317) atom ratios, total C/Fe, increased in the first 10 days of synthesis and then remained about constant. At 21.4 atmospheres, atom ratios, total C/Fe, for samples converted to cementite, were lower after 35 to 40 days of testing than before synthesis. These results are similar to those obtained with Hägg carbide.[4] 3. Although values for maximum carbidic carbon are only approximate, in most cases they show the same trends as phases found in X-ray analyses. An exception is the initial sample in test X-268, in which metallic iron was the major phase. 4. After synthesis with catalysts converted to cementite, this phase was the only carbide identified by X-ray diffraction. 5. Formation of carbonates during synthesis increased sharply with pressure, and the results are similar to those with catalysts converted to Hägg carbide or iron nitride.[4,7] 6. At the temperatures studied, deposition of elemental carbon from synthesis gas does not appear to be an important factor in disintegration of catalysts during synthesis. Disintegration parallels oxidation and appears to be related to structural changes involved in the formation of magnetite. 7. Explanations advanced for composition changes of Hägg carbide during synthesis are adequate for cementite: (a) Water is the principal oxidant and (b) the decrease in carbon content of catalyst in synthesis at 21.4 atmospheres may result from direct hydrogenation of carbide or reaction of water with carbide to produce methane and magnetite.

Discussion

The data indicate that fused iron catalysts, converted to cementite, are active in the Fischer–Tropsch synthesis and that their behavior is qualitatively similar to that of preparations containing Hägg iron carbide or metallic iron. Cementite prepared with carbon monoxide was more active than cementite from methane; the reason for the difference is not known. In synthesis at 7.8 atmospheres, catalysts converted to Hägg carbide or cementite by treatment with carbon monoxide were more active and oxidized less rapidly than reduced catalysts. At 21.4 atmospheres, carbided catalysts had little or no advantage over reduced catalysts with respect to either activity or rate of oxidation. The selectivity of fused catalysts containing metallic iron, Hägg carbide or cementite as initial phase was about the same except that the carbides often had a slightly higher usage ratio, H_2/CO, than reduced catalysts. However, the selectivity of nitrided iron was considerably different from that of reduced or carbided samples, nitrides yielding a product of lower average molecular weight with a larger concentration of oxygenated molecules. At both 7.8 and 21.4 atmospheres, nitrides oxidized at a lower rate and were usually more active than reduced or carbided catalysts.

These and older data demonstrate that iron converted to cementite, Hägg iron carbide, iron nitride or iron carbonitride is at least as active in the Fischer–Tropsch synthesis as the metal. This behavior of interstitial compounds of iron is in sharp contrast to that of carbides of cobalt[13] and nickel,[14] which have very low activities as compared with the metals.

[13] S. Weller, L. J. E. Hofer and R. B. Anderson, THIS JOURNAL, **70**, 799 (1948); R. B. Anderson, W. K. Hall, A. Krieg and B. Seligman, *ibid.*, **71**, 183 (1949).

[14] M. Perrin, Doctoral Dissertation, Univ. of Lyon, 1948; also references in L. J. E. Hofer, *et al.*, *J. Phys. Colloid Chem.*, **54**, 1161 (1950).

BRUCETON, PENNSYLVANIA

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Investigation of the Complexes of Mercury(II) with Ethylenediamine Using the Mercury Electrode[1]

BY JAMES I. WATTERS AND JOHN G. MASON[2]

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Mercury(II) forms complexes with ethylenediamine which are reversibly reduced in alkaline solutions directly to free mercury at the dropping mercury electrode. In solutions containing mercury(II) ions and an excess of ethylenediamine continuous composite anodic–cathodic waves having slopes of about 0.030 volt corresponding to reversible two electron transfers are obtained at more negative potentials than that of aquomercury(II) ions. The potential of a mercury pool as a function of *p*H and ligand concentration has permitted an interpretation of the equilibria and an evaluation of the complexity constants. The equilibrium in ethylenediamine solutions is considerably more complex than that of most other metal ions due to the presence of mixed complexes containing hydroxyl ions as well as hydrogen ions associated with the bound ethylenediamine. The predominant species and their complexity constants at 25° and $\mu = 0.1$ are: $Hg(en)_2^{2+}$, $K_2 = 10^{23.32}$; $Hg(en)^{2+}$, $K_1 = 10^{14.3}$; $Hg(en)(OH)^+$, $K_{101} = 10^{23.8}$; $Hg(Hen)_2^{4+}$, $K_{020} = 10^{12.9}$; $Hg(en)(Hen)^{3+}$, $K_{110} = 10^{18.6}$; and $Hg(en)(Hen)_2^{4+}$, $K_{120} = 10^{22.2}$.

