Acetohydroxamate complexes of some divalent metal ions

ACETOHYDROXAMATE COMPLEXES OF SOME DIVALENT METAL IONS

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OF

SOME DIVALENT METAL IONS

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INTRODUCTION

Studies of the stabilities of the metal complexes of acetohydroxamic acid have been limited to those of iron(III) (1,6) and copper(II) (8). The present investigation was undertaken in an attempt to establish the relative stabilities of the acetohydroxamate complexes of some divalent metal ions. Jannik Bjerrum's (2) well-known titration method seemed to be best suited for this study.

The limits of applicability of Bjerrum's method are set by the stability of the complexes involved, the solubility of the complexes, and the ease of hydrolysis of the free metal ion.

The amount of complex formed at the start of the titration should be very small. This may be reduced by depressing the initial pH or by decreasing the ligand to metal ion ratio. Depressing the initial pH is applicable if the stability of the first complex is not too great. If the first complex is very stable the initial pH must be quite low and a prohibitive amount of mineral acid is required. The measurement of very low pH values is also uncertain. Decreasing the ligand to metal ion ratio has the effect of raising the entire pH range over which complex formation takes place. This procedure is applicable as long as there is sufficient ligand to form the complexes and to prevent hydrolysis. This is likely to occur if the pH at which complex formation becomes essentially complete is much greater than the pH at which the free

metal ion begins to hydrolyze.

In general, if the complex is very stable, Bjerrum's method is not applicable. Thus, Dale (6) found some discrepancy between the values for the formation constant of the first iron(III) acetohydroxamate complex (FeR^{++}, R^{-}= acetohydroxamate ion) determined by a spectrophotometric method and by Bjerrum's method. Later work by Aksnes (1) supported Dale's spectrophotometrically determined value.

Bjerrum's method is also inapplicable if an insoluble complex is formed. Of the metal acetohydroxamates thus far studied only the copper(II) salt has a small solubility. An attempt by Giffin (8) to determine the formation constants of the copper(II) acetohydroxamate complexes by Bjerrum's method failed due to the formation of a precipitate of CuR_2.

In the present work Bjerrum's method was applied to the study of the acetohydroxamate complexes of iron(II), cobalt(II), nickel(II), and copper(II). It was hoped that using sufficiently low concentrations of copper(II) ion would prevent precipitation of CuR_2. Aksnes (1) stated that iron(II) does not form complexes with hydroxamic acids. Thus, one of the reasons for including iron(II) in the present study was to determine whether or not complex formation does take place. (Under Aksnes' experimental conditions it probably did not.) Also, a comparison of the stabilities of the complexes of iron in the two oxidation states seemed worthwhile. The choice of metal ions having successive

atomic numbers was to permit a correlation of the effect of the metal ion on the stability of the complex.

EXPERIMENTAL

APPARATUS

A Beckman Model G pH meter was used for determining titration curves from which equilibrium data were obtained. For standardizing solutions a Beckman H-2 or Zeromatic pH meter was used. These instruments were standardized against Beckman buffers of pH four or seven.

A five ml microburet graduated to 0.01 ml was used. Titrations under a nitrogen atmosphere were carried out in a 400-ml electrolytic beaker covered with a Plexiglas plate drilled to accommodate the electrodes, stirrer shaft, nitrogen delivery tube, and buret tip. Prepurified nitrogen (Olin-Matheson Co.) was used without further purification except for titrations involving iron(II) ion, in which case the nitrogen was passed through alkaline pyrogallol to remove the last traces of oxygen.

MATERIALS

The acetohydroxamic acid was prepared by Mr. Floyd Farha by Hoffmann's method (9). It was recrystallized from ethyl acetate before use. Solutions of the acid were prepared determinately on the day that they were used. All other chemicals were analytical reagent or primary standard grade.

