

volt. Similarly the orientation of water molecules at and in the interface changes with the potential of the mercury, thus affecting the rate of hydration of I. When the electrolyte content in the solution is small, as was the case in our experiment with a very dilute pyridine-pyridinium hydrochloride buffer, the structure of the double layer, especially at more negative potentials, is quite different from that in 0.1 *M* potassium chloride solution, which was the normal salt content in our experiments. In the very dilute buffer no dip in the current-voltage curve and no minimum were observed. Although the exact mechanism of the decreasing rate of the reaction $I + H_2O \rightarrow II$ with increasing negative potential needs further study, there is no doubt that the occurrence of the minimum, as in Fig. 1 (curve III), must be attributed to a decreasing rate of the above reaction at the electrode surface with increasing negative potential.

Summary

1. The polarographic behavior of phenolphthalein has been investigated under widely varying conditions. In 25% ethanol phenolphthalein gives a one-step reduction wave in a *pH* range between 0 and 9. In this range the half-wave potential changes according to $\pi^{1/2}$ (*vs.* S.C.E.) = 0.54 - 0.046 *pH*. The red form of phenolphthalein yields two waves of equal height, each wave giving a well-defined diffusion current. The sum of the two diffusion currents is equal to that of the

single wave observed at lower *pH*. The polarographic reduction of phenolphthalein to phenolphthalin is accompanied by a transfer of two electrons.

2. In the presence of a phosphate buffer of a *pH* of 7 the diffusion current decreases abnormally when the ethanol concentration is increased. In 60% ethanol the "apparent" diffusion current becomes extremely small at 25°. It is concluded that the lactone form of phenolphthalein is not reduced, but its hydrated form is. At alcohol concentrations of 25% or less the rate of hydration at the surface of the electrode is so large that a normal diffusion current is observed. At high alcohol concentrations the "apparent diffusion current" becomes entirely rate- and not diffusion-controlled. Experiments carried out at various temperatures substantiate this interpretation.

3. In 25% ethanol in the presence of a buffer of *pH* 7 the diffusion current remains constant in a potential range between -1.0 and -1.2 volt; it decreases slightly between -1.2 and -1.4 volt and then drops suddenly to attain a small minimum value at a potential of about -1.6 volt. Experimental evidence has been given substantiating the interpretation that the occurrence of the minimum is to be attributed to a decreased rate of transformation of the lactone form into the reducible hydrated form at the surface of the dropping electrode.

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Polarographic Behavior of Nitrospenylhydroxylamine¹

BY I. M. KOLTHOFF AND A. LIBERTI²

The ammonium salt of nitrospenylhydroxylamine, called cupferron, is a well-known analytical reagent, which precipitates a great number of metal ions in acid medium. In connection with a study of the use of cupferron as a reagent in amperometric titrations, the polarographic behavior of nitrospenylhydroxylamine has been investigated over a wide range of *pH*.

Experimental

Materials Used: Cupferron.—Eastman Kodak Co. and G. F. Smith Chemical Co. products were recrystallized from ethanol. The crystals had the appearance of silver-white leaflets (m. p. 163-164°). The solid product was stored in a dark bottle over solid ammonium carbonate to prevent decomposition. A stock solution (0.02 *M*) in water was found to be stable for more than two weeks when kept in the dark in a cool place. The solution is not stable in acid medium, as the phenylnitrosohydroxylamine decomposes. The rate of decomposition increases with decreasing *pH*. When polarograms were determined in acid

medium at a *pH* smaller than 3, a measured volume of an air-free stock solution of cupferron was added to a suitable volume of air-free buffer solution in the cell and the current-voltage curve was determined soon after mixing. In some experiments the lithium salt of nitrospenylhydroxylamine was used, which was prepared from cupferron and lithium hydroxide.

Buffer Solutions.—In the *pH* range between 1 and 5.6 Clark and Lubs buffers served to adjust the *pH*. In the range between *pH* 3 and 10 the universal buffers of Britton and Robinson³ were used. The buffer mixtures were prepared by addition of lithium hydroxide to a solution which was 0.04 *M* in phosphoric, 0.04 *M* in acetic and 0.04 *M* in boric acids. In addition, Clark and Lubs buffers, prepared from boric acid and lithium hydroxide and lithium chloride, were used in the *pH* range between 8 and 10.

