[Contribution from the School of Chemistry of the University of Minnesota]

Polarography of Nitroprusside. Equilibrium Constant of the Reaction Between Nitroprusside and Hydroxyl Ions[1]

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Nitroprusside gives three reduction waves at the dropping mercury electrode, the first two being hydrogen ion independent. It is postulated that the first wave corresponds to the reaction: $Fe(CN)_5NO^{-2} + e \rightarrow Fe(CN)_5NO^{-3}$. The second wave may correspond to $Fe(CN)_5NO^{-3} + e \rightarrow Fe(CN)_5NO^{-4}$. Evidence is presented that the reaction between nitroprusside and hydroxyl ions is given by the equation: $Fe(CN)_5NO^{-2} + OH^- \rightleftarrows Fe(CN)_5NO_2^{-4} + H^+$. $Fe(CN)_5NO^{-2}$ is reducible at the dropping electrode, $Fe(CN)_5NO_2^{-4}$ is not. In alkaline medium $Fe(CN)_5NO_2^{-4}$ can be oxidized at the rotated and stationary platinum electrodes to $Fe(CN)_5NO_2^{-3}$, while $Fe(CN)_5NO^{-2}$ is not oxidized. From spectrophotometric and polarographic data the value of the equilibrium constant (equation 3) has been found equal to 1×10^{-6} at 25° at an ionic strength of 0.5.

Sidgwick[2] states that the nitroprusside ion, $Fe(CN)_5NO^{-2}$, contains iron in the ferrous form while the NO group is present as the nitrosyl, NO^+. Thus nitroprusside ion can be written as $[Fe(II)(CN)_5NO^+]^{-3}$. Although it is not stated in the literature that nitroprusside can be reduced, this would be expected on the basis of the latter formula. As is shown in the present paper, nitroprusside gives various reduction waves upon electrolysis at the dropping mercury electrode.

Nitroprusside resists oxidation in neutral and acid medium, but is oxidized by strong oxidizing agents in alkaline medium to a salt of the red ion $Fe(CN)_5NO_2^{-3}$.[2] In this connection, the reaction between nitroprusside and hydroxyl ions is of interest. According to Cambi and Szegö,[3] the reaction leads to an equilibrium

$$Fe(CN)_5NO^{-2} + 2OH^- \rightleftarrows Fe(CN)_5NO_2^{-4} + H_2O \quad (1)$$

Evidence is given in the present paper that not the $[Fe(CN)_5NO^+]^{-3}$, but the $Fe(CN)_5NO_2^{-4}$ ion is oxidized in alkaline medium. This oxidation involves a simple one electron transfer

$$Fe(CN)_5NO_2^{-4} \longrightarrow Fe(CN)_5NO_2^{-3} + e \quad (2)$$

The potential of the $Fe(CN)_5NO_2^{-4}/Fe(CN)_5NO_2^{-3}$ couple was measured by Davidson[4] who reported a value for E^0 of 0.234 volt *vs.* N.C.E., but stated that the potential varied with time because of the instability of the compounds involved.

In the present study of the polarography of nitroprusside a large decrease of the reduction waves was observed in alkaline medium. When it was assumed that $Fe(CN)_5NO^{-2}$ but not $Fe(CN)_5NO_2^{-4}$ is reduced the equilibrium constant of reaction (1) was calculated to be of the order of 100 times smaller than that reported by Cambi and Szegö.[3] The value was redetermined, making use of polarographic and spectrophotometric data.

The oxidation of nitroprusside in alkaline medium was studied briefly with the rotating and stationary platinum electrodes as indicator electrodes.

Reagents and Apparatus.—The sodium nitroprusside dihydrate used in the experiments was J. T. Baker or Baker and Adamson reagent grade. Most of the stock solutions were kept in sealed polymerization bottles under nitrogen pressure to prevent air oxidation. The nitroprusside solutions are light sensitive and slowly turn green after exposure to light. Our solutions were kept in the dark, but were exposed to diffuse light when samples were taken. New stock solutions were prepared every two or three days.

All other reagents were analytical reagent grade. The phosphate buffers were prepared by mixing appropriate amounts of solutions of mono-, di- and trisodium phosphate. The carbonate buffers were prepared by adding concentrated hydrochloric acid to sodium carbonate solutions. In much of the work a universal buffer solution was used which contained equal moles of acetic, boric and phosphoric acids, adjusted to the desired *p*H with concentrated alkali. This buffer will be referred to as "ABP" buffer. The molarity given is the total molarity of the acids and their salts.

