may possibly be explained by the difference in atomic volume of the two components.

In an explanation of this asymmetry, the importance of atomic size may arise from its effect on the number of nearest neighbors in the mixture. Thus the larger bismuth atoms, in a matrix primarily of smaller gold atoms, will have a larger number of nearest neighbors than the small gold atoms, in a matrix primarily of larger bismuth atoms. To the author's knowledge, no attempt has been made in the literature to evaluate this effect quantitatively, but it may be assumed to play an important part in the understanding of the energetic asymmetry of binary mixtures.

There is also a fair amount of qualitative support for the idea that the magnitude of ΔH is related to a difference in size between the two components. It is, for example, well known that pairs of metals of widely different atomic size frequently show limited miscibility in the liquid state. It may be mentioned that the same point of view underlies discussions of the size factor in connection with solid solubility.

The effect of size differences on specific heat and, consequently, on heat and entropy of mixing gives further support for the same idea. However, although it is clear that this difference in specific heat should contribute toward the measured positive value of ΔH at elevated temperature, one also has to take into account the hypothetical interaction energy at the absolute zero. We are, at the present time, unable to estimate the relative importance of these two factors.

Acknowledgments.—The author is indebted to Miss M. C. Bachelder, Mr. Adolph Roman and Mr. L. J. Howell for carrying out the analytical work involved in the present investigation.

Summary

The thermodynamic properties of the liquid systems bismuth–gold and thallium–gold have been investigated by the electromotive force method.

Both systems show the expected large entropies of mixing, which are believed to originate in the large differences in atomic size between the two components.

In the system bismuth–gold the combined effect of the entropy and a fairly large positive ΔH of mixing (1 kcal./g. atom in the middle of the system) is to give the system a nearly ideal appearance at 700°. In the thallium–gold system the large entropy terms entirely overshadow the heat terms, causing the system to show fairly large negative deviations from Raoult's law.

CHICAGO, ILLINOIS RECEIVED JUNE 19, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Iron with 1,10-Phenanthroline. IV. Application to Investigation of Zinc Phenanthroline Complexes

BY I. M. KOLTHOFF, D. L. LEUSSING AND T. S. LEE[1]

Zinc ion has been shown to form three complexes with 1,10-phenanthroline in aqueous solution: the mono-, di- and tri-1,10-phenanthroline zinc ion. The equilibrium constants for these complexes have been evaluated and found to be 3.7×10^{-7}, 7×10^{-13} and 1×10^{-17} for K_1, K_2 and K_3, respectively, at 25°.

Zinc has been observed to interfere in the colorimetric determination of iron by 1,10-phenanthroline,[2] indicating that 1,10-phenanthroline forms one or more relatively strong complexes with zinc. Additional evidence for the existence of zinc–phenanthroline complexes is that solid zinc triphenanthroline[3] and the similar mono- and tridipyridyl complexes have been described in the literature.[4]

The following investigation has been carried out in order to establish the nature and equilibrium constants of the zinc–phenanthroline complexes in aqueous solutions. This investigation also illustrates how knowledge of the complex ions of one metal (ferrous phenanthroline complexes) may be used in the study of the complex ions of another metal.

The dissociation constant of the mono-phenanthroline-zinc ion was evaluated by allowing zinc and ferrous iron to compete for a limited amount of phenanthroline and measuring the equilibrium concentration of triphenanthroline ferrous ion (ferroin) spectrophotometrically. The dissociation constants of the di- and triphenanthroline zinc complexes were evaluated from experiments in which the equilibrium distribution of phenanthroline between chloroform and aqueous zinc solution was determined. In addition, conductometric measurements were made which verify the results obtained by both of the above methods.

