

[CONTRIBUTION OF BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES]

Studies of the Fischer-Tropsch Synthesis. XV. Cementite as Catalysts

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Reduced, fused-iron catalysts, converted to cementite by direct carburization or by thermal reaction of Hägg iron carbide and iron, were tested in the Fischer-Tropsch synthesis at 7.8 and 21.4 atmospheres. Catalysts containing cementite are active in the synthesis and have similar catalytic properties to Hägg carbide. At 7.8 atmospheres, cementite and Hägg carbide are usually more active and oxidize less rapidly than reduced catalysts; however, at 21.4 atmospheres, the activity and rate of oxidation of carbided and reduced catalysts were about the same.

Introduction

Although cementite (Fe_3C) has been known for many years, no data have been reported on its properties as a catalyst in the Fischer-Tropsch synthesis. Cementite is not produced during the synthesis with iron catalysts in low temperature operation ($< 300^\circ$) and has not been reported in catalysts used in the fluidized or hot-gas recycled processes at temperatures considerably above 300° . However, the formation of cementite under some conditions of the high temperature processes should be possible. The higher carbides, Hägg hexagonal and a carbide of approximate composition FeC , have been found in used Fischer-Tropsch catalysts.^{1,2,3} Iron catalysts converted to Hägg carbide⁴ and to iron nitrides^{5,6} have been shown to be active in the Fischer-Tropsch synthesis. Catalysts converted to Hägg carbide have essentially the same selectivity as reduced catalysts; however, iron nitrides yielded considerably different products than either reduced or carbided catalysts.

In studies of nitrated iron catalysts at the Bureau of Mines, cementite that was obtained by hydrogenation of carbonitrides formed in the synthesis was active in subsequent synthesis.^{6,7} On this basis fused iron catalysts directly converted to cementite were tested in the Fischer-Tropsch synthesis. The present paper describes the preparation of cementite in a fused iron catalyst and its activity, selectivity and composition changes during the synthesis.

Experimental

Tests were made on samples of 6- to 8-mesh fused iron catalyst (our No. D-3001) containing 67.4% iron, 4.61 MgO, 0.57 K_2O , 0.71 SiO_2 and 0.65% Cr_2O_3 . The properties of this catalyst, its reduction and behavior in the Fischer-Tropsch synthesis have been described in previous papers.^{8,9} Methods of conducting the synthesis and analyses of catalysts and reaction products also have been given.⁴ Tests were made at 7.8 and 21.4 atmospheres with $\text{H}_2 + \text{CO}$ gas. The flow of synthesis gas was maintained constant and the temperature varied to maintain an apparent contraction (CO_2 -free) of 63 to 65%.

(1) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *THIS JOURNAL*, **71**, 189 (1949).

(2) K. H. Jack, *Proc. Roy. Soc. (London)*, **A195**, 56 (1948).

(3) H. C. Eckstrom and W. A. Adcock, *THIS JOURNAL*, **72**, 1042 (1950).

(4) J. F. Shultz, W. K. Hall, B. Seligman and R. B. Anderson, *ibid.*, **77**, 213 (1955).

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(6) R. B. Anderson, *Advances in Catalysis*, **5**, 355 (1953).

(7) J. F. Shultz, B. Seligman, J. A. Lecky and R. B. Anderson, *THIS JOURNAL*, **74**, 637 (1952).

(8) W. K. Hall, W. H. Tarn and R. B. Anderson, *ibid.*, **72**, 5426 (1950); *J. Phys. Chem.*, **56**, 688 (1952).

(9) J. T. McCartney and R. B. Anderson, *J. Appl. Phys.*, **22**, 144 (1951).

Preparation of Cementite in Catalysts.—Three methods, all at atmospheric pressure, were employed to prepare cementite: (A) Conversion of Hägg iron carbide to cementite: This method is based on the observation that Hägg carbide reacts with metallic iron to form cementite.^{10a,b} This reaction proceeds more rapidly than the decomposition of Hägg carbide into cementite and free carbon. Reduced catalysts were carburized with carbon monoxide to convert two-thirds of the iron to Hägg carbide in a tilting metal block reactor.⁵ Helium was then passed over the catalyst and the temperature increased to 475° and maintained for 2 hours. The catalyst was dropped into the receiving vessel and cooled in helium.

