

# The Anodic Behavior of Alcohols in Alkaline Solutions

By

Shunzo Koidzumi

(Received July 13, 1934)

---

The evolution of hydrogen and hydrocarbons at the anode by the electrolysis of alcohols in alkaline solutions has been observed by E. Müller and his co-operators.<sup>1)</sup> The reaction resembles closely that of Kolbe's synthesis of hydrocarbons by means of the electrolysis of fatty acid salts. As to the mechanism of this reaction, different explanations have been proposed by E. Müller<sup>2)</sup> and Fr. Fichter<sup>3)</sup>. These explanations, however, have not yet received experimentally conclusive confirmation.

Recently E. Müller and his co-workers, having measured the anode potential in the electrolysis of an alkaline solution containing acetone, formaldehyde<sup>4)</sup> or formic acid<sup>5)</sup>, proposed an explanation for the mechanism of the characteristic reaction. It dwells upon the anodic adsorption of anions. In the electrolysis of formic acid in an alkaline solution, they observed a regular swinging of the anode potential which was accompanied by an intermittent evolution of carbon dioxide at the anode. This fact has aroused much interest as clear evidence for the discharge of the adsorbed formate anion and the spontaneous splitting of the discharged anion into carbon dioxide, leaving hydrogen at the anode as the hydrogen electrode. In the case of formaldehyde, such a swinging of anode potential did not take place; but a jump of the anode potential at a definite current density was observed.

As to the electrolysis of alcohols, not much has yet been studied; only an instance in which the anode potential was measured with some electrodes during the electrolysis of methyl alcohol.<sup>6)</sup> In electrolyzing *n*-propyl alcohol, the present writer<sup>7)</sup>, observed a fairly large evolution of ethane and ethylene along with hydrogen. In this experiment methyl

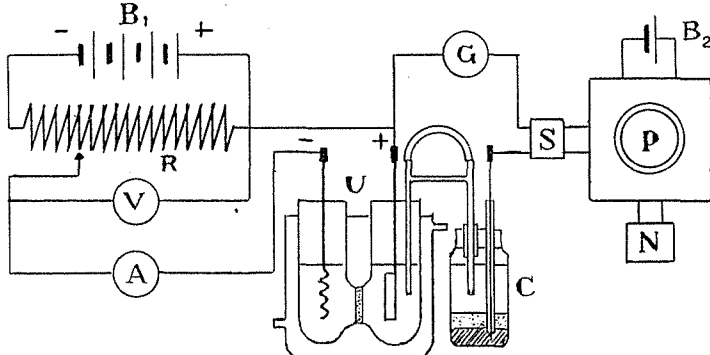
alcohol was used as the solvent to increase the concentration of propyl alcohol. This, however, so complicated the anodic reactions as to make their thorough investigation very difficult. In the present investigation, therefore, the electrolysis of lower alcohols was undertaken as they have great solubility in the concentrated solution of caustic soda, such as methyl and ethyl alcohol; and the relation between the anode potential and the current strength was measured, varying the applied electromotive force and electrodes. A complete analysis of the evolved gases and also of the various substances produced by electrolysis in the solution was simultaneously carried out. As the consequence, evidences showing the anodic adsorption and discharge of anions seem to have been realized. To explain the discharge theory so far experimentally verified the writer tried to apply the "Octet electronic theory" proposed by E. Müller.

( I )

### Electrolytic Oxidation of Methyl Alcohol in an Alkaline Solution

Anode potential and current-potential curve

Apparatus



- |                                     |                                    |
|-------------------------------------|------------------------------------|
| B <sub>1</sub> : Battery (24 volts) | R : Slide Resistance               |
| V : Voltmeter                       | A : Ammeter                        |
| U : Electrolytic Cell               | C : Normal-Calomel Electrode       |
| G : Galvanometer                    | S : Commutator                     |
| P : Potentiometer                   | B <sub>2</sub> : Battery (2 volts) |
| N : Standard Cell.                  |                                    |

For the analysis of electrolyte, an electrolytic cell as shown in the above figure, provided with a diaphragm consisting of a glass filter plate, was used. Anode gases were introduced under a constant pressure into the burette, which was designed by the author<sup>7</sup>.

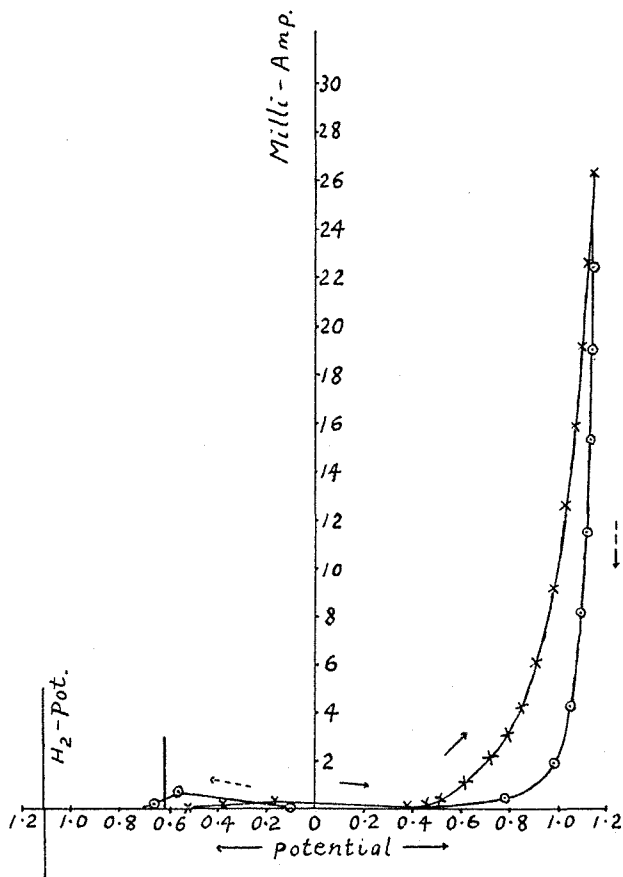
### Experimental

For determination of anode potential and current strength an ordinary U-tube is used as the electrolytic cell.

The electrolyte (20 c.c. of 8N-NaOH + 20 c.c. of CH<sub>3</sub>OH i. e. 4N-NaOH alcoholic solution) is poured into the U-tube, and an anode is immersed in one side of the tube and a platinum spiral in the other

Fig. 1.

Pt  $\left( \begin{array}{l} \phi = 0.5 \text{ mm.} \\ L = 62.0 \text{ mm.} \end{array} \right.$



as the cathode. The temperature of the electrolyte is kept always at 18°C.

First, applying no electromotive force (E. M. F.) the static anode potential ( $\Delta$ ) against the calomel-electrode is measured. Then, the applied E. M. F. is increased at an interval of 5 minutes with the increment of 0.25 volt. The anode potential against the calomel electrode and the current strength corresponding to each applied E. M. F. are measured, and the curve is plotted taking the former (in volt) in abscissa and the latter (in m. Amp.) in ordinate. As shown in Fig. 1, the static potential of platinum anode is  $-0.620$ , being lower than that in the water solution of 4N-NaOH (cf. Fig. 8;  $-0.135$ ), and higher than the reversible hydrogen-electrode potential ( $-1.123$ ; calculated for 4N-NaOH solution). In increasing the applied E. M. F., the ascent of the current-potential curve is scarcely seen in the lower range of the potential against the standard electrode. The curve shows a normal ascent only in the higher range of the anode potential after it has been increased remarkably over the oxygen-electrode potential ( $+0.382$ ; calculated). From  $+0.520$  upward the current rapidly increases along with the potential increase, following the gas evolution. In decreasing the applied E. M. F., the descending current-potential curve, almost similar to the ascending curve but slightly deflected to the nobler side, is obtained. When the electrolysis is over, the static anode potential is found to be  $-1.110$ , which is nearly equal to the hydrogen-electrode potential. The anode may evidently be regarded to have adsorbed much hydrogen at this instant.

Similar current-potential curves are traced with anodes of palladium, gold, rhodium, silver, nickel and copper as in Figs. 2, 3, 4, 5, 6 and 7.

Suspecting that there would be found a break or inflexion of the curve corresponding to the point at which hydrogen and hydrocarbon begin to evolve at the anode, the writer conducted the electrolyses with platinum, rhodium, gold or palladium as anodes, since these metals show the specific nature of evolving hydrogen anodically. Yet no such inflexion could be found, although with nickel and silver anodes an inflexion of the curve in its ascending part was observed nearly at the oxygen-electrode potential. This simply indicates the point at which oxygen begins to be evolved. Neither nickel nor silver has such a specific action to evolve hydrogen anodically. However, some hint was obtained in comparing the current-potential curves traced in the electrolyses of alcoholic solution of 4N-NaOH and aqueous solution of 4N-NaOH containing no alcohol.

Fig. 2.

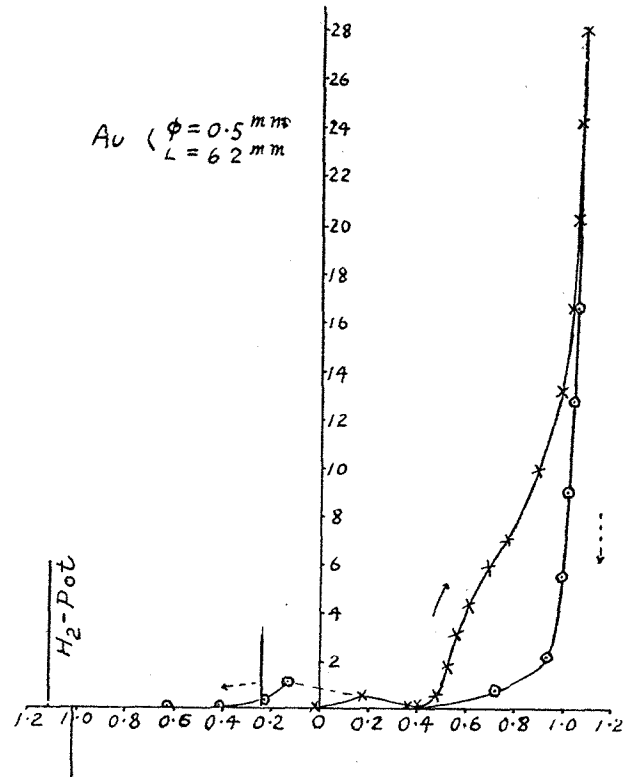


Fig. 3.

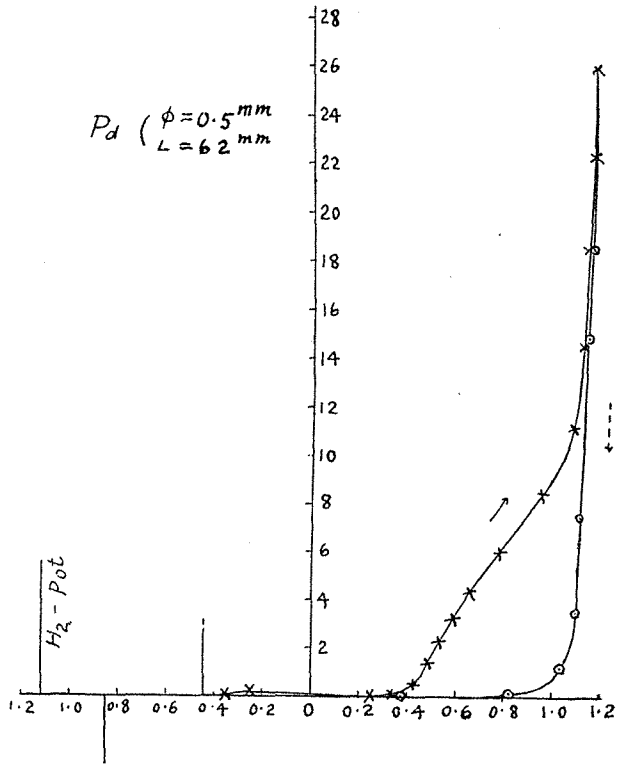


Fig. 4.

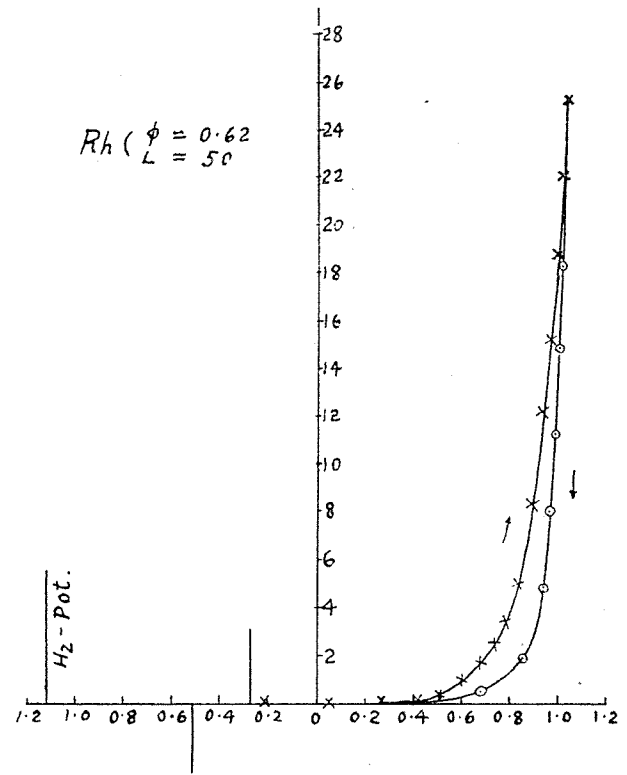


Fig. 5.

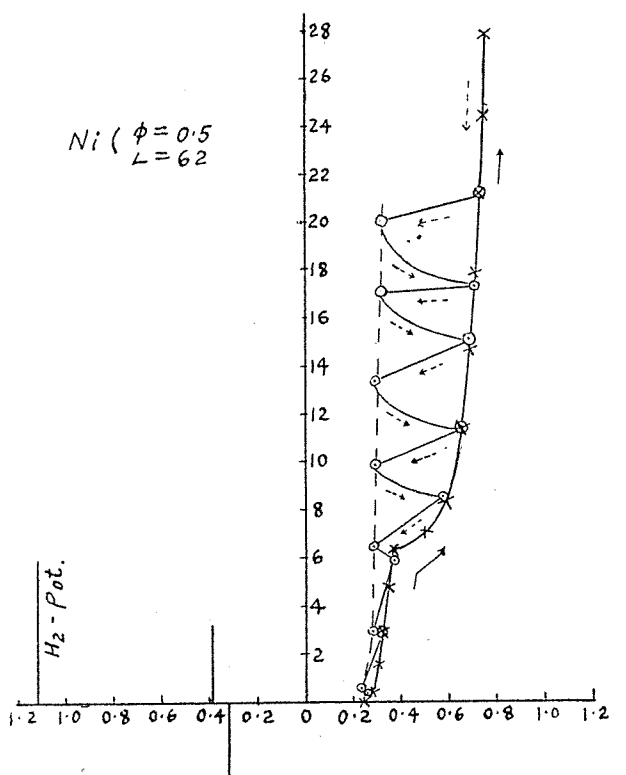


Fig. 6.