Monophenantholine Zinc Ion: Competition Experiments

The molar concentration, y, of *o*-phenanthroline present as zinc complexes in a solution containing zinc, ferrous iron and phenanthroline is given by the expression

$$y = C_{\mathrm{Ph}} - 3[\mathrm{FePh_3}^{++}] - [\mathrm{FePh}^{++}] \qquad (1)$$

where C denotes total, analytical concentration brackets represent actual concentrations, and Ph represents the phenanthroline molecule. Under the experimental conditions used the concentration of free phenanthroline can be neglected in equation

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(1) Department of Chemistry, University of Chicago, Chicago, Illinois.

(2) Smith and Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. Frederick Smith Chemical Co., Columbus, Ohio; E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 271.

(3) F. Blau, *Monatsh.*, **19**, 647 (1898); P. Pfeiffer and Fr. Tapperman, *Z. anorg. allgem. Chem.*, **215**, 273 (1933); P. Pfeiffer and K. Quehl, *Ber.*, **64**, 2667 (1931); **65**, 560 (1932).

(4) F. M. Jeager and J. A. van Dijk, *Z. anorg. allgem. Chem.*, **227**, 273 (1936).

TABLE I

APPARENT INSTABILITY CONSTANTS OF ZINC–PHENANTHROLINE COMPLEXES

$pH = 5.0, C_{Fe^{++}} = 1.86 \times 10^{-4}\ M$

Expt.	$C_{Zn} \times 10^4$	$C_{Ph} \times 10^4$	Extinction at 500 mμ	$[FePh_3^{++}]$[a] $\times 10^5$	$[FePh^{++}]$[b] $\times 10^6$	$y \times 10^4$	"Apparent" values $K_1 \times 10^7$	$K_2 \times 10^{14}$	$K_3 \times 10^{22}$	True value K_1[c] $\times 10^7$
1	22.7	0.91	0.012	0.11	2.1	0.86	3.65	1.08	2.3	3.65
2	18.2	.91	.020	.19	2.5	.83	3.63	1.29	3.4	3.65
3	13.6	.91	.039	.36	3.1	.77	3.60	1.64	5.2	3.75
4	9.1	.91	.0825	.77	3.7	.64	3.72	2.16	9.2	3.70
5	9.1	2.72	.502	4.69	5.9	1.25	3.48	4.16	36	3.75
6	5.45	2.72	.648	6.06	6.0	0.84	3.46	4.74	46	3.71
7	2.72	2.72	.790	7.33	5.9	.46	3.42	5.26	57	3.73
8	0.91	2.72	.890	8.32	5.8	.17	3.28	5.54	64	3.6
9	.68	2.72	.898	8.39	5.8	.14	2.94	5.05	59	3.2
10	.455	2.72	.915	8.55	5.8	.10	2.72	4.75	57	3.0

[a] Calculated from extinction: $[FePh_3^{++}] = \text{Extn.}/1.07 \times 10^4$. [b] Calculated from equation (2). [c] Corrected for the presence of $[ZnPh_2^{++}]$ assuming $K_2 = 7 \times 10^{-13}$.

(1). The concentration of $FePh_2^{++}$ has also been neglected because this ion is not stable in aqueous solutions.[5]

The absorption of light at 500 mμ by solutions containing zinc chloride, ferrous ammonium sulfate, phenanthroline and acetate buffer was shown to be due entirely to $FePh_3^{++}$ ("ferroin"), the $FePh^{++}$ being very pale yellow and the other components being colorless.[5] The concentration of ferroin was, therefore, found directly from the extinction of the solution at 500 mμ. The concentration of $FePh^{++}$ was calculated from equation (2) by successive approximations.

$$[FePh^{++}] = [K_3^{1/3}/K_1]\cdot[FePh_3^{++}]^{1/3}\cdot(C_{Fe} - [FePh_3^{++}] - [FePh^{++}])^{2/3} \qquad (2)$$

where K_3 represents the dissociation constant of ferroin (5×10^{-22} at 25°)[6] and K_1 that of $FePh^{++}$ (1.3×10^{-6} at 25°).[5]

The value of y, calculated from equations (1) and (2) can be used to calculate the apparent dissociation constant of phenanthroline–zinc ion containing n phenanthroline molecules per zinc atom.