(B) Direct preparation with $2\text{H}_2 + \text{CO}$ gas¹¹: Catalysts largely converted to cementite were prepared by carburizing the reduced sample with $2\text{H}_2 + \text{CO}$ gas at a space velocity of 2,500 hr^{-1} and 310° for 6 hours in the tilting reactor. The carburized sample was then dropped into the receiving vessel and cooled in $2\text{H}_2 + \text{CO}$ gas.

(C) Direct preparation with methane: Pure methane was passed over the reduced catalyst at a space velocity of 1,000 hr^{-1} and 500° for 4 hours in the tilting reactor. The catalyst was dropped into the receiver in methane and cooled to room temperature.

These methods produced catalysts containing principally cementite. Most of the samples contained metallic iron in addition to cementite, but other carbides were not found. Table I summarizes conditions of reduction and carburization and the phases detected by X-ray diffraction analysis. Special care was taken in transferring catalysts to avoid oxidation.⁵

Activity and Selectivity.—Activities of reduced and carbided iron at 7.8 and 21.4 atmospheres (absolute) are compared in Figs. 1 and 2, respectively. Activity, A_{Fe} , was corrected to standard synthesis conditions (240° and 65% conversion) by an empirical rate equation and is expressed as cc. of synthesis gas consumed per gram of iron per hour.¹² Although surface areas were determined on some of these samples and could be estimated for the remainder, the activity per gram is usually independent of surface area; hence activity was not expressed per unit surface area. The surface areas per gram of unreduced catalyst are principally a function of reduction temperature⁸: 450° , 10 m^2 ; 500° , 5 m^2 ; 550° , 4 m^2 .

Figure 3 compares product distributions of reduced and carbided catalysts at 7.8 and 21.4 atmospheres, corresponding to data in Figs. 1 and 2. The plot presents the distribution of total hydrocarbons, including oxygenated molecules dissolved in condensed hydrocarbons, water-soluble oxygenated molecules being excluded. Gaseous hydrocarbons and distillation fraction of condensed "hydrocarbons" are shown. Numbers preceded by (=) indicate percentages of olefins; "Br" is bromine number, "OH" weight per cent. hydroxyl group, and "CO" weight per cent. carbonyl group as aldehyde, ketones and acids. The relative usage of H_2 and CO is given in Table II.

The reduction procedures for the catalysts described were in some cases not the same, as shown in Table I. These

(10) (a) H. H. Podgurski, J. T. Kummer, T. W. DeWitt and P. H. Emmett, *THIS JOURNAL*, **72**, 5382 (1950); (b) L. J. E. Hofer and E. M. Cohn, *J. Chem. Phys.*, **18**, 766 (1950).

(11) This preparation may be regarded as an example of the formation of cementite during synthesis. Small yields of higher hydrocarbons are produced; however, the activity is low and the selectivity poor under these conditions.

(12) R. B. Anderson, B. Seligman, J. F. Shultz, R. E. Kelly and M. A. Elliott, *Ind. Eng. Chem.*, **44**, 391 (1952).

TABLE I
PRETREATMENT OF CATALYSTS^c

Test	Reduction in hydrogen			Extent of reduction, %	Gas	Carburization			Phases from X-ray diffract. ^a
	Temp., °C.	Space velocity, hr. ⁻¹	Time, hr.			Temp., °C.	Time, hr.	Atom ratio, C/Fe	
X-152	450	1000	43	90.2	None	α
X-173	550	1980	24	98.0	None	α
X-515	500	1180	24	97.9	None	α
X-249	450	2110	60	97.7	CO	240 ^b	12	0.30	αC
X-317	450	2000	62	96.1	CO	200-276 ^b	10	.36	C
X-343	500	2200	24	100	CO	245-252 ^b	12	.31	Cα
X-329	500	2390	40	98.3	2H ₂ + 1CO	310	6	.42	Cα
X-294	500	2500	24	96.6	CO	150-350	18	.58	χα
X-342	500	1990	24	97.2	CO	150-350	18	.57	χα
X-268	550	2850	20	96.0	CH ₄	500	4	.24	αC
X-276	550	2050	20	97.2	CH ₄	500	6	.40	C

^a Phases listed in order of decreasing intensity of X-ray diffraction pattern: α = metallic iron, C = cementite, and χ = Hägg carbide. ^b After carburization, the catalyst was heated in helium at 475° for two hours. ^c All steps at atmospheric pressure.

