of sulfate ion, $[\text{SO}_4^-]$. Observed value of the rest potential and its pH dependence are in agreement in sodium hydroxide solution with the values expected thermodynamically for the reaction, $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2e^-$, *i. e.*,

$$V_r = 0.926 - 0.059 \text{pH}, \text{ v(N.H.E.) at } 25^\circ\text{C.}^{8)} \quad (3)$$

In sulfuric acid solution, however, the rest potential was independent of pH and close to the reversible potential of the reaction, $2\text{Hg} + \text{SO}_4^- = \text{Hg}_2\text{SO}_4 + 2e^-$, *i. e.*,

$$V_r = 0.615 - (RT/2F) \ln a_{\text{SO}_4^-}, \text{ v(N.H.E.)}. \quad (4)$$

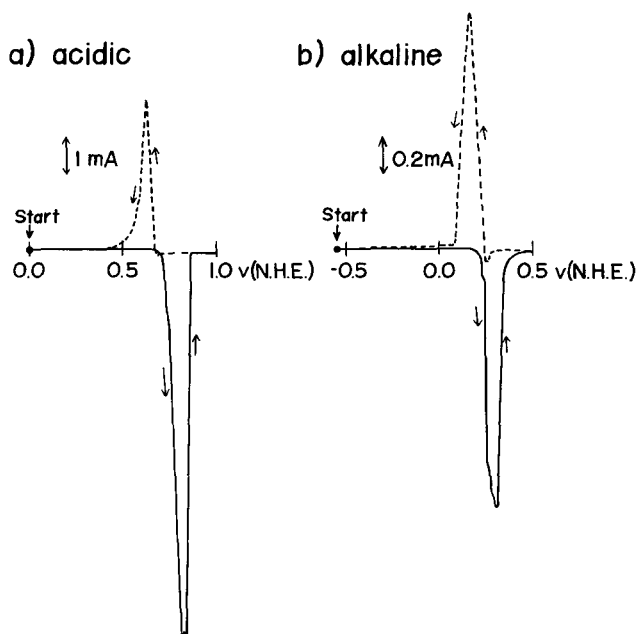


Fig. 10. $I-V$ curves by the potential sweep of anodic polarization with the sweep rate of $4\text{v}/1.1\text{ min.}$
 a, in sulfuric acid solution, $\text{pH}=0.8$; b, in the alkaline solution of $\text{Na}_2\text{SO}_4 + \text{NaOH}$, $[\text{Na}^+] = 1\text{ N}$ and $\text{pH}=11.0$.
 —, anodic current; ---, cathodic current.

The $I-V$ curve was then studied to confirm the presence of HgO or Hg_2SO_4 on the surface at the rest potential. Typical curves in the acidic and alkaline solutions are shown in Fig. 10. Large peaks of the anodic and cathodic currents are observed for the forward and backward sweeps of the anodic polarization, showing formation and exhaustion of the surface compound. It is noticed that in the backward sweep, the cathodic current peak

Hydrogen Electrode Reaction in Alkaline Solutions. I

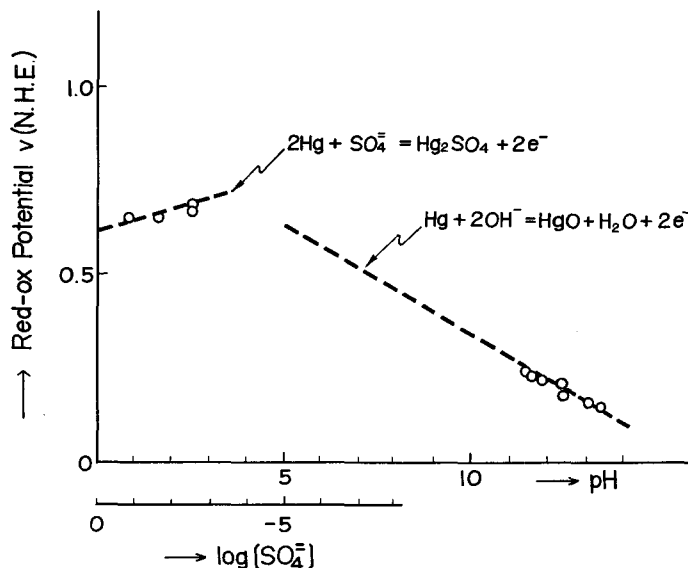


Fig. 11. Red-ox potential as a function of pH and $[\text{SO}_4^{2-}]$ ($25 \pm 0.05^\circ\text{C}$).