Prior to the present investigation the only literature reference to the complex of mercury with ethylenediamine was the tabulated value $10^{23.42}$ for the complexity constant of $Hg(en)_2^{2+}$ in 1 M KNO_3 at 25° in a review by Bjerrum[3] on the basis of unpublished experiments. The present study supports his result and also establishes the species and stability of the several mercury(II) complexes which exist in ethylenediamine solutions at various *p*H's. Since the present paper was first submitted, Nyman, Roe and Masson[4] have reported a value of $10^{22.88}$ at 25° and an ionic strength adjusted to 0.1 with potassium nitrate obtained by polarographic measurements.

Introduction

Anodic mercury polarographic waves at more negative potentials than the terminal wave for the oxidation of the mercury drop in non-complexing electrolytes are usually due to the formation of a

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[1] Presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Kansas City, Mo., April 1, 1954.

[2] Taken in part from a thesis by J. G. Mason submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955.

[3] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[4] C. J. Nyman, D. K. Roe and D. B. Masson, THIS JOURNAL, **77**, 4191 (1955).

precipitate of slightly soluble salts of mercury(I) or very stable complexes of mercury(II). The possibility of obtaining mercury in either the I or II state is due to the rapid equilibrium

$$\mathrm{Hg} + \mathrm{Hg}^{2+} \rightleftarrows \mathrm{Hg}_2{}^{2+} \qquad (1)$$

for which the equilibrium constant is about 81 at 25° and infinite dilution or 83.7 at an ionic strength of 0.1. The former value was given by Latimer[5] and the latter was interpolated from results by Schwarzenbach and Anderegg.[6]

Polarograms obtained during the oxidation of mercury or the reduction of mercury ions are unique in that the electrode itself constitutes the reduced form. Consequently the observed half-wave potential for the reversible reduction of mercury(II) complex in the presence of an excess of ligand is not the true half-wave potential because a very large anodic portion of the composite wave is neglected. This apparent half-wave potential is, as pointed out by Kolthoff and Miller,[7] a function of the concentration of the mercury complex as well as that of the ligand. After establishing the reversibility of the electrode polarographically the authors preferred to investigate the equilibrium by measuring the potential of the quiet mercury pool. Its potential was found to be nearly identical with that of the dropping mercury electrode with no electrolysis except for the iR correction resulting from charging the drop. It has the further advantage that the concentration of the complex at the surface is the same as in the bulk of the solution.

The mercury electrode has recently been used by Infeldt and Sillen[8] to investigate the complexes of mercury(I) and mercury(II) with sulfate and nitrate. They obtained values of 1.05 and 0.5 for the stepwise formation constants of the mercury(I) complexes with nitrate and values of 1.28 and 1.0 for the corresponding mercury(II) complexes. These constants are sufficiently small compared to those with ethylenediamine so that the presence of nitrate should not interfere. However, nitrate was excluded for the final measurements.

Leden's method[9] was used for the evaluation of the equilibrium constants. DeFord and Hume[10] as well as Ringbom and Eriksson[11] have adapted the method to polarographic measurements while Hindman and Sullivan[12] have discussed the use of determinants. In this paper the method is adapted to the potentiometric study of mixed complexes through the use of determinants. According to Leden's procedure one may write general equations for the equilibrium and the corresponding complexity constant

$$\mathrm{M} + i\mathrm{A} \rightleftarrows \mathrm{MA}_i;\ K_i = \frac{(\mathrm{MA}_i)}{(\mathrm{M})(\mathrm{A})^i} \qquad (2)$$

Rearranging the above equation and summing the equations for all species of M, assuming the absence of binuclear complexes, yields

$$(\mathrm{M}) = \frac{\sum\limits_0^N (\mathrm{MA})_i}{\sum\limits_0^N K_i(\mathrm{A})^i} \qquad (3)$$

In this and the following equations (M) represents the concentration of metal ions, (A) represents the concentration of ligand and (MA_i) represents the concentration of the ith complex. N represents the maximum number of complexed ligands. For clarity ionic charges are not included. In these equations the form of the summation is simpler if it starts with $i = 0$. For this hypothetical equilibrium (MA_0) is equivalent to (M) while $(\mathrm{A})^0$ and K_0 are equal to unity.

