255. Oxidation–Reduction Potentials of Metal Complexes in Water: Some Copper Complexes.

By C. J. HAWKINS and D. D. PERRIN.

The stability constants of cuprous and cupric complexes with pyridine, 4-methylpyridine, imidazole, benzimidazole, and 2-methylthioethylamine have been obtained at 20° and $I = 0{\cdot}15$ in a medium consisting essentially of sodium sulphate (for Cu^{I}) and sodium perchlorate (for Cu^{II}) by potentiometric titration. Solutions of the cuprous complexes were prepared by electrolysis of copper in the presence of ligand. Electrode potentials, E_L°, for the Cu^{2+}–Cu^{+} complexes have been calculated from these results. In all cases there is preferential stabilisation of the cuprous state.

FEW values for the oxidation–reduction potentials of corresponding pairs of copper(II)–copper(I) complexes in aqueous solution have so far been published: a recent review[1] listed only four potentials that were considered to be reasonably reliable, namely, for the 1 : 2 complexes with ammonia, imidazole, and ethylenediamine, and for the sulphides. James and Williams[2] later confirmed, to within 0·02 v, the values for the first three of these and also reported oxidation–reduction potentials of 1 : 2 copper complexes in water with morpholine, piperidine, some 1,10-phenanthrolines, 2,2′-bipyridyls, and α-amino-acids. They also studied a more extensive series of 1 : 2 copper complexes with 1,10-phenanthrolines and 2,2′-bipyridyls in 50% dioxan–water, but the relation of the values so obtained to potentials in water is uncertain: in the four cases where aqueous values are also known they are from 84 to 131 mv less positive, and the ranking order (for bipyridyl complexes) is different in the two solvents.[2] Particularly because of its relevance to biological systems, in which reversible oxidation–reduction of copper complexes is known to occur, we have begun a systematic study of the effect of complex formation with a range of ligands upon the redox potential of copper(II)–copper(I) in water.

A severe limitation on the methods that may be used and the extent of complex formation that can be studied is the instability in solution of the free hydrated ion, Cu_{aq}^{+}. This ion readily disproportionates into Cu_{aq}^{2+} and free copper, with an equilibrium constant[3] at 25° of $[Cu^{2+}]/[Cu^{+}]^2 = 1 \times 10^6$, so that the few known copper(I) salts probably owe their stability to complex formation. Hence it is difficult to assess the precision attainable

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[1] Perrin, *Rev. Pure Appl. Chem.*, 1959, **9**, 257.
[2] James and Williams, *J.*, 1961, 2007.
[3] Fenwick, *J. Amer. Chem. Soc.*, 1926, **48**, 860.

by a method such as that of James and Williams[2] in which solid cuprous chloride is added to the system, and in which, presumably, there is competitive complex formation for cuprous ion between the chloride ions and the other ligand. Because of the introduction of undesirable species such as bisulphite or mercurous ions, difficulties also arise if copper(I) ion is generated in the solution by chemical reduction of copper(II) ion. Further, the experimentally measured redox potential of the system can be converted into a standard potential, E_L°, only if the copper(I) and the copper(II) complexes are fully formed or if their stability constants are known. The E_f^* values given by James and Williams,[2] where E_f^* is the formal oxidation–reduction potential for pairs of complexes at specified degrees of formation ($\bar{n}$), deviate from these potentials to an extent which depends on the consecutive stability constants, K, of the complexes. When, as is often the case, $K_1 \gg K_2$ for the cuprous and the cupric complexes, E_f^* at $\bar{n} = 1$ will be almost the same as E_L° for the pair of 1 : 1 copper–ligand complexes; but if, for example, in either series $K_1 = K_2$, the two values of E will be different because at $\bar{n} = 1$ only one-third of the metal is present in the 1 : 1 complex (and the solution contains equal concentrations of metal ion and 1 : 1 and 1 : 2 complexes).

