THE SOLUBILITIES OF SILVER SALTS.

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During the progress of work in the author's laboratory on the cyanide complex radical of metals, there arose a need for the data on the solubilities of cyanide and thiocyanate of metals. Numerous investigators have reported on the solubilities of cyanide, thiocyanate and other salts of metals in water. But the results reported by them are not in good agreement one another. The author measured, at first, the solubilities in water of thiocyanate, bromide, cyanide and carbonate of silver.

The data obtained by previous investigators are shown in the following table.

Table 1.

Solubilities of Silver Salts in Water (moles per liter).

Salts	Temp.	Solubility	Year	Observer
AgSCN	25°C.	1.08×10^{-6}	1903	Kuster and Thiel(1)
	25	1.25×10^{-6}	1903	Abegg and Cox(2)
	25	1.20×10^{-6}	1908	Hill(3)
	25	$1{\cdot}08\times10^{-6}$	1912	Kirschner(4)
	20	0.77×10^{-6}	1903	Böttger(5)
AgBr	25	8.8×10^{-7}	1908	Hill(3)
	25	6.6×10^{-7}	1894	Goodwin(6)
	25	8.1×10^{-7}	1900	Thiel(7)
	18	2.0×10^{-6}	1893	Kohlrausch and Rose(8)
	13	1.8×10^{-6}	1893	Holleman(9)
AgCN	25	2.22×10^{-6}	1904	Lucas(10)
	19.96	1.64×10^{-6}	1903	Böttger(5)
	17.5	3.17×10^{-7}	1903	Abegg and Cox(2)
Ag_2CO_3	25	1.16×10^{-4}	1909	Spencer and Le Pla(11)
	25	1.52×10^{-4}	1903	Abegg and Cox(2)

(1) *Z. anorg. Chem.*, **33** (1903), 139.
(2) *Z. physik. Chem.*, **46** (1903), 11.
(3) *J. Am. Chem. Soc.*, **30** (1908), 74.
(4) *Z. physik. Chem.*, **79** (1912), 245.
(5) *Z. physik. Chem.*, **46** (1903), 603.
(6) *Z. physik. Chem.*, **13** (1894), 645.
(7) *Z. anorg. Chem.*, **24** (1900), 57.
(8) *Z. physik. Chem.*, **12** (1893), 139, 241.
(9) *Z. physik. Chem.*, **12** (1893), 139, 241.
(10) *Z. anorg. Chem.*, **41** (1904), 198.
(11) *Z. anorg. Chem.*, **65** (1909), 14.

Experimental. Silver thiocyanate, bromide, cyanide and carbonate were prepared from the dilute solutions of the corresponding potassium salts by precipitating with purified silver nitrate. The potassium salts were of Kahlbaum and purified by recrystallization before being used. The precipitated silver salts were further purified by washing with conductivity water. The conductivity water which was used in the experiment had a specific conductance of 1.2×10^{-6}. The works have been done in the dark room.

The solubilities have been measured by the potentiometric method. The cell used were of ordinary form composed of the electrodes of pure silver wires, 0.01 mol silver nitrate solution and the saturated solution of silver salts which is to be measured. The saturated solution of ammonium nitrate has been used as the junction liquid. Thus:

(1) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgSCN in 0.1N.KSCN | Ag
(2) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgBr in 0.1N.KBr | Ag
(3) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgCN in 0.01N.KCN | Ag
(4) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | Ag_2CO_3 in 0.1N.Na_2CO_3 | Ag

All the electromotive force measurements were done after the cells had stood in a thermostat the temperature of which was kept constant within 0.1° for about one or two hours to attain equilibrium as indicated by a constancy of electromotive force. For the measurements a potentiometer and a D.L. type mirror galvanometer were used.

The electromotive force of the cells at 18°C. is given by the following equation, the transport number of anion being assumed to be 0.53.

$$e = 0.53 \times 2 \times 0.058 \log \frac{0.01a}{x}$$

The degree of ionization of silver nitrate in 0.01N. solution, a, is 0.93 at 18°C. x is the concentration of silver ion in the 0.1N. solution of potassium thiocyanate, bromide or carbonate and in the 0.01N. solution of potassium cyanide.

The concentrations of the thiocyanate, bromide and carbonate ions are assumed to be 0.01 normal, and that of the cyanide ion 0.1 normal.

The observed electromotive forces of the cells and the solubilities of silver salts calculated therefrom are shown in Tables 2, 3, 4 and 5. The concentrations, in these tables, are given in mol per litre.

Table 2.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgSCN in 0.1N. KSCN | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. KCNS solution	Solubilities of Ag SCN at 18°C.
1	1	0.545	1.2×10^{-11}	1.1×10^{-6}
2	1	0.550	1.0×10^{-11}	1.0×10^{-6}
3	1	0.552	0.9×10^{-11}	0.9×10^{-6}
4	1	0.549	1.1×10^{-11}	1.0×10^{-6}
5	1	0.551	1.0×10^{-11}	1.0×10^{-6}
mean	1	0.549	1.0×10^{-11}	1.0×10^{-6}

Table 3.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgBr in 0.1N. KBr | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. KBr solution	Solubilities of Ag Br at 18°C.
1	2	0.570	4.9×10^{-12}	7.0×10^{-7}
2	2	0.571	4.8×10^{-12}	6.9×10^{-7}
3	2	0.570	4.9×10^{-12}	7.0×10^{-7}
4	2	0.569	5.2×10^{-12}	7.2×10^{-7}
5	2	0.571	4.8×10^{-12}	6.9×10^{-7}
mean	2	0.570	4.9×10^{-12}	7.0×10^{-7}

Table 4.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgCN in 0.01N. KCN | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.01 N. KCN solution	Solubilities of Ag CN at 18°C.
1	2	0.572	4.5×10^{-12}	2.1×10^{-7}
2	2	0.571	4.8×10^{-12}	2.2×10^{-7}
3	2	0.572	4.5×10^{-12}	2.1×10^{-7}
4	2	0.573	4.4×10^{-12}	2.1×10^{-7}
5	2	0.571	4.8×10^{-12}	2.2×10^{-7}
mean	2	0.571	4.6×10^{-12}	2.1×10^{-7}

Table 5.

Ag | 0.01N-$AgNO_3$ | NH_4NO_3 (sat) | Ag_2CO_3 in 0.1N-Na_2CO_3 | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. Na_2CO_3 solution	Solubilities of Ag_2CO_3 at 18°C.
1	2	0.204	4.6×10^{-6}	1.2×10^{-4}
2	2	0.205	4.5×10^{-6}	1.2×10^{-4}
3	2	0.204	4.6×10^{-6}	1.2×10^{-4}
4	2	0.206	4.3×10^{-6}	0.9×10^{-4}
5	2	0.206	4.3×10^{-6}	0.9×10^{-4}
mean	2	0.205	4.5×10^{-6}	1.1×10^{-4}

Summary.

The solubilities of silver cyanide, thiocyanate, bromide and carbonate in water at 18°C. have been determined by the electromotive force measurements, and obtained the values:

Silver cyanide: 2.1×10^{-7} mol per litre
Silver thiocyanate: 1.0×10^{-6} ,, ,, ,,
Silver bromide: 7.0×10^{-7} ,, ,, ,,
Silver carbonate: 1.1×10^{-4} ,, ,, ,,

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