Equation 3 may be substituted into the Nernst equation as

$$E = E_0' + S \log (\mathrm{M}) = E_0' - S \log \frac{\sum\limits_0^N K_i(\mathrm{A})^i}{\sum\limits_0^N (\mathrm{MA})_i} \qquad (4)$$

E indicates the measured potential and E_0' indicates the formal potential of the electrode for the constant ionic strength used in the experiments. For consistency between the polarographic and potentiometric data the European convention of potential signs is employed. S indicates 2.303 RT/nF in the Nernst equation. C_M represents the sum of the concentrations of all species of $\mathrm{M}, \Sigma(\mathrm{MA}_i)$.

$$F_0(\mathrm{A}) = \left(\text{antilog}\,\frac{E_0' - E}{S}\right) C_\mathrm{M} = \sum_0^N K_i(\mathrm{A})^i = 1 + K_1(\mathrm{A})^1 + K_2(\mathrm{A})^2 + K_3(\mathrm{A})^3 \ldots K_N(\mathrm{A})^N \qquad (5)$$

$$F_1(\mathrm{A}) = \frac{\left(\text{antilog}\,\frac{E_0' - E}{S}\right) C_\mathrm{M} - 1}{(\mathrm{A})} = \sum_1^N K_i(\mathrm{A})^{i-1} = K_1 + K_2(\mathrm{A}) + K_3(\mathrm{A})^2 \ldots K_N(\mathrm{A})^{N-1} \qquad (6)$$

If the term antilog $(E_0' - E)/S$ is replaced by $(\mathrm{M})^{-1}$ it becomes evident that these equations are identical with those of Leden.[9]

The first and second complexity constant can be investigated by equation 6 provided only one kind of ligand is present. If the concentration of free ligand, A, is known or can be calculated on the basis of pH and if E_0' is known it is possible to plot the left-hand term of equation 6 along the y-axis *versus* (A) along the x axis. The resulting graph should be linear with a (y) intercept of K_1 and a slope of K_2 in the range of (A) smaller than that at which MA_3 becomes significant. The process can then be continued for MA_3 after obtaining $F_2(\mathrm{A})$ by subtracting K_1 and dividing through by (A). The process is repeated for higher complexes until a straight line of zero slope is obtained for the saturated complex.

If more than one kind of ligand is present, for example the species A, B and C the following general equation and complexity constant may be written

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[5] W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 164.

[6] G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **37**, 1289 (1954).

[7] I. M. Kolthoff and C. S. Miller, This Journal, **63**, 2732 (1941).

[8] G. Infeldt and L. G. Sillen, *Svensk Kem. Tids.*, **58**, 104 (1946).

[9] I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

[10] D. D. DeFord and D. N. Hume, This Journal, **73**, 5321 (1951).

[11] A. Ringbom and L. Eriksson, *Acta Chem. Scand.*, **7**, 1105 (1953).

[12] J. C. Sullivan and J. C. Hindman, This Journal, **74**, 6091 (1952).

$$\mathrm{M} + i\mathrm{A} + j\mathrm{B} + k\mathrm{C} \rightleftarrows \mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k;\ K_{ijk} = \frac{(\mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k)}{(\mathrm{M})(\mathrm{A})^i(\mathrm{B})^j(\mathrm{C})^k} \quad (7)$$

The general expression for F_0 becomes

$$F_0(\mathrm{A, B, C}) = \text{antilog}\,\frac{(E_0' - E)}{S} = \sum_0^N K_{ijk}(\mathrm{A})^i(\mathrm{B})^j(\mathrm{C})^k = 1 + K_{100}(\mathrm{A})^1 + K_{200}(\mathrm{A})^2 + \ldots. + K_{010}(\mathrm{B})^1 + \ldots\ldots. + K_{110}(\mathrm{A})^1(\mathrm{B})^1\ldots\ldots + K_{101}(\mathrm{A})^1(\mathrm{C})^1\ldots.. + K_{111}(\mathrm{A})^1(\mathrm{B})^1\mathrm{C}^1\ldots.. \quad (8)$$