Tetramethylammonium Hydroxide Solution.—An Eastman Kodak Co. product of the bromide of this base was purified by repeated recrystallizations from ethanol-water mixtures. A stock solution of the hydroxide was prepared from the purified bromide with silver hydroxide as described by Peracchio and Meloche.⁴ Buffer solutions prepared from tetramethylammonium hydroxide and phos-

(1) From a Master's thesis (1947) of A. Liberti, submitted to the Graduate School of the University of Minnesota.

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(3) H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1456 (1931).

(4) E. S. Peracchio and V. W. Meloche, *THIS JOURNAL*, 60, 1770 (1938).

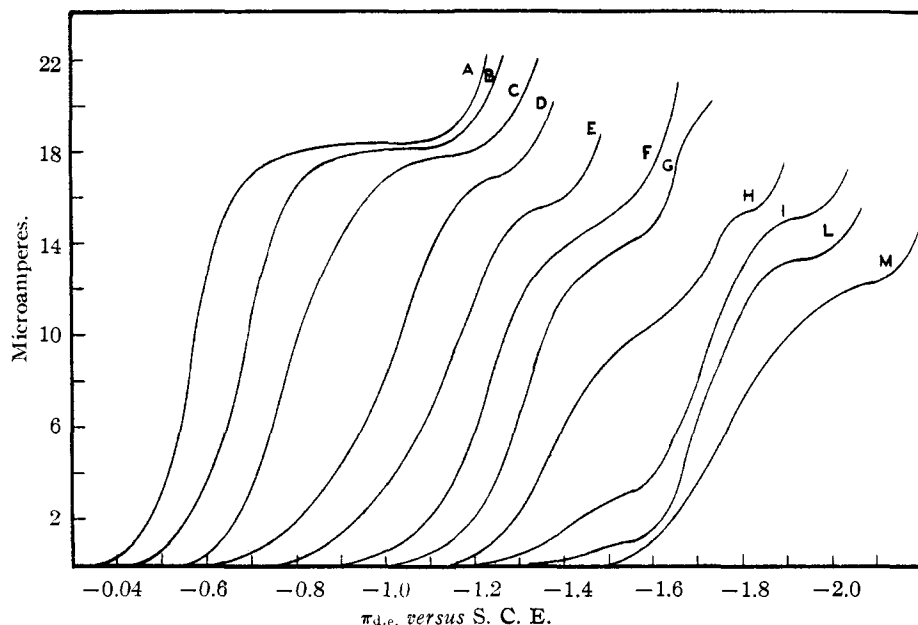


Fig. 1.—Polarograms of cupferron ($8 \times 10^{-4} M$) in buffer solutions at the following pH values: A 1.2, B 2.1, C 3.1, D 4.4, E 5.2, F 5.9, G 6.6, H 7.2, I 7.9, L 8.8, M 12.5.

phoric acid or boric acid were prepared. Polarograms obtained with these buffers gave poorly reproducible and irregular currents near the potentials at which the cupferron waves appeared. For this reason these buffers could not be used in the present polarographic work. On the other hand, well defined waves were obtained in tetramethylammonium hydroxide solutions.

Gelatin Solution.—A 0.1% gelatin solution in water was stored under a layer of toluene to prevent decomposition. When used in a concentration of the order of 0.01%, gelatin was found to eliminate maxima in the polarograms at a pH smaller than 3. At a pH greater than 3 no maxima were observed even in the absence of gelatin.

Determination of Polarograms.—Both the manual polarograph⁵ and the automatic Heyrovsky instrument, Model XI, have been used in this work. In all the experiments an outside saturated calomel electrode (S.C.E.) served as the reference electrode. All the potentials refer to the S.C.E.

Under the experimental conditions the capillary had a drop time t of 3.00 seconds at zero applied e.m.f. and the mass of mercury m flowing out per second was 2.37 mg. The values of m and t were determined in the potential range between 0 and 2 volts. The values of the diffusion current could thus be referred to the same value of $m^2/4t^{3/2}$. The reported values of diffusion or limiting currents are corrected for the residual current and refer to a $m^2/4t^{3/2}$ value at a potential of 0.5 volt.

The electrolysis cell was provided at the bottom with an inlet tube for purified nitrogen. Another inlet tube through the stopper of the cell served for the introduction of nitrogen to the gas phase above the solution during the measurements. All the experiments were carried out in a thermostat at $25.0 \pm 0.1^\circ$.

