359. *The Ultraviolet Absorption Spectra and Stability Constants of Cuprous Cyanide Complexes.*

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The optical densities of aqueous solutions of cuprous cyanide and potassium or sodium cyanide have been measured at 25° and used to derive the molar extinction coefficients of the anions $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, and $[Cu(CN)_4]^{3-}$ from 220 to 320 mμ. The association constant $K_3 = [Cu(CN)_3{}^{2-}]/[Cu(CN)_2{}^-][CN^-]$ is $1{\cdot}27 \times 10^4$ at an ionic strength of about 0·001. The equilibria are all adequately described by the constants derived by earlier workers from infrared spectra.

The ultraviolet absorption spectra of the complex cuprous cyanides are compared with those of other metal cyanides.

WHILE studying plating solutions we had to determine the change in the composition of cuprous cyanide solutions with increasing concentration of added cyanide ion, and found the ultraviolet absorption spectrum a convenient property to measure. Meanwhile, Penneman and Jones,[1] from the infrared absorption spectra of aqueous solutions, determined both concentration and thermodynamic dissociation constants for the equilibria:

$$[Cu(CN)_3]^{2-} \rightleftharpoons [Cu(CN)_2]^- + CN^-; \quad [Cu(CN)_4]^{3-} \rightleftharpoons [Cu(CN)_3]^{2-} + CN^-$$

and Brigando[2] reported the ultraviolet absorption spectra of a number of metal cyanides. However, the solution used by Brigando to measure the spectrum of $[Cu(CN)_4]^{3-}$ contained all three species. The results now reported for very dilute solutions agree well with those from the infrared measurements at much higher concentrations.

EXPERIMENTAL

All measurements were made with a Unicam S.P. 500 spectrophotometer in water-jacketed silica cells at 25° ± 0·02°.

Cuprous cyanide, from " AnalaR " cupric sulphate and potassium cyanide, was dissolved in excess of potassium cyanide solution and reprecipitated with a slight excess of sulphuric acid. The pure white solid was washed with conductivity water and alcohol and dried at 110°. All solutions were prepared from this and recrystallised potassium or sodium cyanide. They were standardised for total cyanide, after distillation, by titration with silver nitrate, and for copper either volumetrically or, for the most dilute solutions, colorimetrically as the *o*-phenanthroline complex. Conductivity water saturated with nitrogen was used throughout. The solutions with total cyanide : copper ratios of less than 2·6 were prepared by adding small known volumes of standard acid (hydrochloric or perchloric) to the cuprocyanide solutions in stoppered flasks.

Results.—The absorption spectra all have two large peaks (with maximum apparent molar extinction coefficients, $\varepsilon_{\text{app.}}$, greater than 1000) at about 210 and 235 mμ. For solutions containing less than 1·0mM-copper and increasing cyanide concentration there are two isosbestic points. For these solutions $\varepsilon_{\text{app.}}$ at 238 mμ increases linearly with increasing ratio of total cyanide to total copper up to about 4·5 (Fig. 1). For more concentrated solutions at this wavelength there is a sharp increase up to ratios of about 3 and then a maximum at about 4. Duplicate solutions with sodium cyanide instead of potassium cyanide gave identical absorption spectra.

Treatment of Results.—Cyanide ion is hydrolysed[3] mainly to cyanate and hydrogen cyanide; hydrogen cyanide gives ammonium formate.[4] We therefore measured the absorbance of solutions of potassium cyanide, sodium cyanate, and sodium formate (Table 1). In all cases the molar extinction coefficients are too small for the concentrations expected to introduce any

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[1] Penneman and Jones, *J. Chem. Phys.*, 1956, **24**, 293.

[2] Brigando, *Bull. Soc. chim. France*, 1957, **4**, 503.

[3] For a review see Deltombe and Pourbaix, Proc. of 6th C.I.T.C.E., London, 1956, p. 138.