Oxygen-free solutions were obtained when necessary by bubbling with Linde 99.99% nitrogen.

Current–voltage curves were recorded with a Sargent model XXI recording polarograph. Diffusion currents were measured manually. Gelatin was used to eliminate a maximum. Spectrophotometric measurements were made with a Beckman model B spectrophotometer. A Beckman model H *p*H meter was used to measure *p*H. Polarographic measurements were made at 25.0°. Spectrophotometric measurements were made at room temperature (25 ± 2°).

Reduction of Nitroprusside at the Dropping Mercury Electrode

Experimental.—The conventional dropping mercury electrode arrangement was used, with the saturated calomel electrode (S.C.E.) as reference electrode. The drop time of the electrode was 5.3 seconds with the electrode and S.C.E. short-circuited, 6.0 seconds at an applied potential of −0.5 volt *vs.* S.C.E., and 4.0 seconds at −1.6 volts; "*m*" was 1.10 mg. second. The sp. reduction waves of nitroprusside were measured in the conventional manner, using buffered and oxygen-free solutions throughout. In alkaline solution the equilibrium of reaction (1) is slowly attained. Polarograms of these solutions were measured after aging them for an hour or more in an atmosphere of nitrogen. Spectrophotometric measurements (*v.i.*) showed that alkaline solutions of nitroprusside undergo a slow, irreversible decomposition. The diffusion currents were corrected for this by measuring them as a function of time and extrapolating the slowly decreasing part of the current–time curves to zero time. The *p*H of each solution was measured after recording its polarogram.

Results.—Nitroprusside is reduced at the dropping mercury electrode in three steps, with half-wave potentials at approximately −0.4, −0.6 and −1.2 volts *vs.* S.C.E. A typical polarogram is shown in Fig. 1. Analysis of the waves shows that waves No. 1 and No. 2 may correspond to one-electron reversible reactions but that wave No. 3 is irreversible. The diffusion current constants of waves No. 1 and No. 2 are independent of nitroprusside concentration from 0.1 to 1.5 millimolar. The values of the constant vary slightly with the ionic strength of the solution. In a given medium, nitroprusside can be determined polarographically by measuring the diffusion currents of the first and, if desired, of the second wave. At an ionic strength of 0.5 (KCl) the diffusion current constant of wave

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(1) This work was carried out under the sponsorship of the Reconstruction Finance Corporation, Synthetic Rubber Division, in connection with the Synthetic Rubber Program of the United States Government.

(2) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford Press, 1950, p. 1344.

(3) L. Cambi and L. Szegö, *Gazz. chim. ital.*, **58**, 71 (1928).

(4) D. Davidson, This Journal, **50**, 2622 (1928).

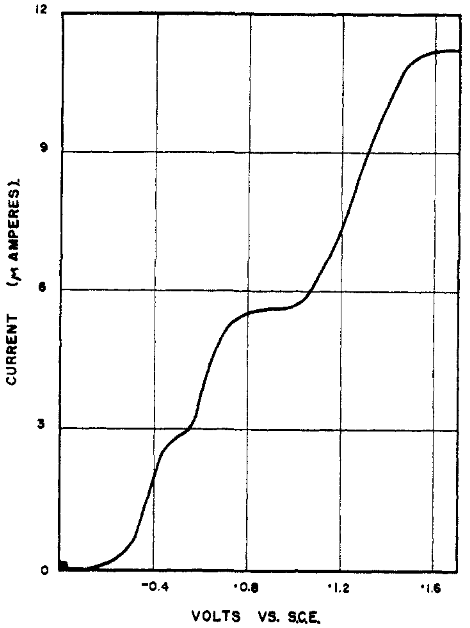

Fig. 1.—Polarogram of 0.001 *M* nitroprusside in 0.02 *M* ABP buffer, 0.5 *M* KCl, *p*H 7.14.

No. 1 at 25° is 1.86 at *p*H between 6 and 9. The effect of *p*H on the diffusion current constants and half-wave potentials of the three nitroprusside waves is summarized in Figs. 2 and 3.