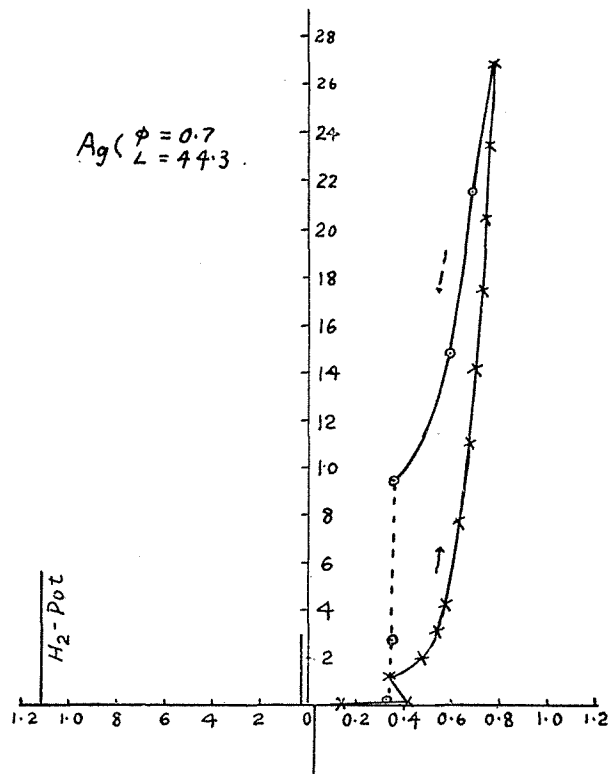


Fig. 7.

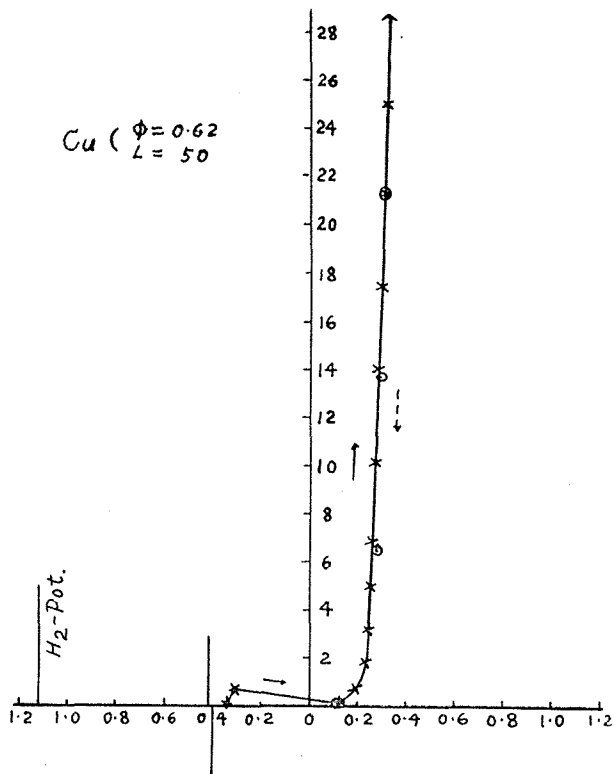


Fig. 9.

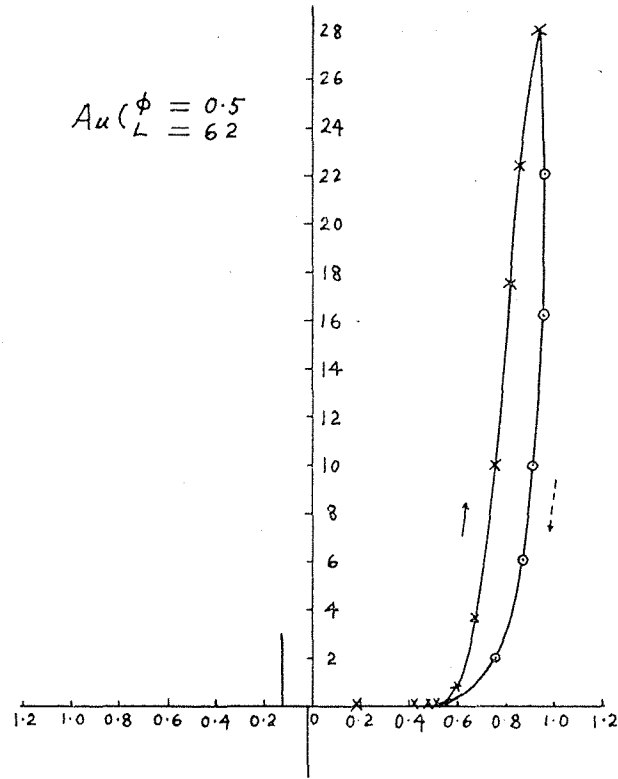


Fig. 8.

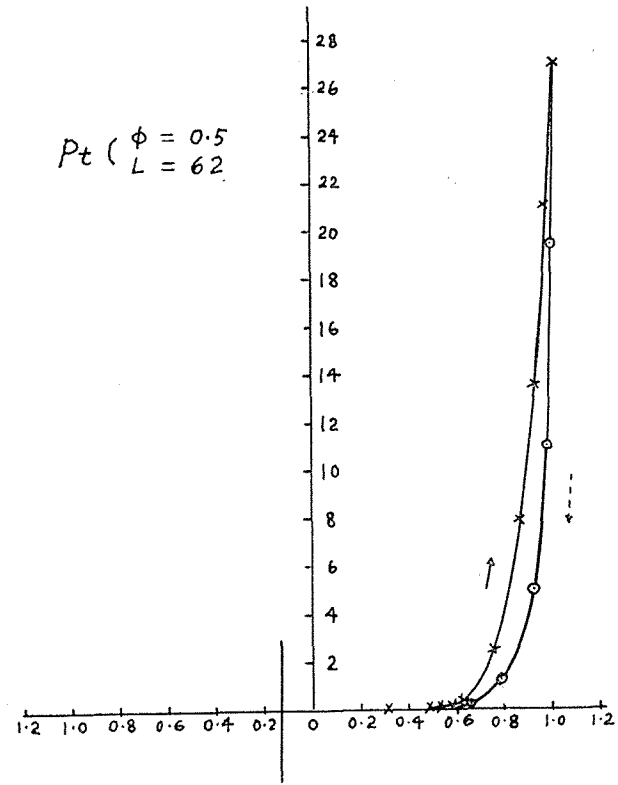




Fig. 10.

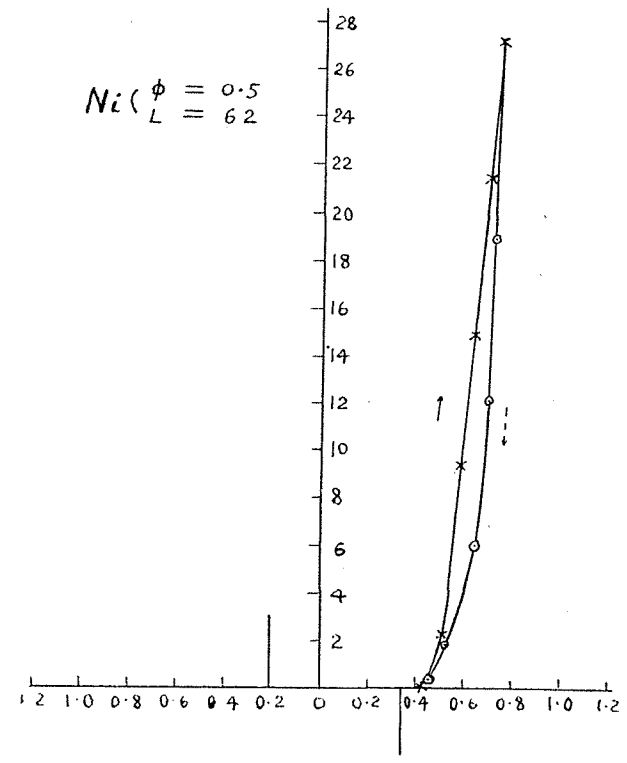
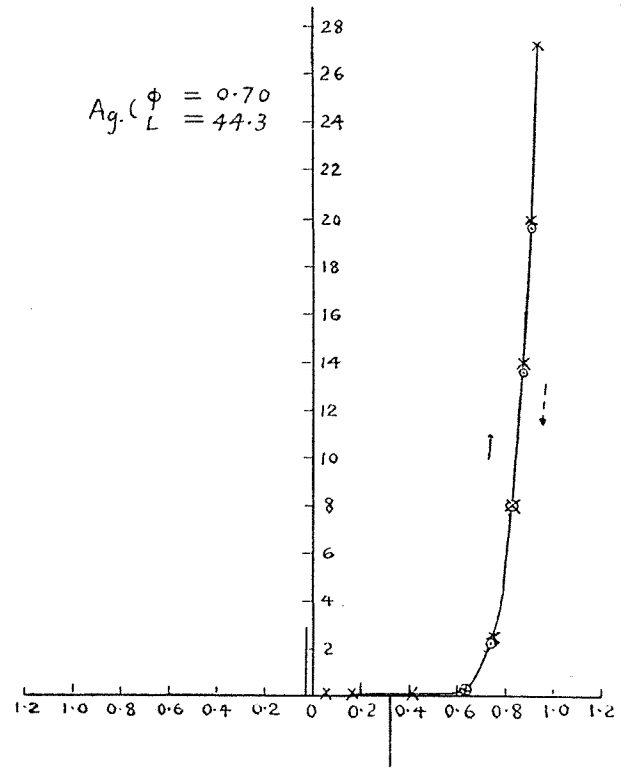


Fig. 11.



The current-potential curve obtained with platinum or gold anode from which hydrogen is evolved in the electrolysis of an alcoholic solution, always stands in the nobler side of the curve which is shown in Fig. 8 or Fig. 9. This fact shows that the adsorption and discharge of alcoholate and glycol anions occur either prior to or simultaneously with those of hydroxyl ions. In other words, the discharge of hydroxyl anions, being obstructed by the accumulation of alcoholate anions, is partially possible. The current-potential curve obtained with nickel or copper anode from which no hydrogen is evolved in the electrolysis of an alcoholic solution is found to stand in the opposite side of the curve, (Fig. 10 or Fig. 11).

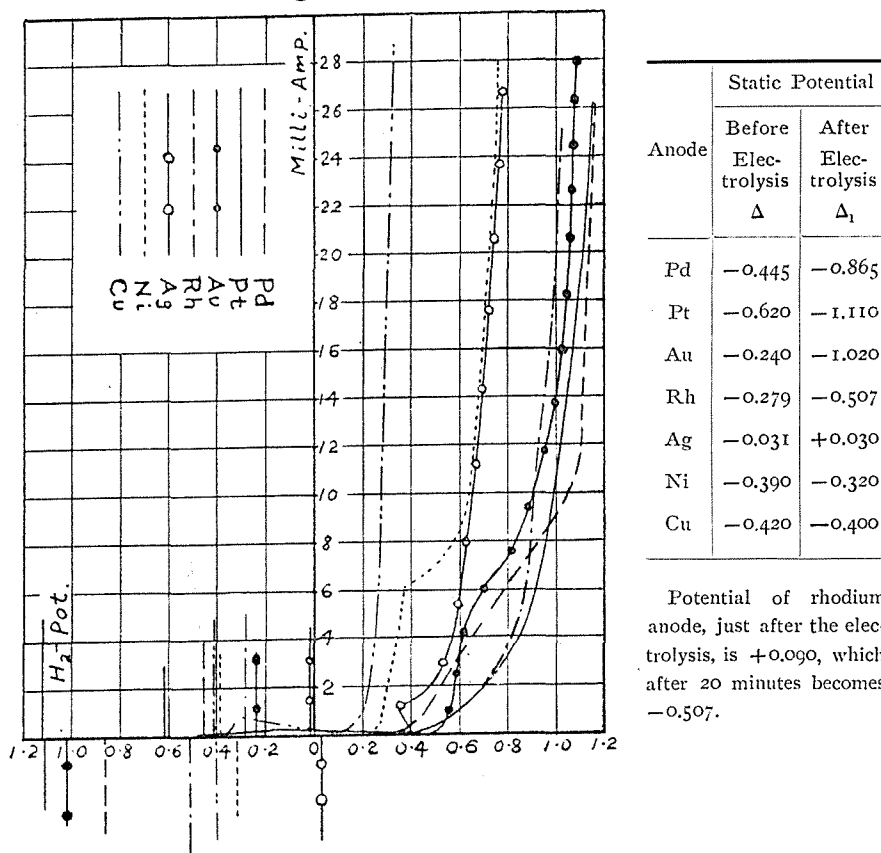
In the case of ordinary anodic oxidation, hydroxyl ions are discharged on the anode, the alcohol and the alcoholate anions acting as a depolarizer. Therefore it is a matter of course that the current-potential curve obtained by the electrolysis of alcoholic solution lies at the lower potential side when compared with the curve obtained by the electrolysis of the solution containing no alcohol.

In the electrolysis of alcoholic solution of 4N-NaOH with the nickel anode, the current-potential curve shows a very regular zigzag movement of anode potential in its descending part as shown in Fig. 5. That is to say, in decreasing the impressed E. M. F., the anode potential is decreased along the ascending curve to +0.742 (amperage=21.1 m. Amp.), but when the impressed E. M. F. is further decreased, the potential suddenly moves to the point on the dotted line, +0.327 (amperage=20.0 m. Amp.) where the evolution of oxygen momentarily ceases (depolarization due to alcohol is at its maximum). A few minutes later, however, owing to the local depletion of the concentration of alcohol (depolarizer) on the anode surface, the anode potential returns to the point on the ascending curve, +0.714 (amperage=17.3 m. Amp.) and oxygen is again evolved. When the anode potential is decreased to the point +0.250, after a repetition of such a zigzag motion, the current becomes very insignificant i. e. 0.5 m. Amp., as in the case of the ascending curve.

A similar but less distinct phenomenon is observed in the case of silver anode.

Next, the ascending parts of the current-potential curves obtained with various anodes in the electrolysis of 4N-NaOH solution containing methyl alcohol, are summarized in the following figure :

Fig. 12.



The Anode Potential at which the gas begins to evolve.

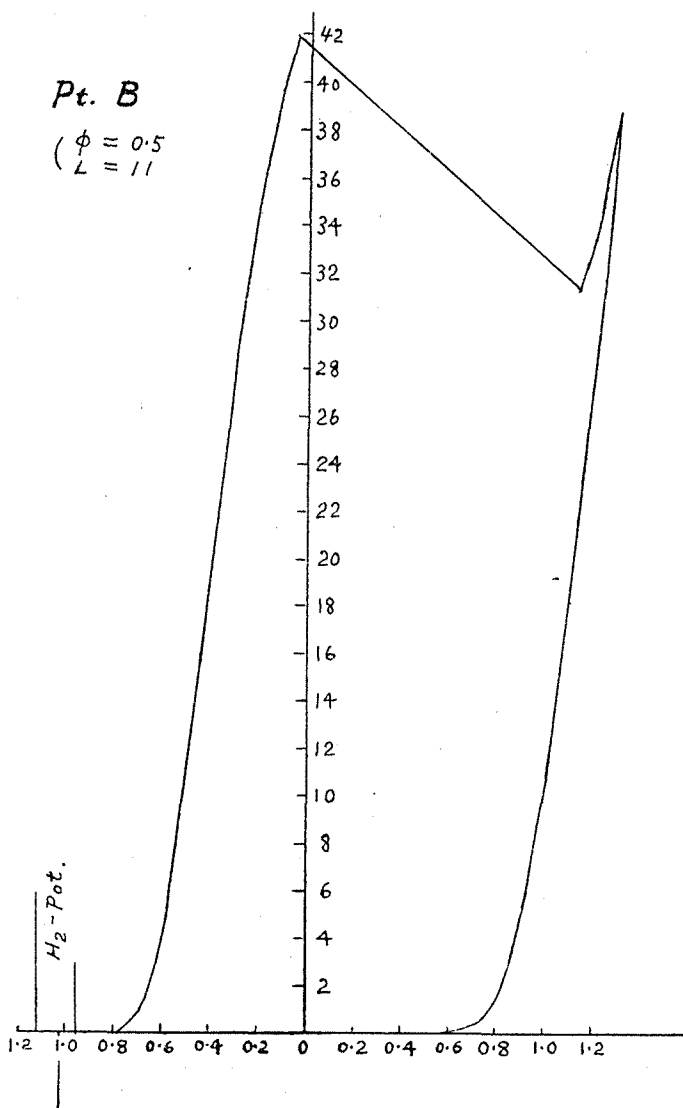
Cu	Ni	Ag	Rh	Au	Pd	Pt
+0.535	+0.376	+0.338	+0.432	+0.480	+0.480	+0.520

In the case of Pt, Pd, Au and Rh anodes which have the characteristics of hydrogen evolution, the ascending part of the curve, where the gas is evolved briskly, lies between +0.8 and +1.2 volt. With the anodes from which no hydrogen is evolved, such as Ag, Ni, and Cu, the curve where the oxygen is evolved lies at the potential lower than +0.8.

