ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART III.

ZINC CYANIDE COMPLEX RADICAL.

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F. Kunschert⁽¹⁾ stated that when a zinc salt is dissolved in a solution of potassium cyanide, the molal ratio of combined to uncombined zinc is usually four to one, though sometimes three to one, and he showed that the salt $K_2Zn(CN)_4$ will be separated to about 16% in KCN and $KZn(CN)_3$, and moreover, in concentrated solutions there exist such ion or salt as $Zn(CN)_4^{--}$, $K_2Zn(CN)_4$ or $BaZn(CN)_4$.

Book of analytical chemistry⁽²⁾ describes as the followings: It produces white precipitate of zinc cyanide by adding potassium cyanide to a solution of a zinc salt. In this case, the reaction take places are:

$$Zn^{++} + 2CN^{-} \rightleftarrows Zn(CN)_2$$
$$Zn(CN)_2 + 2CN^{-} \rightleftarrows Zn(CN)_4^{--}$$

Composition of Zinc Cyanide Ion. A simple titration method has been employed to determine the ratio of combined cyanide to zinc in the complex ion. The method has already been described in the cases of silver cyanide⁽³⁾ and cadmium cyanide.⁽⁴⁾ Zinc cyanide has been prepared from the dilute solution of zinc sulphate and sodium cyanide solution. It is white amorphous precipitate. The results are summarized in the following tables.

Table 1.
Sodium Cyanide and Zinc Cyanide.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to zinc
		Apparent	Actual*	
0.2850	1.1288	0.5978	0.8828	3.09
0.2377	1.2322	0.4944	0.7321	3.08
0.1779	1.3637	0.3629	0.5408	3.04

* This Bulletin, **6** (1931), 61.

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(1) *Z. anorg. Chem.*, **41** (1904), 351.
(2) For example, Treadwell, "Lehrbuch der analytischen Chemie," Vol. 1.
(3) This Bulletin, **4** (1929), 190.
(4) This Bulletin, **6** (1931), 60.

Table 1.—(*Concluded*)

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to zinc
		Apparent	Actual	
0.1199	1.4809	0.2457	0.3656	3.05
0.0770	1.5742	0.1524	0.2294	2.98
0.2469	0.5614	0.5030	0.7499	3.00
0.2005	0.6614	0.4030	0.6035	3.01
0.1853	0.6955	0.3689	0.5543	2.99
0.1767	0.7146	0.3498	0.5265	2.98
0.1524	0.7627	0.3017	0.4541	2.98
0.2003	0.2386	0.4418	0.6421	3.27
0.1735	0.3178	0.3626	0.5361	3.09
0.1482	0.3766	0.3038	0.4520	3.05
0.1110	0.4562	0.2242	0.3552	3.02
0.0937	0.4996	0.1808	0.2745	2.95

Table 2.

Sodium Cyanide and Zinc Sulphate.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.2436	0.0754	0.9890	4.05
0.2159	0.1869	0.8765	4.06
0.1835	0.3231	0.7413	4.04
0.1721	0.3726	0.6918	4.02
0.1366	0.5167	0.5477	4.01
0.0942	0.6872	0.3772	4.00
0.0635	0.8088	0.2556	4.02
0.1415	0.2726	0.5906	4.17
0.1077	0.3938	0.4694	4.34
0.0793	0.5364	0.3268	4.12
0.0894	0.0503	0.3688	4.11
0.0807	0.0963	0.3228	4.00
0.0570	0.1927	0.2264	3.97
0.0466	0.2389	0.1802	3.86

Table 3.

Sodium Cyanide and Zinc Acetate.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0907	0.4944	0.3688	4.06
0.0692	0.5950	0.2682	3.87
0.0351	0.7458	0.1404	4.00
0.0258	0.7710	0.0922	3.58

In the above experiments, the molal ratio of combined cyanide to zinc is three to one in the case of zinc cyanide and sodium cyanide, and four to one is other cases, corresponding to the formulas $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$ respectively.

Stability of the Zinc Cyanide Ion. There is available in the literature very little information on the concentration of zinc ion in zinc cyanide solution. Kunschert⁽¹⁾ stated that the zinc ion concentration is 3×10^{-19} in a molal solution of cyanide ion and 0.1 molal solution of complex ion, which he regards as $Zn(CN)_3^-$. He gives as the stability constant 3.3×10^{17}.

The author have consequently made a series of determinations of the potential differences between a zinc electrode and various zinc salts in sodium cyanide solution. The solutions used in these measurements were made by dissolving the appropriate amounts of pure $Zn(CN)_2$ and $ZnSO_4$ in 100 c.c. portions of 0.5177 molal sodium cyanide solution. The electromotive force measurements were made at 18°C by connecting a normal calomel electrode, through a normal potassium chloride salt bridge, with an electrode of pure zinc rod immersed directly in the solution, which being constantly stirred. The data are summarized in Tables 4 and 5.

Table 4.

$Zn(CN)_3^-$	CN^-	E	E_w	Zn^{++}	K
0.03916	0.15687	1.5471	1.2649	2.717×10^{-18}	3.73×10^{18}
0.02385	0.16079	1.5522	1.2700	1.799×10^{-18}	3.18×10^{18}
0.02000	0.16472	1.5556	1.2734	1.371×10^{-18}	3.27×10^{18}

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(1) *Z. anorg. Chem.*, **41** (1904), 351.