Approximately 0.1 molar stock solutions of cobalt(II), nickel(II), and copper(II) perchlorates were prepared from the appropriate hydrated salts (G. Frederick Smith Chemical Co.). The solutions were standardized by potentiometric titration with

EDTA. A mercury electrode in the presence of a drop of 0.1 molar mercuric-EDTA complex in the solution being titrated indicated the endpoint (15). The source of iron(II) was ferrous ammonium sulfate hexahydrate (Mallinckrodt); stock solutions were prepared determinately just prior to use.

Approximately 0.25 molar solutions of disodium dihydrogen ethylenediamine tetraacetate dihydrate (J. T. Baker Chemical Co.) were standardized potentiometrically against a 0.1 molar standard copper solution. The latter was prepared by dissolving about 0.635 gram of assayed copper foil (J. T. Baker Chemical Co.) in nitric acid. The resulting solution was diluted to 100 ml with water.

Solutions of the mercuric-EDTA complex were prepared in a manner similar to that described by Schmid and Reilley (13) except that the mercuric nitrate and EDTA solutions were more concentrated (0.4 molar). Also, nitric acid was used to effect solution of the mercuric nitrate.

Carbonate-free sodium hydroxide solutions were prepared by dilution of appropriate quantities of filtered 50 percent (about 18 molar) sodium hydroxide (12). Deionized water which had been boiled to remove carbon dioxide was used in the preparation of these and all other solutions. The sodium hydroxide solutions were standardized against potassium acid phthalate (Mallinckrodt).

A 0.1047 normal solution of perchloric acid was prepared from 70 percent acid (J. T. Baker Chemical Co.). It was standardized by comparison with standard sodium hydroxide.

One molar solutions of potassium nitrate were prepared determinately using the dried reagent (Mallinckrodt).

Acetic acid-sodium acetate and ammonium hydroxide-ammonium chloride buffers of pH five and nine, respectively, were used for buffering the solutions being titrated in the potentiometric standardizations of the EDTA and metal salt solutions.

PROCEDURE

In all of the titrations described in this section, the ionic strength of the solution being titrated was adjusted to 0.1 with potassium nitrate. The initial volume of the solution was always 100 ml. The temperature was maintained constant at 25°C. All of the titrations were carried out under a nitrogen atmosphere.

The ionization constant of acetohydroxamic acid was determined by titrating five millimoles of the acid with 1.156 normal sodium hydroxide. The pH at the midpoint of the titration curve gave the negative logarithm of the ionization constant.

Two titrations were required to determine the formation constants of the complexes of a given metal ion. For both titrations the solution being titrated contained five millimoles of acetohydroxamic acid, 0.1 millimole of perchloric acid, and ten millimoles of potassium nitrate. One of the solutions contained, in addition, 0.05 millimole of the appropriate metal ion. Two or three such sets of titrations were carried out for each metal ion. The titrant was approximately 0.1 normal sodium hydroxide.

The perchloric acid was used to depress the initial pH until

complex formation was negligible. The purpose of the large excess of acetohydroxamic acid was to lower the entire pH range of complex formation to such an extent that the reaction was essentially complete at the pH at which the free metal began to hydrolyze (7).

When copper(II) was the metal ion involved, the amount of acetohydroxamic acid was reduced from five millimoles to one millimole.

An "oxygen-free" solution of sodium hydroxide was prepared and used as titrant when the metal ion was iron(II).

DATA AND RESULTS

IONIZATION CONSTANT OF ACETOHYDROXAMIC ACID

At the midpoint of the titration curve of a weak acid

$$pH = pk$$

where k is the ionization constant of the acid.

The value of pk for acetohydroxamic acid was thus found to be 9.40 ± 0.01. The corresponding value of k was 4.0×10^{-10}.

FORMATION CURVES

Bjerrum (2) defined the function $\bar{n}$ as the average number of ligands bound per metal ion. If all of the first complex (MR^{n-1}) is formed before any of the second complex (MR_2^{n-2}) is formed and so on, then, when $\bar{n} = 1/2$, $pk_1 = \log [R^-]$ and similarly, when $\bar{n} = 3/2$, $pk_2 = \log [R^-]$ (5). Thus, pk values can be read directly from a "formation curve," a plot of $\bar{n}$ as a function of $\log [R^-]$. Representative formation curves for the complexes of the metal ions studied are shown in Figures I and II. The corresponding data are given in Table I.

