

*A New Application of the Theory of Corresponding Solutions to
Measurements of the Stabilities of Some Metal Complexes.*

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[Reprint Order No. 6378.]

Solutions of identical absorption spectrum can be prepared containing the same total concentration of ferrous iron, but different proportions of 1 : 10-phenanthroline and a second cation. The theory of such "corresponding solutions," in which two metals are competing for the same ligand, is developed and applied to measurements, by two procedures, of parts of the formation curves for the systems cobalt, nickel, copper, and zinc with 1 : 10-phenanthroline. These confirm the stability constants obtained by a partition method (Irving and Mellor, to be published).

DISCORDANT values have been reported by different authors, using different procedures, for the stability constants of complexes of certain transition metals. The value $\log \beta_3 = 21.15$ obtained for the system Fe^{2+} -1 : 10-phenanthroline by a partition method (Irving and Mellor, to be published) agrees well with the values $\log \beta_3 = 21.5$ by a kinetic method (Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596), 21.3 by an equilibrium method (*idem, ibid.*, p. 2348), and 21.1 by a tracer exchange method (Cook and Long, *ibid.*, 1951, **73**, 4119). But the value 17.1 ± 0.8 has been obtained by potentiometric measurements (Dwyer and Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1946, **80**, 28) and 22.4 is reported by Davies and Dwyer (*Trans. Faraday Soc.*, 1953, **49**, 180; personal communication from Dunstone and Mellor). For the nickel-phenanthroline system the value $\log \beta_3 = 23.9$

recently obtained by a partition method (Irving and Mellor, *loc. cit.*). disagrees with that, 18.3 ± 1.1 , reported by Davies and Dwyer (*loc. cit.*); other discrepancies will be noted in a later paper (Irving and Mellor, *loc. cit.*).

An independent check on the data obtained by our partition procedure was clearly desirable. Polarographic methods are of limited value for this purpose. Thus the reduction of the trisphenanthroline complex may be irreversible, as has been demonstrated for copper (Onstott and Laitinen, *J. Amer. Chem. Soc.*, 1950, **72**, 4724) and the intrinsic difficulty of obtaining individual step-constants from polarographic measurements is now well recognised (cf. Ringbom and Eriksson, *Acta Chem. Scand.*, 1953, **7**, 1105; Eriksson, *ibid.*, p. 1146). Few reversible metal electrodes are suitable for potentiometric studies using the central-ion method (cf. Bjerrum and Nielsen, *ibid.*, 1948, **2**, 297), and any procedures based on changes in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential suffer from several disabilities: (i) phenanthroline forms complexes with both ferrous and ferric ions—although in their calculations Dwyer and Nyholm (*loc. cit.*) ignored the admittedly weaker complexing of ferric ions; (ii) the system comes to equilibrium rather slowly; (iii) the organic component may be irreversibly oxidised. We have, however, succeeded in confirming the values we had previously reported for the stability constants of several transition-metal-phenanthroline complexes by a novel application of the theory of corresponding solutions which is capable of still wider use.

When a series of metal complexes MA_n ($n = 1, 2, \dots, N$) formed from a metal, M, and a ligand, A, are in a stepwise equilibrium governed by stability constants defined by $K_n = [\text{MA}_n]/[\text{MA}_{n-1}][\text{A}]$, or $\beta_n = [\text{MA}_n]/[\text{M}][\text{A}]^n$, it is well known that the ligand number, \bar{n} , is a function only of $[\text{A}]$, the concentration of free ligand (*i.e.*, that which is not bound in any way, *e.g.*, to metal or to hydrogen ions), and the various stability constants $\beta_1, \beta_2, \dots, \beta_N$.

$$\text{Explicitly} \quad \bar{n} = \sum_0^N n \beta_n [\text{A}]^n / \sum_0^N \beta_n [\text{A}]^n \quad \dots \quad (1)$$

where $\beta_0 = 1$, by definition. The fraction of the total metal present in the form MA_n is given by

$$\alpha_n = \beta_n [\text{A}]^n / \sum_0^N \beta_n [\text{A}]^n \quad \dots \quad (2)$$

and the ratio between the concentrations of any two species MA_n and MA_j by

$$r_{n,j} = [\text{MA}_n]/[\text{MA}_j] = \beta_n [\text{A}]^{n-j} / \beta_j \quad \dots \quad (3)$$

