ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART I. SILVER CYANIDE COMPLEX RADICAL.

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As early as 1904 it was stated by Richard Lucas,(1) Morgan,(2) and Kunschert(3) that when a silver salt is dissolved in a cyanide solution, the molal ratio of combined cyanide to silver is usually two to one, though sometimes one to one, corresponding to the formulas $Ag(CN)_2^-$ and $AgCN^-$. In the literature generally, even in recent text books, the complex ion is

(1) *Z. anorg. Chem.*, **41** (1904), 193.
(2) *Z. physik. Chem.*, **17** (1865), 513.
(3) *Z. anorg. Chem.*, **41** (1904), 359.

almost universally given as $Ag(CN)_2^-$. This may be due to the fact that the simplest of the double salts of potassium cyanide and silver cyanide is $KAg(CN)_2$.

Kunschert assumed that the e.m.f. of the concentration cell of copper cyanide in potassium cyanide solution was solely due to the difference in KCN concentration. It is probable, however, that at least an equally important source of potential difference in silver ion concentration was produced through the equilibrium $Ag(CN)_2^- \rightleftarrows Ag^+ + 2CN^-$ by the change in concentration of cyanide.

The works of Kunschert, Morgan and Richard Lucas are only necessary for me to add that their experiment were not well adapted to revealing the composition of the complex ion in solution.

Bonner and Kaura[1] found that in KCN solutions saturated with CuCN the ratio of bound cyanide is always three and the ratio of KCN to CuCN is therefore two instead of 2.5.

Bonner and Kaura determined the ratio of bound cyanide by simple titration method. I tried with this method to determine the ratio of bound cyanide about silver complex ion.

Composition of the silver cyanide ion. In order to determine the ratio of combined cyanide to silver in the complex ion, I have employed a simple titration method. Varying quantities of the desired silver salt were dissolved in 100 c.c. portions of an approximately moral sodium cyanide solution. The "free" cyanide which was not combined with silver to form the complex ion, was determined by titrating with silver nitrate solution using potassium iodide to facilitate the detection of the end point. The difference between the total cyanide, as determined in the original sodium cyanide solution, and the free cyanide in a particular sample, gave the amount of cyanide combined with the silver to form the complex ion. The result are summerized in the following tables.

Table 1.

Sodium Cyanide and Silver Cyanide.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.4660	0.0000	—
0.2061	0.2389	1.21
0.1422	0.1571	1.12
0.1031	0.1089	1.05
0.0770	0.0791	1.02
0.0559	0.0591	1.04
0.0301	0.0289	0.98

(1) *Chem. Met. Eng.*, **34** (1927), 84.

Table 2.

Sodium Cyanide and Silver Chloride.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1868	0.0000	—
0.1549	0.1669	1.04
0.1134	0.1218	1.06
0.0999	0.1050	1.05
0.0883	0.0903	1.02
0.0738	0.0782	1.07

Note: I have determined the concentration of silver nitrate by means of pure sodium chloride solution. In this case, I used potassium bichromate as the indicator.

Table 3.

Sodium Cyanide and Silver Thiocyanate.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.2318	0.0000	—
0.0908	0.0983	1.07
0.0676	0.0739	1.07
0.0560	0.0615	1.09
0.0463	0.0516	1.08
0.0309	0.0323	1.04
0.0193	0.0195	1.01
0.0097	0.0103	1.05

Table 4.

Sodium Cyanide and Silver Oxide.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1852	0.0000	—
0.0445	0.0486	1.09
0.0129	0.0138	1.07
0.0039	0.0048	1.24

Table 5.

Sodium Cyanide and Silver Chromate.[1]

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1882	0.0000	—
0.0357	0.0370	1.04
0.0231	0.0263	1.13
0.0217	0.0251	1.15
0.0179	0.0186	1.03

In all the above solutions the molal ratio of combined cyanide to silver is one to one, indicating the formula $AgCN^-$.

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(1) Prepared by the method given in *Z. anorg. Chem.*, **41** (1904), 69.