Mathematical analysis of the curves of redox potential against the logarithm of ligand concentration, and their first derivatives, can afford potentials and stability constants,[4] but this method does not provide a very good internal check on the consistency of the results. We prefer to obtain, in separate experiments, the stability constants, β, of the copper(I) and copper(II) complexes, and then calculate E_L° by using the identity,[5]

$$E_L^\circ = E^\circ_{Cu^{2+},Cu^+} - 2{\cdot}3026(\boldsymbol{RT}/\boldsymbol{F})(\log \beta_{Cu^{2+}} - \log \beta_{Cu^+}). \qquad (1)$$

In the present work the copper(I) complexes were formed by electrolysis of copper in a solution of the ligand, a method based on that of Náray-Szabó and Szabó,[6] followed by potentiometric titration.

EXPERIMENTAL

" AnalaR " pyridine which had been kept over potassium hydroxide pellets for three months was distilled, yielding a fraction with b. p. 113·5°/714 mm. (lit.,[7] 113·65°/714 mm.). 4-Methylpyridine (from British Drug Houses Ltd.) was refluxed over barium oxide for 4 hr. and distilled; the fraction boiling at 141·5° was collected. Imidazole (from Messrs. L. Light and Co.) was decolorised with charcoal, recrystallised three times from benzene, and dried at 40° *in vacuo*. Benzimidazole (from B.D.H. Ltd.) was decolorised with charcoal, recrystallised four times from aqueous ethanol, and dried at 100° for 12 hr. 2-Methylthioethylamine, prepared by the method of Brighton and Reid[8] and repeatedly distilled, had b. p. 145·5°/720 mm. (lit.,[8] 146·8°/760 mm.). Except for sodium perchlorate which was recrystallised from aqueous ethanol and dried *in vacuo* at room temperature, the remaining reagents were of " AnalaR " grade and were used without further purification.

The electrolysis- and titration-cell was a cylindrical glass vessel of about 200 ml. capacity, closed by a rubber stopper through which passed " Quickfit " ground-glass sockets carrying three electrodes (bright platinum foil, gold foil, and glass), a platinum wire supporting a cylindrical copper anode 1 cm. high and 2 cm. in diameter (constructed from " AnalaR " copper and freshly scoured with steel wool to remove the oxide coating), ancillary attachments (an " Agla " micrometer syringe, thermometer, gas inlet, and outlet through a water-trap), and an alumina thimble. This thimble, which was sealed with a coating of calcium silicate except for an annular strip near its base, contained 0·05M-sodium sulphate, acidified with sulphuric acid, into which dipped the platinum gauze electrode which was the cathode during electrolysis. In addition, the cell was connected to an external saturated calomel electrode by an ammonium

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[4] Tomkinson and Williams, *J.*, 1958, 2010.

[5] Perrin, *J.*, 1959, 290.

[6] Náray-Szabó and Szabó, *Z. phys. Chem.*, 1933, *A*, **166**, 228.

[7] Weissberger, Proskauer, Riddick, and Toops, " Technique of Organic Chemistry, Vol. VII. Organic Solvents," 2nd edn., Interscience Publ. Inc., New York, 1955, p. 243.

[8] Brighton and Reid, *J. Amer. Chem. Soc.*, 1943, **65**, 458.

nitrate–sodium nitrate–agar salt bridge.[9] The potentiometer was a Tinsley instrument (type 4046B), easily readable to 0·1 mv, and was used with a Pye " Scalamp " galvanometer. pH measurements were made on a Cambridge bench-model pH-meter, with 0·050M-potassium hydrogen phthalate (pH 4·00 at 20°) as standard. The solution in the cell was stirred magnetically. Before the electrolysis, oxygen was removed from the system by bubbling nitrogen (commercial " oxygen-free," passed through Fieser's solution and potassium hydroxide, then washed with water) through the solution for 1 hr. For the remainder of the experiment a slight positive pressure was maintained by passing the nitrogen over the surface of the solution. A gas coulometer, which could be read to 0·01 ml. with an accuracy of about 1 : 1000 over the working range, was used to follow the electrolysis. Acid dissociation constants of the ligands, and the stability constants of their copper(II) complexes, were determined in the usual manner by pH-titration in solutions adjusted to an ionic strength of 0·15 by addition of sodium perchlorate. The stability constants were evaluated by the graphical method of Irving and Rossotti.[10] Measurements were made at 20° ± 0·1° and constants are concentration constants.