Experimental Results

As an illustration some representative polarograms in the pH range between 1 and 12.5 are given in Fig. 1. Without correction for the residual current many of the limiting currents appear poorly defined. For this reason the polarograms represented in Fig. 1 give the currents found with

(5) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

the manual apparatus, corrected for the residual current and referred to a constant value of $m^2/4t^{3/2}$. Since at a pH between 1 and 3 the decomposition of phenylnitrosohydroxylamine is rapid, 24 ml. of the supporting buffer solution was made air-free in the cell, 1 ml. of standard air-free cupferron solution was added and the current-voltage curve determined immediately after mixing. The determinations were well reproducible.

Only one wave was found in acid medium, up to a pH of 6.6. The apparent diffusion or limiting current decreased with increasing pH , the change becoming very pronounced when the pH became greater than 6. At pH values between 3 and 6 the limiting current was found to be proportional to the concentration of cupferron added to the buffers. This is illustrated in Fig. 2.

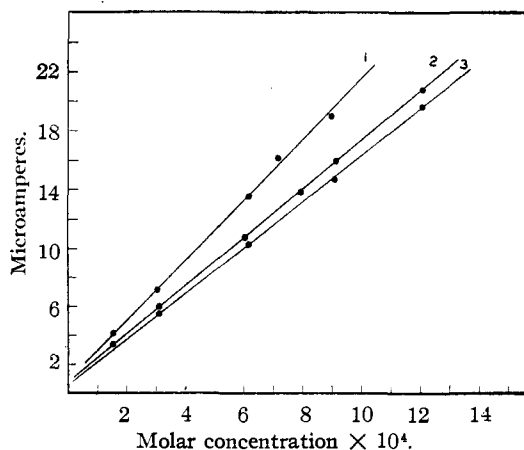


Fig. 2.—Limiting current as a function of concentration at: 1, pH 2.9; 2, pH 5.2; 3, pH 6.6.

A plot of the values of $\log i/(i_d - i)$ versus the potential at a pH of 1 yields a straight line with a slope of 182 mv. This indicates that the reduction is irreversible; as it seems impossible that a reversible reduction would involve three electrons.

In the pH range between 7 and 9 two waves were observed. The first wave was poorly defined (see Fig. 1 and 3); its limiting value was estimated by the tangent method (see Fig. 3). The second wave appeared to attain a constant value at a pH greater than 8.

Only one wave due to reduction of the cupferronate was observed at a pH greater than 9, its height remaining unchanged when the pH was raised to 12.5.

Some of the experimental data are summarized in Table I.

TABLE I

WAVE HEIGHTS AND HALF WAVE POTENTIALS IN 8×10^{-4} M SOLUTIONS OF CUPFERRON AT VARYING pH AT 25°

pH	Supporting electrolyte	Height first wave in μA	$-(\pi^{1/2}/\delta)_1$	Height second wave in μA	$-(\pi^{1/2}/\delta)_2$
1.1	Clark and Lubs; HCl-KCl	18.5	0.672		
1.4	Clark and Lubs; HCl-KCl	18.4	.71		
2.1	Clark and Lubs; Phthalate	18.3	.785		
3.0	Clark and Lubs; Phthalate	17.8	.89		
4.4	Clark and Lubs; Phthalate	16.6	1.10		
5.2	Clark and Lubs; Phthalate	15.5	1.22		
5.9	Britton and Robinson	14.6	1.32		
6.6	Britton and Robinson	13.2	1.405		
7.2	Britton and Robinson	9.0	1.46	6	1.79
7.9	Britton and Robinson	3.8	1.53	11.2	1.81
8.3	Britton and Robinson	2.8	1.56	12.2	1.81
8.8	Britton and Robinson	1.0	1.57	12.2	1.82
10.0	Boric acid-lithium hydroxide	12.2	1.85
12.5	Tetramethylammonium hydroxide	12.2	1.86

The half wave potential of the first wave was found to depend greatly upon the pH . The plot of the half wave potential against the pH yields a straight line with a slope of 128 mv. per pH unit. Thus, the half wave potential $-\pi_{1/2}$ is found to vary with the pH according to $-\pi_{1/2} = -\pi_{1/2}^0 - 0.128 pH$ in which $\pi_{1/2}^0 = -0.58$ v. (versus the S.C.E.) at 25° .

This relation expresses that the half wave potential varies with the square of the hydrogen ion concentration, which is a very unusual relation. The half wave potential of the second wave appears to be practically independent of the pH . Its value was found to be -1.80 v.