The various vertical lines above the abscissa indicate the static potential of anode before electrolysis, and those under the abscissa

indicate that after electrolysis. The static anode potentials of platinum, palladium, rhodium, and gold after electrolysis are deflected towards the hydrogen-electrode potential, becoming baser than those before electrolysis. This fact shows that these electrodes, after electrolysis, are in the state of adsorbing hydrogen. On the contrary, the static

Fig. 13.



anode potentials of copper, nickel and silver after electrolysis, which are deflected to the nobler side when compared with those before electrolysis, tend to approach to the oxygen-electrode potential.

As it is already known that alcohol in an alkaline solution gives off hydrogen by the catalytic action of rhodium black<sup>9)</sup>, it was deemed

Fig. 14.

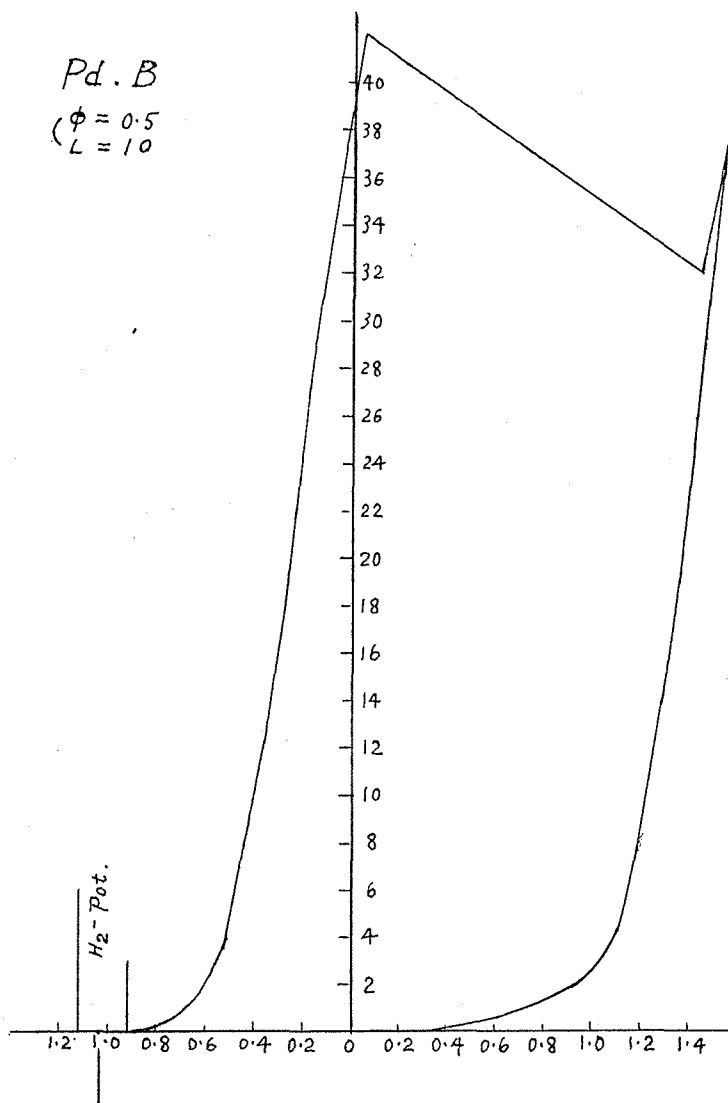


Fig. 16.

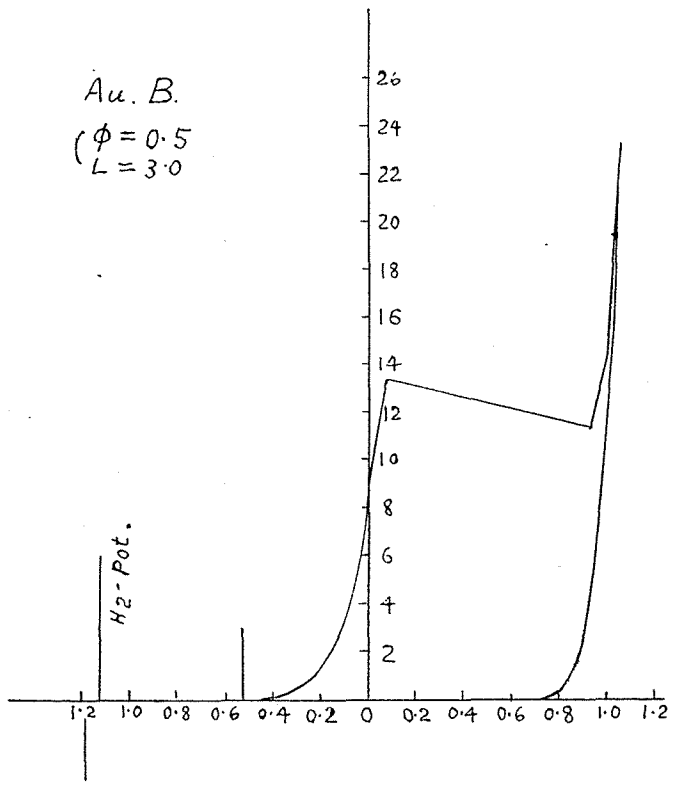
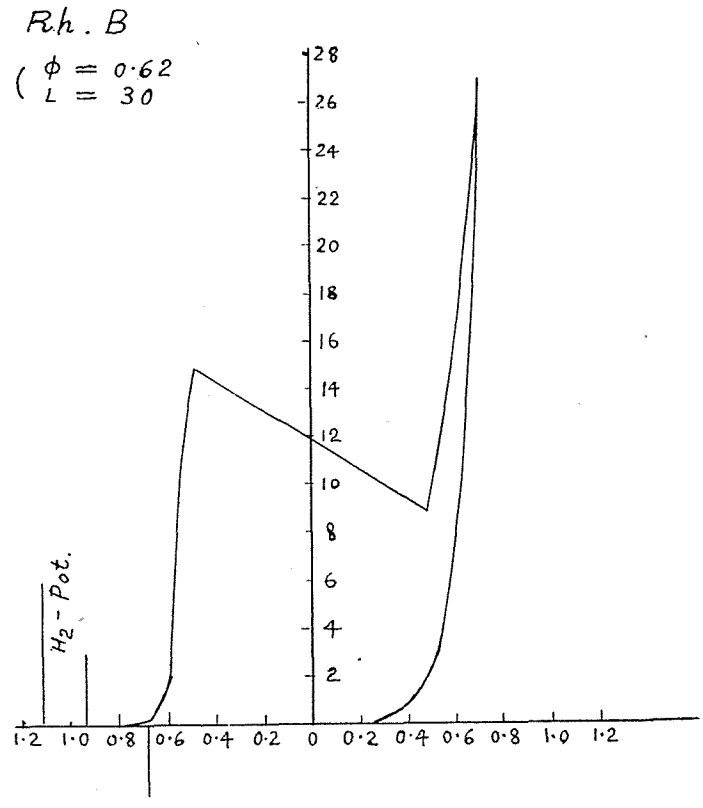


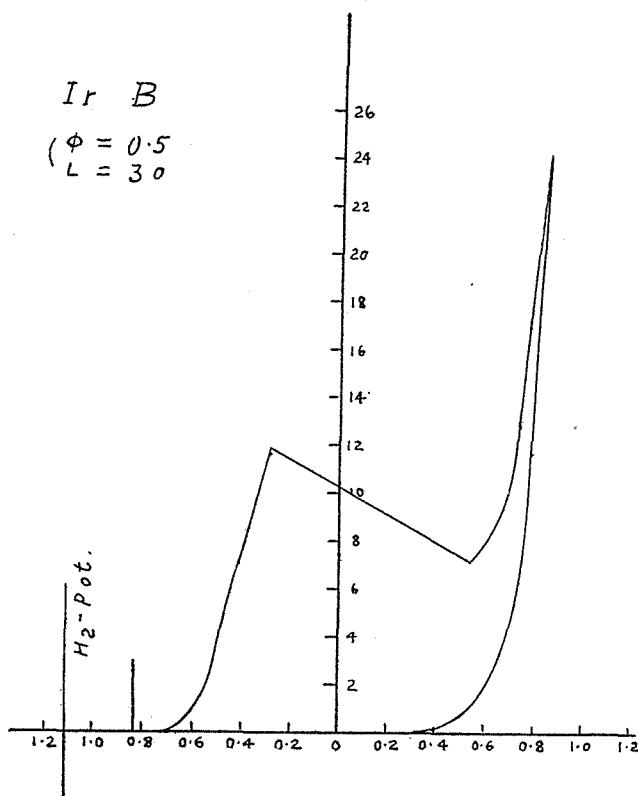
Fig. 15.



necessary to trace the anodic reaction of various metals in a spongy form. Hence, the similar investigation was repeated with Pt, Rd, Pd, and Au coated with the respective black as the anode.

Osmium black and Ruthenium black electrode prepared by the electrolytic method were found hardly serviceable, as the former gradually dissolves and the latter is stripped off in the course of electrolysis. Therefore, the current-potential curves for both anodes could not be obtained.

Fig. 17.



As shown in the figures from 13 to 17 when Pt, Pd, Rh, Au, and Ir black are used as anodes, the current-potential curves show a distinct ascent even in the lower range of potential. Yet in these cases no evolution of anode gas is present. When, however, current density reaches a certain limit, anode gas begins suddenly to be evolved and at the same time the anode potential jumps to the nobler range of potential. From this point the curve again shows a normal ascent,

gas evolution being also increased, along with the increase of applied E. M. F. The ascending limit of the curve in the baser range varies according to the condition of sponginess of the anode metal, but the jump of anode potential is always clearly observed.

### Electrolysis with Spongy Plate Anode

Taking into consideration the fact that the current-potential curve ascends in two different ways, we can naturally presume the possibility of the occurrence of different kinds of anodic oxidation. Hence to investigate these reactions, electrolyses under different conditions were conducted using various spongy anode plates (metal plate coated with a corresponding metal black). In one case, the anode potential was kept in the baser range; in another, in the nobler range. The quantitative analysis of electrolytic products in each case was carefully carried out.

### Analysis of Electrolytic Products

#### (a) Qualitative Analysis

An anode of a platinum plate ( $3 \times 4$ )  $\text{cm}^2$  coated with platinum black was immersed into the anolyte (20 c.c. of methyl alcohol + 20 c.c. of 8N-NaOH) and a platinum spiral cathode into the catholyte (40 c.c. of 4N-NaOH); then the electrolysis was conducted at the temperature of 18°C., retaining the anode potential between  $-0.582$  and  $-0.113$ . After a current of 3 Amp.-hours was passed the electrolyte was diluted with water and neutralized under cooling with 20 c.c. of 8N- $\text{H}_3\text{PO}_4$ , then made acid with 30 c.c. of  $\text{H}_3\text{PO}_4$  (sp. gr. 1.71). The solution (about 250 c.c.) was subjected to distillation. As formaldehyde was detected by Schiff's reagent, the distillate was neutralized with 0.1N-NaOH, and again subjected to distillation. The distillate, free from formic acid, was again tested with the following reagents and the presence of formaldehyde was decisively confirmed.

- 1) Schiff's Reagent.
- 2) With morphine: *Zeit. f. anal. Chem.* **38** (1899), 467.
- 3) With phenylhydrazine hydrochloride; and Na-nitroprusside: Rimini; *Bul. Soc. Chim.* **3**, 20; (1898), 896;  
*J. Ber. d. Pharm.*, (1899), 623; Jean; *Apoth. Ztg.* (1912) 159.
- 4) With milk and conc.  $\text{H}_2\text{SO}_4$  containing  $\text{FeCl}_3$   
Hehner; *Analyst*, **21** (1896), 95; *Zeit. f. anal. Chem.* **36** (1897), 714; **39** (1900), 332;  
William & Sherman; *J. Am. Chem. Soc.*, **27** (1905), 1497.
- 5) Tollen's Reagent
- 6) Romijn's microscopic test; *Zeit. f. anal. Chem.*, **39** (1897) 44.

The residual solution decolorizes permanganate solution and precipitates lead formate by the addition of a lead nitrate solution. The lead contents of the precipitate were determined to be 69.91%, which is practically equal to the theoretical value 69.72% calculated for  $\text{Pb}(\text{HCO}_2)_2$ .

Thus it was confirmed that the products in the electrolyte consisted mainly of formic acid mixed with a small quantity of formaldehyde.



(b) Quantitative Analysis

As to the estimation of formaldehyde and formic acid in the presence of methyl alcohol in an alkaline solution, the method proposed by the present writer was applied as follows:

After the electrolysis, the electrolyte is diluted with water to a volume of 250 c.c. To 25 c.c. (1/10 of the volume) of this solution 0.5 g. of NaCl is added and cooled with ice. The amounts of NaOH and Na<sub>2</sub>CO<sub>3</sub> are determined by the differential titration, according to R. B. Warder,<sup>9)</sup> in order to know the alkalinity and to determine the carbonic acid produced by the electrolysis.

Table I.

Sample solution c.c.	Taken c.c.	0.2025N-HCl used (c.c.)		NaOH in 25 c.c. (g)	Total NaOH g.		Na <sub>2</sub> CO <sub>3</sub> in 25 c.c.	Total Na <sub>2</sub> CO <sub>3</sub> g.
		Phenolphthalein	Methyl-orange					
250	25	147.0	2.75	1.1684	11.684		0.0590	
250	25	147.2	2.75	1.1703	11.703	11.694	0.0590	0.590

The alkalinity of the solution is calculated to be 1.17 N-NaOH from the amount of NaOH determined (11.694 g.) as just suitable to the iodimetric titration of formaldehyde.

Next, to determine the amount of formaldehyde, 50 c.c. of the solution is mixed with an excess of iodine solution, and shaken for one minute. Then the mixture is acidified with 20 c.c. of 4N-HCl and the excess of iodine is titrated with thiosulphate solution.

Table II.