Values of $\bar{n}$ were calculated with the aid of the titration curves. A pair of titration curves for cobalt(II) as the metal ion is shown in Figure III. The horizontal distance (d) between the two curves at a given pH represents the amount of sodium hydroxide required to titrate the hydrogen ion liberated by the formation of the complexes according to the equations

$$M^{++} + HR \longrightarrow MR^{+} + H^{+}$$

TABLE I

Values of $\bar{n}$ and log $[\bar{R}]$

	Cobalt(II)		Nickel(II)	
pH	$\bar{n}$	log $[\bar{R}]$	$\bar{n}$	log $[\bar{R}]$
3.75	0.040	-6.95	0.044	-6.95
4.00	0.044	-6.71	0.044	-6.71
4.25	0.060	-6.46	0.060	-6.45
4.50	0.094	-6.21	0.116	-6.21
4.75	0.131	-5.96	0.181	-5.96
5.00	0.209	-5.71	0.287	-5.71
5.25	0.326	-5.46	0.442	-5.46
5.50	0.473	-5.21	0.612	-5.21
5.75	0.658	-4.96	0.801	-4.96
6.00	0.845	-4.71	0.992	-4.71
6.25	1.046	-4.46	1.185	-4.46
6.50	1.271	-4.21	1.382	-4.21
6.75	1.476	-3.97	1.554	-3.97
7.00	1.662	-3.72	1.711	-3.72
7.25	1.800	-3.47	1.932	-3.47
7.50	1.989	-3.23	2.052	-3.23
7.75	1.919	-2.98	1.972	-2.98
8.00	1.770	-2.74	2.300	-2.75

TABLE I (CONTINUED)

	Copper(II)		Iron(II)	
pH	$\bar{n}$	log $[R^-]$	$\bar{n}$	log $[R^-]$
3.07	0.192	-8.34	-	-
3.25	0.293	-8.16	-	-
3.50	0.524	-7.92	-	-
3.75	0.649	-7.67	0.073	-6.95
4.00	0.784	-7.42	0.103	-6.71
4.25	0.947	-7.18	0.119	-6.46
4.50	1.088	-6.93	0.150	-6.21
4.75	1.213	-6.69	0.185	-5.96
5.00	1.361	-6.44	0.242	-5.71
5.25	1.516	-6.19	0.319	-5.46
5.50	1.667	-5.95	0.418	-5.21
5.75	1.772	-5.70	0.568	-4.96
6.00	1.862	-5.45	0.788	-4.71
6.25	1.921	-5.20	1.022	-4.46
6.50	1.954	-4.96	1.257	-4.22
6.75	2.003	-4.71	1.474	-3.97
7.00	2.019	-4.46	1.673	-3.72
7.25	-	-	1.905	-3.47
7.50	-	-	2.088	-3.23
7.75	-	-	2.235	-2.99
8.00	-	-	2.347	-2.75