The following experimental procedure for the copper(I) complexes was based on the fact that, if E° for $\mathrm{Cu^IL}_x/\mathrm{Cu^0}$ is less positive than E° for $\mathrm{Cu^{II}L}_x/\mathrm{Cu^0}$, then copper(I) complexes will be formed in solution by the anodic electrolysis of copper in a solution of the ligand. A neutral or weakly acid solution of the ligand in sulphuric acid was adjusted to an ionic strength of 0·15 by addition of sodium sulphate. Copper(I) and copper(II) ions were generated in the solution by electrolysis, the quantity, $[\mathrm{Cu^+}] + 2[\mathrm{Cu^{2+}}]$, being known from the gas coulometer. The copper anode was then lifted out of the solution. The potential of the platinum and gold electrodes, with respect to the saturated calomel electrode, and the pH of the solution, were recorded as the solution was titrated with standard 0·05M-sulphuric acid. Because differences between potentials with the platinum and gold electrodes never exceeded 0·4 mv, the average of the two readings at each point was used in the subsequent calculations. Stability constants of the copper(I) complexes were calculated from these results by using the equations developed in the Appendix. Details of a typical experiment are set out in Table 1.

TABLE 1.

Determination of stability constants of copper(I) complexes with 2-methylthioethylamine.

An aqueous solution of 2-methylthioethylamine ($5{\cdot}0 \times 10^{-3}$M), containing sulphuric acid ($2{\cdot}45 \times 10^{-3}$M), was adjusted to $I = 0{\cdot}15$ with sodium sulphate. Copper ions were added by electrolysis, giving $[\mathrm{Cu^I}]_T + 2[\mathrm{Cu^{II}}]_T = 3{\cdot}071 \times 10^{-4}$M. The solution was then titrated with 0·0497M-sulphuric acid.

$[H_2SO_4]$ (μM)	E (mv)	pH	[L] (μM)	r *
2450	78·5	6·51	3·909	41·54
2460	76·7	6·44	3·302	35·70
2469	75·0	6·38	2·888	29·99
2478	73·2	6·32	2·555	26·88
2488	71·3	6·25	2·183	23·83
2497	70·1	6·20	1·931	21·98
2507	68·6	6·13	1·670	19·98
2516	67·2	6·07	1·460	18·65
2526	65·9	6·00	1·248	17·10
2535	65·2	5·95	1·103	16·21
2544	64·2	5·88	0·954	15·20
2554	63·5	5·81	0·815	14·43
2573	61·7	5·69	0·623	12·98
2591	60·3	5·55	0·455	11·89
2610	59·6	5·41	0·332	11·30
2629	59·4	5·27	0·242	11·03
2662	58·6	4·93	0·111	10·41

From these results, by use of equations given in the Appendix, the following values were obtained: $s = 9{\cdot}931$, $t = 4{\cdot}423 \times 10^6$, $u = 9{\cdot}438 \times 10^{11}$. Hence, $\log K_1 = 5{\cdot}65$, $\log \beta_2 = 10{\cdot}98$, at 20°, and $I = 0{\cdot}15$, from $K_1 = t/s$, and $\beta_2 = u/s$.

* $r = (1 + K_1^{\mathrm{II}}[\mathrm{L}] + \beta_2^{\mathrm{II}}[\mathrm{L}]^2 + \ldots) \exp - (nFE/2{\cdot}3026RT)$.

RESULTS AND DISCUSSION

Values obtained in the present work for the acid dissociation constants of the ligands studied, and for the stability constants of their copper(II) complexes are given in Table 2. Published figures, if obtained under comparable conditions, are also listed, together with some results for related substances. Our values for the copper(II) complexes of pyridine and 4-methylpyridine diverge increasingly from those of Bruehlman and Verhoek,[11]

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[9] Perrin, *J.*, 1958, 3120.