[4] Marsh and Martin, *J. Appl. Chem.*, 1957, **7**, 205.

errors into the treatment given below; however, because of this hydrolysis the pH could only be used to calculate the hydrogen cyanide concentration in the most alkaline solutions (pH >10).

TABLE 1.

Wavelength (mμ)	Molar extinction coefficient CN⁻	CNO⁻	HCO₂⁻
250—320		<0·1	
240	—	0·2	0·1
238	8·0	—	—
235	—	0·2	0·4
230	13·5	0·3	1·2
225	18·2	0·4	3·5
220	20·0	0·8	8·1

TABLE 2.

Total Cu	Total CN	pH	*a*	*b*	*c*	$[CN^-]_{free}$
1·512	13·000	10·57	0·004	0·838	0·675	7·338
1·512	10·100	10·49	0·007	0·991	0·519	4·673
1·512	7·785	10·28	0·014	1·199	0·305	2·733
1·264	8·015	10·53	0·009	0·943	0·312	3·536
1·264	6·627	10·48	0·013	1·040	0·211	2·307

The thermodynamic dissociation constants calculated by Penneman and Jones [1] are given in equations (1)—(6), which were used to determine the compositions of solutions containing more than 1·0mM-copper and high cyanide ratios. The only assumptions are that eqn. (1) holds for these very alkaline solutions; that corrections for the ionic activity coefficients (which change very little) can be expressed in terms of eqn. (2); and that all the copper is in the form of a complex. In these equations square brackets represent molar concentrations, the enclosing brackets denoting complex ions being omitted.

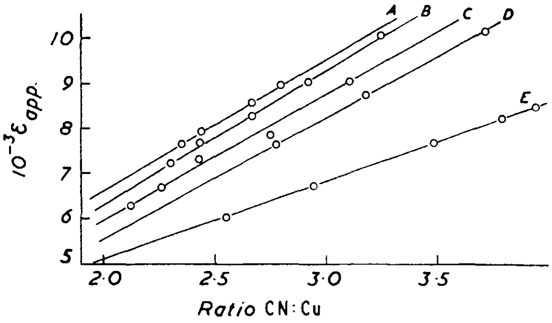


FIG. 1. *Relation of* $\varepsilon_{app.}$ *to* CN : Cu *ratio at* 238 mμ.

Copper: *A*, 0·6883; *B*, 0·4818; *C*, 0·3658; *D*, 0·3093; *E*, 0·2434 mM.

$$\log_{10}[HCN] = \overline{14} + pH + 0{\cdot}5f(I) \quad (1)$$

$$f(I) = I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}});\ \text{where } I = \text{ionic strength} \quad (2)$$

$$[Cu(CN)_3{}^{2-}] = b = \text{Total copper}/(1 + X + Y) \quad (3)$$

$$\log_{10} X = \bar{5}{\cdot}4150 + f(I) - \log_{10}[CN^-] \quad (4)$$

$$\log_{10} Y = 1{\cdot}7160 + 3f(I) + \log_{10}[CN^-] \quad (5)$$

$$[Cu(CN)_4{}^{3-}] = c = bY$$

$$[Cu(CN)_2{}^-] = a = \text{Total copper} - b - c$$

$$[CN^-] = [K^+] - [HCN] - a - 2b - 3c \quad (6)$$

X and *Y* are *a*/*b* and *c*/*b* respectively.

The calculated compositions (mmoles/l.) are given in Table 2. These, combined with the measured optical densities (*x*) at 238 mμ (Fig. 2), show that *x*/*b* is linear with *c*/*b*. The values of ε for $Cu(CN)_3{}^{2-} = \varepsilon_2$ and for $Cu(CN)_4{}^{3-} = \varepsilon_3$ at λ 238 mμ from the intercept and slope are 11,600 and 10,050 respectively.