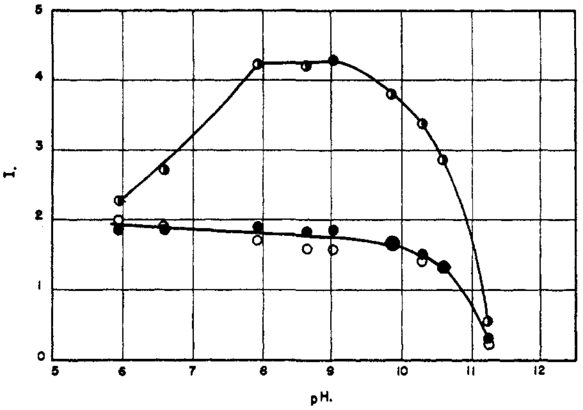

Fig. 2.—Variation of diffusion current constant "*I*" with *p*H: ○, wave No. 1; ●, wave No. 2; ◑, wave No. 3.

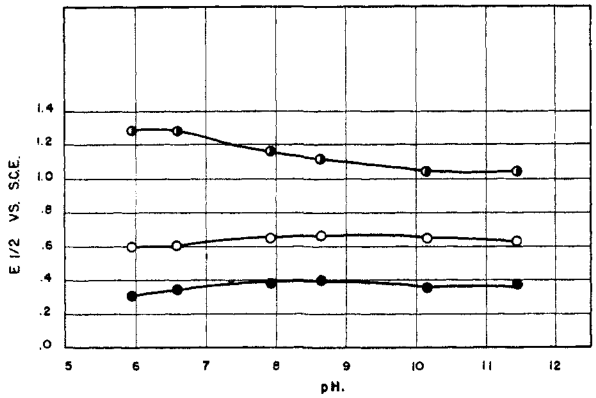

Fig. 3.—Variation of $E_{1/2}$ with *p*H: ●, wave No. 1; ○, wave No. 2; ◑, wave No. 3. Solutions 0.5 *M* in KCl, 0.06 *M* in ABP buffer, 0.001% in gelatin, 0.001 or 0.002 *M* in nitroprusside; temp. 25.0°.

The number of electrons involved in the reductions was derived from the Ilkovic expression $n = I/605D^{1/2}$, where $I = i_d/cm^{2/3}t^{1/6}$. The diffusion coefficient of the nitroprusside ion was calculated from its equivalent conductance with the aid of the equation[5] $D^\circ = 2.67 \times 10^{-7}\,\lambda/Z$. Using the equivalent conductance of nitroprusside ion of 71.0 mhos at 25° as given by Hölzl[6] gives a value of D of 9.45×10^{-6}. Substitution in the Ilkovic equation gives $n = I/1.86$. Values of n calculated from the diffusion current constants in Fig. 2 ($n = 1.00 \pm 0.02$ for wave No. 1, and 0.91 ± 0.09 for wave No. 2) indicate that waves No. 1 and No. 2 involve one electron each, while the apparent n value of wave No. 3 increases from 1.2 at *p*H 5.95 to 2.3 at *p*H 9.02. The n value of wave No. 1 was confirmed by comparing its diffusion current with that of ferricyanide which has about the same diffusion coefficient (8.9×10^{-6}). The ratio of the two waves at the same molar concentration was 1.04.

The diffusion current constant of all three waves decreases abruptly when the *p*H is increased above 10. It has been mentioned that in alkaline solution the nitroprusside ion is transformed into $Fe(CN)_5NO_2^{-1}$ (see equation 1). Assuming that only the $Fe(CN)_5NO^{-2}$ is reducible it is possible to calculate the change of the diffusion current constant with *p*H if the equilibrium constant of reaction (1) is known. In Fig. 4 the experimental diffusion current constant of the first wave, obtained under equilibrium conditions, is plotted as a function of *p*H. The curve calculated from the value of the equilibrium constant given by Cambi and Szegö[3] ($K = 1.35 \times 10^{-4}$) deviates very much from the experimental curve. On the other hand, the curve calculated with our own value of constant of 1×10^{-6} (*v.i.*) is much closer to the experimental curve.