Sample solution c.c.	Taken c.c.	0.1N-I <sub>2</sub> added c.c.	0.1N-Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> used c.c.		0.1N-I <sub>2</sub> (c.c.) used <sup>2</sup> for HCHO	Total HCHO g.
250	50	20.16	18.37	18.36	1.80	0.0135
	50	20.16	18.35			

The total amount of HCHO (g.) = 0.00150 × 1.80 × 5 = 0.0135g. After formaldehyde is determined, 25 c.c. of the residual solution (100 c.c.) is neutralized with 147 c.c. of 0.2025N-H<sub>2</sub>SO<sub>4</sub> and 0.5 g. of NaHCO<sub>3</sub> is next added. The solution is subjected to repeated evaporation (5 times) adding water in each operation. The residue is dissolved in water and made alkaline with 15 c.c. of 1N-NaOH. Heating the solution on a water-bath, sodium formate is oxidized with an excess of permanganate solution. The solution is now acidified and precipitated MnO<sub>2</sub> is dissolved with an excess of oxalic acid. Finally the excess is titrated with permanganate. Thus knowing the amount of permanganate used in the oxidation of formate, the amount of formic acid is calculated.

Table III.

Sample solution c.c.	Taken c.c.	KMnO <sub>4</sub> (0.1044 N) added c.c.	H <sub>2</sub> SO <sub>4</sub> (6N) c.c.	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (0.1N) added c.c. (t)	0.1044N-KMnO <sub>4</sub>		Total 0.1N-KMnO <sub>4</sub> used c.c. (T)	0.1N-KMnO <sub>4</sub> used for HCOOH (T-t)	Total HCOOH g.
					used in back titrat. c.c.	mean c.c.			
250	25	100	20	60	9.70	9.65	114.45	54.45	1.253
	25	100	20	60	9.60				

The total weight of HCOOH = (T-t) × 0.002301 × 10 = 1.253 g.

After the electrolysis, during which the anode potential was kept at the baser or at the nobler range of potential, the electrolytic products were determined by applying the method of analysis as described above. The results, with current efficiencies appended, are tabulated as follows:

### Electrolysis at baser range of potential

Anolyte: 20 c.c. of  $\text{CH}_3\text{OH}$  + 20 c.c. of 8N-NaOH

Catholyte: 40 c.c. of 4N-NaOH

Table IV.

Anode potential	Electric quantity Amp.-hour	Products	Produced amount g.	Current efficiency %	$\text{Na}_2\text{CO}_3$ found g.
Pt black (-0.495) - (-0.473) 18°C	3.149	HCHO HCOOH	0.0135 1.2530	0.77 92.66	0.590
Pt black (-0.704) - (-0.542) 18°C	3.000	HCHO HCOOH	0.0113 1.2200	0.67 94.73	0.590
Pt black (-0.737) - (-0.590) 20°C	3.001	HCHO HCOOH	0.0103 1.2020	0.61 93.33	0.694
Pt black (-0.790) - (-0.582) 30°C	3.000	HCHO HCOOH	0.0172 1.0180	1.02 79.02	1.142
Pd black (-0.565) - (-0.380) 20°C	3.184	HCHO HCOOH	0.0046 1.0590	0.25 77.47	0.684
Rh black (-0.571) - (-0.540) 20°C	1.771	HCHO HCOOH	0.0079 0.7030	0.78 92.45	0.289
Au black (-0.460) - (-0.120) 20°C	0.674	HCHO HCOOH	0.0049 0.3106	1.30 107.60	0.132

Electric quantity: Amp.-hours are determined by use of copper coulometer.

From the analytical results of the electrolytic products an inquiry was made into the mechanism of the reaction. E. Müller's view, which presumes that by the catalytic action of spongy platinum or rhodium the adsorbed alcoholate anion is discharged at comparatively low potential and passing the state of glycol anion changes into formic acid, may be regarded as the most probable. By the use of spongy anode, the current yield for formic acid supercedes 90% when the temperature is kept below 25°C., while that for formaldehyde is always less than



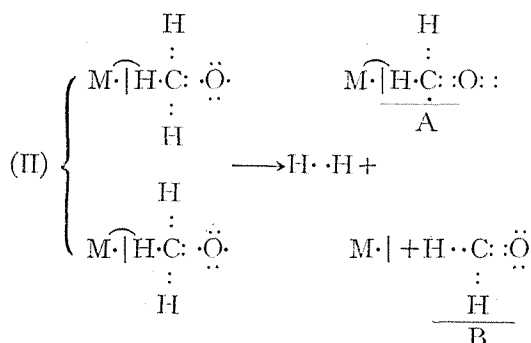
## Electrolysis at nobler range of spongy anode potential

Table V

Anode potential	Electric quantity Amp.-hour	Products	Produced amount g.	Current efficiency %	Na <sub>2</sub> CO <sub>3</sub> found g.
Pt black (+0.437) - (+0.917) 20°C	3.180	HCHO	0.0263	1.48	1.499
		HCOOH	0.8730	63.95	
Pt black (+1.710) - (>+1.9) 20°C	3.159	HCHO	0.1036	5.85	1.650
		HCOOH	0.1644	12.12	
	Total volume of anode gas c.c.	Gas components	Gas evolved(c.c.)	%	
	36.0	H <sub>2</sub>	20.88	58.02	
		CO	9.90	27.50	
CO <sub>2</sub>		0.66	1.83		
O <sub>2</sub>	4.56	12.65			
Pt black Spiral ( $\phi=0.7$ mm $L=70$ mm (>+2.00) 25°C	3.394	HCHO	0.179	9.42	1.896
		HCOOH	0.2012	13.80	
	Total volume of anode gas c.c.	Gas components	Gas evolved(c.c.)	%	
	40.6	H <sub>2</sub>	0	0	
		CO	22.36	55.07	
CO <sub>2</sub>		0.65	1.60		
O <sub>2</sub>		17.59	43.33		

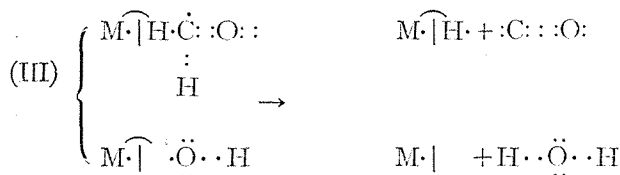
The electrolysis conducted with anode potential in the nobler range produces gaseous hydrogen and formaldehyde, as shown in formula II. This is due to the greater accumulation of the discharged alcoholate anions upon the anode surface caused by the larger current density<sup>(1)</sup>.

In this case the adsorbed aldehyde /A is in a condition unfavorable to change into the adsorbed glycol anion by the direct addition of OH ion, but the liberated aldehyde /B is first hydrated, and the glycol anion thus formed is discharged on the anode surface to produce formic acid. Thus formaldehyde and formic acid are both produced in this instance, and the current efficiency for the former is increased and that for the latter is greatly decreased. This great decrease of formic acid is due to the predominance of the secondary reaction as



already shown in formula (I''), which is verified by the greater formation of sodium carbonate (compare Table V and IV).

At the nobler potential anode (+1.7-+1.9) fairly large quantum of carbon monoxide is evolved together with hydrogen. Probably the aldehyde in the adsorbed state (/A), is affected by the discharged hydroxyl ion to produce water and carbon monoxide, as is shown in Formula III. If this explanation is right, the evolution of carbon



monoxide must be increased with the increase of the anode potential, which naturally increases the discharge of hydroxyl ion. Actually as shown in Table V when the anode potential is raised above +2.0, the anode gas consists merely of carbon monoxide and oxygen containing no hydrogen. In this case too the static anode potential after electrolysis lies between -0.98 and -1.12 showing a good coincidence with hydrogen-electrode potential.

### Electrolysis by Use of Smooth Platinum Anode

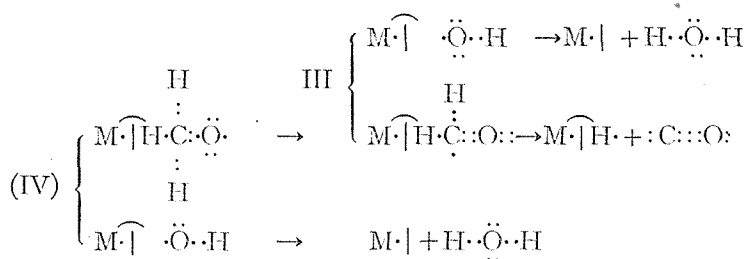
As described above, the evolution of hydrogen at spongy anodes is explained by the adsorptive nature of the anodes. To obtain further confirmation of the above explanation, electrolyses are conducted with various smooth metal anodes at the higher range of potential, and the analysis of evolved gases and the determination of products in electrolyte are carried out. At the lower range of potential, electrolysis with a smooth metal anode is hardly possible as is shown in Fig. 12.

Table VI

	Current density (Amp./cm <sup>2</sup> ) Anode-potential	Gas evolved cc.	Gas composition %				Electric quantity Amp.-hr.	Products	Produced amount g.	Current efficiency %	$\frac{\text{HCHO}}{\text{HCOOH}}$ %	Na <sub>2</sub> CO <sub>3</sub> found g.
			H <sub>2</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>						
1)	$0.5/12=0.0416$ (1.025) - (1.209) -1.120( $\Delta_1$ )	103.3	86.32	1.21	0	12.47	3.073	HCHO HCOOH	0.4513 0.5633	26.22 42.70	61.42	1.106
2)	$1/12=0.0833$ (1.237) - (1.325) -1.123( $\Delta_1$ )	107.3	86.42	1.60	0	11.98	3.097	HCHO HCOOH	0.3377 0.5864	19.46 44.07	44.51	1.189
3)	$2/12=0.1666$ (1.395) - (1.462) -0.895( $\Delta_1$ )	69.2	80.35	4.47	0.53	14.64	3.212	HCHO HCOOH	0.2265 0.5190	12.59 37.63	33.45	1.301
4)	$1/3=0.3333$ >1.8 -0.880( $\Delta_1$ )	73.6	70.91	11.41	0.82	16.86	3.120	HCHO HCOOH	0.2018 0.4558	11.28 34.02	33.16	1.392
5)	$2/3=0.6666$ >2.0 -0.818( $\Delta_1$ )	60.3	51.06	28.10	0	20.84	3.517	HCHO HCOOH	0.1958 0.4574	9.94 30.30	32.80	1.474
6)	$1/\pi 0.05 \times 6.2 = 1.0273$ >2.0 -1.124( $\Delta_1$ )	37.2	0	44.16	5.19	50.65	3.327	HCHO HCOOH	0.1571 0.4391	8.43 30.75	27.43	1.527
7)	Rh $1/\pi 0.062 \times 5.0 = 1.0273$ >2.0 -0.157( $\Delta_1$ )	71.0	0	60.75	0.27	38.97	3.065	HCHO HCOOH	0.2405 0.1864	14.02 14.17	98.94	1.395

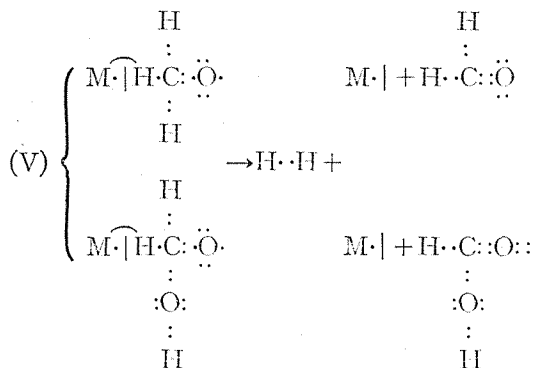


the former entirely ceases and the latter together with oxygen occupies the main portion of the anode gases, when the current density attains the value 1.0273 Amp./cm<sup>2</sup>. Perhaps the current stronger than 0.0833 Amp./cm<sup>2</sup> hinders the reaction (II), increasing the discharge of hydroxyl ions at the anode surface and in consequence the reaction as shown in formula (IV) and (III) is gradually rendered predominant.

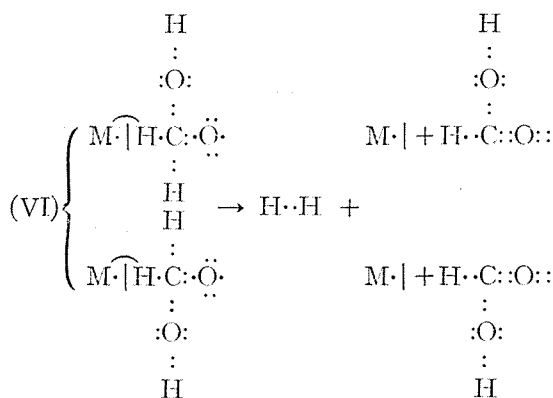


Moreover the fact that the evolution of oxygen remains almost constant, independent of remarkable increase and decrease of carbon monoxide and hydrogen respectively, which are brought about by increasing current density, strongly endorses the view illustrated above by the formula (IV) and (III). Also the fact that the smooth platinum anode, which evolves no hydrogen with the current of 1.0273 Amp./cm<sup>2</sup>, becomes a hydrogen-electrode after electrolysis, may be deemed to confirm this view.

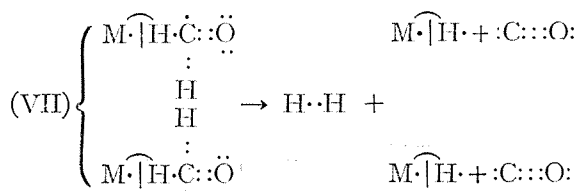
Taking into consideration the fact that the formation of anodic hydrogen and current efficiency for formaldehyde and formic acid, especially for the latter, run almost parallel with each other, the reactions represented by (V) and (VI) may also be regarded to take place.







Reaction (VII) was proved to be improbable from the result of the electrolysis of formaldehyde described below.



Electrolysis of Formaldehyde.

With the current density the same as that cited in Table VI (2) the electrolysis of formaldehyde in an alkaline solution was conducted with the following results:

Anode: smooth platinum plate      Anolyte: 20 c.c. HCHO solution<sup>12)</sup>  
 (3 × 4)cm<sup>2</sup>      + 20 c.c. 8N-NaOH  
 Cathode: platinum spiral      Catholyte: 40 c.c. 4N-NaOH  
 Current density: 0.08<sub>33</sub> Amp./cm<sup>2</sup>      Temperature: 20–25°C.

Table VII.

Anode potential	Gas evolved c.c.	Gas composition %				Electric quantity Amp.-hr.	Product	Pro-duced A-mount g.	Cur-rent Effi-ciency %	Na <sub>2</sub> CO <sub>3</sub> found g.
		H <sub>2</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>					
(1.020) –(1.306) –1.095(Δ <sub>1</sub> )	66.8	75.78	1.56	0.52	22.14	2.980	HCOOH	1.965	76.81	2.444

As shown in Table VII, the anode gas consists mainly of hydrogen, and the current yield for formic acid is fairly large. From



The Influence of Electrode

In order to compare the action of platinum anode to those of rhodium, iridium, gold, and palladium anodes, electrolyses as shown in Table IX were conducted, and also to investigate the difference of anodic nature between such nobler metals and other metals which are generally used as anodes in alkaline solution, various electrolyses as shown in Table X were also carried out.

The analytical results of the electrolytic products were as follows :

Electrode from which Hydrogen is Evolved.

Anodes : Pt, Rh, Ir, Au, Pd. Cathode : Platinum Spiral

Anolyte : 20 c.c. CH<sub>3</sub>OH + 20 c.c. 8N-NaOH Catholyte : 40 c.c.

4N-NaOH

Current density : 0.0833 Amp./cm<sup>2</sup>

Temperature : 20° - 25°C.

Table IX.