$$ZnPh_n^{++} \rightleftharpoons Zn^{++} + nPh \qquad (3)$$

$$K_n = \frac{[Zn^{++}][Ph]_n}{[ZnPh_n^{++}]} \qquad (4)$$

$$K_n = \frac{n}{y}\left(C_{Zn} - \frac{y}{n}\right)\left(\frac{K_3[FePh_3^{++}]}{C_{Fe} - [FePh_3^{++}] - [FePh^{++}]}\right)^{n/3} \qquad (5)$$

Equation (5) gives the apparent value of the dissociation constant of a phenanthroline-zinc ion assuming that only one zinc complex (with n phenanthroline molecules per zinc atom) is present.

In Table I are given the results of a series of experiments and the calculated values of K_n corresponding to n = 1, 2 and 3. The values of K_n for n = 1 (column 8) were found to vary only 10% as the ratio of phenanthroline to total concentration of zinc was varied from 0.04 to 3 (experiments 1–8). On the other hand, K_n for n = 2 varied fivefold and K_n for n = 3 varied twenty-eight fold over the same range. It can be concluded that under the conditions of experiments 1–8 the monophenanthroline-zinc was the only zinc complex present at appreciable concentration.

From the experiments described in the section "di- and triphenanthroline-zinc ions" the dissociation constant of the diphenanthroline zinc was evaluated. Application of this value to the experiments of Table I shows that a very small concentration of the diphenanthroline complex was present in the solutions of experiments 5–10. Upon correcting for the presence of diphenanthroline complex the average value of K_1, the dissociation constant of monophenanthroline zinc was found to be 3.7×10^{-7} (last column, Table I).

In addition to the experiments described above a modification of Job's method of continuous variations[7] was employed to find the predominant species of phenanthroline–zinc complexes present in solutions containing a very low concentration of free phenanthroline. A series of solutions was prepared in which the ferrous ammonium sulfate concentration and the sum of the molar concentrations of zinc and phenanthroline were held constant. The values of y, the equilibrium molar concentration of phenanthroline present as zinc complexes, were calculated from the measured ferroin concentrations and equations (1) and (2) and are given in Table II. Values of y corresponding to different values of R were plotted where

$$R = \frac{C_{Zn}}{C_{Zn} + C_{Ph}} \qquad (6)$$

TABLE II

METHOD OF CONTINUOUS VARIATIONS

$pH = 5.0, C_{Fe} = 1.86 \times 10^{-4}\ M, C_{Zn} + C_{Ph} = 2.72 \times 10^{-4}\ M$

$C_{Zn} \times 10^4$	$C_{Ph} \times 10^4$	R	Extinction at 500 mμ	$[FePh_3^{++}] \times 10^5$	$[FePh^{++}] \times 10^6$	$y \times 10^5$
2.17	0.55	0.80	0.118	1.10	4.2	1.8
2.04	.68	.75	.166	1.55	4.7	1.7
1.95	.77	.72	.190	1.78	4.8	1.9
1.81	.91	.67	.235	2.20	5.1	2.0
1.63	1.09	.60	.305	2.85	5.5	1.8
1.36	1.36	.50	.409	3.82	5.8	1.6
1.08	1.64	.40	.510	4.77	5.9	1.5
0.90	1.82	.33	.582	5.44	6.0	1.3
.77	1.95	.29	.692	5.88	5.8	1.3
.68	2.04	.25	.670	6.26	6.1	1.0
.54	2.18	.20	.725	6.77	6.0	0.9

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(5) I. M. Kolthoff, D. L. Leussing and T. S. Lee, THIS JOURNAL, **72**, 2173 (1950).

(6) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *ibid.*, **70**, 2348 (1948).