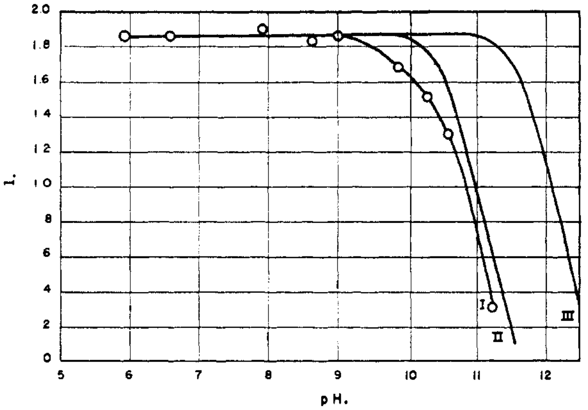

Fig. 4.—Change of diffusion current constant with *p*H. Comparison of experimental and calculated values: I, experimental; II, $K_{eq} = 1.0 \times 10^{-6}$; III, $K_{eq} = 1.35 \times 10^{-4}$ (Cambi and Szegö).

Mechanism of Polarographic Reduction.—Since nitroprusside is a ferrous compound, the first one-electron wave cannot involve the iron, but must be due to the reduction of the NO group. The first reduction may be represented by the equation

$$Fe(CN)_5(NO^+)^{-3} + e \longrightarrow Fe(CN)_5NO^{-3}$$

In this connection it is of interest to mention that the compound $Na_3Fe(CN)_5NO$ has been reported by Hoffmann.[7]

An additional one-electron reduction may give $Fe(CN)_5NO^{-4}$, or could lead to the decomposition of nitroprusside to give $(HNO)_2 + Fe(CN)_5OH^{-4}$. The ion $Fe(CN)_5NO^{-4}$ has been reported,[8] but its existence is not well established.

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(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 45.

(6) F. Hölzl, *Wien-Monatsh.*, **56**, 79 (1930).

(7) K. A. Hoffmann, *Z. anorg. Chem.*, **12**, 146 (1896).

(8) J. Giral, *Anales. soc. españ. fís. quím.*, **21**, 236 (1923).

Wave No. 3 is hydrogen ion dependent and highly irreversible. No postulation of the electrode reaction involved can be made at the present time.

Oxidation of Nitroprusside at the Rotating Platinum Electrode

The oxidation of nitroprusside in alkaline medium occurs at such a positive potential that its anodic wave cannot be observed at the dropping mercury electrode. At the rotating platinum electrode an anodic wave is observed.

A platinum wire microelectrode rotated at 1100 r.p.m. was used as the anode, with a saturated calomel electrode as the cathode. The polarogram was recorded using a Sargent model XXI polarograph. The potential was applied from +0.9 to 0.0 volt *vs.* S.C.E. It was found that the shape of the *c–v* curve was different when the potential was applied in the reverse direction (from 0.0 to +0.9 volt). In all measurements the potential was applied from plus to minus. In the oxidation of ferrocyanide at the rotating platinum electrode it is reported[9] that no wave occurs when the potential is applied from minus to plus, but that a diffusion current is obtained when the potential is varied from plus to minus.

Current–voltage curves were recorded of solutions at *p*H 9.2, 10.5, 11.1, 11.5. At *p*H 9.2, 0.1 *M* borax was used as a buffer, and 0.2 *M* phosphate buffers at higher *p*H. Oxygen was not removed from the solutions. Fifty ml. of the buffer solution was placed in a beaker and the residual current recorded from +0.9 to 0.0 volt *vs.* S.C.E. Then 1 ml. of 0.01 *M* nitroprusside was added and the solution allowed to stand for 15 minutes before recording the current–voltage curve. The polarograms obtained are shown in Fig. 5. The anodic limiting current of nitroprusside increases as the *p*H is raised, indicating that the alkaline form of nitroprusside, $Fe(CN)_5NO_2^{-4}$, is being oxidized.

