[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIA INVOLVING SOME COMPLEX IONS OF SILVER AND THE FREE ENERGY OF SOME SILVER COMPOUNDS[1]

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Complex ions of silver are formed by the combination of silver ion with ammonia, cyanide, sulfite, thiosulfate, nitrite, thiocyanate, chloride, bromide, iodide and a few other substances. They fall into two classes: those formed from the ions of strong acids, including the halides and thiocyanates, in which case no one complex predominates, and those formed by the combination of silver ion with neutral, weakly basic, or weakly acidic substances in which only a single complex is predominantly present. The equilibria involving the latter class may be treated in a manner comparable to the treatment of simple ion equilibria. The latter class includes the ammonia and cyanide complexes, and it is with these that this paper is chiefly concerned.

When silver chloride is added to aqueous ammonia, silver ammonia complex is formed in accordance with the equation

$$AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l) \qquad (1)$$

If we define K_m' by the equation[2]

$$K_m' = m(Ag(NH_3)_2^+)m(Cl^-)a^2\,(H_2O)/a^2\,(NH_4OH(aq.)) \qquad (2)$$

it is obvious from the definition of the activity coefficient that the true equilibrium constant, K, is equal to $\gamma_\pm{}^2K_m'$, where $\gamma_\pm$ is the activity coefficient of the complex salt. The activity of the water is included in the activity of the aqueous ammonia by definition and it will be found in the following article[3] that the activity coefficient of the ammonia in aqueous silver ammonia chloride is equal to the molality of the ammonia. If, then, we plot the logarithm of the reciprocal square root of K_m' against a function of the ionic strength, or its square root ($\mu^{1/2}$), the curve is similar to that obtained by plotting the logarithm of the activity coefficient ($\log \gamma_\pm$) of a simple univalent salt against the same function of the ionic strength. The extrapolation to infinite dilution is made by superimposing our plot upon the similar plot for a suitable strong electrolyte.[2a] The logarithm of the reciprocal square root of K then coincides with the origin of the reference plot. From the value of $\log (1/K^{1/2})$ and the measured values of

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[1] Abridged paper; original received December 22, 1927.

[2] The method of extrapolation is a modification of that adopted by (a) Randall and Vietti, THIS JOURNAL, **50**, 1526 (1928). Reference to the present work was made by (b) Randall, *Trans. Faraday Soc.*, **23**, 502 (1927). See also (c) Randall, *ibid.*, **23**, 498 (1927); (d) Bray and MacKay, THIS JOURNAL, **32**, 1207 (1910), and (e) Johnston, *ibid.*, **37**, 2001 (1915), used similar equilibrium constants.

[3] Randall and Halford, *ibid.*, **52**, 192 (1930).

$\log (1/K_m'^{1/2})$ the activity coefficient of the complex salt may be obtained for a given ionic strength, for by definition

$$\log \gamma_{\pm} = \log (1/K_m'^{1/2}) - \log (1/K^{1/2}) \qquad (3)$$

In a reaction in which the complex is formed by the addition of an ion as cyanide or sulfite, rather than by reaction with a neutral molecule as ammonia or hydrocyanic acid, another method of extrapolation must be employed. For example, in the reaction

$$AgI(s) + 2CN^- = Ag(CN)_2^- + I^-;\ K = a(Ag(CN)_2^-)a(I^-)/a^2(CN^-) \qquad (4)$$

the value of K is probably not far different from the stoichiometrical equilibrium constant K_m; and if $\log K_m$ is plotted against the square root of the ionic strength, a straight line will be obtained if the activity coefficients of the cyanide complex and iodide ion are not far different from that of cyanide ion. In many cases K is obtained with sufficient accuracy by taking the numerical average of K_m.

The Solubility of Silver Chloride in Aqueous Ammonia.—$AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l)$.—Silver chloride was prepared by adding silver nitrate (0.5 M) to a slight excess of ammonium chloride (0.1 M) in the presence of very dilute nitric acid. After filtering and washing thoroughly, the precipitate was dried at 100°. At all times care was taken to avoid prolonged exposure to light. Aqueous ammonia was prepared by diluting U. S. P. ammonium hydroxide to the desired strength. The resulting solutions were found to be free from carbonate. Toluene was distilled before use, about 20% being discarded in the initial and final fractions.