Anode Anode potential	Gas evolv- ed c.c.	Gas composition %				Elect. quant. Amp.- hour	Product	Produced amount g.	Cur- rent yield %	Ratio of yield %	Na <sub>2</sub> CO <sub>3</sub> found g.
		H <sub>2</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>						
Pt (1.237) -(1.325) -1.123(Δ <sub>1</sub> )	107.3	86.42	1.60	—	11.98	3.097	HCHO HCOOH	0.3377 0.5864	19.46 44.07	44.16	1.189
Rh (0.870) -(1.017) -1.120(Δ <sub>1</sub> )	56.7	77.14	1.66	2.33	18.87	3.007	HCHO HCOOH	0.1858 0.6207	11.04 48.08	22.96	1.001
Ir (1.020) -(1.479) -1.125(Δ <sub>1</sub> )	41.4	70.34	—	1.58	28.07	2.961	HCHO HCOOH	0.2311 0.7970	13.93 69.70	22.22	1.264
Au (1.026) (1.186) — -1.126(Δ <sub>1</sub> )	36.7	74.35	2.95	2.95	19.72	4.365	HCHO HCOOH	0.1457 0.8045	5.96 42.92	13.89	1.343
Pd (1.220) -(1.535)	101.0 (110 mins.)	0	3.38	0	96.62	3.844	HCHO	0.2773	12.88	39.23	1.027
	101.0 (105 mins.)	2.90	2.17	0	94.93		HCOOH	0.5415	32.82		
-1.097(Δ <sub>1</sub> )	109.8 (145 mins.) 311.8	4.37	0.92	0	94.71						

Electrode from which no Hydrogen is Evolved.

The electrolytic conditions are the same as in Table IX.

Table X.

Anode Anode potential	Gas evol- ed c.c.	Gas composition %				Elect. quant. Amp.- hour	Product	Produced amount g.	Cur- rent yield %	Ratio of yield %	Na <sub>2</sub> CO <sub>3</sub> found g.
		H <sub>2</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>						
Ag (0.550) —(1.700) +0.275(Δ <sub>1</sub> )	32.0	0	0	0	100.00	3.166	HCHO	0.0416	2.35	4.62	1.106
							HCOOH	0.7684	56.51		
Ni (0.340) —(0.495) —0.140(Δ <sub>1</sub> )	35.8	0	0	1.77	98.23	4.041	HCHO	0.2157	9.53	19.19	1.159
							HCOOH	0.8616	49.66		
C (1.170) —(1.386) +0.206(Δ <sub>1</sub> )	22.1	0	0	1.42	98.58	4.137	HCHO	0.2005	8.65	16.43	1.264
							HCOOH	0.9353	52.65		
Cu (0.426) —(0.520) —0.010(Δ <sub>1</sub> )	2.4	0	0	0	100.00	3.109	HCHO	0.0748	4.29	14.34	1.474
							HCOOH	0.3993	29.92		
Fe (0.603) —(0.651) —0.120(Δ <sub>1</sub> )	151.0 (60 mins.)	0	0.29	0.29	99.42	2.826	HCHO	0.1030	6.51	32.18	0.263
	150.5 (60 mins.)	0	0.20	0.40	99.40						
	152.5 (60 mins.)	0	0.11	0.51	99.38						
	454.0										

As shown in Table IX, platinum, rhodium, iridium, gold, and palladium anodes are ascertained to have the properties of evolving hydrogen as was inferred from current-potential curves. With palladium anode, only a small amount of hydrogen is evolved, as it remains mostly occluded in the anode. The palladium plate after electrolysis is found to bend backward against the cathode, as its surface facing the cathode expands by occluding much hydrogen. After electrolysis all electrodes above mentioned show their static anode potentials very near to the hydrogen-electrode potential.

With silver, nickel, copper, iron and also carbon anode no hydrogen is evolved and their static anode potential after electrolysis is found far different from the hydrogen-electrode potential.

In examining the products in the electrolytic solution after electrolyses, no distinct difference is recognizable between the two cases, as shown in Table IX and Table X. This fact can only be understood by explaining the reaction of anodic evolution of hydrogen according to the mechanism as illustrated in Table VIII. No special products other than formaldehyde and formic acid are produced even when anodic hydrogen is evolved. But in this case the ratio of the current yield for formaldehyde to that for formic acid is generally greater than the ratio which is found when only ordinary electrolytic oxidation occurs.

## ( II )

### The Electrolytic Oxidation of Ethyl Alcohol in an Alkaline Solution

#### Anode Potential and Current-potential Curves

In the electrolytic oxidation of methyl alcohol, it was found that the static anode potential, especially after the electrolysis, and the current-potential curve traced during the electrolysis, were closely related with the anodic evolution of hydrogen. To ascertain how the electrolysis of ethyl alcohol takes place the current-potential curves were traced with various anodes.

As shown in Fig. 19, the current-potential curve ascends only in a slight degree in the baser range of potential against the normal-electrode, and the anode gas is not evolved as in the case of methyl alcohol. When the anode potential is raised to the nobler range to exceed the oxygen-electrode potential, the curve begins to show a normal ascent accompanying the gas evolution. The descending curve is almost similar to the ascending curve but is deflected slightly to the nobler side. The static anode potential after electrolysis is  $-1.050$ , lying near the hydrogen-electrode potential.

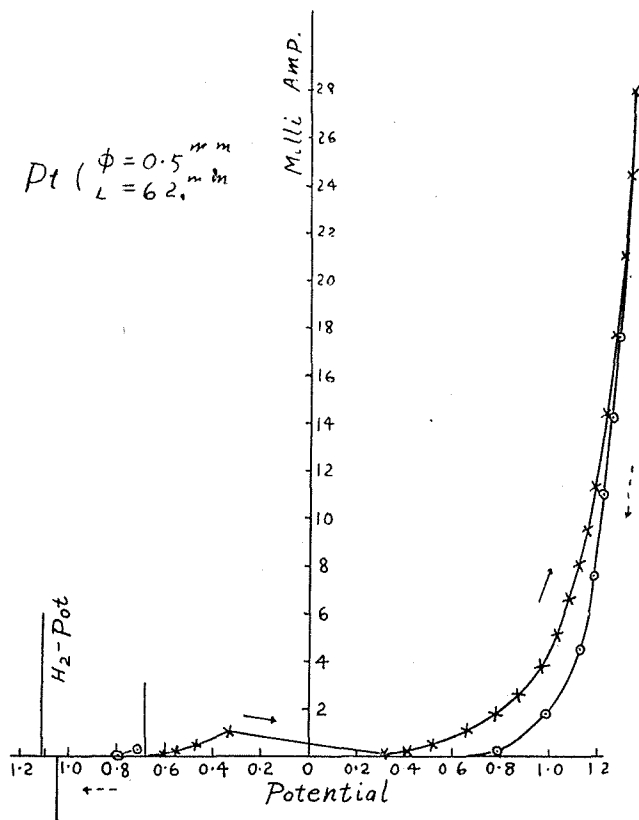
Anode: Platinum wire  $\phi=0.5$  m.m. ;  $L=62.0$  m.m.

Cathode: Platinum spiral

Electrolyte: 20 c.c. of  $\text{CH}_3\text{CH}_2\text{OH}$  + 20 c.c. of 8N-NaOH

Temperature:  $18^\circ\text{C}$ .

Fig. 19.



The curves for rhodium, gold, palladium, silver, nickel, and copper anodes, traced in the similar manner, are illustrated in Figs. 20, 21, 22, 23, 24, and 25.

The curves for rhodium, gold, and palladium, as shown in Fig. 20; 21; 22, show a similar type of ascending in the nobler range as in the case of methyl alcohol, but the ascending curve for palladium is deflected much more to the less noble potential than in the case of methyl alcohol and also to the lower potential side of the curve obtained in the blank electrolysis.

With silver anode, no instability of anode potential near the oxygen-electrode is found. The descending curve shows a good coincidence with the ascending one. Moreover, the curve obtained in this electrolysis is deflected to the nobler side of the curve obtained in the blank experiment. The curve for the nickel anode as shown

Fig. 21.

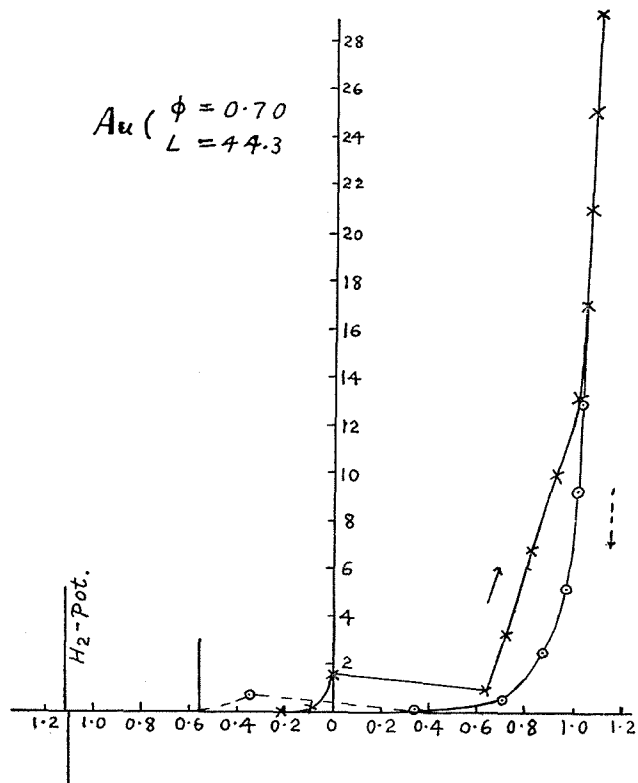
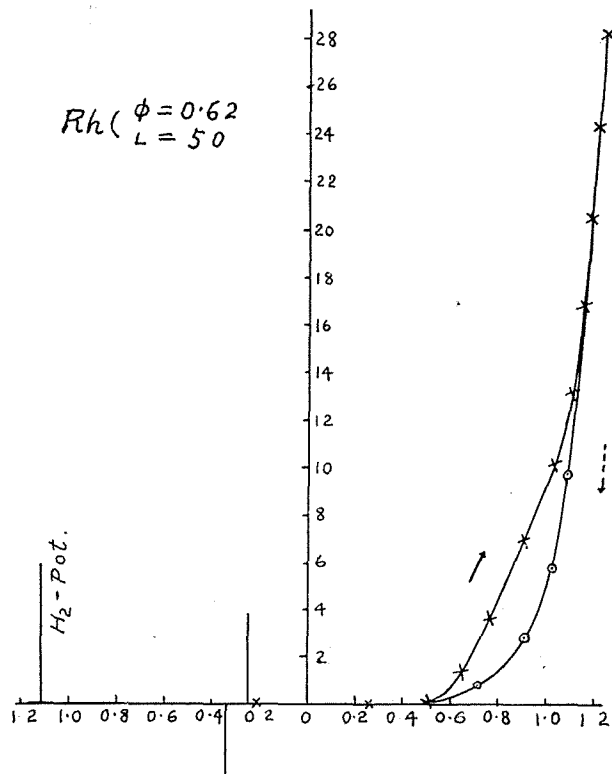
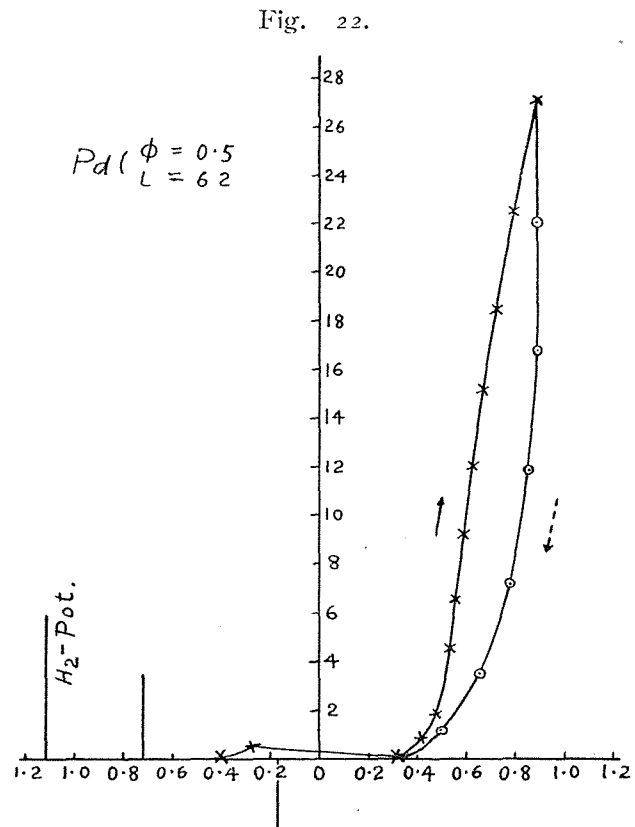
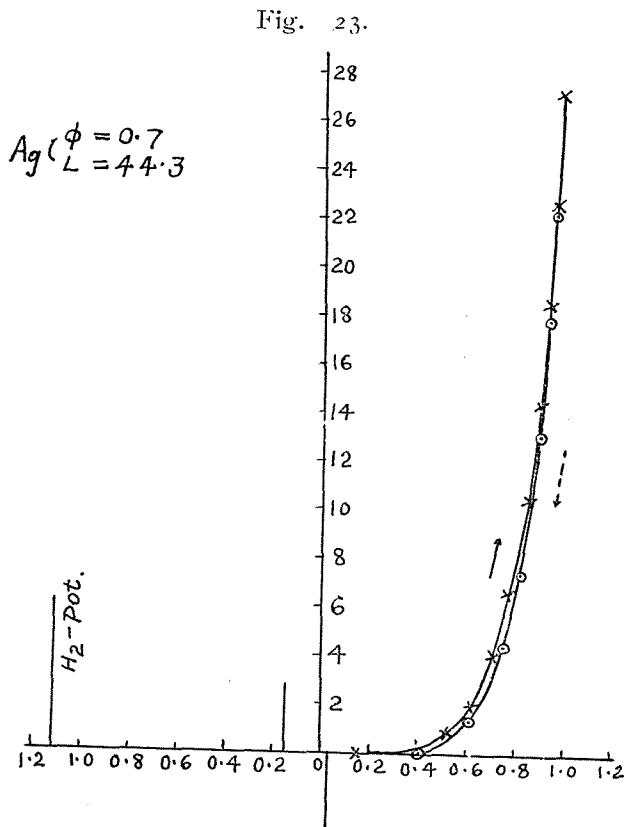
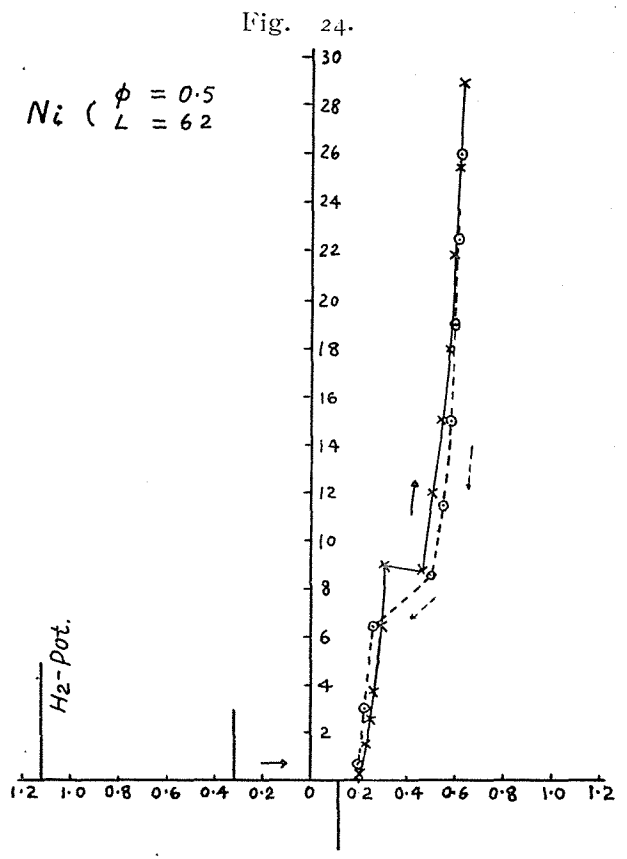
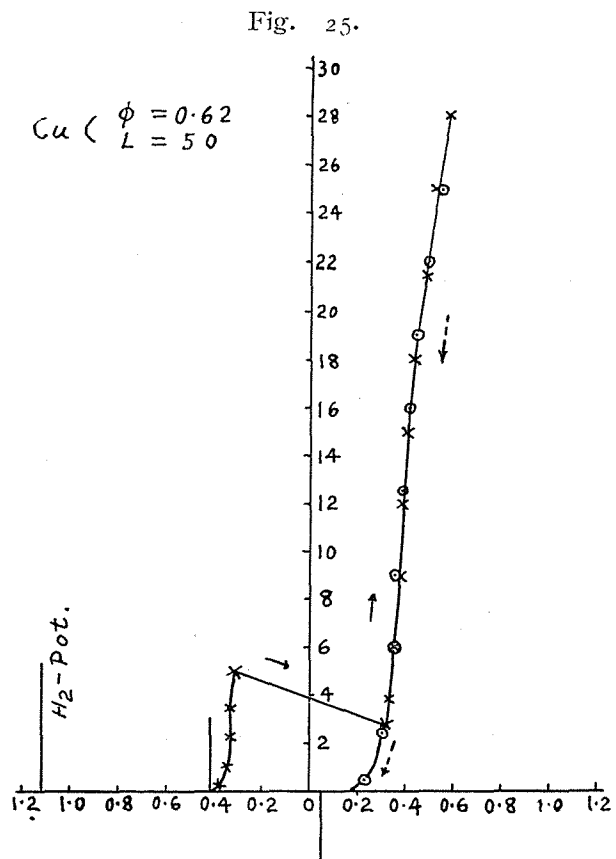


Fig. 20.