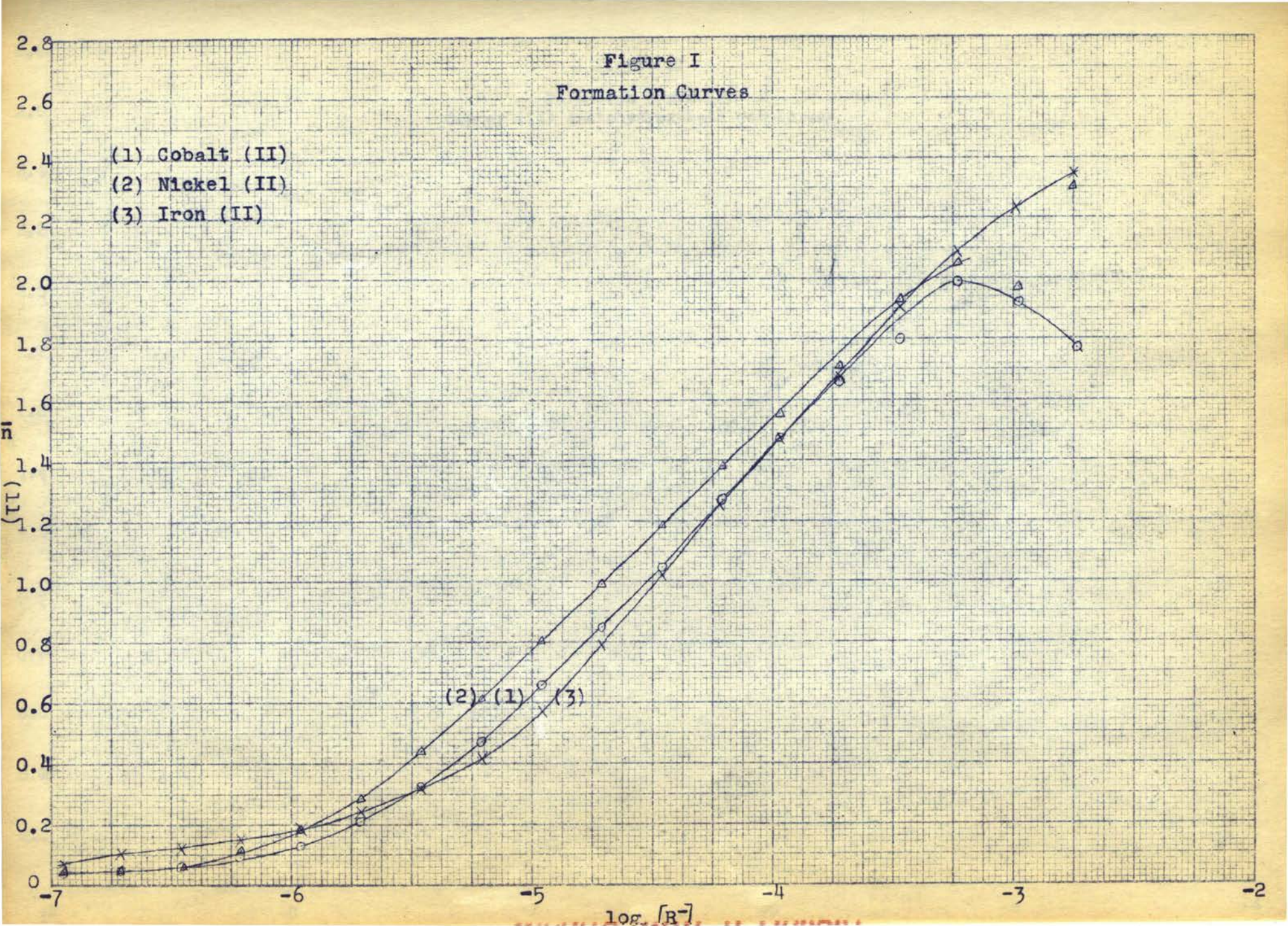