Since α_n and $r_{n,j}$ are functions only of $[\text{A}]$ and the stability constants $\beta_1, \beta_2, \dots, \beta_N$, they are also functions of \bar{n} ; but they do not contain terms specifically relating to the total concentrations of metal or ligand in the system. Now if C_M is the total concentration of metal present, and C_A the total concentration of ligand available for complex formation with it (*i.e.*, excluding the amount bound to protons or to any other metal present), we have

$$\bar{n}_M = (C_A - [\text{A}])/C_M$$

$$\text{or} \quad C_A = \bar{n}_M \cdot C_M + [\text{A}] \quad \dots \quad (4)$$

Any increase in the total concentration of metal from C_M to C_M' (or C_M'' , ...) will produce a decrease in \bar{n}_M which can be exactly compensated by an increase in the total concentration of ligand from C_A to C_A' (or C_A'' ...), so that

$$\bar{n}_M = (C_A - [\text{A}])/C_M = (C_A' - [\text{A}])/C_M' = (C_A'' - [\text{A}])/C_M'' = \dots$$

\bar{n} and $[\text{A}]$ remaining the same in all cases. Clearly an infinite number of solutions could be prepared for which the values of C_A and C_M satisfy the linear equation (4) where \bar{n} and $[\text{A}]$ are now constants. Such solutions are said to be "corresponding" (Bjerrum, *Kgl. Dansk Videnskab. Selskab.*, 1944, **21**, No. 4; Fronaeus, *Acta Chem. Scand.*, 1951, **5**, 139) and it follows from (2) and (3) that α_n (and $r_{n,j}$) is the same for all of them. Conversely, any physical property which permits the quantitative measurement of α_n (or $r_{n,j}$) may

serve to establish the "correspondence" between solutions, and equation (4) can then be solved for \bar{n} and $[A]$. The determination of the values of the constants $\beta_1, \beta_2, \dots, \beta_n$ from pairs of values of \bar{n} and $[A]$ has been discussed previously (Irving and Rossotti, *J.*, 1953, 3397).

FIG. 1. The absorbancy, A_s , at 510 m μ , of solutions containing 8×10^{-5} M-ferrous iron and increasing concentrations of 1:10-phenanthroline. The concentration of cobalt, C_M , in curves 1, 2, 3, 4, and 5 was 0, 1.2 , 1.6 , 2.4 , and 3.2×10^{-4} M.

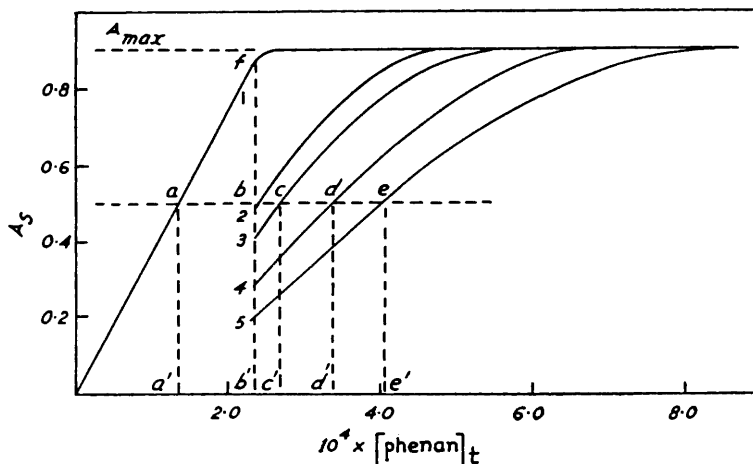
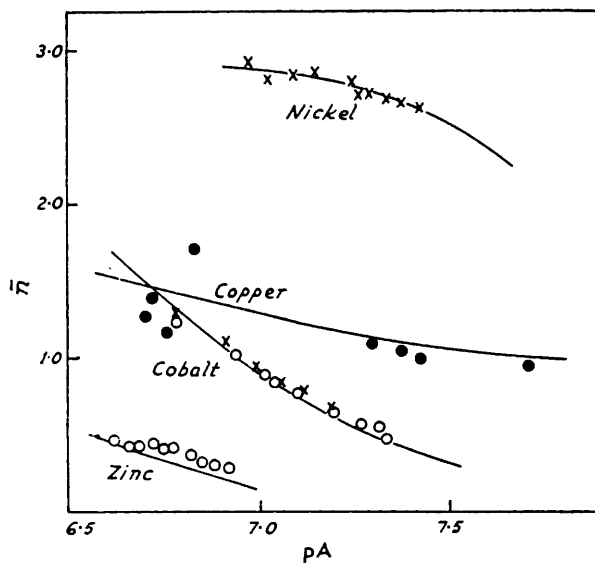


FIG. 2. The results of spectrophotometric determination of the stability constants of metal-phenanthroline complexes. The full lines are formation curves drawn by using stability constants obtained previously by a partition method.