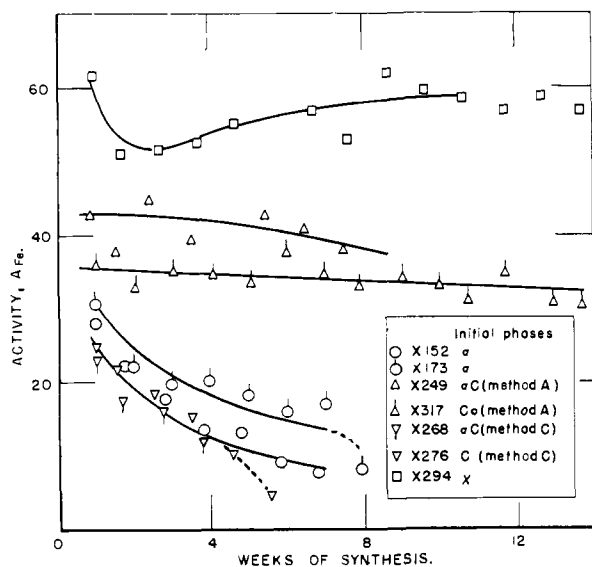


Fig. 1.—Activities of reduced and carburized catalysts at 7.8 atm. as a function of time. Symbols denoting phases defined in Table I.

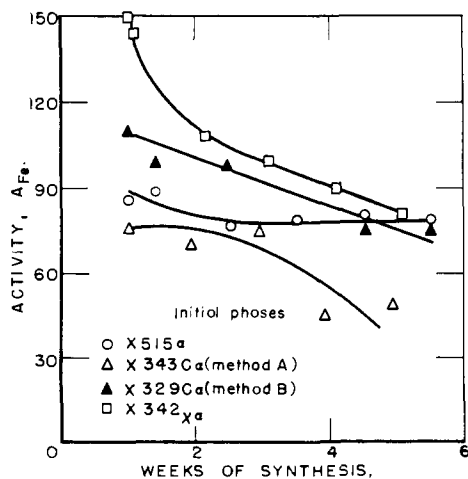


Fig. 2.—Activities of reduced and carburized catalysts at 21.4 atm. as a function of time. Symbols denoting phases defined in Table I.

TABLE II
USAGE RATIOS (H₂/CO) FOR TESTS OF FUSED CATALYSTS WITH 1H₂:1CO^c

Test	Carbiding gas	Usage ratio, ^a H ₂ /CO	Initial ^b phases
7.8 atmospheres (absolute)			
X-152	None	0.72	α
X-173	None	.70	α
X-249	CO	.81	αC
X-268	CH ₄	.77	αC
X-276	CH ₄	.79	C
X-294	CO	.76	χα
X-317	CO	.83	C
21.4 atmospheres (absolute)			
X-329	2H ₂ + 1CO	0.85	Cα
X-342	CO	.79	χα
X-343	CO	.76	C
X-515	None	.76	α

^a Averages of weeks 2 to 6. ^b Phases listed in order of decreasing intensity of X-ray diffraction pattern: α = metallic iron, C = cementite, χ = Hägg carbide. ^c Average contraction 62 to 65%.

differences, however, do not seriously complicate the interpretation, since (a) synthesis behavior is relatively independent of reduction conditions in the temperature range, 450-550°, and (b) sufficient data are presented to permit cross comparison.

TEST NUMBER	7.8 ATM				21.4 ATM				
	X 152	X 317	X 294	X 276	X 173	X 342	X 343	X 329	X 515
CARBONING GAS	None	CO	CO	CH ₄	None	CO	CO	2H ₂ +1CO	None
* TEMPERATURE, °C	270	235	229	270	259	243	257	247	248
* SPACE VELOCITY, hr. ⁻¹	97	83	106	100	97	334	287	322	303
* CONTRACTION, %	65	63	64	63	63	63	62	64	65
* ACTIVITY, A _{Fe}	14	34	53	14	20	104	55	89	80
PHASES PRESENT	α	C	χ	C	α	χ	Cα	Cα	α