For reasons given in the discussion section the height of the first and of the second waves at a pH of 8.25 were determined as a function of the height, h , of the mercury in the reservoir. In these experiments the lithium salt of nitrosophenylhydroxylamine was used instead of cupferron in order to eliminate the ammonium wave. The experiments were carried out in boric acid-lithium hydroxide buffers. The measured values of the limiting currents were corrected again for the residual

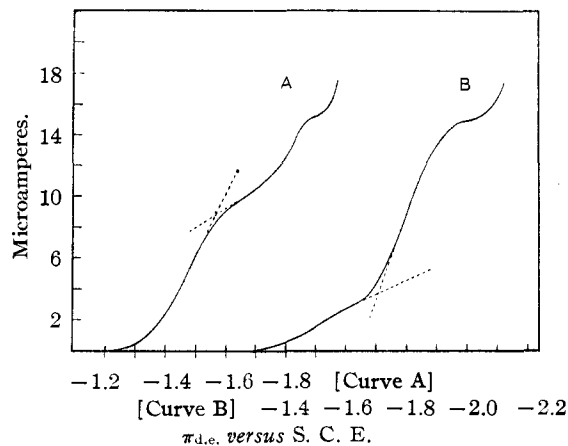


Fig. 3.—Polarograms of 8×10^{-4} M cupferron at pH 7.2 (curve A) and pH 7.9 (curve B).

current and referred to a constant value of $m^2/s^2t^{1/2}$. The results are given in Table II.

TABLE II

VALUES OF THE FIRST (i_1) AND THE SECOND (i_2) LIMITING CURRENTS AT pH 8.25 AS FUNCTION OF THE HEIGHT OF MERCURY IN THE RESERVOIR

Height h of mercury in reservoir in cm.	Drop time t in seconds	i_1	i_2	$i_2/h^{1/2}$
94	2.4	2.80	13.55	1.40
75	3.0	2.80	12.20	1.41
56	4.2	2.76	10.64	1.42
39	6.3	2.70	8.60	1.37

It is seen that the height of the first wave is not affected by the height of the mercury in the reservoir, while that of the second wave is proportional to the square root of the height of the mercury. Therefore, the height of the second wave is diffusion controlled, like that of an ordinary diffusion current.

Discussion

(1) From the fact that in the pH range between 7 and 9 two reduction waves are observed it is evident that the acid form of nitrosophenylhydroxylamine and its anion are reduced at different potentials. However, in the acid range at a pH greater than 3 the height of the wave of the acid form is much greater than corresponds to the concentration of the undissociated acid in the bulk of the solution. Only at a pH smaller than 2 does the limiting current correspond to the true diffusion current of the undissociated acid. From the work of Hantzsch⁶ and of Pyatnitokii⁷ it is estimated that the ionization constant K_a of phenylnitrosophenylhydroxylamine at 25° is equal to 5.3×10^{-5} . Assuming that the limiting value of the current of 18.5μ in 8×10^{-4} M cupferron solution at pH 1 is the true diffusion current of the

(6) A. Hantzsch, *Ber.*, **35**, 265 (1902).

(7) V. Pyatnitokii, *Zhur. Anal. Khim.*, **1**, 135 (1946); *Chem. Abs.*, **41**, 725 (1947).

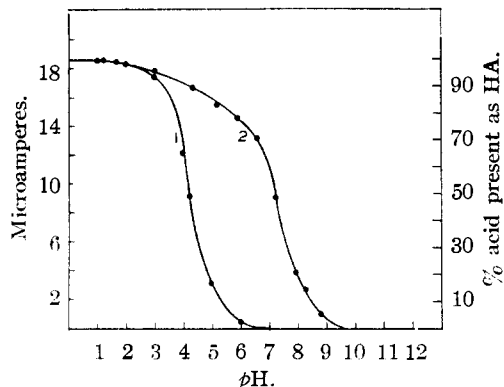


Fig. 4.—Curve 1, dissociation curve of nitrosophenylhydroxylamine; curve 2, change of the limiting current of the acid form of nitrosophenylhydroxylamine.

acid, the values of i_d at higher pH can be calculated. Plotting the calculated values against pH yields curve 1 in Fig. 4. Curve 2 represents the limiting currents due to the acid form observed at varying pH . It is seen that the mid-way point is shifted 3 units to a higher pH . The reason for this shift is that upon reduction of the free acid at the surface of the electrode, more acid is formed as a result of the association of hydrogen ions with the anions A^- of the acid