Table 5.

$Zn(CN)_4^{--}$	CN^-	E	E_w	Zn^{++}	K
0.03460	0.10442	1.5532	1.2710	1.668×10^{-18}	1.77×10^{20}
0.02428	0.10589	1.5588	1.2766	1.068×10^{-18}	1.81×10^{20}

In Tables 4 and 5, E are the measured electromotive forces and E_w are the potentials of the zinc electrode referred to normal hydrogen electrode, taking the value for the single potential of the normal calomel electrode as 0.2822 volt.(1) The zinc ion concentration, C, was found by the next equation.

$$E_w = E_0 - 0.02885 \log c$$

where E_0 is the standard electrode potential of the zinc ion-zinc electrode which is given as 0.7581 volt.(2) From the calculated value of (Zn^{++}), K can be determined from the expression:

$$K = \frac{Zn(CN)_3^-}{(Zn^{++})\,(CN^-)^3} \text{ and } K = \frac{Zn(CN)_4^{--}}{(Zn^{++})\,(CN^-)^4}$$

Table 6.

$Zn(CN)_3^-$	CN^-	E	E_h	E_{Zn}	H^+	Zn^{++}	K
0.03916	0.15687	1.5471	−0.3157	1.2324	1.14×10^{-11}	4.94×10^{-17}	2.05×10^{17}
0.02385	0.16079	1.5528	−0.3158	1.2364	1.13×10^{-11}	2.64×10^{-17}	2.14×10^{17}
0.02000	0.16472	1.5556	−0.3159	1.2397	1.12×10^{-11}	2.02×10^{-17}	2.20×10^{17}

Table 7.

$Zn(CN)_4^{--}$	CN^-	E	E_h	E_{Zn}	H^+	Zn^{++}	K
0.03460	0.10442	1.5532	−0.3130	1.2402	1.41×10^{-11}	1.95×10^{-17}	1.47×10^{19}
0.02428	0.10589	1.5588	−0.3132	1.2456	1.39×10^{-11}	1.27×10^{-17}	1.51×10^{19}

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(1) Lewis and Randall, "Thermodynamics" (1923), p. 407.

(2) Ibid., p. 420.

In Tables 6 and 7, E is the measured electromotive force; E_h the correction required to give the potential (E_{Zn}) referred to the normal hydrogen electrode, and K the stability constant. The hydrogen ion concentrations in these solutions were calculated from the ionization constant of HCN⁽¹⁾ as 2.06×10^{-9} and that for water⁽²⁾ as 1.005×10^{-14}.

From the law of mass action we have obtained for the dissociation of hydrocyanic acid:

$$\frac{(\mathrm{CN}^-)\,(\mathrm{H}^+)}{(\mathrm{HCN})} = K \quad \dots\dots\dots\dots \quad (1)$$

and, since

$$(\mathrm{H}^+)\,(\mathrm{OH}^-) = K_w \quad \dots\dots\dots\dots \quad (2)$$

we have

$$\frac{(\mathrm{CN}^-)}{(\mathrm{HCN})} = \frac{K}{K_w}\,(\mathrm{OH}^-) \quad \dots\dots\dots\dots \quad (3)$$

The concentration of the undissociated sodium cyanide may be neglected, since the salt may be regarded as completely dissociated. The hydrolysis of sodium cyanide takes place according to the equation.

$$\mathrm{NaCN} + \mathrm{H_2O} = \mathrm{HCN} + \mathrm{NaOH}$$

and the sodium hydroxide may, also be regarded as completely dissociated. Therefore, the concentration of the OH ion produced by the hydrolysis is equal to the concentration of the undissociated HCN produced at the same time according to the equation.

$$\mathrm{CN}^- + \mathrm{H_2O} = \mathrm{OH}^- + \mathrm{HCN} \quad \dots\dots\dots\dots \quad (4)$$

Now, from (3) we have

$$(\mathrm{HCN}) = (\mathrm{OH}^-) = \frac{(\mathrm{CN}^-)}{(\mathrm{OH}^-)} \times \frac{K_w}{K}$$

so

$$(\mathrm{CN}^-) = \frac{K(\mathrm{OH}^-)^2}{K_w} \text{ or } (\mathrm{OH}^-)^2 = \frac{(\mathrm{CN}^-)\,K_w}{K} \quad \dots\dots \quad (6)$$

Therefore, the concentration of the hydrogen ion was calculated from the equations (6) and (2) and the value of E_h was calculated by the next equation.

$$E_h = 0.02885 \log (\mathrm{H}^+)$$

To determine the zinc ion concentration we may write,

$$E_{Zn} = E_o - 0.02885 \log c$$

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(1) Lewis and Randall, "Thermodynamics" (1923), p. 589.

(2) Ibid., p. 486.

where E_0, the standard electrode potential of Zn^{++}, is taken as 0.7581 volt. From the calculated value of Zn^{++}, K can be determined from the above expression.

The fact that K remaines constant are an added evidence for the formulas $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$.

Conclusion. The composition of the zinc cyanide complex ion are probably $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$ at all concentrations.

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