The values of the constants can be solved by the use of determinants in the following form where different subscripts are placed after (A) to indicate different concentrations.

$$D = \begin{vmatrix} 1 + K_{100}(\mathrm{A})_1{}^1 + K_{200}(\mathrm{A})^2 + \ldots\ldots\ldots\ldots & K_{ijk}(\mathrm{A})_1{}^i(\mathrm{B})_1{}^j(\mathrm{C})_1{}^k \\ 1 + K_{100}(\mathrm{A})_2 + K_{200}(\mathrm{A})^3 + \ldots\ldots\ldots. & K_{ijk}(\mathrm{A})_2{}^i(\mathrm{B})_2{}^j(\mathrm{C})_2{}^k \\ \cdots\cdots\cdots\cdots & \cdots\cdots \\ \cdots\cdots\cdots\cdots & \cdots\cdots \\ 1 + K_{100}(\mathrm{A})_{i+j+k}\cdots\cdots\cdots & \cdots\cdots \end{vmatrix} \neq 0 \quad (9)$$

$F_0(\mathrm{A})(\mathrm{B})(\mathrm{C})$ can be calculated from the electrode potentials according to (8) and (A) (B) and (C) can usually be calculated on the basis of *p*H measurements. The function must be calculated for as many different solutions as there are unknown equilibrium constants. If a complex species does not exist in relatively large concentration in any of the solutions then its calculated value may be a small difference of large numbers or even negative in sign due to experimental deviations. After obtaining preliminary values for the constants it is possible to calculate the various terms on the right side of the equation. From these it is possible to calculate the theoretical relative abundance of the various complex species in the various solutions as well as the theoretical value of F_0. The values of F_0 can then be recalculated for solutions containing significant but different concentrations of the possible species.

In order to analyze the polarographic waves for reversibility it was assumed that the equilibrium of ethylenediamine with hydrogen ions was attained rapidly and that a large excess of ethylenediamine was added to the solutions. It was further assumed that the rates of diffusion of the various mercury complexes were equal. Then

$$i = kI_c \sum_0^N (\mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k) - (\mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k)_0 \quad (10)$$

$$i_{dc} = kI_c \sum_0^N (\mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k) \quad (11)$$

where i and i_{dc} are the polarographic current and the cathodic diffusion currents, respectively, corrected for charging current, k is the capillary characteristic, I_c is the diffusion current constant and the subscript, zero, indicates the concentration at the electrode surface. Substitution of equations 10 and 11 into equation 4 yields

$$E = E_0' - S \log \sum_0^N K_{ijk}(\mathrm{A})^i(\mathrm{B})^j(\mathrm{C})^k + S \log kI_c + S \log (i_{dc} - i) \quad (12)$$

This equation is valid for either anodic or cathodic currents. The current, i, has a negative sign if anodic, and a positive sign if cathodic while i_{dc} is zero if the solution contains no mercury. Since the first three terms on the right are constant, a plot of E *versus* $\log (i_d - i)$ should yield a straight line having a slope of S, provided the electrode reaction is reversible. It is evident that the apparent half-wave potential varies with i_{dc} and therefore with the mercury concentration.

The concentrations of free en and Hen$^+$ were calculated as described in the earlier paper[13] using the values $10^{-7.20}$ and $10^{-10.00}$ for the acidity constants for the successive dissociation of two hydrogen ions from $\mathrm{H_2en^{2+}}$. These were determined from curves for the titration of 0.04928 *M* ethylenediamine with perchloric acid at 25° and with the ionic strength adjusted to 0.1 with sodium perchlorate using the glass electrode.