From Fig. 4 it is seen that at a pH greater than 6 the current due to the equilibrium concentration of HA is negligibly small and that the limiting current is determined entirely by the rate of formation of HA at the surface of the electrode. This current may be called the kinetic current. The polarographic behavior of nitrosophenylhydroxylamine in acid medium is very similar to that of pyruvic acid and of phenylglyoxalic acid discussed by Brdička and Wiesner.⁸ These authors derived the following expression for the limiting value of the kinetic current (i_k)₁

$$(i_k)_1 = \frac{\mu k [H^+] a c K_a}{(K_a + [H^+]) (\mu k [H^+] + a \cdot 10^3 / n F y q)} \quad (2)$$

in which k is the rate constant of reaction (1), μ is the thickness of the layer around the electrode where the association takes place, a is the constant in the Ilkovič equation $i_d = ac$, c is the total concentration (dissociated plus undissociated) of the acid with ionization constant K_a , n is the number of electrons involved in the reduction, Fy the faraday, and q the average surface of mercury per drop.

When the concentration of HA in the bulk of the solution is not negligibly small the total current i_t due to the reduction of the acid form becomes

$$i_t = (i_d)_{HA} + i_k \quad (3)$$

in which $(i_d)_{HA}$ is the diffusion current of the acid

(8) R. Brdička and K. Wiesner, *Coll. Czechoslov. Chem. Commun.*, **12**, 138 (1947).

corresponding to the reduction of the undissociated acid present in the bulk of the solution. It can be shown⁸ that when i_t is equal to one half of the maximum value of $(i_d)_{HA}$ (in our case found at pH of 1)

$$\mu k = \frac{K_a - [H^+]}{(K_a + [H^+])[H^+]} \times \frac{a \cdot 10^3}{n F y q} \quad (4)$$

Under our experimental conditions, a had a value of 0.0230 and q of 0.0189. Using these figures in equation (3) a value of μk of 3.34×10^4 is found. Brdička and Wiesner estimate that μ is of the order of 10^{-7} cm. Using this value, a rate constant k (equation 1) of the order of 3.3×10^{11} is found. This value is only an approximation, because equation (2) has been derived on the basis of some simplifying assumptions. A highly mathematical and more exact treatment is given by Koutecky and Brdička.⁹

Using the above value of μk it is possible to calculate the limiting kinetic currents at various pH . The values thus obtained are plotted in Fig. 5 and are compared with the experimental values found by subtracting the calculated values of $(i_d)_{HA}$ from i_t (equation 3). Considering that equation (2) is only approximately valid the agreement between the calculated and experimental values is satisfactory.

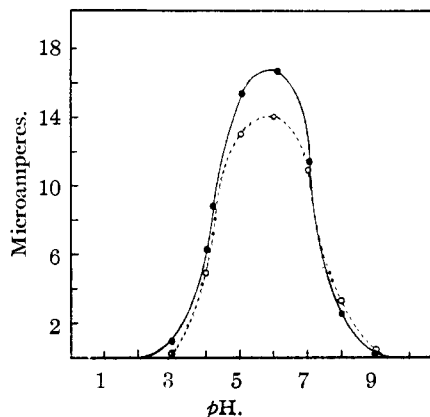


Fig. 5.—Change of the kinetic current at varying pH . The dotted curve shows the experimental values and the drawn curve the calculated values.

The correctness of the interpretation of the polarograms in acid medium is supported by the effect of the height of mercury in the reservoir upon the first and the second waves at a pH of 8.25. At this pH $(i_d)_{HA}$ is equal to zero and the height of the first wave is equal to $(i_k)_1$. Moreover, at this pH , $a \cdot 10^3 / n F y q$ is much greater than $\mu k [H^+]$. Hence, at this pH

$$i_1 = (i_k)_1 = \frac{\mu k [H^+] a c n F y q}{(K_a + [H^+]) a \cdot 10^3} \quad (5)$$

It is seen that a cancels in equation (5) and that the height of the first wave becomes proportional

(9) J. Koutecky and R. Brdička, *Coll. Czechoslov. Chem. Commun.*, **12**, 337 (1947).

to q . Since the surface of the mercury is proportional to $m^{2/3}t^{2/3}$ the height of the mercury in the reservoir should not have any effect on i_1 at a pH of 8.25. Indeed, it is seen from Table II that the pressure of the mercury does not affect i_1 . On the other hand i_2 is diffusion controlled; therefore, i_2 varies with the square root of the height of the mercury in the reservoir.