(7) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

As R was varied from 0 to 1 the value of y was limited first by the total concentration of zinc and then by the total concentration of phenanthroline. In Fig. 1 the experimental points are compared with a theoretical curve calculated by assuming that monophenanthroline–zinc is the only zinc complex present and that the value of the dissociation constant K_1 is that calculated from the experiments of Table I. The agreement between the theoretical curve and the experimental points is satisfactory. A theoretical curve (II) was also calculated on the assumption that the only zinc complex present was $ZnPh_2^{++}$. A hypothetical value of the dissociation constant (5×10^{-14}) was chosen so as to give agreement of the theoretical curve with the experimental points in the region where R is small. There is no agreement of curve II with the points in the region where R is large, indicating that diphenanthroline-zinc is not the predominant species. A theoretical curve corresponding to the triphenanthroline-zinc ion would show still less agreement with the experimental points.

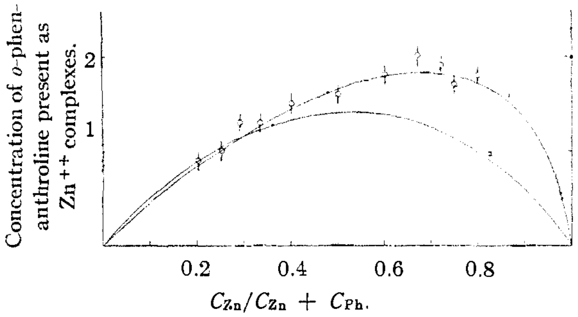

Fig. 1.—Method of continuous variations: $C_{Fe} = 1.86 \times 10^{-4}$ M. $C_{Zn} + C_{Ph} = 2.72 \times 10^{-4}$ M, $pH = 5.0$: curve I, calculated from values of $K_{ZnPh^{++}} = 3.7 \times 10^{-7}$; curve II, calculated from apparent value of $K_{ZnPh_2^{++}} = 5.0 \times 10^{-14}$. Circles are experimental points.

It should be mentioned here that in all of the experiments of Tables I and II an excess of ferrous ion over phenanthroline was present. Consequently the concentration of free phenanthroline was so small that the diphenanthroline– and triphenanthroline–zinc complexes would not be expected to form (see Fig. 2).

Experimental Details of Competition and Method of Continuous Variations

Zinc chloride and 1,10-phenanthroline solutions, buffered at pH 5.0 (acetate buffer) were mixed in varying proportions and diluted to the desired volume using the pH 5.0 buffer. A 20-ml. aliquot was removed, bubbled with nitrogen and 2 ml. of a freshly prepared 2.04×10^{-3} M ferrous ammonium sulfate solution was added. This amount of ferrous solution is in slight excess of that required to react quantitatively for the formation of ferroin with all the o-phenanthroline present. The solution was again bubbled with nitrogen and allowed to come to equilibrium at 25°. Equilibrium was reached within one to three hours. The equilibrium concentration of the ferroin was then measured spectrophotometrically.

Di- and Triphenanthroline-zinc Ions.—Experiments in which phenanthroline was allowed to distribute between aqueous zinc solution and chloroform were carried out to study the zinc complex ions $ZnPh_n^{++}$ where n is greater than 1. For such experiments it was necessary first to determine the distribution coefficient, K_d, of free phenanthroline between chloroform and water. The value of K_d was found by determining the amount of phenanthroline extracted by chloroform from an aqueous solution containing phenanthrolium chloride and hydrochloric acid.

$$K_d = [Ph]_{CHCl_3}/[Ph] \quad (7)$$

$$= [Ph]_{CHCl_3}[H^+]\gamma_{H^+}/K_a[PhH^+]\gamma_{PhH^+} \quad (8)$$

where brackets represent equilibrium concentrations in the aqueous phase unless otherwise specified, K_a is the acid dissociation constant of the phenanthrolium ion (1.1×10^{-5}), and γ represents activity coefficients in the aqueous phase. The value of $[Ph]_{CHCl_3}$ was determined spectrophotometrically (see Experimental details). The values of the other terms in equation (8) were calculated as