Treatment of Dilute Solutions given in Fig. 1.—These solutions were assumed to contain only

$[Cu(CN)_2]^-$, and $[Cu(CN)_3]^{2-}$, both absorbing at 238 mμ. The concentration of hydrogen cyanide was ignored and the following equations used $\{\varepsilon_1$ applies to $[Cu(CN)_2]^-\}$:

$$\begin{aligned} a + b &= \text{Total copper} = y \\ \varepsilon_{\text{app.}} &= (a/y)\varepsilon_1 + (b/y)\varepsilon_2 \\ &= \varepsilon_1 + \alpha_2(\varepsilon_2 - \varepsilon_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7) \\ 2a + 3b + [CN^-]_{\text{free}} &= \text{total cyanide; } b/a = K_3[CN^-]_{\text{free}} \\ &(\text{Total cyanide/Total copper}) - 2 = Z \end{aligned}$$

FIG. 2. *Plots of c/b against x/b at (A) 235 mμ and (B) 238 mμ.*

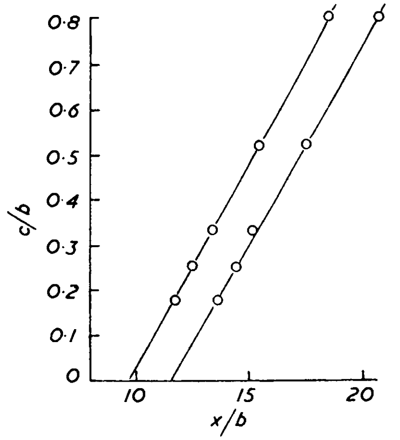


FIG. 3.

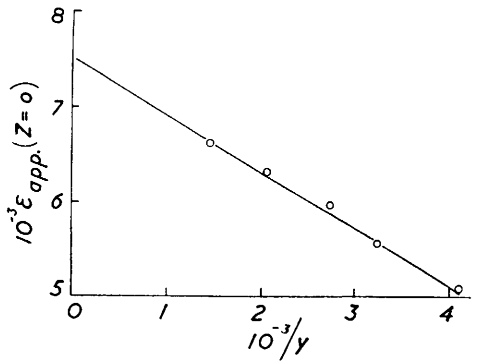


FIG. 4. *Plots of* $\varepsilon_{\text{app.}}$ *against* α_2 *at (A) 205 mμ and (B) 238 mμ.*

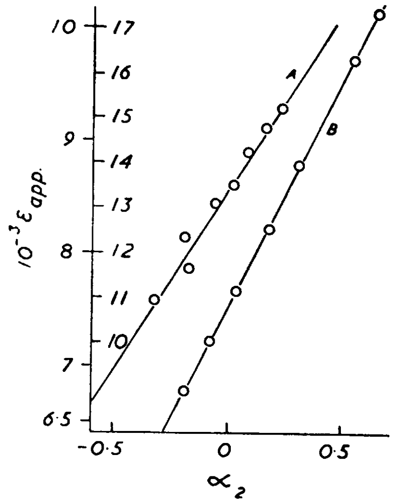
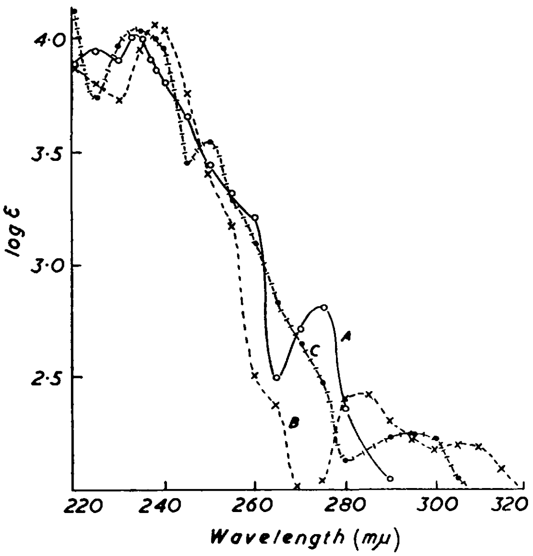


FIG. 5. *Ultraviolet spectra of (A)* $[Cu(CN)_2]^-$, *(B)* $[Cu(CN)_3]^{2-}$, *and (C)* $[Cu(CN)_4]^{3-}$.