[10] Irving and Rossotti, *J.*, 1953, 3397.

[11] Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

TABLE 2.

Acid dissociation constants and copper(II) complex stability constants in water at 20° and an ionic strength of 0·15.

Ligand	pK_a	log K_1^{II}	log β_2^{II}	log β_3^{II}	log β_4^{II}
Pyridine	5·32 ± 0·00	2·65	4·86	6·90	8·45
	5·45[a]	2·52[a]	4·38[a]	5·69[a]	6·54[a]
4-Methylpyridine	6·19 ± 0·02	2·56	5·39	7·66	9·54
	6·26[a]	2·82[a]	4·97[a]	6·58[a]	7·74[a]
Imidazole	7·20 ± 0·03	4·26	7·87	10·73	12·98
	7·09[b]	4·20[b]	7·67[b]	10·51[b]	12·51[b]
	7·11[c]	4·36[c]	7·93[c]	10·78[c]	12·84[c]
Benzimidazole	5·68 ± 0·02	3·56	6·34	9·00	10·97
	5·58[d]	3·43[d]	6·41[d]	8·92[d]	10·92[d]
2-Methylthioethylamine	9·56 ± 0·02	5·30	9·68		
	9·45[e]		10·68[e]		
Ammonia	9·40[f]	4·31[g]	7·98[g]	11·02[g]	13·32[g]
Ethylenediamine	7·49,[h] 10·17[h]	10·72[h]	20·03[h]		

[a] At 25° and $I = 0·5$, from Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401. [b] At 25° and $I = 0·135$, from Mickel and Andrews, *ibid.*, 1955, **77**, 5291. [c] At 22·5° and $I = 0·16$, from Edsall, Felsenfeld, Goodman, and Gurd, *ibid.*, 1954, **76**, 3054. [d] At 25° and $I = 0·16$, from Lane and Quinlan, *ibid.*, 1960, **82**, 2994. [e] At 30° and $I = 1·0$, from Gonick, Fernelius, and Douglas, *ibid.*, 1954, **76**, 4671. [f] At 20° and $I = 0$, from Bates and Pinching, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 419. [g] At 18° and $I = 2$, from Bjerrum, *Kgl. danske Videnskab. Selskab, mat.-fys. Medd.*, 1931, **11**, No. 5. [h] At 25° and $I = 1$, from Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 307.

which appear to be based on Bjerrum's approximations (not valid here because differences in the series $K_1 > K_2 > K_3 > K_4$ are not great) that the reciprocals of ligand concentration at $\bar{n} = 0·5$, 1, 1·5, and 2 are equal respectively to K_1, $\beta_2^{1/2}$, $\beta_3^{1/3}$, and $\beta_4^{1/4}$. Table 3 gives the corresponding copper(I) stability constants and the oxidation–reduction potentials, $E_L°$, for corresponding pairs of cupric and cuprous complexes. These have been calculated from the stability constants by using eqn. (1) and Fenwick's value[3] of 0·167 v for $E°_{Cu^{2+},Cu^{+}}$ at 25°. Table 3 also records copper(II)–copper(I) couples in aqueous solution which are representative of most of the results previously published.

TABLE 3.

Stability constants of copper(I) complexes, and electrode potentials of copper(II)–copper(I) couples in water at 20° and an ionic strength of 0·15.