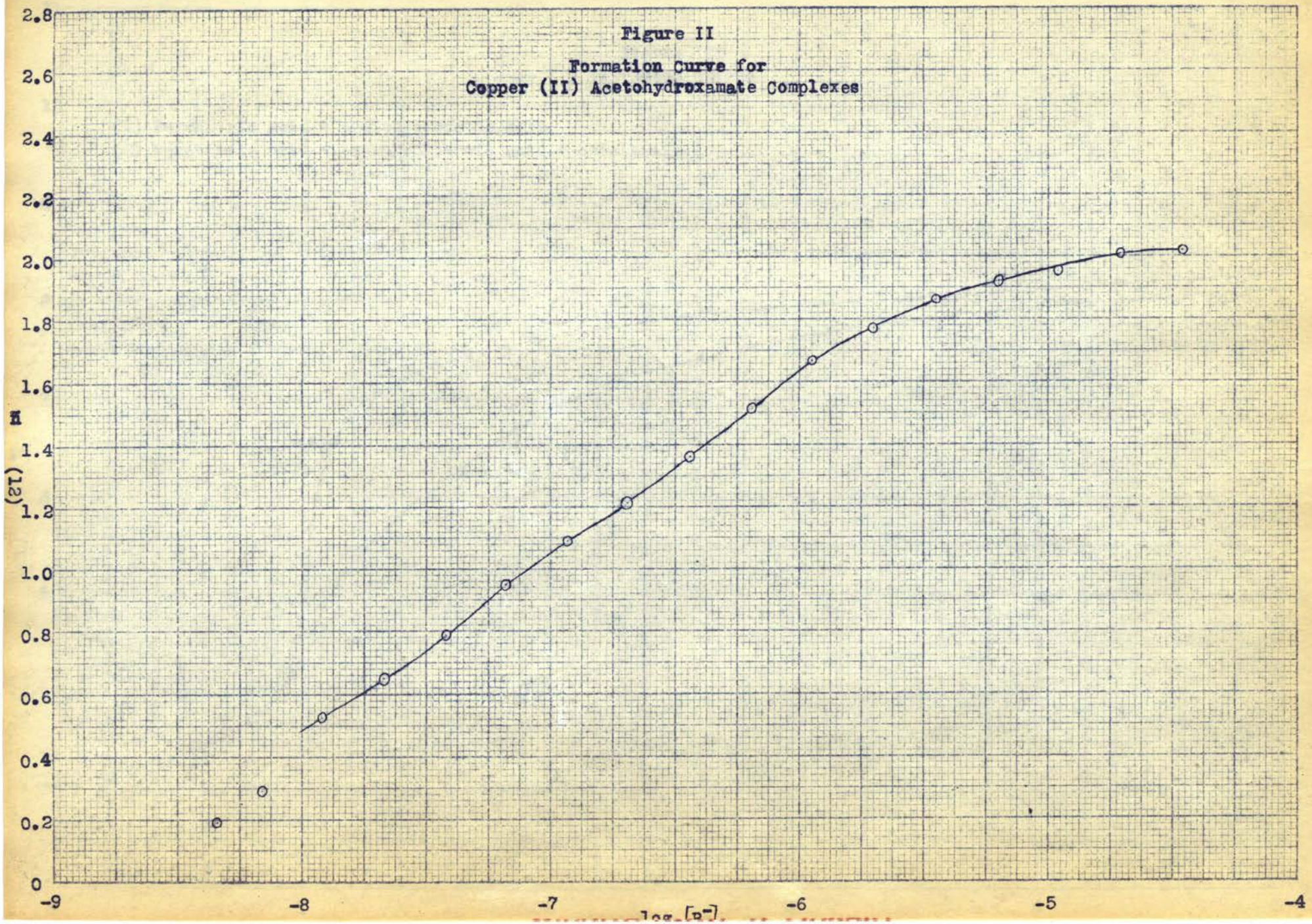


