22. *Physicochemical Studies of Complex Formation involving Weak Acids. Part XII. The Complex Anions of Cuprous and Auric Cyanides.*

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OUR knowledge of the composition of the cuprocyanide and auricyanide ions is not entirely satisfactory. Treadwell and Girsewald (*Z. anorg. Chem.*, 1904, **38**, 92), from a study of the colour intensity of the solutions of copper sulphate and potassium cyanide in the absence and the presence of ammonia, considered that the compounds, $K_2Cu(CN)_3$ and $K_3NH_4[Cu(CN)_3]_2$, might exist in solution, whilst Kunschert (*ibid.*, 1904, **41**, 359), from the potentials of a silver electrode immersed in potassium cyanide solutions of silver and cuprous cyanides, was led to believe that both anions, $Cu(CN)_3''$ and $Cu(CN)_4'''$, were formed (see also Moles and Isaguirre, *Anal. Fís. Quím.*, 1921, **19**, 23). Glasstone (J., 1929, 705), who titrated potentiometrically with a copper electrode a suspension of cuprous cyanide by potassium cyanide, found that a well-defined inflexion, indicating a rapid diminution in the cuprous-ion concentration, was obtained soon after 2 equivs. had been added. This was considered to point to the formation of $Cu(CN)_3''$. It is a curious fact, that although many potassium cuprous cyanides have been isolated in crystalline form, the complex cyanide, $K_2Cu(CN)_3$, has not been prepared, and moreover, Bassett and Corbet (J., 1924, **125**, 1660) conclude from an isotherm of the appropriate ternary system that there is no indication of this particular salt at 25°.

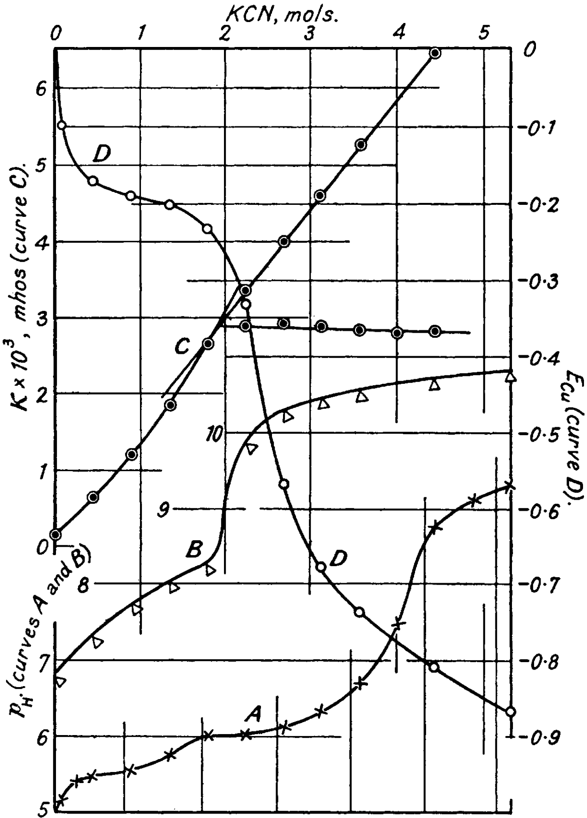
Complex auricyanides have been described by Himly (*Wied. Ann.*, 1842, **42**, 337) and Lindborn (*Ber.*, 1877, **10**, 1725), but the nature of the complex anion formed in solution has not been investigated.

We have now studied the complex cyanide ions by means of (*a*) the vapour-pressure method of estimating hydrolysed hydrogen cyanide (Harman and Worley, *Trans. Faraday Soc.*, 1924, **20**, 502; Britton and Dodd, J., 1931, 2332), (*b*) glass-electrode p_H measurements, and (*c*) conductivity. The results point to the existence in solution of the complex anions, $Cu(CN)_3''$ and $Au(CN)_4'$, only.

EXPERIMENTAL.

I. *Copper*.—It is well known that, on addition of potassium cyanide to a solution of copper sulphate, cyanogen is liberated, and according to Friend (" Text Book of Inorganic Chemistry,"

FIG. 1.



1924, II, 287), cupric cuprocyanide, $Cu[Cu(CN)_2]_2,5H_2O$, is precipitated. On heating, it is completely converted into cuprous cyanide.