Ligand	log K_1^{I}	log β_2^{I}	$E°_{1:1}$ (v)	$E°_{2:2}$ (v)	E_f* (2 : 2) (v)
Pyridine	3·17	6·64	0·197	0·270	
	3·90[a]	6·60[a]			
4-Methylpyridine	4·30	7·65	0·268	0·298	
Imidazole	5·78	10·98	0·255	0·348	0·317[a]
		10·44,[a] 10·87[a]			
		10·8[b]			
Benzimidazole	4·47	9·73	0·220	0·364	
2-Methylthioethylamine	5·65	10·98	0·187	0·243	
Ammonia	5·93[c]	10·86,[c] 11·2[d]		0·34[e]	0·308[a]
Ethylenediamine		11·4,[a] ~10·8[f]		−0·38[e]	−0·360[a]
2,2′-Bipyridyl					0·120[a]
1,10-Phenanthroline					0·174[a]
Morpholine					0·250[a]
Piperidine					(?0·145)[a]
Glycine					−0·160[a]

[a] At 25° and $I = 0·3$, from James and Williams, *J.*, 1961, 2007. [b] At 25° and $I = 0·15$, from Li, White, and Doody, *J. Amer. Chem. Soc.*, 1954, **76**, 6219. [c] At 18° and $I = 2$, from Bjerrum, *Kgl. danske Videnskab. Selskab, mat.-fys. Medd.*, 1934, **12**, No. 15. [d] At room temp. and $I = 2$, from Stackelberg and von Freyhold, *Z. Elektrochem.*, 1940, **46**, 120. [e] Estimated from lit., Perrin, *Rev. Pure Appl. Chem.*, 1959, **9**, 257. [f] Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 307.

From eqn. (1) it can be seen that changes in the electrode potentials of copper(II)–copper(I) complexes reflect differences in the relative stabilities of the two series of complexes, so that the preferential stabilisation of one of the valency states of copper can be ascertained by inspection of the oxidation–reduction potential. (It is only in this context that the word, " stabilisation," will be used without further qualification.) Thus, results in Table 3 indicate that (with the doubtful [2] exception of piperidine) in aqueous solutions all monodentate amines preferentially stabilise copper(I) in (presumably linear) 1 : 1 and 1 : 2 complexes. This may be because the lone-pair electrons on nitrogen atoms in amines are more polarisable than those on the oxygen atoms of water molecules, and the Cu^+ ion is more polarisable than is Cu^{2+}, so that there is greater orbital overlap and stronger covalent-bond formation in copper(I)–amine complexes than in either copper(II)–amine complexes or the hydrated metal ions. Orgel [12] has postulated that *d–s* mixing can impart added stability to a linear copper(I) complex. This hybridisation, coupled with the greater crystal field strength of ammonia than of water, may also explain in part the preferential stabilisation of copper(I) [rather than copper(II)] in 1 : 1 and 1 : 2 amine complexes.

Conversely, it is convenient to examine the stability constants of related copper(II) and copper(I) complexes with a view to understanding the resulting oxidation–reduction potentials. Frequently, the stability constants of a cation with a series of related ligands follow approximately the relation, $\log K = a \,.\, \mathrm{p}K_a + b$, where a and b are constants. This is true, for example, for Ag^+ in 1 : 1 complexes with primary amines,[11] with $a \approx 0{\cdot}25$. It has been suggested [13] that a and b are useful measures of the σ-acceptor and π-donor strengths of the cation concerned. On the other hand, $\log \beta_2$ for the Ag^+ complexes shows little change in going from ammonia to ethylamine, which differ in pK by 1·4.[14] Comparable generalisations might be expected for Cu^+. Hence, the closeness of the $\log K_1{}^{\mathrm{I}}$ and $\log \beta_2{}^{\mathrm{I}}$ values for the copper complexes with ammonia and 2-methylthioethylamine, in conjunction with the similarity of their pK_a values, strongly suggests that in its 2-methylthioethylamine complexes, Cu^+ is co-ordinated only through the amino-group. By similar reasoning, ethylenediamine behaves towards Cu^+ as a monodentate ligand. In both these cases this is probably a consequence of the greater ionic radius of Cu^+ than of Cu^{2+} and the requirement that, whereas there is a bond angle of 90° for a square planar or distorted octahedral Cu^{2+} complex, an angle of 109° would be necessary if Cu^+ formed a tetrahedral complex with a bidentate ligand: neither 2-methylthioethylamine nor ethylenediamine is able to form such a 5-membered chelate ring with Cu^+. Steric requirements permit a 6-membered ring to be formed by 1,3-diaminopropane with Cu^+, so that the 1,3-diaminopropane complexes of Cu^+ should be more stable than those with ethylenediamine (as is found for Ag^+): [15] at the same time the Cu^{2+} complexes become less stable than those with ethylenediamine. In the Cu^{2+} series, $\log K_1$ and $\log \beta_2$ for the complexes with 2-methylthioethylamine are about 1 and 2 logarithmic units higher than for ammonia, because rather weak chelation, involving ring formation by the metal through the sulphur and nitrogen atoms, can occur. The very strong chelation of Cu^{2+} by ethylenediamine causes the marked increase in $\log \beta_2$ of over 12 logarithmic units relative to ammonia. Because of this effect, E° for the 1 : 2 copper complexes of 2-methylthioethylamine is only 0·13 v less positive than for the ammonia complexes, but E° for the ethylenediamine complexes is less positive by 0·67 v. The value of $-0{\cdot}160$ v for $E_f{}^*$ corresponding to the 1 : 2 copper glycine complexes [2] (which is representative of the α-amino-acids so far studied), together with $\log \beta_2 = 15{\cdot}1$ for the copper(II) complex,[14] leads to $\log \beta_2{}^{\mathrm{I}} = 9{\cdot}6$ and suggests that here, too, Cu^+ is co-ordinated only though the amino-group.