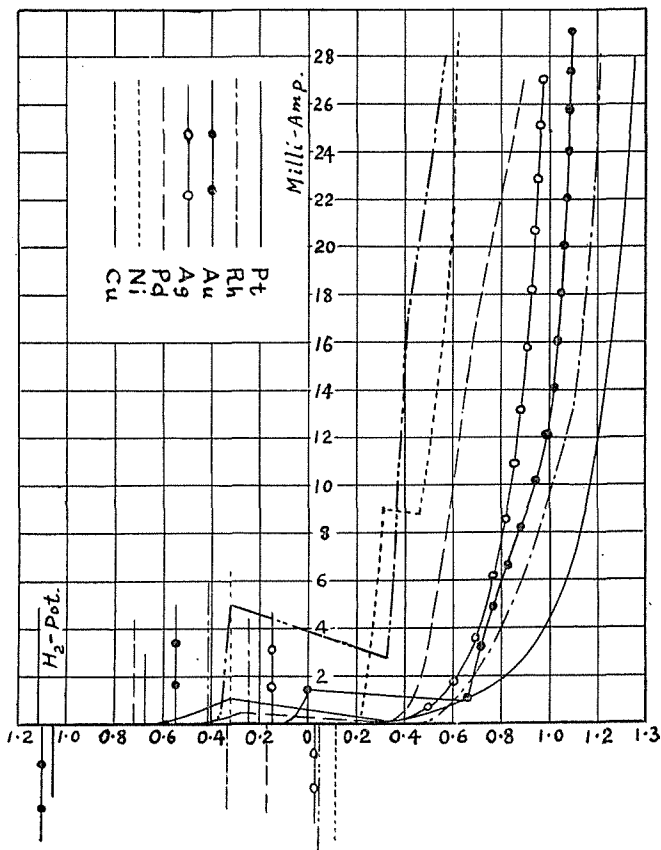
in Fig. 24. shows a clear break near the oxygen-electrode potential as in the case of methyl alcohol. However the transition or the zigzag motion of anode potential in the descending curve cannot be observed

Anode	Static Potential	
	Before Electrolysis ( $\Delta$ )	After Electrolysis ( $\Delta_1$ )
Pt	-0.680	-1.050
Rh	-0.250	-0.340
Au	-0.560	-1.100
Ag	-0.150	+0.026
Pd	-0.723	-0.170
Ni	-0.325	+0.120
Cu	-0.418	+0.040

though observable in the case of methyl alcohol. For copper, the curve is almost similar to that obtained in the electrolysis of methyl alcohol.

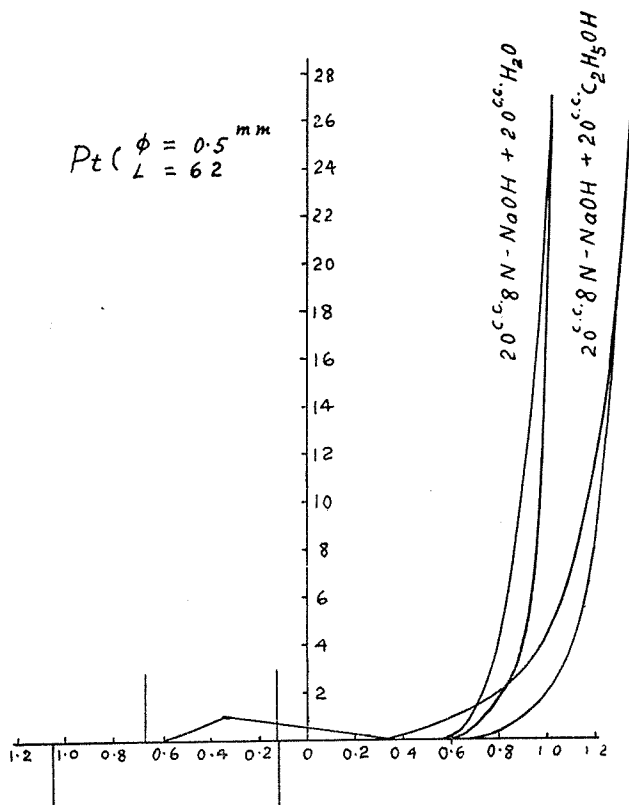
The ascending part of the current-potential curves previously traced for the smooth metal anodes of platinum, rhodium, gold, silver, palladium, nickel, and copper may be summarized and illustrated as in Fig. 26.

Fig. 26.



As shown in the above table, the static anode potentials of platinum, rhodium, and gold, after electrolysis, are deflected more to the baser potential than their static anode potential before electrolysis. The static anode potentials of silver, palladium, nickel, and copper anodes after electrolysis are, however, deflected more to the nobler side than those before electrolysis. In comparing the current-potential curves obtained in the electrolyses of alcoholic solution of 4N-NaOH with those obtained in the electrolyses of aqueous solution of 4N-NaOH, the former curves are deflected to the nobler potential side of the latter curves in the cases of platinum, rhodium, gold, and silver anodes; and in the case of palladium, nickel, and copper anodes, the former curves are deflected to the baser side of the latter. In order to show clearly these relations the cases of platinum and gold anodes are illustrated in Fig. 27 and Fig. 28, and the cases of palladium and nickel anodes in Fig. 29 and Fig. 30.

Fig. 27.



From the investigation of the current-potential curves for the various smooth metal anodes, it is seen that when platinum, rhodium, gold, and silver are used as anodes in the electrolysis of ethyl alcohol in an alkaline solutions, the discharge of alcoholate ions takes place prior to or simultaneously with the discharge of hydroxyl ions. Accordingly the anodic evolution of hydrogen and hydrocarbons can be expected. On the contrary, in the case of palladium, nickel, and copper anodes no special reactions other than ordinary anodic oxidation can be expected. As to the silver anode, its current-potential curve (Fig. 23) is slightly deflected to the nobler side of the curve obtained by the blank experiment (Fig. 11), but its static anode potential after electrolysis becomes nobler than that before electrolysis. Hence prediction of the special anodic reaction on silver electrode is somewhat difficult.

Fig. 28.

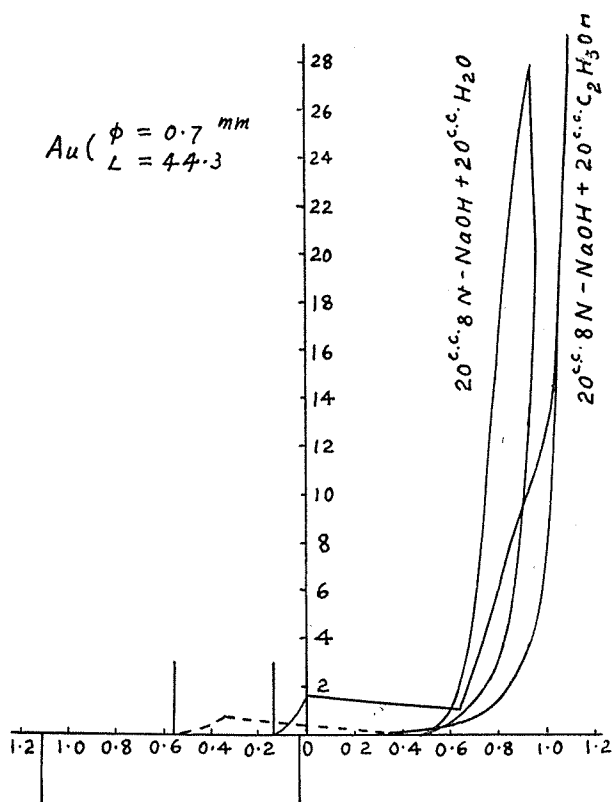


Fig. 29.

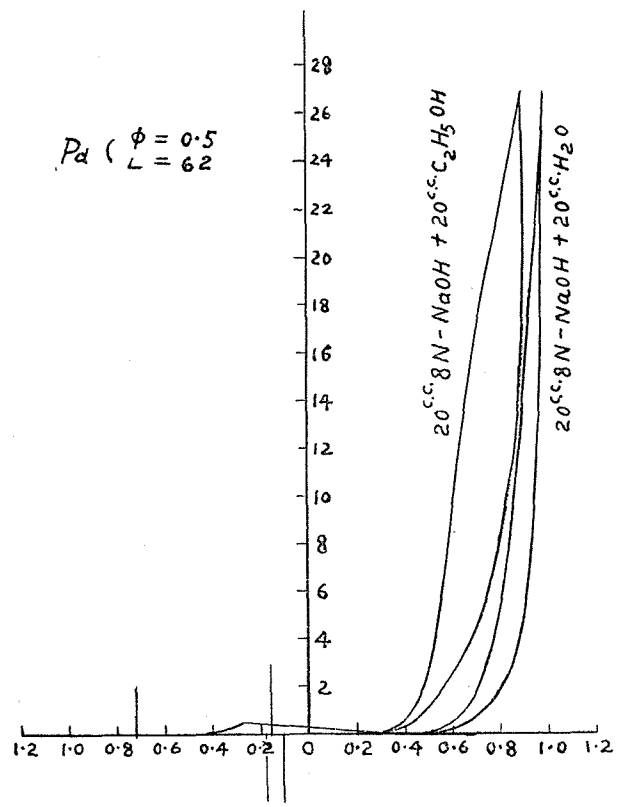


Fig. 30.

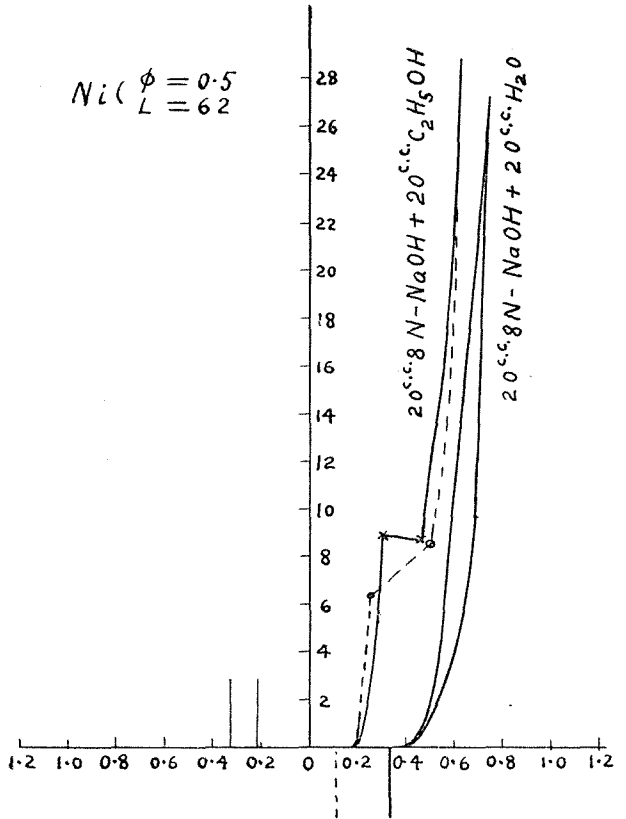


Fig. 32.

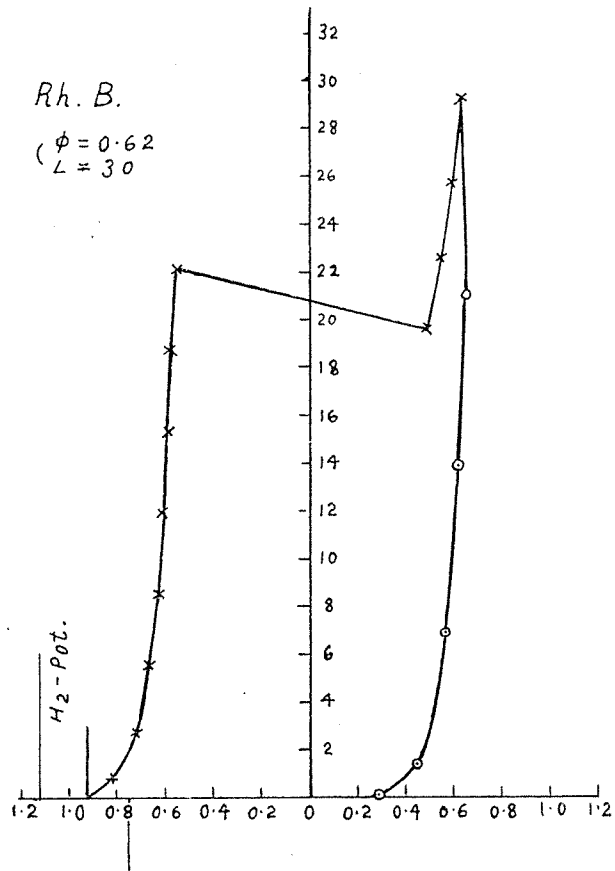


Fig. 31.

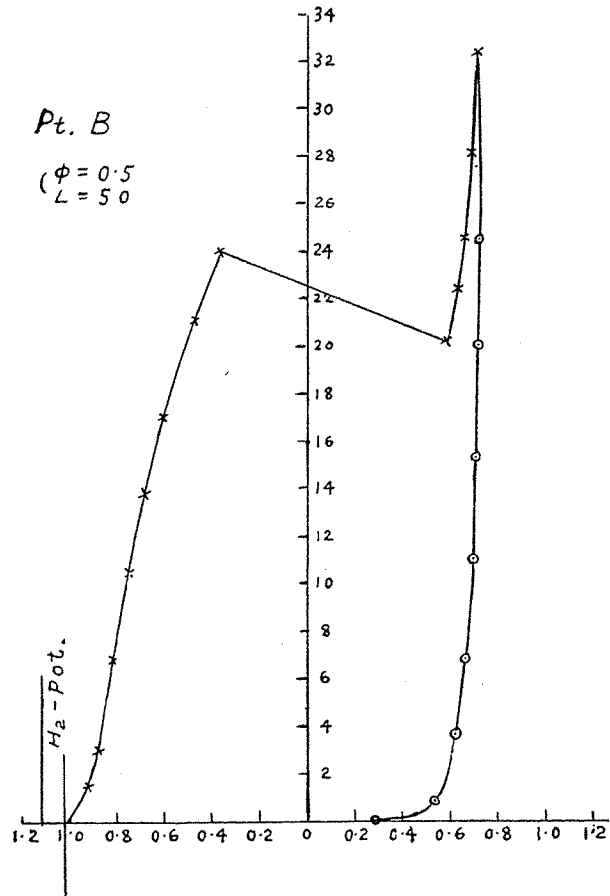


Fig. 34.