The value +0.5930 volt *versus* the saturated calomel electrode (S.C.E.) was used as the formal potential for the $\mathrm{Hg^{2+}/Hg}$ electrode. This is similar to that calculated by Matyska and Kossler[14] for an ionic strength of 0.1 at 25° except for a correction of −0.001 volt based on the results of Schwarzenbach and Anderegg.[6]

Experimental

Apparatus.—The polarographic measurements were made with a manual polarograph described by Watters.[15] The capillary used in the polarographic experiments delivered 1.278 mg. of mercury per second and had a drop time of 5.89 seconds at the potential of the saturated calomel electrode. Its capillary characteristic, $m_0{}^{2/3}t_0{}^{1/6}$, was accordingly 1.664 mg.$^{2/3}$ sec.$^{-1/2}$.

For the final potentiometric measurements, a saturated calomel reference electrode was separated from the cell by a solution of saturated KCl and a 6-mm. salt bridge containing 0.1 *M* $\mathrm{NaClO_4}$ in 3% agar agar. A new bridge was used for each series of experiments and the cell was placed in the bath about one hour before starting the series of measurements. The cell contained a mercury pool electrode and the solution was purged with nitrogen before each measurement. The potential measurements were made with a Rubicon type B high precision potentiometer in conjunction with a Rubicon D.D. spotlight galvanometer having a sensitivity of 0.01 microamperes per mm.

A Beckman model G *p*H meter using the general purpose glass electrode was used and was standardized with Beckman buffers having *p*H values of 10, 7 and 4 placed in the cell.

All of the experiments were performed in a water-bath at 25.0 ± 0.1° and the ionic strength was adjusted to 0.1 *M* by $\mathrm{KNO_3}$ in the polarographic experiments and by $\mathrm{NaClO_4}$ in the potentiometric experiments.

The preparation and storage of carbonate-free 0.4928 *M* ethylenediamine has already been described.[13] The standard 0.1 *M* mercury(II) perchlorate solution was prepared by dissolving a weighed amount of mercury(II) oxide in a slight excess of perchloric acid. The molarity was verified electrolytically using a weighed mercury cathode. The standard 0.2 *M* perchloric acid was prepared by dilution of 60% reagent grade perchloric acid. The standard 1.0 *M* sodium perchlorate, reagent grade, solution was prepared from anhydrous sodium perchlorate.

In the final experiments stock solutions were prepared to contain 0.01 to 0.0001 *M* $\mathrm{Hg^{2+}}$ and 0.05 to 0.0005 *M* ethylenediamine in basic and acidic solutions. The basic solution also contained 0.1 *M* sodium perchlorate. The acidic solution was prepared to contain 0.1 *M* perchloric acid. Solutions of intermediate *p*H were prepared by mixing in

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[13] J. I. Watters and E. D. Loughran, THIS JOURNAL, **75**, 4819 (1953).

[14] B. Matyska and I. Kossler, *Coll. Czech. Chem. Commun.*, **16**, 221 (1951).

[15] J. I. Watters, *Rev. Sci. Inst.*, **22**, 851 (1951).

various ratios, the acidic and basic solutions having the same total mercury and ethylenediamine concentrations.

Results and Discussion

Continuous anodic–cathodic polarograms were obtained at various *p*H values with solutions 1 millimolar in mercury(II) ion, 0.025 *M* in ethylenediamine, 0.1 *M* in total nitrate, and 0.004% in gelatin. The anodic diffusion currents were not so well defined as the cathodic ones. This is reasonable since it will be shown that ethylenediamine adds stepwise. Thus it is probable that the bis-complex is formed at the beginning of the anodic wave and the mono-complex near the anodic diffusion current region. Consequently mercury(II) ion in the presence of an excess of ethylenediamine was used in the experiments.

In analyzing the polarographic waves, the plot of E *versus* log $(i_{dc} - i)$ yielded linear graphs having reciprocal slopes of 0.029 to 0.034 volt in the *p*H range of 11 to 7, respectively. This indicates a reversible two electron transfer in this *p*H range. The shift of these waves in the alkaline *p*H range was 0.0593 volt per tenfold change in (en) due to *p*H variation. This indicates the presence of two ligands in the complex with excess ethylenediamine. In the more acidic solutions at a *p*H decreased to 5 the reciprocal slope increased to 0.058 volt indicating that the electrode reaction was not completely reversible, at least for an actual electrolysis of mercury(II) directly to free mercury. The diffusion current constant of the mercury(II) complex was essentially independent of *p*H, having a value 3.56 microamperes millimolar^{-1} mg.$^{-2/3}$ sec.$^{1/2}$.