The method of applying the theory of corresponding solutions to the present problem is illustrated by Fig. 1. Curve 1 shows the effect of increasing total concentrations of 1:10-phenanthroline, $[\text{phenan}]_t$, on the absorbancy at 510 m μ of a solution 8×10^{-5} M with respect to ferrous iron and of a constant ionic strength 0.1M. Curve 2 was obtained by making similar measurements on solutions containing 1.2×10^{-4} M-cobaltous ion in addition to the previous concentration of ferrous iron, the temperature and ionic strength remaining

the same. Curves 3, 4, and 5 refer to measurements in which the concentration of cobalt was increased progressively to 1.6, 2.4, and $3.2 \times 10^{-4}\text{M}$ respectively. The absorbancy at 510 $\text{m}\mu$ is due essentially to the red tris-complex $\text{Fe}(\text{phenan})_3^{2+}$. The reduction in absorbancy as the cobalt concentration is increased while the total concentration of phenanthroline remains constant (ordinate bb') is due to the smaller concentration of phenanthroline available for forming complexes with iron consequent upon the formation of the species $\text{Co}(\text{phenan})_2^{2+}$, $\text{Co}(\text{phenan})_3^{2+}$, and $\text{Co}(\text{phenan})_3^{2+}$. Mixtures having the same absorbancy, A_s (e.g., a , b , c , d , and e), are "corresponding" solutions and, since the total concentration of iron is the same in each, identical concentrations of Fe^{2+} , $\text{Fe}(\text{phenan})_2^{2+}$, $\text{Fe}(\text{phenan})_3^{2+}$, and free phenanthroline must be present. It follows that the whole of the phenanthroline represented by the concentration difference $a'b'$ must have formed complexes with the cobalt present in solution 2; the whole of the phenanthroline represented by the concentration difference $c'd'$ must have formed complexes with an amount of cobalt equivalent to the difference in cobalt concentration between solutions 3 and 4, viz., $0.8 \times 10^{-4}\text{M}$. In this way are obtained ten values for C_N (where $N = \text{Co}$) and ten corresponding values for C_A (where $A = \text{phenan}$), the concentration of ligand bound uniquely to the metal N.

$$\text{Then } \frac{C_A}{C_N} = \frac{[\text{NA}] + 2[\text{NA}_2] + 3[\text{NA}_3]}{[\text{N}] + [\text{NA}] + [\text{NA}_2] + [\text{NA}_3]} = \bar{n}_N \quad \dots \quad (5)$$

As predicted theoretically, plots of C_A against C_N gave a family of straight lines (not reproduced), all passing through the origin. In this way the value of \bar{n}_N , the degree of formation of the system of complexes NA_n ($n = 1, 2, \dots, N$) can be obtained corresponding to each absorbancy, A_s , in Fig. 1. The method of corresponding solutions has previously been applied to the study of complexes of a single metal such that values of \bar{n} and $[\text{A}]$ are obtained from the same measurements as shown in equation (4). When two metals are competing for the same ligand, as in the present procedure, values of $[\text{A}]$ must be obtained indirectly. Since all solutions of a particular absorbancy are "corresponding," the constant value of $[\text{phenan}]$ in solutions b , c , d , and e containing both cobaltous and ferrous ions is identical with the value of $[\text{phenan}]$ in solution a which contains only ferrous iron. Since $A_s = \epsilon l [\text{Fe}(\text{phenan})_3^{++}]$, and $A_{\text{max.}} = \epsilon l C_{\text{Fe}}$, where ϵ is the molecular extinction coefficient of the tris-complex at 510 $\text{m}\mu$ and l is the length of the optical cell,

$$\begin{aligned} A_s/A_{\text{max.}} &= [\text{Fe}(\text{phenan})_3^{++}]/C_{\text{Fe}} \\ &= \beta_3[\text{phenan}]^3/(1 + \beta_1[\text{phenan}] + \beta_2[\text{phenan}]^2 + \beta_3[\text{phenan}]^3) \quad \dots \quad (6) \end{aligned}$$