The pH and $[\text{SO}_4^{2-}]$ are controlled by changing the respective composition of NaOH, Na_2SO_4 and H_2SO_4 in solution. Dotted lines show relations expected thermodynamically by Eq. (3) for HgO and Eq. (4) for Hg_2SO_4 .

is initiated with small anodic current peak. We take the potential at the latter peak as the red-ox potential characteristic of the surface compound, since the peaks of the anodic and cathodic currents are located respectively at the right and left hand sides of this potential as seen in Fig. 10. The red-ox potential thus defined is plotted against the pH or the logarithm of $[\text{SO}_4^{2-}]$ in Fig. 11. Results are in agreement with Eq. (3) or (4) as indicated by the dotted lines. Thus, it is concluded that the rest potential is determined by the presence of HgO or Hg_2SO_4 on the electrode surface according as the solution is alkaline or acidic.

The peak area ratio of the cathodic to the anodic current is found close to unity in the alkaline solution but much less than unity in the acidic solution, *i.e.*, 0.2~0.5. These facts are understood from the small solubility of HgO which is basic substance and the relatively large solubility of Hg_2SO_4 in comparison with HgO. The mercuric oxide formed during the forward sweep will remain on the surface without dissolution and be subjected to the reduction during the backward sweep, thus resulting in the ratio of unity, whereas the mercurous sulfate formed will dissolve in part into the solution

and only the rest is reduced, in consequence giving the ratio much less than unity. It is also possible in the case of Hg_2SO_4 that the cation of Hg_2^{++} is further oxidized to mercuric ion during the anodic sweep and dissolves into the solution.

§ 3 Discussion

Sodium deposition

Experimental results, described above indicate that the accumulation of sodium occurs at the potential of *ca.* -1.6 v to an extent detectable by the present experimental method.

Further experiments showed that the accumulation occurs even at $V_{\text{INV}} = -1.5$ v, when the potential sweep was interrupted at V_{INV} for 15 sec during which the electrode was kept at V_{INV} . Hence, the commencement potential of -1.6 v should be understood as the value characteristic of the present experimental technique and has no physical meaning.

ERDEY-GRÚZ and VÁZSONYI-ZILAHY¹¹⁾ observed the equilibrium potential of dilute amalgams. They found that the potential of the amalgam containing sodium less than 10^{-3} g-atom/l is nearly constant independent of the sodium concentration but shifts sharply to negative value by more than one volt by increasing the concentration of sodium from 10^{-3} to about 3×10^{-3} g-atom/l, and then decreases almost linearly with logarithm of the concentration. The equilibrium potential of the amalgam containing 10^{-2} g-atom/l of sodium in 1N Na^+ solution is estimated from the figure¹¹⁾ at -1.72 v. LEWIS and KRAUS¹²⁾ also reported the value of -2.1525 v (referred to the normal calomel electrode) for the equilibrium potential of the amalgam of 0.206 wt % Na in 1N Na^+ solution. JOFA¹³⁾ quoted in his paper the following equation for the equilibrium potential of the dilute sodium amalgam,

$$V = -1.844 + 0.059 \log (a_{\text{Na}^+}/a_{\text{Na(Hg)}}), \quad (5)$$

where a_{Na^+} and $a_{\text{Na(Hg)}}$ are the activity (g-atom/l) of sodium ion in solution and sodium in amalgam respectively. The activity, $a_{\text{Na(Hg)}}$, is calculated from the above equation at, for example, $V_{\text{INV}} = -1.8$ v and $a_{\text{Na}^+} = 1$, as 1.8×10^{-1} g-atom/l, which turns out 8.7×10^{-3} coulomb for the present droplet of the hanging electrode (radius, 0.05 cm). This quantity is in agreement in order of magnitude with the observed value of Q at $V_{\text{INV}} = -1.8$ v as seen from Fig. 8. At higher cathodic polarization, it might be possible to have the intermetallic compounds, since GERKE¹⁴⁾ and BENT and FORZIATI¹⁵⁾ reported the equilibrium potentials of -1.92 and -2.0 v, respectively for the intermetallic compounds of NaHg_5 and NaHg_2 .