Therefore, by substitution in eqn. (7)

$$\varepsilon_{\text{app.}} = Z\varepsilon_2/\{1 - (1/Ky)[1 \div (1 - \alpha_2)]\} + (1 - \alpha_2)\varepsilon_1 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equation (8) was used by reading the values of the apparent extinction coefficients extrapolated to $Z = 0$ from Fig. 1 and plotting them against $1/y$ (Fig. 3). The intercept ε_1 is

7540 and $1/K_3$, found by dividing the slope by ε_1, is $7{\cdot}85 \times 10^{-5}$, giving $K_3 = 1{\cdot}27 \times 10^4$: the ionic strength of these solutions varied from 0·0006 to 0·0012. When this value was substituted in eqn. (4), x/b was altered by less than 1% and c/b by less than 0·3% which did not alter the calculated extinction coefficients ε_2 and ε_3 by as much as the experimental error of ±1%. Optical densities at below 230 mμ needed correction for the absorption of $[Cu(CN)_2]^-$, although this was always less than 2%. The values of ε_2 and ε_3 plotted in Fig. 5 were obtained in this way.

ε_1 at other wavelengths was obtained from the apparent extinction coefficients plotted in Fig. 3 by using the values of ε_1 and ε_2 at 238 mμ to calculate α_2 [eqn. (7)]. Typical plots of α_2 against $\varepsilon_{app.}$ are given in Fig. 4. ε_1 and ε_2 at different wavelengths were read from such graphs. The values of ε_2 from both sets of solutions agreed within experimental error.

DISCUSSION

The positions and maximum extinction coefficients for the three copper complexes are given in Table 3. The data for $[Au(CN)_2]^-$ and $[Ni(CN)_4]^{2-}$ were given by Brigando.[2]

TABLE 3.

$[Cu(CN)_2]^-$	$\lambda_{max.}$ (mμ)	225	234	(260)	274	—	—
	$\log_{10} \varepsilon_{max.}$	3·962	4·025	(3·214)	2·813	—	—
$[Cu(CN)_3]^{2-}$	$\lambda_{max.}$	—	238	(255)	(265)	285	305
	$\log_{10} \varepsilon_{max.}$	—	4065	(3·176)	(2·731)	2·415	2·204
$[Cu(CN)_4]^{3-}$	$\lambda_{max.}$	—	235	250	(275)	295	—
	$\log_{10} \varepsilon_{max.}$	—	4·041	3·549	(2·477)	2·230	—
$[Au(CN)_2]^-$	$\lambda_{max.}$	230	240	—	—	—	—
	$\log_{10} \varepsilon_{max.}$	3·02	3·50	—	—	—	—
$[Ni(CN)_4]^{2-}$	$\lambda_{max.}$	—	268	288	310	328	—
	$\log_{10} \varepsilon_{max.}$	—	4·02	3·60	2·83	2·64	—

Parentheses indicate shoulders.

The similarities between the two linear ions and also between the higher complexes is obvious. This pattern has also been found for the hexacyanides of some tervalent transition-metal ions.[2] It has been shown [5] that not only for those transition-metal complexes which are usually assumed to be chiefly "ionic" but also for the mono- and tris-dipyridyl and *o*-phenanthroline complexes, similar intense ultraviolet bands may be considered to be derived from those of the ligands which are shifted towards longer wavelengths by *electrostatic* interaction with the metal ion. For the hexacyanides the red shift increases in the order Fe < Co < Cr < Mn, which suggests that this simple picture is also applicable to these complexes. The general pattern of the spectra for copper and gold remains the same as that of transition-metal complexes; silver cyanide solutions absorb below 220 mμ. There is no correlation here between charge and radius of the metal ion and the red shift, which does however increase with increasing stability as measured by the dissociation constants which are given here for the three copper complexes and which for the singly charged cyanides indicate decreasing stability in the order gold > copper > silver.[1]

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[5] Schläfer, *Z. phys. Chem.* (*Frankfurt*), 1956, **8**, 373.