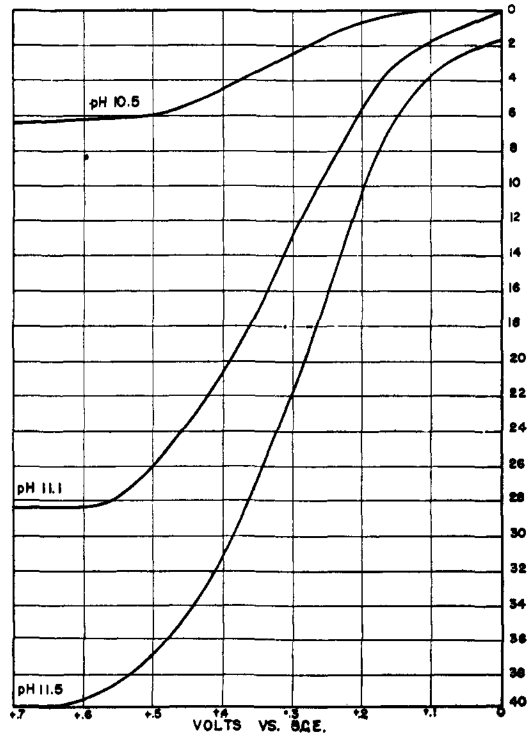

Fig. 5—Oxidation of 2 × 10^{-4} *M* nitroprusside at the rotating platinum electrode (in 0.2 *M* $HPO_4^{=}$–$PO_4^{\equiv}$ buffer). Waves corrected for residual current of electrolyte.

The electron change involved was determined by comparison of the ratio of limiting current to concentration of the nitroprusside solutions, with the same ratio measured for the one electron reduction of ferricyanide under the same experimental conditions. Since the diffusion coefficients of nitroprusside and ferricyanide are about the same, the i_{lim}/c values for the two reactions should be proportional to their apparent "*n*" values. For ferricyanide, i_{lim}/c was measured as 230 microamp-millimole^{-1}-liter^{-1}. At *p*H 11.5 where the nitroprusside is almost entirely in the $Fe(CN)_5NO_2^{-4}$ form, i_{lim}/c for nitroprusside was 220, giving an "*n*" value for the nitroprusside oxidation of 0.96. The reaction may be represented by

$$Fe(CN)_5NO_2^{-4} \longrightarrow Fe(CN)_5NO_2^{-3} + e$$

The observed half-wave potentials became more negative with increasing *p*H, varying from +0.34 volt *vs.* S.C.E. at *p*H 10.15 to +0.29 volt at *p*H 11.5.

A few electrolysis experiments were also carried out with a stationary platinum electrode of 1.5 cm. length as the anode *vs.* a saturated calomel electrode. The temperature was maintained at 25.0° during the experiments. The electrolyte was a 0.14 *M* phosphate buffer of *p*H 11.1 with a nitroprusside concentration of 2.7 millimolar. Oxygen was not removed from the solution. The curves were measured manually, allowing 5 to 10 minutes for establishment of the diffusion layer at each potential. Figure 6 shows the current–voltage curves of solutions which had aged for the indicated period of time. The anodic limiting current increases continuously during the aging, and after four days reached a value more than twice that observed originally, despite the fact that the solution had lost its yellow color and a yellow-tan precipitate had formed. Measurement of the cathodic *c–v* curve with the dropping mercury electrode showed that all nitroprusside had decomposed in the aged solutions. Calculations from the equilibrium constant of the nitroprusside–hydroxyl reaction (*v.i.*) indicated that the $Fe(CN)_5NO^{-2}$ concentration should have been 1.1 millimolar at *p*H 11.1. Apparently, the alkaline solution had decomposed giving products which were oxidizable at the platinum electrode but not reducible at the D.M.E.

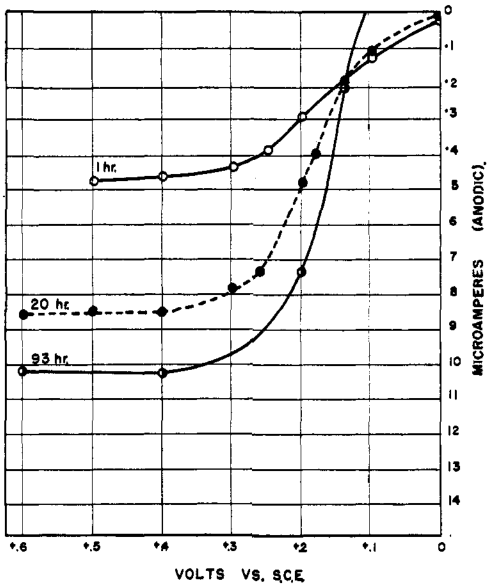

Fig. 6.—Anodic wave of nitroprusside at the S.P.E.; solution, 2.7 × 10^{-3} *M* nitroprusside, 0.143 *M* phosphate buffer, *p*H 11.