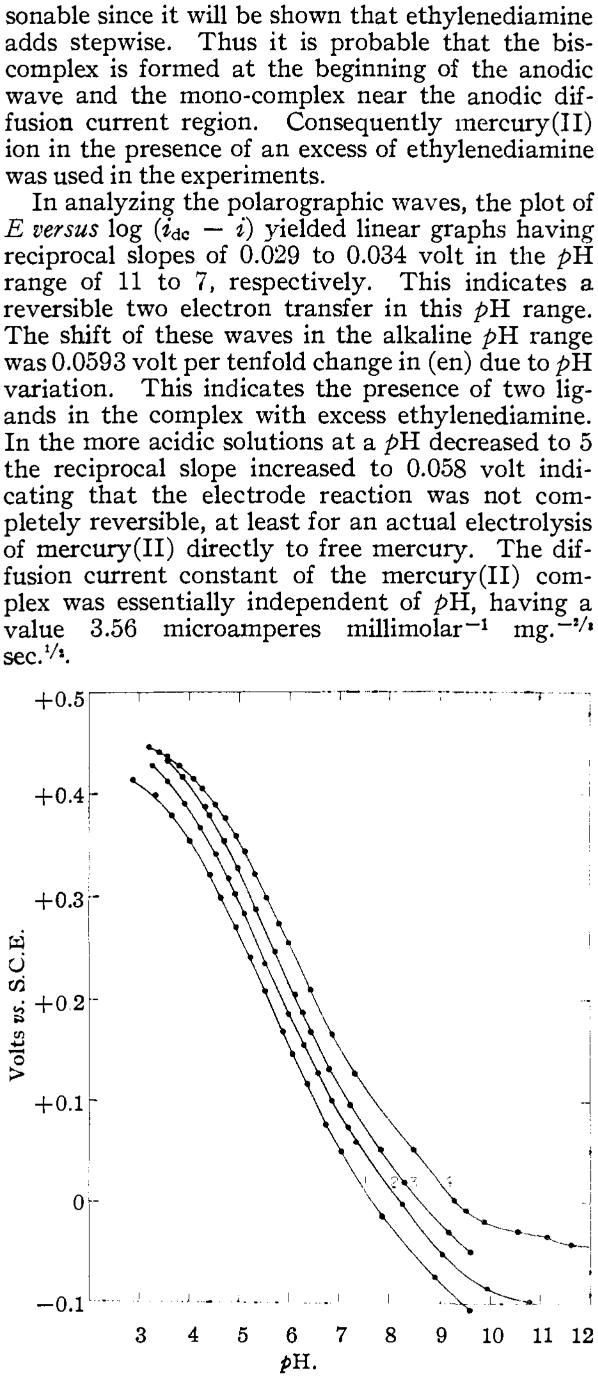

Fig. 1.—Effect of varying the *p*H on the potential of the mercury pool in the following solutions: 1, 0.0001 *M* $Hg(ClO_4)_2$, 0.05 *M* en, $\mu = 0.1$ with $NaClO_4$; 2, 0.001 *M* $Hg(ClO_4)_2$, 0.05 *M* en, $\mu = 0.1$; 3, 0.01 *M* $Hg(ClO_4)_2$, 0.07084 *M* en, $\mu = 0.1$; 4, 0.001 *M* $Hg(ClO_4)_2$, 0.005 *M* en, $\mu = 0.1$.

The excellent continuity of the polarograms across the zero current axis indicated that the electrode reaction might be essentially reversible for the small currents used to measure the potential at conditions of equilibrium with the bulk of the solution. To test the reversibility of the electrode under these conditions the potential of a mercury pool was measured in solutions containing various concentrations of mercury(II) ion and ethylenediamine. The *p*H was varied from basic to the acidic extreme by mixing the solutions as already described. These results are shown in Fig. 1. True equilibrium was attained immediately because the same values were obtained independently of the order in which the reagents were mixed and there was no drift in potential with time. The dropping mercury electrode yielded identical values for a current equal to the residual current. A comparison of curves 1, 2 and 3 in which the mercury(II) concentration was varied 100-fold while the excess ethylenediamine remained essentially constant shows a shift of 0.030 volt per tenfold change in mercury(II) concentration throughout the *p*H range of 9.5 to 3.5. This verifies the reversibility of the electrode process. Furthermore, the essential absence of binuclear complexes is verified since their presence in relatively large amounts would have resulted in a shift approaching 0.015 volt. A similar comparison of curves 2 and 4 reveals a corresponding shift of 0.059 volt per tenfold change in concentration of ethylenediamine, not complexed. This indicates a predominance of complex ions containing two ethylenediamine molecules.