The increase of pK_a from pyridine to 4-methylpyridine, and from benzimidazole to imidazole, is reflected in the higher stability constants of the copper(I) and (II) complexes of 4-methylpyridine and imidazole. Except for the 1 : 2 complexes in the imidazole series, increases are greater with the cuprous, than with the cupric, complexes, leading to an

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[12] Orgel, *J.*, 1958, 4186.

[13] Jones, Poole, Tomkinson, and Williams, *J.*, 1958, 200.

[14] Bjerrum, Schwarzenbach, and Sillén, " Stability Constants, Parts I and II," *Chem. Soc. Spec. Publ.*, Nos. 6 and 7, 1957 and 1958.

[15] Schwarzenbach, Maissen, and Ackermann, *Helv. Chim. Acta*, 1952, **35**, 2333, 2337.

increase in E_L° with pK_a. However, this result may not have much significance because the differences are comparable with the scatter observed in the E_t^* (2 : 2)–pK_a plot for copper–phenanthroline complexes in 50% dioxan–water,[2] where the average effect was a decrease in E_t^* as pK_a increased.

Pyridine and benzimidazole have comparable pK_a values and, in both cases, co-ordination of metals involves the tertiary nitrogen.[16] However, for the copper(I) complexes of benzimidazole, log K_1 and log β_2 are respectively 1·3 and 3·1 logarithmic units higher than for pyridine. Similarly, for the copper(II) complexes the differences are 0·9 and 1·5. Relative to values for primary amines, the stability constants of the copper(I)–pyridine complexes are rather low. Thus, in silver complexes, log β_2 for the pyridine complex is similar to the value for a primary amine of comparable pK_a, and about 1 logarithmic unit greater than predicted from results for tertiary aliphatic amines.[11] By analogy, because the pK_a value of pyridine is lower by 4·2 than that of 2-methylthioethylamine, log β_2^{I} for the copper–pyridine complex would be expected to be lower by about 2 logarithmic units; the observed difference is 4·3. These considerations suggest that π-bonding is not a major factor in the copper–pyridine complexes.

The high stability constants of the copper(I) complexes of imidazole, and the resulting higher values of E_L° for the copper(II)–copper(I) couples, suggest that in biological systems the imidazole groups of histidine molecules in peptides and proteins are likely binding sites for copper ions which form parts of reversible oxidation–reduction systems.

APPENDIX

Method of calculating stability constants of copper(I) complexes from the pH-dependence of the e.m.f. of the cell, Pt/Cu^{2+},Cu^+, ligand//sat. cal.

