ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART II. CADMIUM CYANIDE COMPLEX RADICAL.

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P. Walden[1] and V. Tafeln[2] stated that when a cadmium cyanide is dissolved in a solution of potassium cyanide, the molal ratio of combined cyanide to cadmium is four to one, corresponding to the formula $Cd(CN)_4^{--}$.

(1) *Z. anorg. Chem.*, **23** (1900), 375.
(2) *Ber.*, **35** (1902), 2668.

It may be due to the fact that the simplest of the double salts of potassium cyanide and cadmium cyanide is $2KCN \cdot Cd(CN)_2$.

Books of analytical chemistry[1] describe the following facts. By adding potassium cyanide to a solution of a cadmium salt, it produces white precipitate of amorphous cadmium cyanide and this cyanide is soluble in excess of the reagent.

$$Cd^{++} + 2CN^- \rightarrow Cd(CN)_2$$
$$Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{--}$$

V. Tafeln[2] also stated that when a cadmium sulfocyanide is dissolved in a solution of potassium sulfocyanide, it produces potassium cadmium sulfocyanide, the formula of which is $Cd(CNS)_2 \cdot 2KCNS \cdot 2H_2O$, and moreover showed that there are the following complex compounds of cadmium.

(1) $Cd(CNS)_3M$ (2) $Cd(CNS)_4M_2$ (3) $Cd(CNS)_6M_4$

Composition of the Cadmium Cyanide Ion. In the present investigation, a simple titration method was used for the determination of the ratio of combined cyanide to cadmium in the complex ion. The method has already been described in the case of silver cyanide.[3] The results are shown in the following tables.

Table 1.

Sodium Cyanide and Cadmium Cyanide.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to cadmium
		Apparent	Actual*	
—	2.51344	—	—	—
0.16181	2.20600	0.30744	0.46925	2.90
0.15809	2.20516	0.30828	0.46637	2.95
0.13924	2.23496	0.27848	0.41772	3.00
0.08626	2.34437	0.16907	0.25533	2.96
0.03679	2.43986	0.07358	0.11037	3.00
0.02231	2.46772	0.04572	0.06803	3.05
0.01565	2.48057	0.03287	0.04852	3.10
—	1.48376	—	—	—
0.17050	1.16264	0.32112	0.49162	2.88
0.12759	1.21801	0.26575	0.39334	3.08
0.08714	1.29552	0.18824	0.27538	3.16
0.05070	1.37303	0.11073	0.16143	3.07

* The actual concentration of combined cyanide is equal to the apparent concentration plus the concentration of cadmium.

(1) For example, Treadwell, "Lehrbuch der analytischen Chemie," Vol. 1.
(2) *Z. anorg. Chem.*, **37** (1903), 447.
(3) This Bulletin, **4** (1929), 190.

The cadmium cyanide, $Cd(CN)_2$, has been prepared by decomposing barium cyanide with cadmium sulphate. It crystallizes in small colourless rhombic prisms. The barium cyanide, $Ba(CN)_2 \cdot 2H_2O$, has been obtained by passing hydrocyanic acid into a solution of barium hydroxide, the hydrocyanic acid being obtained by boiling the mixture of potassium ferrocyanide solution and sulphuric acid with the addition of cuprous chloride to decompose completely, thus:

$$K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + FeSO_4 + 2K_2SO_4$$

Table 2.

Sodium Cyanide and Cadmium Sulphate.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.17895	1.30431	0.51717	2.89
0.12013	1.46710	0.35438	2.95
0.08544	1.56089	0.26059	3.05
0.05608	1.64268	0.17880	3.01
—	0.50935	—	—
0.08455	0.26021	0.24914	2.94
0.07383	0.29343	0.21593	2.92
0.06254	0.32111	0.18824	3.00
0.05154	0.35433	0.15502	3.00

Table 3.

Sodium Cyanide and Cadmium Chloride.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.45695	0.53745	1.28403	2.81
0.27383	1.01368	0.80780	2.95
0.10658	1.49854	0.32294	3.03
—	1.48376	—	—
0.23133	0.80831	0.67545	2.91
0.15305	0.98548	0.49828	3.25
0.09789	1.17736	0.30640	3.13
0.05095	1.32989	0.15387	3.02

The cadmium sulphate and cadmium chloride which had been purified by recrystallization were used in these cases.

In all the above solutions the molal ratio of the combined cyanide to cadmium is three to one, indicating the formula to be $Cd(CN)_3^-$.

Stability of the Cadmium Cyanide Ion. There is, in the literature, no available information on the concentration of cadmium ion in cadmium cyanide solutions.

The author determined the potential differences between a cadmium electrode and various solutions of cadmium cyanide in sodium cyanide. The solutions used in these measurements were made by dissolving the appropriate amounts of pure cadmium cyanide in 50 c.c. of 0.77762 mol sodium cyanide solution. The electromotive force measurements were made at 25°C. by connecting a normal calomel electrode, through a saturated potassium chloride salt bridge, with an electrode of pure cadmium wire immersed directly in the solution, which being constantly stirred. The measured potentials remained constant over one hour. The data are summarized in Table 4.

Table 4.

$Cd(CN)_3^-$	CN^-	E	E_w	Cd^{++}	K
0.08920	0.22327	1.1567	0.8745	1.47×10^{-17}	5.45×10^{17}
0.07348	0.23097	1.1799	0.8977	1.12×10^{-17}	5.32×10^{17}
0.05502	0.24124	1.1851	0.9029	7.45×10^{-18}	5.26×10^{17}
0.02712	0.25661	1.1971	0.9149	2.90×10^{-18}	5.53×10^{17}

In Table 4, E is the measured electromotive force, and E_w is the potential of the cadmium electrode referred to the normal hydrogen electrode, taking the value for the single potential of the normal calomel electrode as -0.2822 volt.(1) The cadmium ion concentration, c, was found by the next equation

$$E_w = E_0 - 0.0295 \log c,$$

where E_0 is the standard electrode potential of the cadmium ion—cadmium electrode and is given by Lewis and associates as 0.3976 volt.(2) From the calculated value of (Cd^{++}), K can be determined from the expression:

(1) *J. Am. Chem. Soc.*, **42** (1920), 1128.

(2) Lewis and Randall, "Thermodynamics" (1923), p. 433.

$$K=\frac{Cd(CN)_3^-}{(Cd^{++})(CN^-)^3}$$

The fact that K remaines constant is an added evidence for the formula $Cd(CN)_3^-$.

Conclusion. The composition of the cadmium cyanide complex ion is probably $Cd(CN)_3^-$ at all concentrations.

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