Curve *A* (Fig. 1) was constructed from the p_H values, measured with the glass electrode and the electrometer triode system, of a series of copper sulphate solutions which had been treated with various proportions of potassium cyanide and kept for 24 hours to reach equilibrium. To several 10 c.c. portions of 0·1*M*-copper sulphate, the required amount of potassium cyanide was added, the mixture diluted to 100 c.c. with water, placed in stoppered bottles, and the p_H measured after the above period. A small inflexion occurs with 2 mols. of potassium cyanide, and a larger one with 4—5 mols. The p_H values subsequently set up reveal buffer action, evidently caused by the conversion of some of the dissolved cyanogen into cyanic acid and hydrogen cyanide (Naumann, *Z. Elektrochem.*, 1910, **16**, 772). Greenish-brown precipitates were formed in those solutions to which less than 3·5 mols. of potassium cyanide had been added : greater quantities gave clear colourless solutions.

Curve *B* (Fig. 1) illustrates the effect of adding increasing amounts of potassium cyanide to 100 c.c. of solution in which 0·1 g. of pure cuprous cyanide ultimately dissolved. The conductivities of these solutions at 25° are plotted as curve *C*, and the potentials, E_{Cu} (N-H $= 0$), which they set up at a copper electrode are represented in curve *D*. The copper electrode was coated with an electrodeposited layer from a copper sulphate solution, and gave a potential of 0·2795 volt in 0·01*M*-copper sulphate, thus indicating a normal electrode potential of 0·343 volt, in good accord with that found by Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **207**, 112).

A sharp inflexion occurs in *B* with exactly 2 mols. of potassium cyanide per mol. of cuprous cyanide, and a break appears in the conductometric curve, *C*. Hence the complex cyanide is $K_2Cu(CN)_3$, and the fact that no further potassium cyanide is incorporated in the complex salt is seen from the p_H values and the conductivities thereafter attained. This is contrary to the location of the inflexion, between 2 and 3 mols. of potassium cyanide, in the copper-electrode curve *D*. In the potentiometric titration described by Glasstone (*loc. cit.*), the inflexion occurs with slightly less potassium cyanide. The potentials set up with the first 2 mols. of potassium cyanide were steady and reproducible, but afterwards they became increasingly uncertain. Glasstone has pointed out that copper can dissolve spontaneously in cyanide solutions with liberation of hydrogen, and this may be the explanation of the erratic behaviour of the copper electrode and the delay in the inflexion of curve *D*.

Table I records data regarding the hydrolysed hydrogen cyanide, the concentrations of which were determined by Harman and Worley's method. After deducting the concentration of the hydrogen cyanide set free by hydrolysis from the excess potassium cyanide (see Part V, J., 1932, 1941), the amount of hydrogen cyanide originating from the complex cyanide was found, and thence the percentage hydrolysis of the complex cyanide was calculated, each cyanide group being considered to take part in the hydrolysis. The ratios [CN′]/[HCN] were obtained from the p_H values, thus : $p_H = 9{\cdot}32 + \log[CN']/[HCN]$, $p_{K_{HCN}}$ being 9·32, and from the various observed concentrations of hydrogen cyanide the concentrations of cyanide ions were calculated. The final column of Table I gives the ratios of these concentrations to those of the potassium cyanide in excess of that required to form the complex cyanide. These values are of the order 0·8—0·9, and therefore provide further support for the view that the complex salt is $K_2Cu(CN)_3$. It is also seen that the complex cyanide is comparatively stable, for it is but slightly hydrolysed, and also that it is unaffected by the presence of an excess of potassium cyanide.

Table I.

Concn. × 10³.		$\frac{KCN}{CuCN}$.	[HCN] × 10⁴.			Hydrolysis of complex, %.	p_H.	$\frac{[CN']}{[KCN]}$.
$K_2Cu(CN)_3$.	KCN.		Obs.	KCN.	$K_2Cu(CN)_3$.			
2·79	0	0·5	0·4	0	0·4	0·48	7·38	—
5·58	0	1·0	0·6	0	0·6	0·32	7·85	—
8·37	0	1·5	0·8	0	0·8	0·29	8·14	—
11·16	0	2·0	1·6	0	1·6	0·48	9·40	—
11·16	5·58	2·5	5·26	3·66	1·6	0·48	10·22	0·8
11·16	11·16	3·0	6·79	5·19	1·6	0·48	10·47	0·9
11·16	16·74	3·5	7·96	6·36	1·6	0·48	10·56	0·8
11·16	22·32	4·0	8·96	7·36	1·6	0·48	10·63	0·8
11·16	44·64	6·0	12·00	10·50	1·5	0·48	10·85	0·9

An analysis was made of the specific conductivities of the solutions containing excess of potassium cyanide. Assuming that the specific conductivities of the complex cyanide and the potassium cyanide are additive, and knowing that of the latter, it is possible to compute that of the former, and thence its equivalent conductivity. Table II has thus been obtained. The concentration of the complex cyanide formed was 0·02232*N* in each case.

Table II.