Values of $[\text{phenan}]$ corresponding to any value of A_s were read off from a large-scale graph (not reproduced) of $A_s/A_{\text{max.}}$ against $[\text{phenan}]$, using $\log \beta_1 = 5.85$, $\log \beta_2 = 11.15$, and $\log \beta_3 = 21.15$. Although the value adopted for β_3 is confirmed by several independent methods (p. 3457), there is no independent check on the values chosen for β_1 and β_2 ; but it can readily be shown that the predominating species in this system are the ions Fe^{2+} and $\text{Fe}(\text{phenan})_3^{2+}$, the intermediate species $\text{Fe}(\text{phenan})_2^{2+}$ and $\text{Fe}(\text{phenan})_2^{2+}$ never contributing more than a few percent to the total composition (cf. Fig. 3 in Irving, Cabell, and Mellor, *J.*, 1953, 3417), so that the graph of equation (6) is scarcely modified even by considerable variation in the values adopted for β_1 and β_2 . Fig. 2 (crosses) shows how closely the values for \bar{n}_N and pA ($= -\log_{10} [\text{A}]$) for the system cobalt-1 : 10-phenanthroline agree with those obtained by the partition method (Irving and Mellor, *loc. cit.*) which were used to plot the formation curves shown as solid lines.

The unusual features of the system ferrous ions-1 : 10-phenanthroline already mentioned, and the fact that $K_3 \gg K_1 > K_2$, permit a further simplification in experimental procedure. Let A_0 be the absorbancy and $[\text{phenan}]_0$ the concentration of free ligand for a solution containing ferrous iron at a concentration, C_{Fe} , and phenanthroline at a concentration, C_A , somewhat less than $3C_{\text{Fe}}$; let A_1 be the absorbancy and $[\text{phenan}]_1$ the concentration of free ligand after addition of another metal N, at a concentration C_N , and

let $A_{\max.}$ be the absorbancy of the first solution after the addition of excess of phenanthroline. Since $A_{\max.} = \epsilon l C_{\text{Fe}}$ as before, we have for the first solution

$$C_A = 3(A_0 C_{\text{Fe}}/A_{\max.}) + [\text{phenan}]_0$$

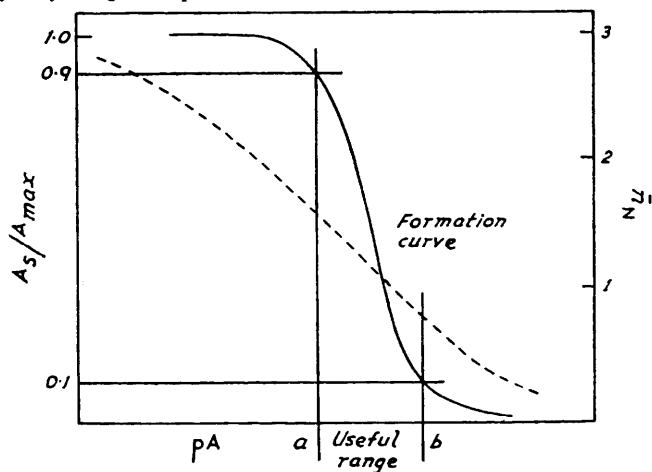
and for the second solution

$$C_A = 3(A_1 C_{\text{Fe}}/A_{\max.}) + [\text{phenan}]_1 + \bar{n}_N C_N$$

whence $\bar{n}_N = \{[\text{phenan}]_0 - [\text{phenan}]_1 + 3C_{\text{Fe}}(A_0 - A_1)/A_{\max.}\}/C_N$. . . (7)

Under the experimental conditions employed, the change in free-ligand concentration is negligible in comparison with the last term in the numerator of equation (7), which simplifies to $\bar{n}_N = 3C_{\text{Fe}}(A_0 - A_1)/A_{\max.}C_N$. The corresponding value of $[\text{phenan}]$ is obtained, as before, from the graph of equation (6). The results for cobalt are shown (open circles) in Fig. 2. The agreement with the more rigorous spectrophotometric procedure is quite satisfactory, and by using the simpler procedure values for \bar{n}_N and corresponding values of pA were obtained for $N =$ nickel, copper, and zinc, and $A = 1 : 10$ -phenanthroline. These results are shown in Fig. 2 where the full lines were drawn with