Hydrogen Electrode Reaction in Alkaline Solutions. I

Kinetics of sodium deposition

Equation (2) gives the integrated quantity of the deposited sodium during the cathodic potential sweep up to V_{INV} . Thus, differentiation of Eq. (2) gives the empirical relation between the current density, i , and the potential, V , for the reaction, $\text{Na}^+ + e^- \longrightarrow \text{Na}(\text{Hg})$ as

$$i = i_0 \exp(-\alpha FV/RT), \quad (6)$$

where the suffix, INV, is omitted and

$$i \equiv (dQ/dt)/A \quad (7. a)$$

$$i_0 \equiv (-k[\text{Na}^+] \alpha F/RT)(dV/dt)/A \quad (7. b)$$

A ; Surface area.

The quantity, i_0 , is the current density for the reaction at the reversible potential of the normal hydrogen electrode. The i_0 was independent of the sweep rate as seen from Eq. (7. b) and the fact that the constant k in Eq. (7. b) or (2) is inversely proportional to the sweep rate at the rapid scanning of the potential (2-3, (ii), or Fig. 6). Equation (6) is written for the case of $[\text{Na}^+] = 1\text{N}$ as

$$-V(\text{volt}) = 1.76 + 0.133 \log i, \quad (8)$$

where the slope 0.133 v is the mean value of the slopes obtained in 1N, 0.1N and 0.01N Na^+ solutions.

Hydrogen evolution and sodium deposition

The present Tafel relation in Fig. 2 (curve, 2) is observed in the potential range more negative than the potential of -1.6v , where the sodium accumulation becomes detectable and is enhanced exponentially with higher cathodic polarization. Consequently, it is concluded that the present Tafel relation is affected to a great extent by the contribution owing to the sodium deposition and is not attributed purely to the hydrogen evolution reaction itself. Thus, the activity of mercury itself is hardly determinable in the present system.

Equation (8) is represented by curve 4 in Fig. 2. One can see that the discharge of sodium ion occurs quite rapidly in comparison with the hydrogen evolution reaction observed by BOCKRIS and WATSON in the alkaline solution. This is in harmony with the conclusion³⁻⁵⁾ that the discharge of sodium ion is one of the elementary steps of hydrogen evolution reaction, and that the rate-determining step is the following step which gives hydrogen

H. KITA and T. KURISU

molecule with reaction of the deposited sodium with water molecule.

In acidic solution, however, the rate of hydrogen evolution reaction is much accelerated as seen in Fig. 8 (curve, 1) and exceeds the rate of the deposition of sodium which is independent of pH. Thus, in acidic solution there is no room for sodium to be an intermediate of the hydrogen evolution. It might be expected that at around pH=5, the rates of the both reactions become comparable, if the Tafel line of hydrogen evolution shifts by 59 mv per pH in the negative direction of potential.

Literatures

- 1) H. KITA, This Journal, **13**, 151 (1965).
- 2) H. KITA, J. Electrochem. Soc., **113**, 1095 (1966).
- 3) J. O'M. BOCKRIS and R. G. H. WATSON, J. phys. chim., **49**, C70 (1952).
- 4) R. NOTOYA and A. MATSUDA, This Journal, **14**, 165, 192, 198 (1966).
- 5) T. OHMORI and A. MATSUDA, *ibid.*, **15**, 201 (1967), **17**, 39 (1969).
- 6) J. D. ROSS, R. D. DEMARS and I. SHAIN, Anal. Chem., **28**, 1768 (1956).
- 7) O. NAGASHIMA and H. KITA, This Journal, **15**, 49 (1967).
- 8) W. M. LATIMER, "Oxidation Potentials" 2nd ed., Prentice-Hall, Inc., (1952).
- 9) J. O'M. BOCKRIS and H. KITA, J. Electrochem. Soc., **108**, 676 (1961).
- 10) J. HEYROVSKÝ, Disc. Faraday Soc., **1**, 212 (1947).
- 11) T. ERDEY-GRÚZ and A. VÁZSONYI-ZILAHY, Z. phys. Chem., **A 177**, 292 (1936).
- 12) G. N. LEWIS and C. A. KRAUS, J. Am. Chem. Soc., **32**, 1459 (1910).
- 13) E. A. JOFA, Zhur. Fiz. Khim., **28**, 1163 (1954).
- 14) R. H. GERKE, J. Am. Chem. Soc., **45**, 2507 (1923).
- 15) H. E. BENT and A. F. FORZIATI, J. Am. Chem. Soc., **58**, 2220 (1936).