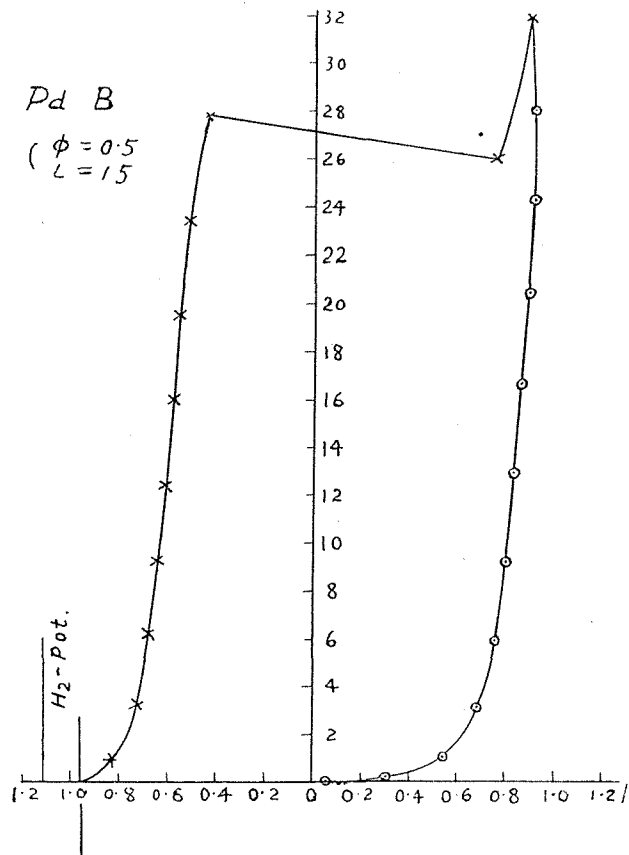
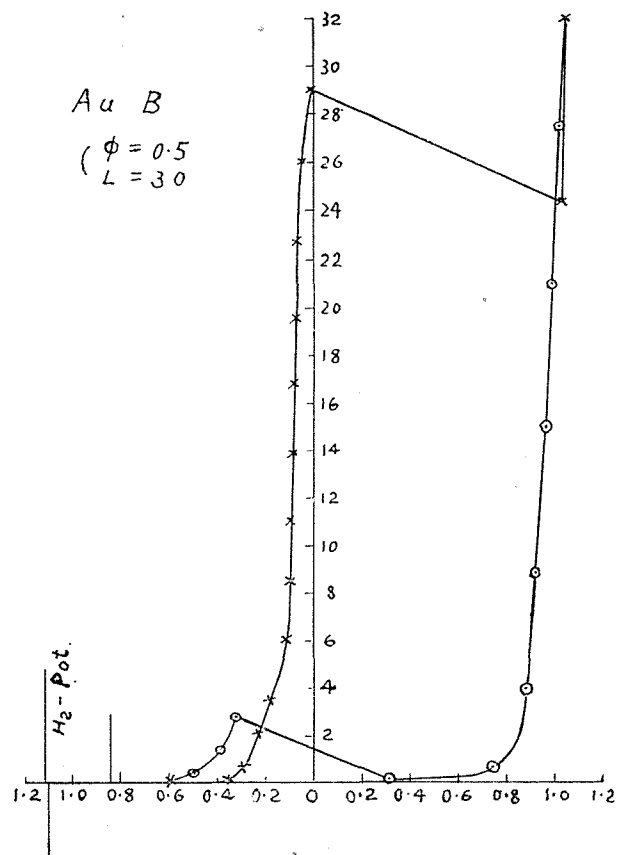


Fig. 33.



The current-potential curves for the spongy anodes of platinum, rhodium, gold and palladium are then traced as in Figs. 31, 32, 33, 34.

The facts that the current-potential curves for these spongy anodes ascend distinctly in the lower potential range against the Calomel-electrode, with no accompanying evolution of anode gas, and that when current density reaches a certain limit, anode gas is suddenly evolved and at the same time the anode potential jumps over to the nobler potential range, are similarly observed in this case as in that of methyl alcohol. So that, a close examination of the electrolyses with spongy anode plates was conducted limiting the potentials in a certain limit. The quantitative analysis of electrolytic products in each case was also made.

### Analysis of Electrolytic Products

As acetaldehyde, acetic acid and formic acid were confirmed to have been produced as the electrolytic products, their determination in the presence of ethyl alcohol in an alkaline solution was performed according to the method contrived by the present author.

The electrolyte is first neutralized, under cooling with ice, by adding carefully 8N-H<sub>3</sub>PO<sub>4</sub> then acidified with 30 c.c. of phosphoric acid (sp. gr. 1.71). The solution is subjected to distillation by use of a special distillation apparatus. The distillation is repeated 5 times, adding 50-70 c.c. of water in each distillation and finally the distillation is continued till about 40 c.c. of boiling solution (145-155°C.) is left as the residue. The volume of the total distillate is now made exactly 500 c.c. by adding the wash water of the apparatus. Taking 50 c.c. of the distillate, acetaldehyde is determined by means of Rocques' method, and in 400 c.c. of it (carbonic acid is previously expelled by passing the air free from carbon dioxide) the amount of total acids acetic and formic is determined by acidimetric titration. To the neutral solution thus obtained, 0.5 g. of sodium bicarbonate is added, and subjected to repeated distillation (in each operation about 50 c.c. of water is added and evaporation is repeated 4 times) under diminished pressure in a current of carbon dioxide, in order to expel alcohol and aldehyde. Dissolving the residue in hot water the formic acid in this solution is determined gravimetrically using the mercuric chloride method. From the amount of formic acid thus determined and that of total acids the amount of acetic acid is determined by calculation.

Table XI

(1)

Total distillate c.c.	Distillate taken c.c.	Water c.c.	NaHSO <sub>3</sub> solution c.c.	0.10121N-I <sub>2</sub>		0.10121N-I <sub>2</sub> used for CH <sub>3</sub> CHO c.c.	CH <sub>3</sub> CHO in 50 c.c. g.	Total CH <sub>3</sub> CHO g.
				Titration value c.c.	Mean c.c.			
500	0	50	50	32.85	32.86	2.02	0.00449	0.0449
	0	50	50	32.87				
	50	0	50	30.85	30.84			
	50	0	50	30.83				



(2)

Total distillate c.c.	Distillate taken c.c.	c.c. of 0.1N-NaOH used in titration of (CH <sub>3</sub> COOH + HCOOH)	c.c. of 0.1N-NaOH		CH <sub>3</sub> COOH in 400 c.c. g.	Total CH <sub>3</sub> CHO g.
			for HCOOH	for CH <sub>3</sub> COOH		
500	400	127.30	2.229	125.07	0.7508	0.9385

(3)

Total distillate c.c.	Distillate taken c.c.	After alcohol and acetaldehyde are expelled by evaporation the residue is dissolved in 100 c.c. of water.	1N-HCl added c.c.	CH <sub>3</sub> COONa 15% soln. added c.c.	HgCl <sub>2</sub> soln. added c.c.	Hg <sub>2</sub> Cl <sub>2</sub> ppted. g.	HCOOH in 400 c.c. g.	Total HCOOH g.
500	400		1.00	50	60	0.1052	0.01026	0.0128

In Table XI (2), the volume (c.c.) of 0.1N-NaOH for HCOOH is calculated from the amount of formic acid (0.01026 g.) determined by gravimetric method, as shown in Table (3).

Electrolysis at the Basar Range of Spongy Anode Potential.

Anolyte: 20 c.c. of CH<sub>3</sub>CH<sub>2</sub>OH + 20 c.c. of 8N-NaOH

Catholyte: 40 c.c. of 4N-NaOH

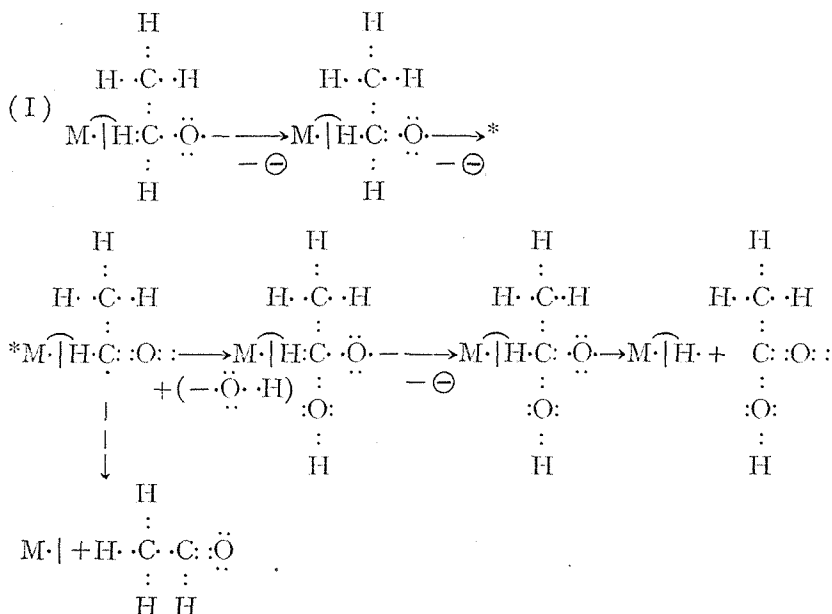
Temperature: 20°C.

Table XII

Anode potential		Electric quantity Amp.-hr.	Products	Produced amount g.	Current efficiency %
1)	Pt black (-0.895) - (-0.370)	2.128	CH <sub>3</sub> CHO	0.0449	2.57
			CH <sub>3</sub> COOH	0.9385	78.74
			HCOOH	0.0128	1.05
2)	Rh black (-0.790) - (-0.560)	2.053	CH <sub>3</sub> CHO	0.0250	1.47
			CH <sub>3</sub> COOH	0.9400	89.14
			HCOOH	0.0102	0.88
3)	Au black (-0.470) - (-0.200)	2.053	CH <sub>3</sub> CHO	0.0105	0.62
			CH <sub>3</sub> COOH	1.0911	94.88
			HCOOH	0.0043	0.37
4)	Pd black (-0.895) - (-0.341)	2.751	CH <sub>3</sub> CHO	0.0286	1.27
			CH <sub>3</sub> COOH	1.4017	91.01
			HCOOH	0.0043	0.27

As shown in the above table the electrolytic product obtained by the electrolyses with these spongy anodes at the basar range of potential against calomel-electrode, consists mainly of acetic acid, its current

yield being fairly great. The mechanism of this reaction may be illustrated as follows:



### Swinging of Anode Potential

When current density is suitably small and also in such a condition as the migration of anions to anode and their discharge on the anode surface can be effected uniformly, a regular swinging of anode potential, as illustrated in Fig. 35, is observed. The figure shows the swinging of anode potential that took place after 87 minutes of electrolysis with a current of 0.25 Amp.

Anode: Platinum plate ( $3 \times 4$ )cm<sup>2</sup> blacked

Cathode: Platinum net

Anolyte: 30 c.c. of CH<sub>3</sub>CH<sub>2</sub>OH + 30 c.c. of 8N-NaOH

Catholyte: 60 c.c. of 4N-NaOH

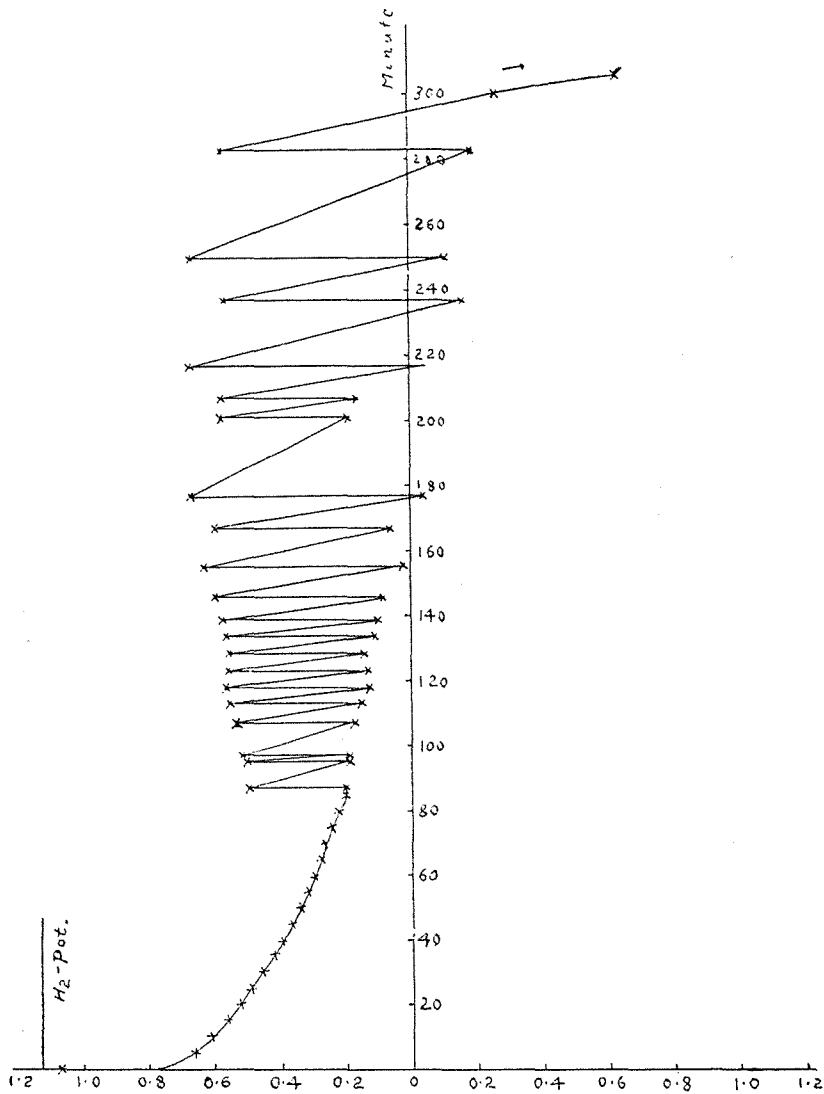
Current density: 0.25 Amp./12cm<sup>2</sup>

Temperature: 17°C.

Electrolytic bath: a porcelain cylinder is used as diaphragm, with the distance between the two electrodes uniform.

In this electrolysis, just before the commencement of the oscillation of anode potential i. e. after 80 minutes of electrolysis, a yellow film, perhaps due to the formation of aldehyde resin, forms on the anode surface. As electrolysis progresses, the colouration is gradually deepened to orange, and the amplitude of potential swinging gradually

Fig. 35.



enlarged. At the end of 5 hours, the anode potential suddenly jumps over to the nobler range. Throughout this electrolysis there is no evolution of anode gas.