Equilibrium Constant and Rate of the Reaction of Nitroprusside with Hydroxyl Ions

The equilibrium constant of the reaction between nitroprusside and hydroxyl ions has been determined spectrophotometrically by Cambi and Szegö.[8] They reported a value of 1.35 × 10^{-4} for the constant

$$K_{eq} = [Fe(CN)_5NO^{-2}][OH^-]^2/[Fe(CN)_5NO_2^{-4}] \quad (3)$$

at 15°. Our polarographic data (see Fig. 3) indicate that this constant is much smaller than 10^{-4} at 25°.

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[9] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1088 (1941).

Spectrophotometric Measurements.—The equilibrium constant of the reaction of nitroprusside with hydroxyl ions was determined by spectrophotometric measurements of the concentration of the yellow $Fe(CN)_5NO_2^{-4}$ ion as a function of *p*H. In agreement with Cambi and Szegö, we find that $Fe(CN)_5NO_2^{-4}$ shows a plateau of high absorbance between 350 and 400 mμ. We measured the extinction of the $[Fe(CN)_5NO_2^{-4}]$ at 385 mμ. Extinction cells were Corex, 1.000 cm. in thickness. The solutions used were 0.85 millimolar in nitroprusside, 8 millimolar in phosphate buffer, and 0.5 molar in potassium chloride. The *p*H of the solutions varied from 10.8 to 11.42. It was found that at *p*H above 12 the yellow color of the solution faded appreciably within an hour, evidently due to decomposition of the nitroprusside. Consequently, it was not possible to measure the extinction at high enough *p*H to ensure the presence of 100% of the colored form. Extinctions at all *p*H's were measured as functions of time and extrapolated to zero time to correct for this decomposition. The extinction coefficient and equilibrium constant were determined using the method of Stearns and Wheland.[10] In addition to the equations for the extinction coefficient, $\log I_0/I = k(Fe(CN)_5NO_2^{-4})$, and for the equilibrium constant, the quantity k' is defined as

$$k' = \frac{\log I_0/I}{[Fe(CN)_5NO^{-2}] + [Fe(CN)_5NO_2^{-4}]} \qquad (4)$$

Eliminating the nitroprusside concentrations from the three equations gives

$$1/k' = 1/k + K_{eq}/k[OH^-]^2 \qquad (5)$$

This expression is linear, with $1/k'$ and $1/[OH]^2$ the variables. A plot of $1/k'$ *vs.* $1/[OH^-]^2$ then has a slope of K_{eq}/k and an intercept at $1/k$. $1/k'$ was calculated at *p*H between 10.8 and 11.42, using values of $\log I_0/I$ corrected for the decomposition of the nitroprusside. These values are plotted against $1/[OH^-]^2$ in Fig. 7. (To facilitate plotting, both sides of equation 5 were multiplied by 10^{-6}.) The slope of the line obtained is 7.1×10^{-10} mole³ liter⁻³ cm. Its intercept at $1/[OH^-]^2 = 0$ is 6.8×10^{-10} liter-mole⁻¹·cm.⁻¹. The molar extinction coefficient, k, is then calculated to be 1.47×10^3 liter-mole⁻¹-cm.⁻¹, and the equilibrium constant, K_{eq}, is equal to 1.0×10^{-6} mole²-liter⁻² at 25°. This value of K_{eq} is about one hundredth that reported by Cambi and Szegö.

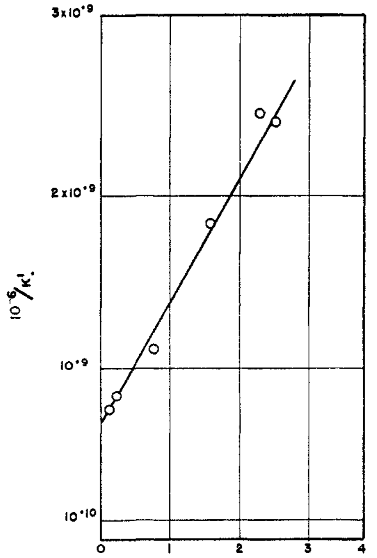

Fig. 7.—Plot of equation: $10^{-6}/k^1 = 10^{-6}/k + (K_{eq}(10^{-6})/K(OH^-)^2)$.