Figure I
Formation Curves
(1) Cobalt (II)
(2) Nickel (II)
(3) Iron (II)
$\bar{n}$ (II)
log. [R⁻]
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-7
-6
-5
-4
-3
-2
(2)
(1)
(3)

Figure II

Formation Curve for
Copper (II) Acetohydroxamate Complexes



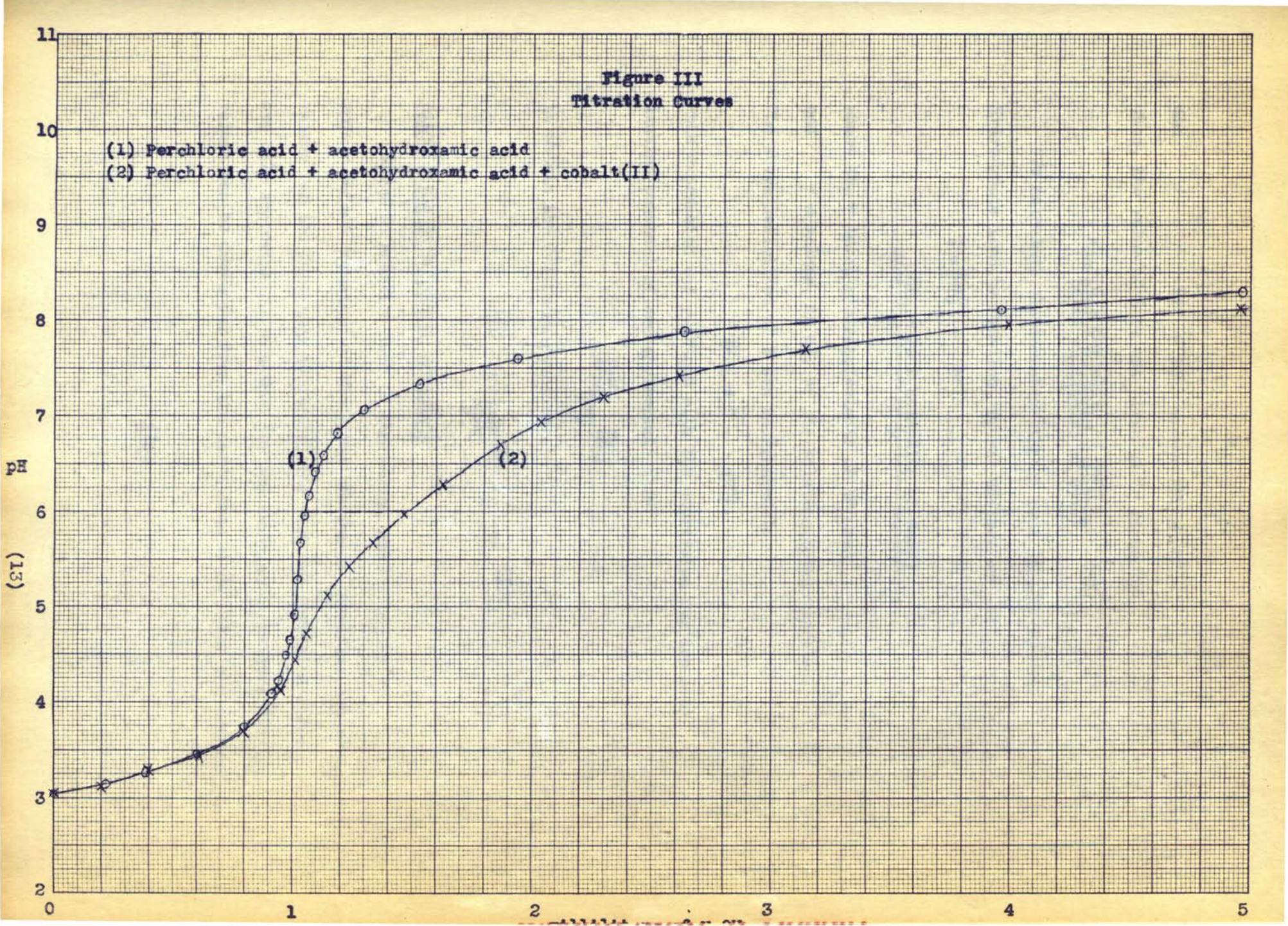


Figure III
Titration Curves
(1) Perchloric acid + acetohydroxamic acid
(2) Perchloric acid + acetohydroxamic acid + cobalt(II)
pH
(13)
(1)
(2)
11
10
9
8
7
6
5
4
3
2
0
1
2
3
4
5

and $$MR^+ + HR \longrightarrow MR_2 + H^+.$$

Thus, the value of $\bar{n}$ at the given pH is given by

$$\bar{n} = \frac{\text{d x normality of NaOH}}{\text{total millimoles of metal}} \quad (5).$$

To calculate the concentration of free ligand (acetohydroxamate ion), a function, B, was defined as

$$B = [HR] + [R^-]$$

$$= \frac{HR_T - (\text{d x normality of NaOH})}{V}$$

where HR_T = total milliequivalents of HR used

and V = volume, in ml, of the solution being titrated.