DISTRIBUTION OF TOTAL HYDROCARBONS, PERCENT (INCLUDES OXYGENATED MATERIAL)	7.8 ATM				21.4 ATM				
	X 152	X 317	X 294	X 276	X 173	X 342	X 343	X 329	X 515
100	C ₁	C ₁	C ₁	C ₁	C ₁	C ₁	C ₁	C ₁	C ₁
90						C ₂ +52	C ₂ +60	C ₂ +58	C ₂ +39
80	C ₂ +22	C ₃ +C ₄	C ₃ +C ₄	C ₃ +C ₄	C ₂ +18	C ₃ +C ₄	C ₃ +C ₄	C ₃ +C ₄	C ₃ +C ₄
70	C ₃ +C ₄	+80	+76	+84	C ₃ +C ₄	+80	+82	+83	+79
60	<185*	<185*	<185*	<185*	<185*	<185*	<185*	<185*	<185*
50	Br 66	Br 62	Br 45	Br 71	Br 69	Br 63	Br 63	Br 63	Br 59
40	OH 0.2	OH 0.5	OH 0.5	OH 0.4	OH 0.7	OH 2.4	OH 2.6	OH 2.7	OH 1.1
30	CO 0.7	CO 0.7	CO 0.7	CO 0.7	CO 0.7	CO 0.7	CO 0.7	CO 0.7	CO 0.7
20	185-352	185-352	185-352	185-352	185-352	185-352	185-352	185-352	185-352
10	352-464	352-464	352-464	352-464	352-464	352-464	352-464	352-464	352-464

Fig. 3.—Selectivity of reduced and carburized catalyst. Symbols denoting initial phases defined in Table I. * Average synthesis conditions.

At 7.8 atmospheres, the catalysts converted to cementite by thermal treatment of Hägg carbide and iron (X-249 and X-317) had high constant activities for as long as 14 weeks (Fig. 1). The average activity of these preparations was about twice that of the corresponding reduced sample (X-152), and the activity of the reduced sample decreased sharply with time. The behavior of cementite was similar to that observed for Hägg carbide (X-294), except that Hägg carbide was more active. The activity of cementite prepared from methane (X-268 and X-267) decreased rapidly with time, and the average activity was somewhat less than observed for the corresponding reduced catalyst (X-173).

In the synthesis at 21.4 atmospheres, however, the activity of the carbides decreased steadily with time, whereas the activity of the reduced catalyst remained essentially constant (Fig. 2). Hägg carbide (X-342) was most active at this pressure. The activity of cementite prepared by method B (X-329) was intermediate between that of Hägg carbide (X-342) and reduced catalyst (X-515). Cementite prepared from Hägg carbide and metallic iron (X-343) had a lower activity than reduced catalyst (X-515).

At 7.8 atmospheres, the selectivity of catalysts converted to cementite (Fig. 3) appears to be essentially independent of operating temperature; however, the catalysts operating at the higher temperatures (X-268 and X-276) were those carburized with methane, the other two (X-249 and X-317) having been prepared by thermal reaction of Hägg carbide with iron. The carburized catalysts produced a material of higher average molecular weight than that from reduced catalyst (X-152 and X-173). Usually for a given catalyst with the same pretreatment, the average molecular weight decreases with increasing temperature and, on this basis, the only positive statement that can be made from this group of data is that the catalysts carburized with methane yield a higher molecular weight product than reduced catalysts.

At 21.4 atmospheres, the average molecular weight of the product was greater than in corresponding tests at 7.8 atmospheres. However, no simple explanation can be offered for these data on the basis of initial phases or operating temperature.

At 7.8 atmospheres, the usage ratios, H_2/CO , with carburized catalysts (Table II) were significantly higher than with reduced catalysts, but in most tests at 21.4 atmospheres the usage ratios were about the same. In these experiments,

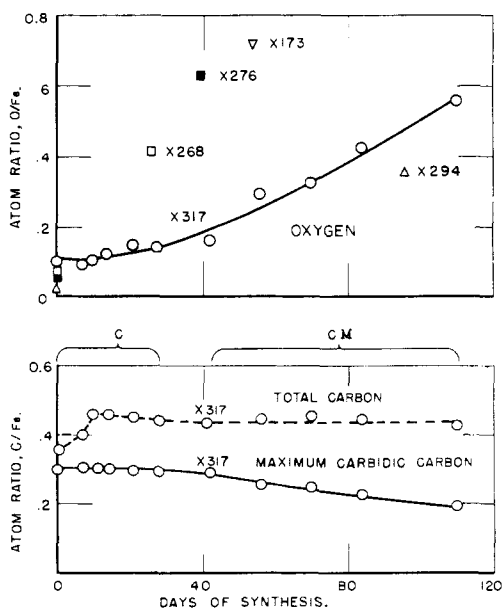


Fig. 4.—Composition changes of catalyst D3001 (converted to cementite by thermal reaction of Hägg carbide with iron) in synthesis at 7.8 atm. in test X317. For comparison the oxygen content is shown for catalysts containing initially metallic iron (X173), Hägg carbide (X294) and cementite from methane (X268 and X276).

the usage ratio is principally determined by the relative production of water and carbon dioxide and probably reflects the relative rates of a primary synthesis reaction producing water and a subsequent water-gas shift reaction.