$$[PhH^+] = C_{Ph} - [Ph]_{CHCl_3} \quad (9)$$

$$[H^+] = C_{H^+} - [PhH^+] \quad (10)$$

where C_{Ph} represents the sum of total concentrations of phenanthroline in both phases (equal volumes of both phases were used in all experiments). Equations (9) and (10) are based on the assumption that no appreciable concentrations of phenanthrolium chloride or of hydrochloric acid exist in a chloroform phase in equilibrium with an aqueous phase. This was established experimentally. The ratio $\gamma_{H^+}/\gamma_{PhH^+}$ of equation (8) was assumed to be unity. The experimental results are given in Table III. It is seen that the value of K_d remained essentially constant when the values of total concentrations of phenanthroline and acid were varied over a wide range. The average value of K_d at 25° is $9 \pm 1 \times 10^2$.

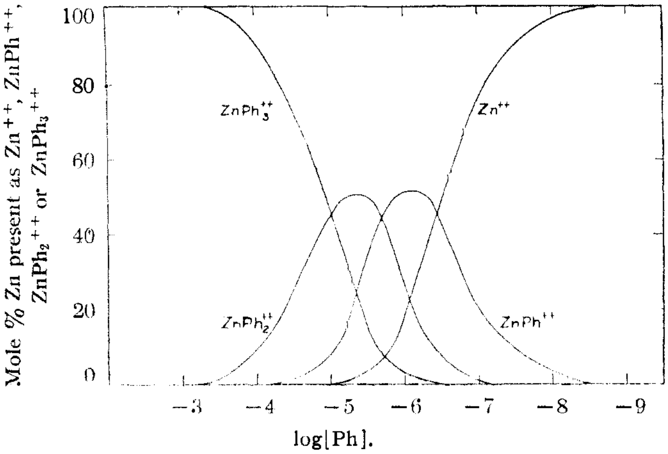

Fig. 2.—Relative amounts of zinc as aquo-zinc ion and as o-phenanthroline complex ions as a function of free phenanthroline concentration in the solution.

The concentration of free phenanthroline in an

TABLE III

DETERMINATION OF THE DISTRIBUTION COEFFICIENT OF 1,10-PHENANTHROLINE BETWEEN CHLOROFORM AND WATER

Ionic strength = 0.1 M, $K_a = 1.1 \times 10^{-5}$

C_{Ph} $M \times 10^4$	C_{H^+} M	$[Ph]_{CHCl_3}$ $M \times 10^4$	$[PhH^+]$ $M \times 10^4$	$[H^+]$ $M \times 10^4$	K_d $\times 10^{-2}$
981	0.0606	468	513	93	7.7
251	.0101	184	67	34	8.5
195	.0101	139	56	45	10
9.8	.0101	5.01	4.8	96	9.9
0.93	.0101	0.46	0.47	101	9.0
				Av.	9 ± 1

aqueous zinc–phenanthroline solution (acid or buffer absent) was found by calculation from the concentration of phenanthroline in an equilibrated chloroform phase (see equation 7). From the concentration of free phenanthroline in the aqueous zinc solution the value of $\bar{n}$ the average number of phenanthroline molecules complexed per zinc atom, could be calculated according to the method of J. Bjerrum.[8]

$$\bar{n} = (C_{Ph} - [Ph]_{CHCl_3})/C_{Zn} \qquad (11)$$

where C_{Ph} again represents the sum of the total molar concentrations of phenanthroline in both phases (equal volumes of chloroform and aqueous phase were used). Equation (11) is based on the assumption that the concentration of free phenanthroline in the aqueous phase is negligible as compared with the concentration of phenanthroline in the zinc complex ions, an assumption that is entirely justified under the present experimental conditions. It is also assumed that free phenanthroline is the only component of the aqueous solution that is extracted to an appreciable extent into the chloroform layer. It was established experimentally that complex molecules such as phenanthroline-zinc nitrate or sulfate are not extracted from the aqueous phase into the chloroform phase.