The above definition of B was rearranged to

$$[HR] = B - [R^-].$$

This expression was combined with the expression for the ionization constant of acetohydroxamic acid

$$\frac{[H^+]\ [R^-]}{[HR]} = k$$

to obtain the following equation:

$$[R^-] = \frac{B}{\frac{[H^+]}{k} + 1} \quad (5).$$

CALCULATION OF FORMATION CONSTANTS

Since in practice some of the second complex begins to appear before formation of the first complex is complete, the pk values for the formation constants read from the formation curve are only approximate. A method for the calculation of more precise values can be developed from the definition of $\bar{n}$. When the maximum

number of ligands which can be bound to a single metal ion is two, $\bar{n}$ can be defined symbolically as

$$\bar{n} = \frac{[MR^+] + 2[MR_2]}{[M^{++}] + [MR^+] + [MR_2]} .$$

The expressions

$$k_1 = \frac{[MR^+]}{[M^{++}][R^-]}$$

and

$$k_1 k_2 = \frac{[MR_2]}{[M^{++}][R^-]^2}$$

can be used to transform this equation for $\bar{n}$ into Bjerrum's "formation function" (2),

$$\bar{n} = \frac{k_1[R^-] + 2k_1k_2[R^-]^2}{1 + k_1[R^-] + k_1k_2[R^-]^2} .$$

The formation function can be written as two simultaneous equations by employing two values of $\bar{n}$ and the corresponding concentrations of free ligand. These simultaneous equations can be solved for the formation constants, k_1 and k_2. By solving these equations Block and McIntyre (3) have derived a simple and convenient set of formulas which permit the direct calculation of k_1 and k_2.

Values of the formation constants of the acetohydroxamate complexes studied were calculated by means of these formulas. The values obtained are listed in Table II.

TABLE II

Formation Constants

Metal Ion		k_1	k_2
Cobalt(II)*		1.2×10^5	1.1×10^4
		1.1×10^5	0.9×10^4
		1.1×10^5	1.0×10^4
	(average)	1.1×10^5	1.0×10^4
Nickel(II)*		2.0×10^5	1.3×10^4
		1.9×10^5	1.5×10^4
	(average)	2.0×10^5	1.4×10^4
Copper(II)*		8.0×10^7	1.7×10^6
		7.7×10^7	1.8×10^6
	(average)	8×10^7	1.8×10^6
Iron(II)**		1.6×10^5	1.2×10^4
		1.1×10^5	1.6×10^4
		0.7×10^5	2.3×10^4
		1.2×10^5	0.9×10^4
		1.0×10^5	1.1×10^4
		0.8×10^5	1.3×10^4
	(average)	$\sim 10^5$	$\sim 10^4$

*Each of the values above the line is an average of five or six values computed from data derived from a single pair of titration curves. The values below the line are averages of the

values above the line.

**Each pair of values for k_1 and k_2 above the line was computed from a single set of data. Each group of three pairs of values was computed from data from a single pair of titration curves.

DISCUSSION AND CONCLUSIONS

Since the pH measurements determine the maximum obtainable precision in Bjerrum's method, the experimental conditions should be adjusted to minimize the effect of the normal uncertainties in the pH measurements.

Experimentally, $\bar{n}$ is the number of hydrogen ions produced per metal ion. Thus, it is necessary that the only reaction producing hydrogen ions be the formation of the complexes, and that the only reaction consuming hydrogen ions be the reaction with the hydroxide ions of the titrant.

Except in the region of high $\bar{n}$ values these conditions were best realized in the determination of the formation constants of the cobalt(II) and nickel(II) complexes.

The formation curve for the cobalt(II) complexes generally exhibited a maximum which approached a $\bar{n}$ value of two. That it did not always do this suggests that this behavior might have been due to errors in pH measurements.

The points for the formation curve of the nickel(II) complexes were too scattered at $\bar{n}$ values much above two to define a curve. Those values which appeared to exceed two were not at all reproducible.