From the identities,

$$E = E^\circ_{\mathrm{Cu^{2+},\,Cu^+}} - (\boldsymbol{RT}/n\boldsymbol{F}) \ln (a_{\mathrm{Cu^+}}/a_{\mathrm{Cu^{2+}}}) + E_{\mathrm{j}}$$

(where E_j is the liquid junction potential),

$$1/[\mathrm{Cu^+}] = (1 + K_1^{\mathrm{I}}[\mathrm{L}] + \beta_2^{\mathrm{I}}[\mathrm{L}]^2 + \ldots)/[\mathrm{Cu^I}]_T,$$

$$1/[\mathrm{Cu^{2+}}] = (1 + K_1^{\mathrm{II}}[\mathrm{L}] + \beta_2^{\mathrm{II}}[\mathrm{L}]^2 + \ldots)/[\mathrm{Cu^{II}}]_T,$$

we have:

$$E = E^\circ_{\mathrm{Cu^{2+},\,Cu^+}} - (\boldsymbol{RT}/n\boldsymbol{F}) \ln ([\mathrm{Cu^I}]_T/[\mathrm{Cu^{II}}]_T) - (\boldsymbol{R}\mathrm{T}/n\boldsymbol{F}) \ln (f_{\mathrm{Cu^+}}/f_{\mathrm{Cu^{2+}}}) + (\boldsymbol{RT}/n\boldsymbol{F}) \ln [(1 + K_1^{\mathrm{I}}[\mathrm{L}] + \ldots.)/(1 + K_1^{\mathrm{II}}[\mathrm{L}] + \ldots..)].$$

If $[\mathrm{Cu^I}]_T/[\mathrm{Cu^{II}}]_T$ and the activity coefficient ratio remain constant, then:

$$E = E_T + (\boldsymbol{RT}/n\boldsymbol{F}) \ln [(1 + K_1^{\mathrm{I}}[\mathrm{L}] + \ldots)/(1 + K_1^{\mathrm{II}}[\mathrm{L}] + \ldots)],$$

where E_T is a constant. This can be written in the form,

$$r = s + t[\mathrm{L}] + u[\mathrm{L}]^2 + \ldots.. \quad \text{(i)},$$

where

$$r = (1 + K_1^{\mathrm{II}}[\mathrm{L}] + \beta_2^{\mathrm{II}}[\mathrm{L}]^2 + \ldots) \exp - (n\boldsymbol{F}E/2{\cdot}3026\boldsymbol{RT}),$$

$$s = \exp n\boldsymbol{F}E_T/2{\cdot}3026\boldsymbol{RT},\ t/s = K_1^{\mathrm{I}}, \cdot u/s = \beta_2^{\mathrm{I}}, \text{ etc.}$$

Values of K_1^{II}, β_2^{II}, . . ., can be found from other experiments by conventional methods, so that r can be evaluated (if necessary by an iterative process) at each point of the titration. The

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[16] Li, White, and Doody, *J. Amer. Chem. Soc.*, 1954, **76**, 6219.

sets of points, r_i, $[L]_i$, $[L]^2{}_i$ . . ., so obtained have to be fitted to the surface described by eqn. (i). This is done by minimising the quantity,

$$\sum (r_i - r)^2 = \Sigma (r_i - s - t[L]_i - \ldots)^2,$$

as in the method of least squares, to give the simultaneous equations:

$$\sum \{(s - r_i) + t[L]_i + u[L]_i^2 + \ldots\} = 0,$$
$$\sum \{(s - r_i)[L]_i + t[L]_i^2 + u[L]_i^3 + \ldots\} = 0,$$
$$\sum \{(s - r_i)[L]_i^2 + t[L]_i^3 + u[L]_i^4 + \ldots\} = 0,$$

which can be solved to give s, t, u, . . ., and hence E_T, $K_1{}^{\mathrm{I}}$, $\beta_2{}^{\mathrm{I}}$.

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DEPARTMENT OF MEDICAL CHEMISTRY, INSTITUTE OF ADVANCED STUDIES,
AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, AUSTRALIA.

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