The dissociation constants of the phenanthroline zinc complexes are related to $\bar{n}$ by the following equation which can be derived from equation (11) (see J. Bjerrum[8])

$$0 = \bar{n} + (\bar{n} - 1)\frac{[Ph]}{K_1} + (\bar{n} - 2)\frac{[Ph]^2}{K_2} + (\bar{n} - 3)\frac{[Ph]^3}{K_3} \qquad (12)$$

where [Ph] represents the concentration of free phenanthroline in the aqueous phase.

In Table IV are shown the values of $\bar{n}$ and [Ph] found for a series of solutions containing different amounts of zinc and phenanthroline. The values of $\bar{n}$ and [Ph] from each experiment, together with the value of K_1 given above, were substituted into equation (12) to yield a series of linear equations, each containing two unknowns, K_2 and K_3. Various pairs of the linear equations were solved for K_2 and K_3. Values of 4, 7, 5, 7 and 8 × 10^{-13}, respectively, were found from the following pairs of experiments: 1 and 3, 1 and 4, 2 and 3, 2 and 4, 3 and 4. For the same pairs of experiments the calculated values of K_3 were 1.2, 1.7, 0.9, 1.0 and 0.6 × 10^{-17}, respectively. It can be concluded that the dissociation constant of the diphenanthroline-zinc ion is 7 × 10^{-13} and that of the triphenanthroline-zinc ion is about 1 × 10^{-17}. It should be noted (see Experimental details) that these dissociation constants refer to solutions of constant ionic strength of 0.1.

TABLE IV

DETERMINATION OF $\bar{n}$: DISTRIBUTION EXPERIMENTS

$[Ph]_{CHCl_3}/[Ph]_{H_2O} = 9 \times 10^2$ $C_{Zn} = 0.00128$ M

Expt.	C_{Ph} $M \times 10^3$	$[Ph]_{CHCl_3}$ $M \times 10^3$	$[Ph]_{H_2O}$ $M \times 10^6$	y $M \times 10^3$	n
1	19.6	16.6	18	3.0	2.34
2	11.9	8.97	10	2.9	2.27
3	4.88	2.64	2.9	2.24	1.75
4	2.36	0.92	1.0	1.44	1.12
5	0.472	0.128	0.14	0.344	0.27

Experiment 5 of Table IV was not suitable for the calculation of K_2 or K_3, because only relatively small amounts of the diphenanthroline- and triphenanthroline-zinc complexes were present. However, if the above values of K_2 and K_3 are substituted into equation (12), together with $\bar{n}$ and [Ph] of Experiment 5, a value of 4.6 × 10^{-7} is calculated for K_1. This is in fair agreement with the value 3.7 × 10^{-7} calculated from the data of Table I.

In Fig. 2 are shown the relative molar concentrations of zinc present as the aquo-zinc ion and as phenanthroline-zinc ions under various conditions. It should be realized that the relative amounts of the different species depend only on the concentration of free phenanthroline and are affected by acidity and the total concentrations of phenanthroline and zinc only insofar as they affect the concentration of free phenanthroline. Figure 2 shows that if log [Ph] is less than −7.2, monophenanthroline-zinc and aquo-zinc only are present. On the other hand, if log [Ph] is between −5.5 to −6.0, all three complexes, as well as aquo-zinc, are present in appreciable amounts. If log [Ph] is greater than −3, essentially all of the zinc would be expected to be present as triphenanthroline-zinc. Unfortunately, it was not possible to investigate experimentally the region of log [Ph] greater than −3 because of the formation of a precipitate, probably $ZnPh_3(NO_3)_2$.

Experimental Details

The chloroform used was Merck, reagent grade, containing 0.7% ethyl alcohol.

***o*-Phenanthroline** solutions in chloroform were prepared by dissolving the required amount of *o*-phenanthroline-monohydrate in a small volume of chloroform and then filtering through glass wool in order to remove the excess water. The solution was then diluted to the proper volume.