In the region of high $\bar{n}$ values ideal conditions were best realized in the determination of the formation constants of the copper(II) complexes. This was probably due in part to the large slopes of the titration curves in the region where $\bar{n}$ values near

two were measured.

The formation curve for the copper(II) system was not well defined in the region of small $\bar{n}$ values. This was probably due to the considerable amount of complex formation that took place during the initial horizontal portion of the titration curves where the distance d could not be accurately measured. The formation curve leveled off at $\bar{n}$ values very near two.

The use of the low concentration of copper(II) ion eliminated the problem, encountered by Giffin (8), of formation of a precipitate of CuR_2. However, the large formation constants of the copper(II) acetohydroxamate complexes made it impractical to depress the initial pH as much as was desirable.

Bjerrum's method might yield better results in the study of these complexes by using appropriate mixed solvents as suggested by Giffin (8). Irving and Rossotti (10) have described a method for the determination of formation constants in mixed solvents which does not require a knowledge of hydrogen ion concentration or activity.

Schwarzenbach and Freitag (14) have used a modification of Bjerrum's method for determining the formation constants of complexes of high stability. Such a modification might be of value applied to the copper(II) acetohydroxamate complexes.

The value for the formation constant, k_1, of the first copper(II) acetohydroxamate complex (CuR^+) obtained in the present work was 8×10^7. This was in good agreement with the value, 9.38×10^7, determined by Giffin (8) using a spectrophotometric

method.

The formation curve for the iron(II) complexes was distorted in the region of small $\bar{n}$ values due to the oxidation of some of the iron(II) to iron(III) and subsequent formation of iron(III) complexes. Most of the oxidation was probably caused by oxygen which had not been removed from the titrant. The formation curve reached values considerably larger than two and showed no marked tendency to level off. This was perhaps due to hydrolysis or the formation of a higher complex. These possibilities might merit further investigation.

The iron(II) complexes can probably be dealt with satisfactorily by taking sufficient precautions to prevent oxidation of the metal ion. A larger excess of acetohydroxamic acid might be necessary since, according to Britton (4), iron(II) hydrolyzes at a lower pH than do cobalt(II) and nickel(II).

The order of stability of the acetohydroxamate complexes of the various metal ions determined in the present work was

$$Cu^{++} \gg Ni^{++} > Co^{++} > Fe^{++}.$$

The position of iron(II) was somewhat in doubt. This order agrees with that given by Mellor and Maley (11) which was determined from data for different ligands.

The values for the formation constants of the iron(III) acetohydroxamate complexes determined by Dale (6) were 1.7×10^{11}, 1.3×10^{9}, and 3.2×10^{7} for k_1, k_2, and k_3, respectively. These were much larger than the 10^{5} and 10^{4} for k_1 and k_2 of the iron(II) complexes obtained in the present work.

The value obtained for the ionization constant of acetohydroxamic acid is compared in Table III with other values which have been determined by the same method.

TABLE III

Ionization Constant of Acetohydroxamic Acid

Source	k	Conditions
Dale (6)	5.0×10^{-10}	$t = 25^{\circ}C$; $\mu = 0.3$
Wise and Brandt (16)	4.0×10^{-10}	$t = 20^{\circ}C$; μ unadjusted
present work	4.0×10^{-10}	$t = 25^{\circ}C$; $\mu = 0.1$

SUMMARY

The formation constants of the acetohydroxamate complexes of four divalent metal ions were determined at a temperature of 25°C and an ionic strength of 0.1. The values obtained are listed in the following table.

Metal Ion	k_1	k_2
Cobalt(II)	1.1×10^5	1.0×10^4
Nickel(II)	2.0×10^5	1.4×10^4
Copper(II)	8×10^7	1.8×10^6
Iron(II)	$\sim 10^5$	$\sim 10^4$

The ionization constant of acetohydroxamic acid was determined for the same conditions of temperature and ionic strength. The value obtained was 4.0×10^{-10}.

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