The electrolytic products in the electrolyte after this electrolysis were determined as follows :

Electric quantity Amp.-hrs.	Products	Produced amount g.	Current efficiency %
1.27	CH <sub>3</sub> CHO	0.0591	5.66
	CH <sub>3</sub> COOH	0.6197	87.14

At first the present writer presumed that the swinging of anode potential is caused by the adsorption of acetaldehyde formed on the anode surface and its spontaneous splitting. From the result of the analysis of electrolytic products, however, the writer was convinced that the swinging is mainly due to the adsorption of discharged glycol anions formed on the anode surface and their splitting into acetic acid.

#### Electrolysis at the Nobler Range of Spongy Anode Potential.

Electrolytic conditions are the same as in the electrolysis with spongy anode at baser range of potential except that the anode potential is raised to the nobler range.

Table XIII.

Anode Anode potential	Gas evolv- ed c.c.	Gas composition				Electric quantity Amp.- hour	Products	Produced amount g.	Cur- rent yield %
		CH <sub>4</sub> %	CO %	CO <sub>2</sub> %	O <sub>2</sub> %				
Pt black (+0.600)– (+0.700)	72.0	1.0	13.90	0.35	84.75	3.059	CH <sub>3</sub> CHO CH <sub>3</sub> COOH HCOOH	0.0680 0.7362 0.0401	2.70 44.93 2.29
Rh black (+0.209)– (+0.527)	88.3	0	15.32	0.59	84.09	3.217	CH <sub>3</sub> CHO CH <sub>3</sub> COOH HCOOH	0.0394 0.7643 0.0376	1.49 42.43 2.04
Au black (+1.000)– (+1.050)	90.2	0	4.02	0.51	95.47	2.880	CH <sub>3</sub> CHO CH <sub>3</sub> COOH HCOOH	0.0450 1.0050 0.0173	1.90 62.30 1.05
Pd black (+0.750)– (+0.930)	97.4	0	2.44	0.65	96.91	2.797	CH <sub>3</sub> CHO CH <sub>3</sub> COOH HCOOH	0.0423 1.1044 0.0110	1.84 70.47 0.69

As shown in the above table, in the electrolyses with spongy anodes at the nobler range of potential, the yield of acetic acid is generally not so great, and the anode gas consists mainly of oxygen containing some carbon monoxide. In any case evolution of anodic hydrogen and hydrocarbons can scarcely be observed.

Electrodes from which Hydrogen and Hydrocarbons are evolved.

Table XIV.

Anode Anode potential	Elect. quant. Amp.-hr.	Gas evolved cc.	Gas composition %							Product	Produced amount g.	Current yield
			CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>			
Pt (1.280)–(1.350) –1.010(Δ <sub>1</sub> )	3.056	101.6 (110 mins.)	0	1.30	6.97	0.91	22.99	43.73	24.09	CH <sub>3</sub> CHO	0.0681	2.71
		46.9 (70 mins.)	0	1.30	3.30	1.99	20.30	34.84	36.75	CH <sub>3</sub> COOH	0.7081	41.38
		148.5								HCOOH	0.2246	12.83
Pt (1.467)–(1.554) –1.060(Δ <sub>1</sub> )	4.293	101.0 (106 mins.)	0	1.27	6.80	1.00	23.01	43.70	24.22	CH <sub>3</sub> CHO	0.0963	2.73
		100.8 (146 mins.)	0	2.90	2.50	2.02	20.22	33.75	38.61	CH <sub>3</sub> COOH	0.8634	35.91
		201.8								HCOOH	0.4795	19.51
Rh (0.755)–(1.005) –0.340(Δ <sub>1</sub> )	3.052	81.5	0	0.73	2.23	1.83	24.35	43.83	17.03	CH <sub>3</sub> CHO	0.0688	2.74
										CH <sub>3</sub> COOH	0.7291	42.66
										HCOOH	0.2406	13.77
C (0.893)–(1.455) –0.104(Δ) –0.296(Δ <sub>1</sub> )	3.059	62.7	0	0.73	3.69	1.97	7.14	72.18	14.29	CH <sub>3</sub> CHO	0.0594	2.36
										CH <sub>3</sub> COOH	0.9365	56.46
										HCOOH	0.1399	7.99
Ir (1.670)–(2.00) –0.320(Δ) –1.044(Δ <sub>1</sub> )	2.970	18.1	0.35	1.80	12.70	2.20	23.80	33.10	26.05	CH <sub>3</sub> CHO	0.0494	2.03
										CH <sub>3</sub> COOH	0.5557	33.41
										HCOOH	0.0696	4.095

However, as anodic evolution of hydrogen and hydrocarbons seems to occur evidently on the smooth platinum anode rather than on the spongy one, electrolyses were conducted with various smooth anodes, and the anode gases as well as the electrolyte products were quantitatively analysed.

### Electrolyses using various smooth metal anodes

Anolyte: 20 c.c. of  $\text{CH}_3\text{CH}_2\text{OH}$  + 20 c.c. of 8N-NaOH

Catholyte: 40 c.c. of 4N-NaOH

Current density: 0.0833 Amp./ $\text{cm}^2$

Temperature: 20°–25°C.

Electrodes from which Hydrogen and Hydrocarbons are evolved.

Table XIV

Electrodes, from which Hydrogen but not Hydrocarbon is evolved.

Table XV.

Anode potential	Elect. quant. Amp.-hr.	Gas evolved c.c.	Gas composition %							Products	Produced amount g.	Current yield %
			$\text{CO}_2$	$\text{C}_2\text{H}_4$	$\text{O}_2$	CO	$\text{H}_2$	$\text{CH}_4$	$\text{C}_2\text{H}_6$			
Au (1.020)– (1.080) –1.100( $\Delta_1$ )	2.880	107.6 (90 mins.)	0	0	87.62	0	11.24	1.15	0	$\text{CH}_3\text{CHO}$	0.0557	2.35
		84.0 (90 mins.)								$\text{CH}_3\text{COOH}$	0.7638	47.35
		191.6	0	0.46	77.25	1.52	20.16	0.61	0	HCOOH	0.0173	1.05
Ag (1.066)– (1.425) –0.026( $\Delta_1$ )	3.058	119.9	0	0	64.70	0	35.30	0	0	$\text{CH}_3\text{CHO}$	0.0207	0.82
										$\text{CH}_3\text{COOH}$	1.4561	85.09
										HCOOH	0.0129	0.74

Electrodes, from which neither Hydrogen nor Hydrocarbon are evolved.

Table XVI.

Anode potential	Elect. quant. Amp.-hr.	Gas evolved			Gas composition %			Products	Produced amount g.	Current yield %
		Total c.c.	Time min.	c.c.	$\text{CO}_2$	CO	$\text{O}_2$			
Pd (1.360)–(1.342) –0.173( $\Delta_1$ )	2.863	546.8	60	105.5	0	0	100.00			
			60	110.0	0	0	100.00	$\text{CH}_3\text{CHO}$	0.0690	2.93
			60	110.5	0	0	100.00	$\text{CH}_3\text{COOH}$	0.0535	3.34
			60	111.0	0	0	100.00			
			60	109.8	0	0	100.00	HCOOH	0.0118	0.71

Table XVI. (Continued)

Anode Anode Potential	Elect. quant. Amp.- hr.	Gas evolved			Gas composition %			Products	Pro- duced amount g.	Cur- rent yield %
		Total c.c.	Time min.	c.c.	CO <sub>2</sub>	CO	O <sub>2</sub>			
Pd  (1.360) - (1.421) - 0.172(Δ <sub>1</sub> )	3.439	666.7	60	111.2	0	0	100.00	CH <sub>3</sub> CHO	0.0601	2.13
			60	111.5	0	0	100.00			
			60	111.0	0	0	100.00	CH <sub>3</sub> COOH	0.0632	3.28
			60	110.9	0	0	100.00			
			60	111.0	0	0	100.00	HCOOH	0.0208	1.05
			60	111.1	0	0	100.00			
Ni  (0.411) - (0.574) + 0.120(Δ <sub>1</sub> )	3.021	104.3	180	104.3	0	0.14	99.86	CH <sub>3</sub> CHO	0.0719	2.89
								CH <sub>3</sub> COOH	1.2139	71.76
									HCOOH	Trace
Fe  (0.655) - (0.704) - 0.545(Δ) - 0.180(Δ <sub>1</sub> )	2.828	542.7	40	108.0	0	0	100.00	CH <sub>3</sub> CHO	0.0443	1.90
			35	107.5	0.21	0	99.79			
			35	107.4	0.20	0	99.80	CH <sub>3</sub> COOH	0.2151	13.58
			35	110.3	0.20	0	99.80			
			35	109.5	0.20	0	99.80	HCOOH	0	0
Cu  (0.462) - (0.510) - 0.405(Δ <sub>1</sub> )	3.073	15.5	180	15.5	0	0	100.00	CH <sub>3</sub> CHO	0.0445	1.76
								CH <sub>3</sub> COOH	1.4844	86.26
									HCOOH	0

As shown in Table XIV, when platinum, iridium, rhodium or carbon are used as the anode, the anode gas consists mainly of methane and ethane, containing some hydrogen and a little ethylene and carbon monoxide. In examining the relation between the gaseous products and the products in the electrolyte, it is found that, when the anode gas consists mainly of hydrocarbon, the production of formic acid in the electrolyte is distinctly great. In the case of iridium anode the yield of formic and acetic acids is somewhat decreased. As iridium plate was not at hand, a small foil (0.58 cm<sup>2</sup> of active surface) was used as anode, and a current of 0.04 Amp. was passed for 75 hours. Therefore the current density and the electric quantity are the same as in the other electrolysis though the current concentration is greatly changed. This may be the cause of the small difference in the current yield. In the electrolysis with carbon anode, methane is found as the main component of anode gas; and the yield of acetic acid is greater whereas that of formic acid is less.

As shown in Table XV, when gold is used as anode, the main constituent of the anode gas is oxygen mixed with a moderate quantum of hydrogen and a little hydrocarbon. When silver anode is used, oxygen and hydrogen are evolved, producing acetic acid in a greater quantity and formic acid in far smaller quantity.

As shown in Table XVI, when palladium, nickel, iron and copper are used as anodes, the anode gas consists only of oxygen, containing neither hydrogen nor hydrocarbon and there is no production of formic acid in the electrolytes.

To confirm the theory thus put forward to explain the special anodic behaviors of alcohol, the electrolytic oxidation reaction of acetaldehyde was examined under the same condition as in the case of ethyl alcohol and the products both of the gases and of the electrolytes were analysed.

#### The Electrolytic oxidation of Acetaldehyde in an Alkaline Solution.

Anode: Platinum plate ( $3 \times 4$ )cm<sup>2</sup>

Anolyte: 20 c.c. of 14.66% acetaldehyde solution<sup>13)</sup> + 20 c.c. of 8N-NaOH

Cathode: Platinum spiral

Catholyte: 40 c.c. of 4N-NaOH

Current density: 0.0833 Amp./cm<sup>2</sup>

Temperature: 20°C.

Table XVII.

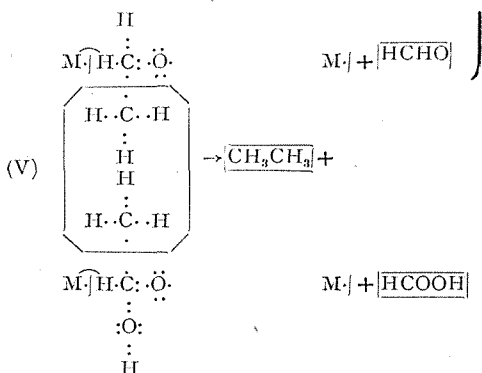
Anode potential	Electric quantity Amp.-hr.	Gas evolved c.c.	Gas composition %				Products	Produced amount g.	Current efficiency %
			CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	O <sub>2</sub>			
Pt (1.475)– (1.519) –0.947(Δ) –0.289(Δ <sub>1</sub> )	3.049	86.6	0.39	3.14	15.69	80.78	CH <sub>3</sub> COOH HCOOH	0.7026 0.1517	20.10 2.89

As shown in the above table, in the electrolysis of acetaldehyde, the anodic evolution of saturated hydrocarbons and hydrogen does not occur, and the anode gas consists mainly of oxygen, containing some carbon monoxide and a little unsaturated hydrocarbon. The current efficiency for acetic acid formation is not satisfactory and that for formic acid is far less. The considerable amount of aldehyde polymerises so as to form resin. It thus becomes clear that the evolution of hydrogen





Table XVIII. (Continued)



### Summary

In the electrolytic oxidation of methyl alcohol and ethyl alcohol in an alkaline solution, the anode potentials under various conditions were measured and the current-potential curves were traced. By investigating these current-potential curves it is possible to anticipate the evolution or the non-evolution of hydrogen and hydrocarbons from the corresponding anode.

As a result of the analyses of the gaseous products evolved on the anode and of the products produced in the electrolyte, it was ascertained that the anodic evolution of hydrogen and hydrocarbons is due to some characteristic property existing between the anode and alcohol. In the electrolysis of methyl alcohol, for example, platinum, rhodium, gold, iridium, and palladium anodes evolved hydrogen; in the case of ethyl alcohol, platinum, rhodium, iridium, and carbon anodes evolve hydrogen and hydrocarbons; and the anodes of gold and silver only hydrogen.

From the results of the analysis both of the gaseous products and the products in the electrolyte, together with the results of the measurement of the anode potentials, the mechanism by which hydrogen and hydrocarbons are evolved anodically was sought for. By assuming adsorption and splitting of organic ions to the anode and explaining them according to the electronic "Octet theory" all the facts so far observed seem to be explained without any contradictions.

In conclusion the author wishes to express his cordial thanks to Prof. Motooki Matsui, for his kind advice and encouragement through-

out this work; and also to take this opportunity of expressing his appreciation to the Imperial Academy of Japan for the fund granted to Prof. Matsui which defrayed a part of the expence of this work.

### Reference

- 1) Zeit. f. Elekt. Chem., **20** (1914), 367; Ann., **420** (1920), 241.
  - 2) Zeit. f. Elekt. Chem., **27** (1921), 54; **27** (1921), 563; **28** (1922), 101.
  - 3) Helv. Chim. Acta, **1** (1918), 146; Zeit. f. Elekt. Chem., **27** (1921), 489.
  - 4) Zeit. f. Elekt. Chem., **34** (1928), 704.
  - 5) Zeit. f. Elekt. Chem., **34** (1928), 256.
  - 6) Zeit. f. Elekt. Chem., **35** (1929), 34.
  - 7) Mem. Col. of Sci. Kyoto Imp. Univ., Vol. XI, No. 5.
  - 8) Zeit. f. Elekt. Chem., **27** (1921), 563.
  - 9) Treadwell-Hall. Anal. Chem. Vol. II, 6th Ed. 486.  
Küster; Z. anorg. Chem., **13** (1897), 134.
  - 10) E. Müller u. Tanaka; Zeit. f. Elek. Chem., **34** (1928) 259.
  - 11) Current density is in direct proportion to anode potential but with spongy anode direct calculation of current density is impossible owing to the difficulty of attaining the identical degree of sponginess.  
12) Since commercial formaline solution may contain methyl alcohol, in this experiment formaldehyde solution is prepared by distilling paraformaldehyde over phosphoric acid, and the aldehyde content is determined to be 14.65% (2.931 g. in 20 c.c.) by means of G. Romijn's method.  
13) The sample solution of acetaldehyde is determined, by means of Rocques' method, to contain 2.932 g. of  $\text{CH}_3\text{CHO}$  in 20 c.c.
-