Substitution of the data into equation 6 for $F_1(A)$ yielded $K_2 = 10^{23.31} {}^{+0.10}$ for $Hg(en)_2{}^{2+}$ in the alkaline *p*H range. Furthermore, the values of $F_1(A)$ reached a constant value of $K_1 = 10^{14.45}$ below a *p*H of 4.15 but started to rise below a *p*H of 3.35. That this final rise was due to the presence of increasing concentrations of $Hg_2{}^{2+}$ in the equilibrium mixtures below a *p*H of 3.55 was proved in the following way. An excess of concentrated hydrochloric acid was added to portions of all of the solutions in this *p*H range after equilibrium with the mercury electrode. The white precipitate, Hg_2Cl_2, formed in increasing amounts as the *p*H decreased below 3.55 but no trace of turbidity was evident above this *p*H. When portions of the solutions were treated with an excess of ethylenediamine the solutions instantly turned gray or black due to the dismutation of $Hg_2{}^{2+}$ to Hg^{2+} and free mercury. Between the alkaline range where $F_1(A)$ indicated that $Hg(en)_2{}^{2+}$ predominated and the acid range of 4.5 to 3.5 where $Hg(en)^{2+}$ apparently predominated the agreement of the data with $F_1(A)$ was only fair. Accordingly experiments were performed using Bjerrum's method. The theoretical and experimental formation curves based on the formation of these two complexes were somewhat similar but the agreement was considerably less than could be accounted for by experimental error. To account for the deviation the possibility of the ligands, OH^- and Hen^+, entering the complexes was considered. Schwarzenbach and his co-workers[16] have established the

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[16] G. Schwarzenbach, H. Ackermann, B. Maissen and G. Anderegg, *Helv. Chim. Acta*, **35**, 2337 (1953).

TABLE I

LOGARITHMS OF CONTRIBUTIONS OF VARIOUS COMPLEX SPECIES TO F_0

Each term has the value log K_{ijk} $(en)^i(Hen^+)^j(OH^-)^k$; theoretically the sum of their antilogs should equal F_0.

A. 0.01 *M* $Hg(ClO_4)_3$, 0.07084 *M* en, $\mu = 0.1$; B. 0.001 *M* $Hg(ClO_4)_2$, 0.005 *M* en, $\mu = 0.1$.

	*p*H	Expt. log F_0	Theor. log F_0	$Hg(en)^{2+}$	$Hg(en)_2^{2+}$	$Hg(Hen)_2^{4+}$	$Hg(en)(Hen)^{3+}$	$Hgen(Hen)_2^{4+}$	$Hg(en)OH^+$
A	9.66	19.70	19.70	12.5	19.7	10.0	15.4	17.3	17.7
	7.20	14.77	14.86	9.9	14.5	9.7	12.6	14.6	12.6
	5.33	8.30	8.37	6.5	7.7	6.6	7.5	8.1	7.3
	3.55	3.39	3.34	3.0	0.7	3.0	2.3	1.0	2.0
B	9.30	16.77	16.70	11.0	16.7	7.7	12.7	13.7	9.6
	7.31	12.75	12.46	8.8	12.4	7.4	10.4	11.2	11.7
	5.30	6.17	6.16	5.2	5.1	4.1	5.1	4.3	6.0
	4.24	3.37	3.42	3.2	1.0	2.1	2.1	0.3	2.9

