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

NICKEL CYANIDE COMPLEX RADICAL.

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H. E. Williams(1) showed that nickel cyanide dissolved very readily in a solution of an alkaline cyanide, forming an orange-red solution of a double nickel cyanide of type, $M_2Ni(CN)_4$.

The following description is found in the book of analytical chemistry.(2) It produces an apple-green gelatinous precipitate by adding potassium cya-

(1) Cyanogen Compounds p. 66 (1915).
(2) Treadwell, Lehrbuch der analytishen Chemie, Vol. 1.

nide to a solution of a nickel salt, and this cyanide is soluble in excess of the reagent.

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

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

Composition of Nickel Cyanide Ion. Nickel cyanide has been prepared by adding a solution of an alkaline cyanide to an excess of a nickel sulphate solution. In this case, author had an apple-green gelatinous precipitate of nickel cyanide, The precipitated nickel cyanide was purified by washing with conductivity water. Also nickel sulphate and nickel nitrate were purified by recrystallization. Then the ratio of combined cyanide to nickel in the complex ion was determined by a simple titration method.[1]

The results are summarized in the following tables.

Table 1.

Sodium Cyanide and Nickel Cyanide.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio of combined cyanide to nickel
0.1535	1.3308	0.6293	4.09
0.1456	1.3517	0.5926	4.07
0.1298	1.3922	0.5205	4.01
0.1195	1.4156	0.4765	3.98
0.1665	1.0109	0.6693	4.02
0.1372	1.0728	0.5488	4.00
0.1038	1.1344	0.4204	4.05
0.0988	1.1476	0.3972	4.03
0.0581	0.6363	0.2330	4.01
0.0390	0.6754	0.1556	3.99
0.0237	0.7064	0.0941	3.97
0.0165	0.7225	0.0635	3.85

Author obtained red colour solutions by adding pure nickel cyanide to 1.6531 and 1.3472 molal solutions of sodium cyanide, and also an orange colour solution by using 0.7530 molal solution of sodium cyanide.

(1) This Bulletin, **4** (1929), 190; ibid., **6** (1931), 60; ibid., **6** (1931), 89.

Table 2.
Sodium Cyanide and Nickel Sulphate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0804	1.3295	0.3236	4.02
0.0662	1.3767	0.2764	4.17
0.0638	1.4001	0.2530	3.96
0.0578	1.4354	0.2177	3.78
0.0556	0.8000	0.2236	4.02
0.0519	0.8059	0.2177	4.19
0.0472	0.8295	0.1941	4.11
0.0444	0.8353	0.1883	4.24
0.0389	0.4471	0.1529	3.93
0.0352	0.4589	0.1411	4.00
0.0317	0.4706	0.1294	4.08
0.0289	0.4824	0.1176	4.06

Table 3.
Sodium Cyanide and Nickel Nitrate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0891	0.7269	0.3555	3.99
0.0731	0.7915	0.2909	3.98
0.0586	0.8488	0.2336	4.00
0.0549	0.8612	0.2212	4.03
0.0418	0.4544	0.1672	4.00
0.0379	0.4712	0.1524	4.02
0.0277	0.5124	0.1111	4.01
0.0212	0.5377	0.0859	4.05

In these cases of the Tables 2 and 3, author obtained red colour solutions by adding nickel sulphate or nitrate solution to the 1.0653 and 1.0824 molal sodium cyanide, and also orange colour solutions by adding nickel salts solutions to the 0.8000, 0.6000, and 0.6236 molal sodium cyanide solutions.

In all these experiments, the molal ratio of combined cyanide to nickel is four to one for all nickel salts, corresponding to the formula $Ni(CN)_4^{--}$. Hence it may be probably that the composition of the cyanide complex radical of nickel is $Ni(CN)_4^{--}$.

Stability of the Nickel Cyanide Ion. There is no available information on the concentration of nickel ion in nickel cyanide solution.

The potential differences between a nickel electrode and various solutions of nickel cyanide in sodium cyanide has been determined. The solutions used in these measurements were made by dissolving the appropriate amounts of pure nickel cyanide in 100 c.c. of 0.7852 mol NaCN solution. The electromotive force measurements were carried out at 25° C. by connecting a normal calomel electrode, through a normal KCl salt bridge, with an electrode of pure nickel wire immersed directly in the solution being constantly stirred. The obtained data are summarized in Table 4.

Table 4.

$Ni(CN)_4^{--}$	CN^-	E	E_w	Ni^{++}	K
0.06995	0.12511	0.7767	0.4946	4.92×10^{-10}	5.8×10^{13}
0.05316	0.14243	0.7863	0.5041	2.34×10^{-10}	5.6×10^{13}
0.02278	0.15591	0.7976	0.5154	7.33×10^{-11}	5.4×10^{13}

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

$$E_w = E_o - 0.0295 \log c$$

where E_o is the standard electrode potential of nickel ion– nickel electrode and its value is 0.22 volt.(2) From the calculated value of (Ni^{++}), stability constant can be determined as follows:

$$K = \frac{Ni(CN)_4^{--}}{(Ni^{++})(CN^-)^4}$$

It will be noticed that K remains nearly constant in the Table 4. Therefore, we may conclude that in this case the complex ion is also $Ni(CN_4^{--})$.

Conclusion. The composition of the nickel cyanide complex ion is probably $Ni(CN)_4^{--}$ through all concentrations.

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(1) Lewis and Randall, Thermodynamics (1923), p. 407.
(2) Noyes and Sherrill, Chemical Principle (1920), p. 260.