Silver chloride, aqueous ammonia and toluene were placed in bottles with ground glass stoppers secured by small rubber caps and rotated in a thermostat at 25° for a period exceeding twenty-four hours. The mixtures were allowed to settle for several hours before analysis. To prevent loss of ammonia by evaporation, samples were forced by pressure from the reaction bottles through absorbent cotton filters into flasks containing a known weight of 0.1 M hydrochloric acid (standardized against sodium carbonate) in excess. The ammonia was extracted from the toluene by excess of standard acid, with methyl orange as the indicator since methyl red was found to dissolve in the toluene. The excess acid was titrated (methyl red, weight buret against sodium hydroxide). Samples for the determination of silver were received in excess of nitric acid and the silver was weighed as silver chloride.

The concentration of free ammonium hydroxide was calculated by subtracting twice the silver concentration plus the calculated ammonium ion from the total ammonia concentration (moles per 1000 g. of water in vacuum).

Experiments by Reychler[4] on the freezing points of solutions of the nitrate and sulfate of silver ammonia complex led to the formula $Ag(NH_3)_2^+$. Konowalow[5] and later Gaus,[6] from vapor pressure, and Berthelot and Delépine,[7] from the heat effects attending the addition of silver nitrate in excess to aqueous ammonia and of aqueous ammonia in excess to silver nitrate, obtained the same formula. The work of Whitney and Mel-

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[4] Reychler, *Ber.*, **28**, 555 (1895).

[5] Konowalow, *Z. physik. Chem.*, **28**, 558 (1898).

[6] Gaus, *Z. anorg. Chem.*, **25**, 236 (1900).

[7] Berthelot and Delépine, *Compt. rend.*, **129**, 326 (1899).

cher,[8] which included transference, freezing point and conductivity experiments, led to a similar result. More recently, de Wijs[9] has presented evidence that in saturated solutions of the base $Ag(NH_3)_2OH$ the average number of ammonia molecules per silver molecule is slightly greater than two. Our experiments with silver chloride solutions, in which the ratio of free ammonia is high in comparison to the complex ion concentration, suggest the presence of small amounts of the higher forms, but at present we are unable to present definite evidence as to the constitution of the complex. Our treatment is independent of the existence of small amounts of the higher forms.

The results of our measurements are given in Table I. Cols. 1 and 2 give the total molality of ammonia and silver constituents, Cols. 3 and 4 the molality of ammonium ion and of undissociated ammonium hydroxide as calculated[10] by the method of approximations, on the basis that the formula of the complex ion is $Ag(NH_3)_2^+$, and Cols. 5 and 6 the functions log $(1/K_m'^{1/2})$ and $\mu^{1/2}$.

TABLE I

SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIA AT 25°

Total $m(NH_3)$	Total $m(Ag)$	Calcd. $m(NH_4^+)$	Calcd. $m(NH_4OH)$	Log $(1/K_m'^{1/2})$	$\mu^{1/2}$
0.1089	0.005665	0.0015	0.0960	1.229	0.0835
1.3039	.0895	.0051	1.1198	1.097	.307
1.710	.1256	.0065	1.4525	1.063	.363
1.8782	.1379	.0068	1.5956	1.064	.380
2.1339	.1628	.0074	1.8009	1.054	.413
2.6400	.2151	.0085	2.2014	1.010	.473
2.9091	.2395	.0090	2.4211	1.005	.498

The values of log $(1/K_m'^{1/2})$ are plotted in Fig. 1 against the square root of the ionic strength. We also show the values of this constant as calculated from the data of other authors.[11]

By superimposition of the plot of Fig. 1 upon the standard activity coefficient curve,[2a] we find that the activity coefficient of the aqueous silver ammonia chloride is slightly less than that given by the limiting curve[2a]

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[8] Whitney and Melcher, THIS JOURNAL, **23**, 68 (1903).

[9] De Wijs, "Thesis," Delft, **1923**.

[10] $NH_4OH(aq.) = NH_4^+ + OH^-$; $K_{298\cdot 1} = 18.1 \times 10^{-6}$ [Noyes and Kanolt, *Publ. Carnegie Inst.*, Washington, D. C., No. 63, 285 (1907)]. The activity coefficient in the mixture was taken as that of sodium hydroxide [see Randall and Failey, *Chem. Reviews*, **4**, 291 (1927)].