formation of a complex of the latter with silver(I) ion. Silver(I) like mercury(II) tends to form linear sp complexes but silver's bonds are considerably weaker. Finally a calculation of the complexity constant for the postulated $Hg(Hen)_2^{2+}$ by Bjerrum's empirical relation[3] between it and the second acidity constant yielded a value of $10^{13.0}$. If this constant were correct appreciable concentrations of the species should exist in some of the solutions. Accordingly determinants were solved for complex mercury(II) ions containing the ligands en, Hen^+, and OH^- alone or in mixtures with a maximum coordination number of 4. Only the following species yielded consistent positive values: $Hg(en)_2^{2+}$ $K_2 = 10^{23.3}$; $Hg(en)^{2+}$, $K_1 = 10^{14.3}$; Hg(en)(OH)$^+$, $K_{101} = 10^{23.8}$; $Hg(Hen)_2^{4+}$, $K_{020} = 10^{12.9}$; $Hg(en)(Hen)^{3+}$, $K_{110} = 10^{18.6}$; $Hg(en)(Hen)_2^{4+}$, $K_{120} = 10^{22.2}$. The calculated contributions of these species to F_0 are tabulated in Table I. The discrepancy between the observed and calculated voltage did not exceed 1 millivolt for any of the solutions in the *p*H range of 3.5 to 9.5. Surprisingly the mixed hydroxyl complex $Hg(en)(OH)^+$ contributed to F_0 through a large range of *p*H especially in the dilute solutions. It was not possible to obtain reliable values for $Hg(Hen)^{3+}$ due to the formation of mercury(I) at low *p*H values.

Our value $10^{12.9}$ for the bonding of two Hen^+ ions to mercury(II) is in excellent agreement with the predicted value $10^{13.0}$. By analogy with ammonia[3] which has the consecutive formation constants $10^{8.8}$, $10^{8.7}$, $10^{1.0}$ and $10^{0.78}$ one may estimate the corresponding values for adding Hen^+ to mercury(II) to be $10^{6.5}$, $10^{6.4}$, $10^{0.9}$, $10^{0.7}$ yielding a mean formation constant $\sqrt[2]{K_{020}} = 10^{6.5}$ for linear sp bonding and $\sqrt[4]{K_{040}} = 10^{4.8}$ for tetrahedral sp^3 bonding. For sp^3 tetrahedral bonding with ethylenediamine $\sqrt[2]{K_2} = 10^{11.7}$. According to Kolthoff[17] the first formation constant of mercury with hydroxyl ion is $10^{11.84}$, at 18°. Garrett and Howell[18] have confirmed his results. The mean value for linear sp hydroxyl formation constant must be close to $10^{11.8}$. Assuming the complexes to contain water molecules in the unfilled positions one calculates the corresponding predicted values in Table II. These results indicate that the calculated constants are at least of the right order of magnitude. The strong bonding with OH^- suggests, in case of $Hg(en)^{2+}$, that the bound en and water may rearrange to form bound Hen^+ and OH^-, thus $Hg(Hen)(OH)^+$. The estimated constant for this complex should be in the order of $10^{14.2}$ which is very close to the observed value. This calculation involves the subtraction of 4 which is equal to log K_W - log K_{enH^+} from the product of the mean Hen^+ and OH^- constants in order to express the constant in terms of (en) rather than $(Hen^+)(OH^-)$. Since these experiments do not permit the verification of this rearrangement, the former formula and the corresponding expression for the formation constant have been retained. Our experimental value for $Hg(Hen)(en)^{3+}$ is less reliable than the others since it did not predominate in any of the solutions. These results indicate that the tendency of mercury complexes to hydrolyze plays an important role in its complex equilibria in relatively low ligand concentrations.

TABLE II

Complex	log *K* (expt.)	log *K* (predicted)
$Hg(en)_2^{2+}$	23.3 ± 0.1	(23.3)
$Hg(en)^{2+}$	14.3 ± 0.1	(11.7), 14.2[a]
$Hg(en)(OH)^+$	23.8 ± 0.3	23.5
$Hg(en)(Hen)^{3+}$	18.6 ± 1.0	16.5
$Hg(en)(Hen)_2^{4+}$	22.3 ± 0.3	21.3
$Hg(Hen)_2^{4+}$	12.9 ± 0.1	13.0

[a] Assumed to rearrange to $Hen^+ + OH^-$.

COLUMBUS, OHIO

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[17] I. M. Kolthoff, *Chem. Weekbl.*, **14**, 1016 (1917).

[18] A. B. Garrett and W. W. Howell, THIS JOURNAL, **61**, 1730 (1939).