SOLUBILITIES OF METALLIC CYANIDES.

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In the author's previous paper[1] the solubilities of cyanide and thiocyanate of silver in water were published. Sherrill[2] determined the solubility of mercuric cyanide in water. But we have no information on the solubilities of cyanides of other metals. Author measured, hence, the solubilities of cyanides of cadmium, zinc, nickel, and cobalt.

In order to determine these solubilities the following cells are used.

Cd (amalgam), Cd^{++} (a_1) ‖ Ca^{++} (a_2), Cd (amalgam)

Zn (amalgam), Zn^{++} (a_1) ‖ Zn^{++} (a_2), Zn (amalgam)

Ni (amalgam), Ni^{++} (a_1) ‖ Ni^{++} (a_2), Ni (amalgam)

Co (amalgam), Co^{++} (a_1) ‖ Co^{++} (a_2), Co (amalgam)

The following two equations have been used to determine the electromotive force.

$$E_c = \frac{RT}{2F} \ln \frac{a_2}{a_1} \qquad (1)$$

$$E_l^{(3)} = \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (2)$$

where E_c represents the electromotive force of electrodes, E_l, the liquid potential at the contact of two solutions, a_1 and a , the activities of cadmium-, zinc-, nickel-, and cobalt-salts, and also Λ_C and Λ_A are the ionic conductances of the cation and of the anion, and V_C and V_A are the valences of the cation and of the anion respectively, the term Λ_A was replaced by the mean value of the two anion conductances.

Experimental.

Cyanides of cadmium, zinc, nickel and cobalt were prepared from the dilute solutions of corresponding potassium salt by precipitating with purified sulphates of these metals respectively. Potassium salts used were

(1) This Bulletin, **5** (1930), 345.
(2) *Z. physik. Chem.*, **43** (1903), 735.
(3) Noyes and Sherrill: Chemical Principles, p. 263 (1922).

of Kahlbaum and purified by recrystallization. The precipitated salts were further purified by washing with conductivity water.

Cadmium chloride, zinc chloride, nickel nitrate, and cobalt nitrate were purified by washing five times with conductivity water. Conductivity water used in the experiments had a specific conductance of 1.5×10^{-6}.

The amalgams were made by electrolysing a 10% solutions of pure cadmium sulphate, zinc sulphate, nickel nitrate, and cobalt nitrate with mercury as a cathode, and the amalgams contained about 2.5% of metals. The cells used were of ordinary form. The electromotive force of the cells were measured after being kept in a thrmostat at $18° \pm 0.1$ for about one hour. Constants necessary to carry out the calculation are given in the Tables 1 and 2.

Table 1.

Salt	Moles per litre of water	Activity coeff.	Activity
$CdCl_2$	0.01	0.532(1)	5.32×10^{-3}
$ZnCl_2$	0.0033	0.799(2)	2.63×10^{-3}
$Ni(NO_3)_2$	0.005	0.776(3)	3.88×10^{-3}
$Co(NO_3)_2$	0.01	0.380(4)	3.80×10^{-3}

Table 2.

Ion	Ionic Conductance at 18°C.	Ion	Ionic Conductance at 18°C.
Cd^{++}	46.4	Cl^-	65.5
Zn^{++}	47.0	CN^-	58.6
Ni^{++}	44.0	NO_3^-	61.8
Co^{++}	43.0		

The values in Table 2 were taken from the data of Noyes and Falk(5), except that for the cyanide ion which was determined by the following method.

(1) *J. Am. Chem. Soc.*, **41** (1919), 1787.
(2) Lewis and Randall "Thermodynamics" p. 420 (1923).
(3) and (4) The values were calculated from the data of "Thermodynamics" p. 382 (1923).
(5) *J. Am. Chem., Soc.*, **34** (1912), 459.

The conductivity was measured by the ordinary bridge method, using the cell of uniform diameter. The assembly for the measurements consisted of measuring bridge with a thin wire platinum-iridium, resistance wire, oscillater, and a tunable telephone. The slide wire and the resistance box were calibrated before the conductivity work was begun. The cell constants of the conductivity cell were determined with 1/50 normal solution of potassium chloride. The specific conductance of the sodium cyanide solutions were measured at 18°±0.1° C. after being kept in the thermostat for one hour. The results are summarized in the Table 3.

Table 3.

Concentration of NaCN	Cell Constant	Specific Conductance		Equivalent Conductance
		appearent	corrected	
1 Mol	0.228	73188×10^{-6}	73186×10^{-6}	73.186
0.1	0.228	7843×10^{-6}	7841×0^{-6}	78.41
0.01	0.228	829.9×10^{-6}	828.4×10^{-6}	82.84
0.001	0.228	95.76×10^{-6}	94.26×10^{-6}	94.26

We obtained 102 as the value of Λ_∞ at the infinite dilution of sodium cyanide by extrapolation from the data in Table 3, and subsequently 58.6 as the value of ionic conductance of CN^-.

Calculation.

The measured electromotive forces are as follows:

	Cell	E at 18°C.
(1)	Cd (amalgam), $Cd(CN)_2$ (sat) ‖ $CdCl_2$ (0.01 M), Cd (amalgam)	0.02700
(2)	Zn (amalgam), $Zn(CN)_2$ (sat) ‖ $ZnCl_2$ (0.0033 M), Zn (amalgam)	0.08705
(3)	Ni (amalgam), $Ni(CN)_2$ (sat) ‖ $Ni(NO_3)_2$ (0.005 M), Ni (amalgam)	0.04300
(4)	Co (amalgam), $Co(CN)_2$ (sat) ‖ $Co(NO_3)_2$ (0.01 M), Co (amalgam)	0.05050

We have the equation (3) by adding the equations (1) and (2).

$$E = E_c - E_l = \left[\frac{1}{2} - \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \right] \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \cdots\cdots\cdots (3)$$

(1) For the 0.01 molal solution of cadmium chloride, the value of activity a_2 is 5.32×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 46.4 and 62.05, respectively and

$$0.02700=\left[\frac{1}{2}-\frac{\frac{46.4}{2}-62.05}{46.4+62.05}\right]0.0577\log\frac{5.32\times10^{-3}}{a_1}$$

then, we obtain

$$a_1=1.51\times10^{-3}$$

(2) For the 0.0033 molal solution of zinc chloride, the value of activity is 2.63×10^{-3} and the value of Λ_C and Λ_A at 18°C. are 47 and 62.05. Therefore,

$$0.08705=\left[\frac{1}{2}-\frac{\frac{47}{2}-62.05}{47+62.05}\right]0.0577\log\frac{2.63\times10^{-3}}{a_1}$$

then

$$a_1=4.49\times10^{-5}$$

(3) For the 0.005 molal solution of nickel nitrate, the value of activity is 3.88×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 44 and 60.2. Then,

$$0.0430=\left[\frac{1}{2}-\frac{\frac{44}{2}-60.2}{44+6.02}\right]0.0577\log\frac{3.88\times10^{-3}}{a_1}$$

and

$$a_1=5.35\times10^{-4}$$

(4) For the 0.01 molal solution of cobalt nitrate, the value of activity is 3.80×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 43 and 60.2, therefore,

$$0.0505=\left[\frac{1}{2}-\frac{\frac{43}{2}-60.2}{43+60.2}\right]0.0577\log\frac{3.80\times10^{-3}}{a_1}$$

and

$$a_1=3.77\times10^{-4}$$

Summary

(1) Ionic conductance of CN^- was determined.

(2) The activities, i.e. solubilities of cyanides of cadmium, zinc, nickel, and cobalt were calculated.

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