$\frac{KCN}{CuCN}$.	$10^3\kappa$ obs.	$10^3\kappa_{KCN}$, calc.	$10^3\kappa_{K_2Cu(CN)_3}$.	Λ $\frac{1}{2}K_2Cu(CN)_3$.
2·184	3·37	0·50	2·87	129
2·621	3·97	1·05	2·91	130
3·058	4·595	1·73	2·87	129
3·494	5·23	2·42	2·81	129
5·242	7·64	4·81	2·83	127

In view of the approximate nature of the assumptions involved, the data in cols. 4 and 5 are sufficiently constant to justify the belief that 2 mols. of potassium cyanide combine with only one of cuprous cyanide. Moreover, the extrapolated equivalent conductivity of the complex cyanide is of magnitude similar to that of other complex cyanides (cf. Part V, *loc. cit.*, p. 1952).

II. *Tervalent Gold.*—Curves *E* and *F* (Fig. 2) refer respectively to the p_H values, measured with the glass electrode, and the specific conductivities at 25°, of solutions 0·002857*M* with respect to sodium aurichloride, $NaAuCl_4$, and containing increasing amounts of potassium cyanide, which had been shaken in stoppered bottles for 24 hours before the measurements were made. Curve *E* reveals that low p_H values prevailed during the reaction with 4 mols. of potassium cyanide, a sudden increase then taking place, and that with more potassium cyanide the p_H values were such that free alkali cyanide was indicated in the solution. Vapour-pressure measurements, made by the picric acid method, on the free hydrogen cyanide present in each of the solutions (Table III), show that in all cases up to 4 mols., the potassium cyanide had converted the theoretical quantity of auric chloride into $KAu(CN)_4$. Hence the low p_H's were caused by the considerable hydrolysis of the unattacked auric chloride (see Britton and Dodd, J., 1932, 2464). Curve *F* also shows that the complex $KAu(CN)_4$ was formed. Table III gives some typical hydrolysis and p_H data, and, like Table I, shows that the complex auricyanide is exceptionally stable, and that $KAu(CN)_4$ is very probably the only complex gold cyanide existing in potassium cyanide solutions.

FIG. 2.

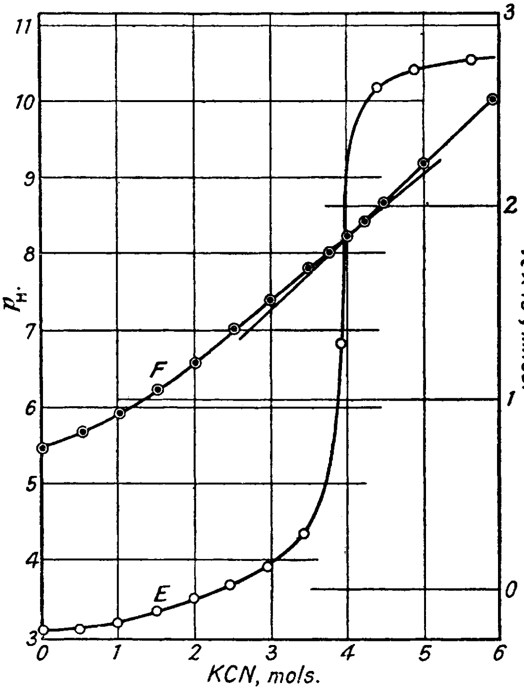


TABLE III.

Concn. × 10³.		$\frac{KCN}{NaAuCl_4}$.	[HCN] × 10⁴.			Hydrolysis of complex, %.	p_H.	$\frac{[CN']}{[KCN]}$.
$KAu(CN)_4$.	KCN.		Obs.	KCN.	$KAu(CN)_4$.			
0·714	0	1	0·6	0	0	2·1	3·16	—
1·428	0	2	0·8	0	0	1·4	3·58	—
2·143	0	3	0·9	0	0	1·0	3·93	—
2·857	0	4	0·3	0	0	0·26	8·00	—
2·857	1·428	4·5	1·94	1·71	0·23	0·20	10·20	1·0
2·857	2·857	5·0	2·80	2·57	0·23	0·20	10·38	1·1
2·857	4·285	5·5	3·40	3·17	0·23	0·20	10·48	1·1
2·857	5·714	6·0	3·90	3·68	0·22	0·19	10·54	1·1

After subtraction of the specific conductivity of the sodium chloride present when 4 mols. of potassium cyanide had reacted with 1 mol. of the aurichloride, the specific conductivity caused by the potassium auricyanide was $3{\cdot}30 \times 10^{-3}$ mho, and as the equivalent concentration was $0{\cdot}002857N$, it follows that the equivalent conductivity was 115·5 mhos, a value slightly greater than that of potassium argenticyanide.

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