0.0128 *M* zinc nitrate stock solution was prepared by dissolving the C. P. monohydrate in water. This solution was then standardized against potassium ferrocyanide according to the method of Kolthoff and Stenger.[9] The potassium ferrocyanide was standardized against 0.0100 *M* zinc nitrate solution prepared from Merck reagent grade metal.

Procedure.—Fifty-ml. solutions of the proper concentrations of *o*-phenanthroline in chloroform were shaken at 25° with equal volumes of 0.00128 *M* zinc nitrate solution which was brought to an ionic strength of 0.1 *M* with potassium nitrate. Equilibrium was established in a few minutes. The chloroform layers were analyzed for *o*-phenanthroline by shaking aliquots with a measured volume of aqueous 2 *N*

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(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

(9) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 301.

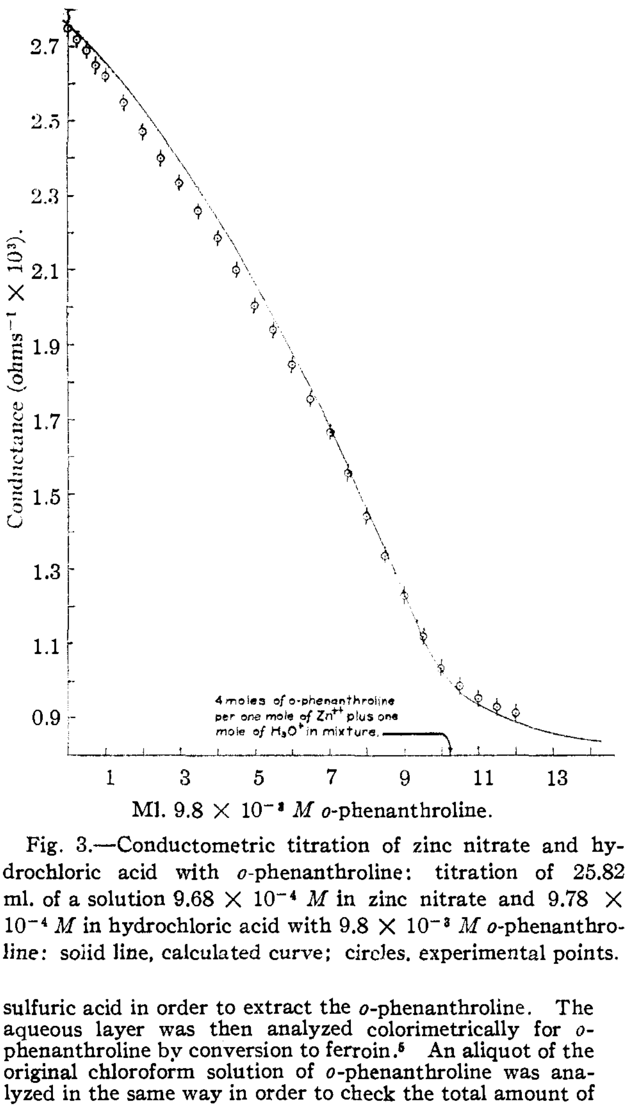

Fig. 3.—Conductometric titration of zinc nitrate and hydrochloric acid with *o*-phenanthroline: titration of 25.82 ml. of a solution 9.68 × 10^{-4} *M* in zinc nitrate and 9.78 × 10^{-4} *M* in hydrochloric acid with 9.8 × 10^{-3} *M* *o*-phenanthroline: solid line, calculated curve; circles, experimental points.

sulfuric acid in order to extract the *o*-phenanthroline. The aqueous layer was then analyzed colorimetrically for *o*-phenanthroline by conversion to ferroin.[5] An aliquot of the original chloroform solution of *o*-phenanthroline was analyzed in the same way in order to check the total amount of *o*-phenanthroline in the system.

Conductometric Measurements.—Conductometric measurements were made in order to test the validity of the results described above. In preliminary experiments it was found that the molar conductivities of the aquo-zinc ion and of all three phenanthroline-zinc ions are nearly equal in aqueous solution. This is apparent from the fact that the titration curve obtained when phenanthroline solution is titrated with zinc is a nearly straight line with constant slope.