FIG. 3. Schematic representation of the formation curve for an arbitrary metal-1 : 10-phenanthroline system superimposed on a graph representing the variation in the fraction of trisphenanthrolineferrous ion present as a function of the free ligand exponent.



the stability constants previously reported (*loc. cit.*). Agreement is excellent for complexes of nickel, cobalt, and copper. The data now obtained for zinc lie just above the formation curve calculated with the values $\log \beta_1 = 6.4$, $\log \beta_2 = 11.95$, and $\log \beta_3 = 17.05$. A slightly better fit is given by increasing the value of $\log \beta_1$ to 6.5, without changing the values for the other two constants.

It has been assumed in the foregoing treatment that none of the optical absorbancy at $510 \text{ m}\mu$ is due to the second cation N^{2+} , or to any of its complexes NA^{2+} , NA_2^{2+} , or NA_3^{3+} . This was, of course, verified experimentally.

Although the new procedures could be applied to studies of complexes of various metals with, *e.g.*, dipyrindyl—provided accurate values for the stability constants of its ferrous complexes were available—and many obvious extensions can be envisaged, they cannot provide data for plotting a complete formation curve for the competing metal, N . The reasons for this appear in Fig. 3 which represents schematically the plot of $A_s/A_{\max.}$ as a function of pA (solid line) for the system ferrous iron-1 : 10-phenanthroline. The accuracy with which measurements of the ratio $A_s/A_{\max.}$ can be made falls off as $A_s \rightarrow 0$, and as $A_s \rightarrow A_{\max.}$, so that, if only values within the range $0.1 \geq A_s/A_{\max.} \geq 0.9$ are acceptable, only those "corresponding" solutions can be studied for which the free ligand concentration lies within the range $a \geq pA \geq b$. The portion of the formation curve (broken lines) accessible to study is therefore limited as shown in Fig. 3. But, depending on the

magnitude of the stability constants of the complexes formed by the competing metal, N, the useful range will cover different portions of the respective formation curves, as shown in Fig. 2.

EXPERIMENTAL

Absorbancies were measured with a Unicam Spectrophotometer, model S.P. 500, with matched Corex cells in a cell compartment at $25^\circ \pm 0.1^\circ$ (thermostat). Recrystallised "AnalaR" reagents were employed and the cobalt salt was tested for the absence of nickel and iron.

System, Cobaltous Ions-1 : 10-Phenanthroline.—(a) *Full procedure.* A stock solution of iron and phenanthroline was made up to contain ferrous iron ($2 \times 10^{-4}\text{M}$), 1 : 10-phenanthroline ($5.94 \times 10^{-4}\text{M}$), hydrochloric acid (0.01M), potassium chloride (0.22M), and hydroxylamine hydrochloride (0.5%). To 10 ml. portions were added x ml. of a cobaltous solution (0.01M), y ml. of 0.10% aqueous 1 : 10-phenanthroline monohydrate, and 5 ml. of 0.1M-sodium acetate, and the total volume was made up to 25 ml. at 25° . The following absorbancies, A_s , were obtained at 510 μ with 1-cm. cells.

| | | | | | | |
|-----------|-------|-------|-------|-------|-------|-------|
| $x = 0.3$ | y | 0.0 | 0.4 | 0.8 | 1.2 | 1.6 |
| | A_s | 0.494 | 0.700 | 0.842 | 0.898 | 0.905 |
| $x = 0.4$ | y | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 |
| | A_s | 0.42 | 0.568 | 0.825 | 0.900 | 0.950 |
| $x = 0.6$ | y | 0.0 | 0.4 | 0.8 | 1.5 | 2.5 |
| | A_s | 0.290 | 0.464 | 0.616 | 0.818 | 0.898 |
| $x = 0.8$ | y | 0.00 | 0.5 | 1.0 | 1.5 | 3.0 |
| | A_s | 0.203 | 0.382 | 0.558 | 0.702 | 0.903 |