Polarographic Measurements.—Assuming that only the $Fe(CN)_5NO^{-2}$ form is reducible at the dropping mercury electrode, the rate of the reaction between nitroprusside and hydroxyl ion was measured at varying *p*H by following the change in the nitroprusside limiting current at the dropping electrode in alkaline solutions as a function of time. Twenty-five ml. of a solution 0.005 *M* in nitroprusside, 0.12 *M* in ABP buffer adjusted to *p*H 8, and 0.5 *M* in potassium chloride was placed in a polarograph cell. After removing dissolved oxygen by bubbling with nitrogen, the diffusion current of the first nitroprusside reduction wave was measured at −0.5 volt *vs.* S.C.E. A known volume of air-free sodium hydroxide solution was added to raise the *p*H, and the solution thoroughly mixed. The decrease in the current was then measured as a function of time, using the manual polarograph. The time at which the alkali was added was taken as the start of the reaction. The current measured before the addition of the alkali was corrected for the volume increase by the alkali and taken as the current at zero time. The *p*H of the solution was measured while the reaction was in progress. The current decreased rapidly during the first 20 minutes, and more slowly, but continuously, thereafter. In order to find the equilibrium value of the current a correction was applied for the slow decomposition in a similar manner as was done in the spectrophotometric measurements. Qualitative evidence of the irreversible decomposition of nitroprusside was obtained by reacidifying alkaline nitroprusside solutions after they had stood for some time and comparing the current with the current originally measured at *p*H 8. The current increased upon adjustment of the *p*H to 8, but never to its original value.

The rate of the reaction of nitroprusside with hydroxyl ion was measured at *p*H between 9.5 and 11.5. Typical current–time curves are shown in Fig. 8. In deriving equations for reaction rates it was assumed that the rate of the forward reaction is proportional to the concentration of $Fe(CN)_5NO^{-2}$, and the rate of the reverse reaction proportional to the concentration of $Fe(CN)_5NO_2^{-4}$. At a given *p*H the rate of formation of $Fe(CN)_5NO^{-2}$ then is given by

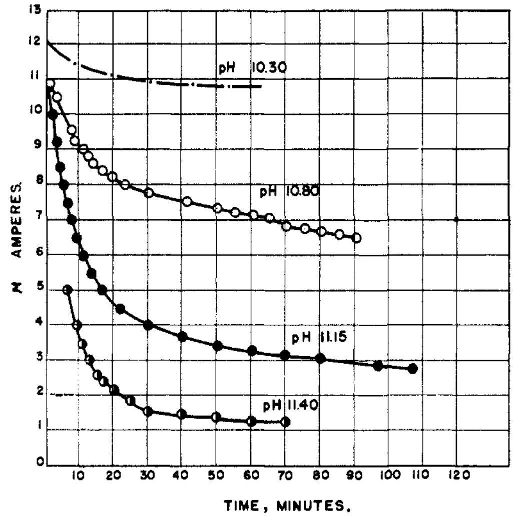

Fig. 8.—Diffusion current *vs.* time: alkaline nitroprusside solutions, 0.005 *M*.

$$dC_1/dt = -k_1C_1 + k_2C_2 \qquad (6)$$

where $C_1 = [Fe(CN)_5NO^{-2}]$ and $C_2 = [Fe(CN)_5 \cdot NO_2^{-4}]$. If nitroprusside is present only in these two forms

$$C_2 = C_0 - C_1 \quad \text{where } C_0 = \text{total nitroprusside} \qquad (7)$$

Then

$$dC_1/dt = -(k_1 + k_2)C_1 + k_2C_0 \qquad (8)$$

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[10] R. S. Stearns and G. W. Wheland, This Journal, **69**, 2025 1947).

Integrating this expression from $t = 0$ to $t = t$, and from C_0 to C_1 gives

$$\log\left[\frac{C_1}{C_0} + \frac{K_2}{K_1}\left(\frac{C_1}{C_0} - 1\right)\right] = -\left[\frac{K_1 + K_2}{2.303}\right]t \quad (9)$$

At equilibrium, t is considered to be infinite and $[Fe(CN)_5NO^{-2}] = C_{eq}$. Therefore

$$k_2/k_1 = C_{eq}/(C_0 - C_{eq}) \quad (10)$$

Substituting this for k_2/k_1 in equation (9) and rearranging gives

$$\log\left[\frac{C_1}{C_0}\left(1 + \frac{C_{eq}}{C_0 - C_{eq}}\right) - \frac{C_{eq}}{C_0 - C_{eq}}\right] = -\left[\frac{k_1 + k_2}{2.303}\right]t \quad (11)$$

A plot of $\log\ [C_1/C_0(1 + C_{eq}/(C_0 - C_{eq})) - C_{eq}/(C_0 - C_{eq})]$ *vs.* time should be linear, with a slope equal to $-(k_1 + k_2)/2.303$. A typical plot of this type is shown in Fig. 9. Values of k_1 and k_2 calculated by simultaneous solution of equations (10) and (11) are given in Table I.