(2) It has been mentioned that the limiting current measured at a pH of 1 corresponds to the true diffusion current of the nitrosophenylhydroxylamine. Assuming that the diffusion coefficient of this acid is equal to that of the benzoate ion, it is possible to calculate the number of electrons n involved in the reduction. From the Ilkovič equation it is found that

$$n = \frac{i_a}{0.605 cD^{1/2}m^2/t^{1/2}}$$

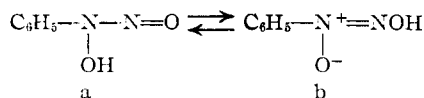
In $8 \times 10^{-4} M$ cupferron solution at a pH of 1, i_a was found equal to 18.5 microamperes, while $m^2/t^{1/2}$ was 2.14. Taking D equal to 8.81×10^{-6} yields a value of 6.0 for n . Hence six electrons are involved in the reduction of nitrosophenylhydroxylamine.

On the other hand in alkaline medium where we are dealing with the reduction of the anion the diffusion current was found to be equal to two thirds of that at a pH of 1. Hence the reduction of the anion involves four electrons.

Various structures have been suggested for nitrosophenylhydroxylamine. Angeli¹⁰ proposed the structure $C_6H_5-N=NOH$, while Hantzsch¹¹

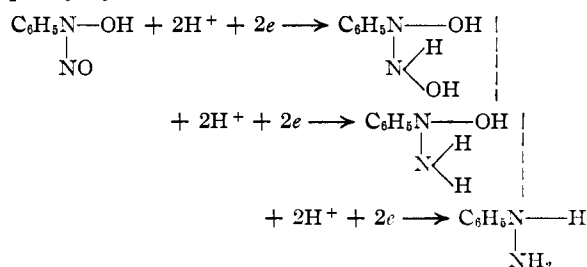
prefers $C_6H_5-N(OH)-NO$. Diehl¹² suggested that

the two forms are in tautomeric equilibrium. Considering the relatively strong acid character of nitrosophenylhydroxylamine G. Fieser and M. Fieser¹³ assume that there is an equilibrium between the nitrosohydroxy form, a, and the more strongly acid amine oxide form, b



The reduction of nitro- and nitroso- compounds occurs in steps. In acid medium, in which the reduction at the dropping electrode involves six

electrons the final reaction product must be the phenylhydrazine



In alkaline medium the reduction involves four electrons and the anion $C_6H_5N^+(O^-)-NO$ (Hantzsch)

or $C_6H_5-N^+=NO^-$ (Fieser and Fieser) apparently

is reduced to $C_6H_5-N(O^-)-NH_2$

Summary

1. Nitrosophenylhydroxylamine solutions at a pH of 1 yield a diffusion current corresponding to a reduction which involves 6 electrons. At a pH greater than 9 the anion of the acid gives a diffusion current corresponding to an electron transfer of 4. The half wave potential of the acid wave varied with the pH : $\pi_{1/2} = -0.58 - 0.128 pH$ vs. S.C.E.; the half wave potential of the alkaline wave is -1.80 v. and does not vary with the pH .

2. Only one wave is found in acid medium up to a pH of about 6.6, two waves are found in the pH range between 6.6 and 9.0; at higher pH only one wave is found.

3. In the acid range at a pH greater than 3 the height of the wave is much greater than corresponds to the concentration of the undissociated acid in the bulk of the solution. This is explained by the fact that the current is partly controlled by the rate of formation of acid at the surface of the electrode: $H^+ + A^- \rightarrow HA$. Using Brdička and Wiesner's⁸ formulation a rate constant of the order of 3.3×10^{11} is calculated. When the kinetic current is very small with regard to the diffusion current the former becomes independent of the height of the mercury in the reservoir. This is found to be true at a pH of 8.25, where the height of the first wave (kinetic current) is independent of the height of mercury in the reservoir, while the second wave is diffusion controlled.

(10) A. Angeli, *Gazz. chim. ital.*, **60**, 352 (1931).

(11) A. Hantzsch, *Ber.*, **64**, 695 (1931).

(12) H. Diehl, *Chem. Rev.*, **21**, 751 (1937).

(13) G. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath Co., Boston, 1944.