Composition and Phase Changes.—Analytical data for catalyst samples before and after synthesis are presented in Table III, and Fig. 4 shows composition changes during the course of a 7.8-atmosphere test of a catalyst converted to cementite by method A. For comparison, typical data for oxygen content of reduced catalysts and samples converted to cementite by two different methods are included in this figure. Samples that had been used in synthesis were extracted with boiling toluene before analyses. The phases present were determined by X-ray diffraction. Chemical analyses were made for total content of iron and carbon, and oxygen was estimated by difference. Analyses for carbonates were made on a few representative samples by measuring the amounts of carbon dioxide evolved on acidifying the catalyst. The carbon dioxide evolved was 1–2 weight per cent. at 7.8 atmospheres and 6.4 weight per cent. at 21.4 atmospheres.

TABLE III

COMPOSITION AND PHASE CHANGES DURING SYNTHESIS

Test	Time, days	Atom or mole ratios			Phase from X-ray analyses ^b
		O/Fe	CO ₂ /Fe	Computed maximum carbidic C/Fe ^a	
7.8 atmospheres (absolute)					
X-249	0	c	c	c	αC
	55	0.395	c	0.354	C,M
X-268	0	.033	c	.237	αC
	26	.415 (.351) ^d	0.031	.318 (.287) ^d	CαM
X-276	0	.022	c	.401	C
	40	.632 (.561) ^d	.036	.559 (.523) ^d	CM
X-294	0	.024	c	.573	χ _α
	96	.357	c	.710	χ _M
X-317	0	.108	c	.363	C
	105	.562 (.528) ^d	0.18	.428 (.410) ^d	CM
X-173	0	.027	c	0.000	α
	54	.716	c	.292	Mα _χ
21.4 atmospheres (absolute)					
X-329	0	0.049	c	0.420	CαM
	40	1.298	c	.351	Mα
X-342	0	0.061	c	.573	χ _α
	37	1.47 (1.255) ^d	.110	.487 (.377) ^d	MαS
X-343	0	0.051	c	.308	Cα
	35	1.300 (1.047) ^d	.126	.299 (.173) ^d	MαC
X-515	0	0.017	c	0.000	α
	39	1.069	c	0.258	Mα _χ

^a Maximum carbide content assuming that all of the iron is present as Fe_3O_4 and Fe_3C . ^b Phases present in order of decreasing intensity of diffraction pattern: α = metallic iron, M = magnetite, C = cementite, χ = Hägg carbide, S = magnesite ($MgCO_3$) or siderite ($FeCO_3$). ^c Not determined. ^d Calculated, assuming carbon dioxide is present as $MgCO_3$.

In used carbided catalysts, the concentration of metallic iron is usually very small, and an estimate could be made of the maximum amount of carbidic carbon by assuming that iron was present only as carbide or magnetite. Previous work suggested that carbon dioxide was present principally as magnesium carbonate,^{6,7} and the data in parentheses in Table III were adjusted on this basis.

Pertinent results of Table III and Fig. 4 may be summarized as: 1. Atom ratios O/Fe increased during synthesis, approaching the value for magnetite in tests at 21.4 atmospheres. Catalysts converted to cementite by treatment with carbon monoxide or $2H_2 + 1CO$ oxidized at about the same rate as those made from Hägg carbide and iron; however, cementite prepared from methane (X-268 and X-276) oxidized more rapidly. Its higher rate of oxidation may have resulted from operation at higher temperatures, required to maintain constant conversions. These preparations oxidized at about the same rate as the corresponding reduced catalyst. 2. At 7.8 atmospheres (X-

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 carbide 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, H₂/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 cobalt¹³ 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 Electrode¹

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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 pH 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)₂²⁺, $K_2 = 10^{23.32}$; Hg(en)²⁺, $K_1 = 10^{14.3}$; Hg(en)(OH)⁺, $K_{101} = 10^{23.8}$; Hg(Hen)₂⁴⁺, $K_{020} = 10^{12.9}$; Hg(en)(Hen)³⁺, $K_{110} = 10^{18.6}$; and Hg(en)(Hen)₂⁴⁺, $K_{120} = 10^{22.2}$.

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)₂²⁺ in 1 M KNO₃ at 25° in a review by Bjerrum³ 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 pH's. Since the present paper was first submitted, Nyman, Roe and Masson⁴ 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

(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).