TABLE I

RATE CONSTANTS OF THE REACTION OF NITROPRUSSIDE WITH HYDROXYL IONS

*p*H	Slope of log *vs.* time plot	Measured $[Fe(CN)_5NO^{-2}]$, C_0	C_{eq}	k_1	k_2
10.8	0.059	4.44	3.14	0.040	0.095
11.0	.050	4.56	1.78	.070	.045
11.2	.059	4.38	1.52	.088	.047
11.3	.058	4.52	0.88	.107	.026
11.4	.063	4.33	0.60	.124	.020

In the above derivation it has not been considered that k_1 and k_2 are functions of the hydroxyl ion concentration. Writing $k_1' = ak_1$ and $k_2' = bk_2$, it is seen from Table II that the least variation of k_1' is found with $a = 1/(OH^-)$ and of k_2' with $b = 1/(H^+)$.

TABLE II

VALUES OF CONSTANTS k_1' AND k_2' AND k_{eq}

	k_1'		k_2'		
*p*H	$a = 1/(OH)^- \times 10$	$a = 1/(OH^-)^2 \times 10^{-4}$	$b = 1/(H^+) \times 10^{-7}$	$b = 1/(H^+)^2 \times 10^{-20}$	$K_{eq} \times 10^7$ (in eq. 13)
10.8	6.3	10.0	6.0	3.8	9.5
11.0	7.0	7.0	4.5	4.5	6.4
11.2	6.3	4.5	6.7	9.4	10.7
11.3	6.0	3.4	4.6	8.2	7.7
11.4	5.0	2.0	5.0	12.5	10.1

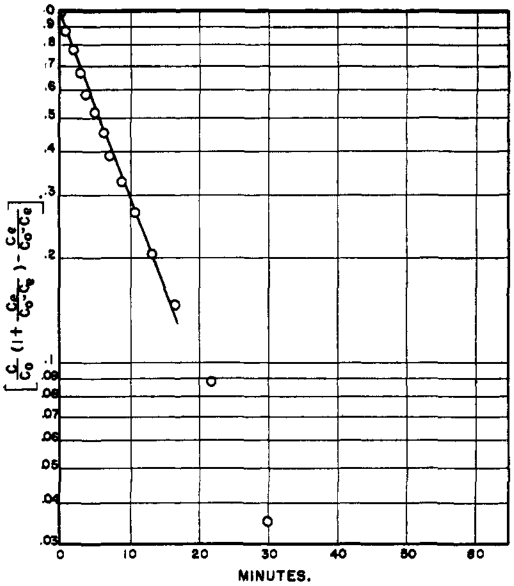

Fig. 9.—Alkaline nitroprusside solution, *p*H 11.2; plot of equation: $\log\ [C_1/C_0(1 + (C_e/(C_0 - C_e)) - C_e/(C_0 - C_e)] = -k_1 + k_2/2.303\ t$.

The rate equation with these reaction rate constants becomes

$$dC_1/dt = -k_1'[OH^-]C_1 + k_2'[H^+]C_2$$

This corresponds to the reaction

$$Fe(CN)_5NO^{-2} + OH^- \rightleftarrows Fe(CN)_5NO_2^{-4} + H^+$$

with an equilibrium constant

$$K'_{eq} = [H^+][Fe(CN)_5NO_2^{-4}]/[OH^-][Fe(CN)_5NO^{-2}] \quad (12)$$

Evidently $K'_{eq} = K_w/K_{eq}$, where K_{eq} is the equilibrium constant in equation (3). Thus

$$K_{eq} = K_w/K'_{eq} = k_2'K_w/k_1' \quad (13)$$

Using the values of k_1' and k_2' from columns 2 and 4 of Table II yields the values of K_{eq} in the last column of Table II. The average value of 9×10^{-7} calculated from the polarographic measurements agrees well with that of 1.0×10^{-6} obtained spectrophotometrically.

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