Additional data (not reproduced) obtained with solutions containing 0.3, 0.5, 0.7, and 0.9 ml. of 0.01M-cobaltous sulphate were included in the curves shown in Fig. 1. Values of C_A and C_N for corresponding solutions at various arbitrary values of the absorbancy, A_s , were plotted as abscissæ and ordinates respectively. The following are typical values of the calculated degrees of formation :

| | | | | | | |
|---|-------|-------|-------|-------|------|------|
| Absorbancy, A_s | 0.30 | 0.42 | 0.50 | 0.60 | 0.70 | 0.80 |
| Slope of graph, \bar{n} | 0.672 | 0.775 | 0.840 | 0.945 | 1.10 | 1.29 |
| Percentage of the tris-complex, $100A_s/A_{\text{max}}$ | 33.2 | 46.4 | 55.2 | 66.3 | 77.3 | 88.4 |
| $-\log_{10}$ [phenan] | 7.19 | 7.11 | 7.055 | 6.99 | 6.91 | 6.78 |

(b) *Shortened procedure.* 10 ml. of the above stock solution of iron and phenanthroline, 5 ml. of 0.1M-sodium acetate, and x ml. of cobaltous solution (10^{-3}M) were made up to 25 ml. at 25° . The absorbancy, $A_0 = 0.875$ (1-cm. cell) when $x = 0$, was increased to $A_{\text{max}} = 0.885$ by adding an excess of 1 : 10-phenanthroline. $C_{\text{Fe}} = 8.0 \times 10^{-5}\text{M}$. The other measurements and calculations were as follows :

| | | | | | | | | |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| x (ml.) | 0.5 | 1.5 | 3.0 | 4.0 | 6.0 | 8.0 | 9.0 | 1.1 * |
| A_1 | 0.785 | 0.651 | 0.500 | 0.417 | 0.283 | 0.196 | 0.160 | 0.104 |
| $10^4 C_N$ | 0.2 | 0.6 | 1.2 | 1.6 | 2.4 | 3.2 | 3.6 | 4.4 |
| \bar{n}_N | 1.22 | 1.01 | 0.84 | 0.78 | 0.67 | 0.575 | 0.54 | 0.47 |
| $-\log_{10}$ [phenan] | 6.78 | 6.94 | 7.04 | 7.10 | 7.19 | 7.27 | 7.31 | 7.33 |

* A 10^{-3}M -solution of cobaltous sulphate was used for this experiment.

For measurements with other metals 10^{-3}M -solutions of nickel, zinc, or cupric sulphate were used in place of the cobaltous sulphate; hydroxylamine hydrochloride was omitted in measurements of the copper-phenanthroline system. The following is a summary of the results :

Nickel (x was varied from 0.1 to 2.0 ml.; A_s from 0.80 to 0.09) :

| | | | | | | | | | | |
|-----------------|------|------|------|------|------|------|------|------|------|------|
| pA | 6.97 | 7.02 | 7.09 | 7.14 | 7.24 | 7.26 | 7.29 | 7.33 | 7.37 | 7.42 |
| \bar{n} | 2.89 | 2.78 | 2.83 | 2.84 | 2.78 | 2.71 | 2.70 | 2.68 | 2.65 | 2.61 |

Zinc (x was varied from 0.3 to 5.0 ml.; A_s from 0.87 to 0.68) :

| | | | | | | | | | | |
|-----------------|------|-------|-------|-------|-------|-------|------|-------|------|------|
| pA | 6.92 | 6.89 | 6.86 | 6.82 | 6.77 | 6.75 | 6.72 | 6.68 | 6.66 | 6.62 |
| \bar{n} | 0.28 | 0.295 | 0.315 | 0.365 | 0.416 | 0.395 | 0.42 | 0.395 | 0.40 | 0.45 |

Copper (x was varied from 0.10 to 6.0 ml.; A_s from 0.81 to 0.015) :

| | | | | | | | | |
|-----------------|------|------|------|------|------|------|------|------|
| pA | 6.70 | 6.72 | 6.76 | 6.83 | 7.29 | 7.37 | 7.42 | 7.70 |
| \bar{n} | 1.25 | 1.37 | 1.18 | 1.70 | 1.09 | 1.06 | 0.98 | 0.93 |

We express our indebtedness to Messrs. Imperial Chemical Industries Limited for the gift of chemicals, and to Messrs. British Celanese Ltd. for the award of a Senior Studentship to one of us (D. H. M.).