A test of the values of K_1, K_2 and K_3 can be made by comparing the experimental and theoretical curves for the titration of a mixture of hydrochloric acid and zinc nitrate with phenanthroline. In this titration both zinc and hydronium ion compete for the added phenanthroline. The conductivity of the solution at any point in the titration therefore depends on the relative values of the dissociation constants of the phenanthrolium ion and of the phenanthroline-zinc ions. This dependence is especially marked because of the large difference in molar conductivities of the phenanthrolium and hydronium ions.

In Fig. 3 are shown data for the titration with 0.0098 *M* phenanthroline of a solution 0.001 *M* in hydrochloric acid and 0.001 *M* in zinc nitrate at 25°. The points are experimental and the solid curve is calculated from molar conductivities and from the values of K_1, K_2, K_3 and K_a given above. The agreement is satisfactory.

The shape of the titration curve is interesting and is explained as follows. If an equimolar mixture of hydrogen and zinc ions were to be titrated with *o*-phenanthroline there would be a competition between the aquo-zinc and the hydronium ion for *o*-phenanthroline. If the hydrogen ion were a much stronger acid than the zinc ion toward phenanthroline, a sharp break in the conductance would be found after additions of one mole of this base. If the zinc were infinitely stronger than the hydrogen ions, there would be hardly any change in the conductance (corrected for dilution upon addition of base until three moles of base are added, assuming that $ZnPh_3^{++}$ is the stable form. From Fig. 3 it is seen that in reality the situation is between these two extremes, the hydrogen ions not being consumed completely until after the addition of about four moles of base per one mole of zinc plus one mole of hydrogen ions in the solution. Thus, the break in the conductance occurs when the zinc is present as $ZnPh_3^{++}$ and the hydrogen ions as PhH^+.

The conductivities of the solutions in this series of experiments were measured with a Model RC conductivity bridge of the Industrial Instruments, Inc., using a cell, the cell-constant of which was 0.230 as determined with 0.00100 *M* potassium chloride. The molar conductivity of 0.00100 *M* zinc nitrate solution was determined to be 236 ohm^{-1} and that of 0.00100 *M* triphenanthroline-zinc nitrate to be 200 (by measuring the conductivity of a mixture which was 0.00100 *M* in zinc nitrate and 0.00500 *M* in 1,10-phenanthroline). In experiments in which a solution of 0.001 *M* 1,10-phenanthroline was titrated with 0.0128 *M* zinc nitrate no change of slope in the titration curve was observed in the regions of the di- and mono-phenanthroline-zinc complexes and excess zinc nitrate. On the basis of the above experiments it was assumed for the present purposes that the molar conductivities of the di- and mono-phenanthroline-zinc ion are the same as that of the aquo-zinc ion.

The value of the molar conductivity of 1,10-phenanthrolium chloride (hydrolysis completely suppressed by presence of excess phenanthroline) has been previously reported as 104.5.[5] The value calculated from the equation of MacInnes[10] for 0.003 *M* hydrochloric acid (a solution of about the same ionic strength as that used in the titration) is 418.

In carrying out the titrations 25.0 ml. of a mixture which was 0.00101 *N* in hydrochloric acid and 0.00100 *M* in zinc nitrate was pipeted into the conductivity cell, which had been washed with water and drained. The cell was thermostated at 25° and successive volumes of 0.0098 *M* *o*-phenanthroline solution were added from a buret upon stirring. A constant reading was attained immediately. As the conductivity cell could not be dried before the addition of the acid-zinc solution a slight dilution of the initial solution occurred. In order to find the initial concentration of the titrated hydrochloric acid-zinc nitrate solution at the beginning of the titration the conductance of this mixture was determined separately. The dilution was then calculated from the ratio of the initial concentration to that of the undiluted mixture. This procedure is sufficiently accurate since the dilution effect was only of the order of 3% (0.82 ml.).

Acknowledgment.—Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out this investigation.

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