[11] (a) Bodländer and Fittig, *Z. physik. Chem.*, **39**, 597 (1901); (b) Straub, *ibid.*, **77**, 332 (1911); (c) Whitney and Melcher, Ref. 8. The values given by Whitney and Melcher are in concentration units. More weight should be given to their values in the dilute solutions as the data for converting concentrations to molalities is not known. (d) The data and calculations are given by Randall in the section on Free Energy, "International Critical Tables," Vol. VII, McGraw-Hill Book Co., New York, **1930**.

of the Debye–Hückel equation. We take log $(1/K^{1/2})$ equal to 1.272 ± 0.002, hence

$$\mathrm{AgCl(s)} + 2\mathrm{NH_4OH(aq.)} = \mathrm{Ag(NH_3)_2^+} + \mathrm{Cl^-} + 2\mathrm{H_2O(l)};\ K_{298.1} = 2.858 \times 10^{-3};\ \Delta F^\circ_{298.1} = 3472 \text{ cal.} \quad (5)$$

The values of the logarithm of activity coefficient of the silver ammonia chloride at round molalities are given in Table II.

Table II

Activity Coefficient of Silver Ammonia Chloride

m	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Log γ	−0.017	−0.024	−0.040	−0.056	−0.080	−0.126	−0.176	−0.248	−0.382

The Solubility of Silver Oxide in Aqueous Ammonia.—$^1/_2\mathrm{Ag_2O(s)} + 2\mathrm{NH_4OH(aq.)} = \mathrm{Ag(NH_3)_2^+} + \mathrm{OH^-} + {}^3/_2\mathrm{H_2O(l)}$. In this reaction the values of K_m' calculated from the distribution ratios of ammonia between toluene and water do not correct completely for the activity of the water since the reaction of two moles of ammonia produces only 1.5 moles

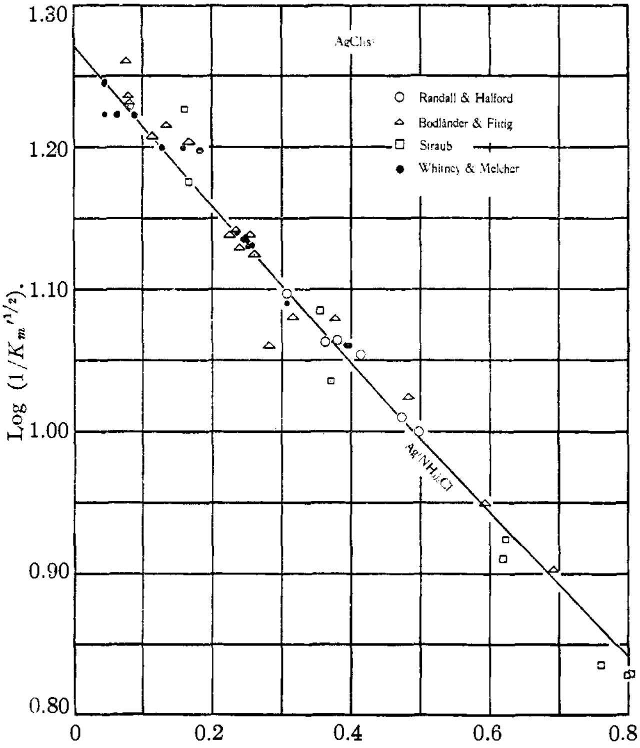

Fig. 1.—Solubility of silver chloride in aqueous ammonium hydroxide at 25°.

of water. The reciprocal square root of the equilibrium constant is given by

$$1/K^{1/2} = a(\mathrm{NH_4OH(aq.)})/[a(\mathrm{Ag(NH_3)_2}^+)a(\mathrm{OH})^- a^{3/2}(\mathrm{H_2O})]^{1/2} \qquad (6)$$

Since by definition

$$a(\mathrm{NH_4OH(aq.)}) = \gamma' m(\mathrm{NH_4OH})a(\mathrm{H_2O}) \qquad (7)$$

then

$$1/K_m'^{1/2} = \gamma' m(\mathrm{NH_4OH})a^{1/4}(\mathrm{H_2O})/m(\mathrm{Ag(NH_3)_2}^+)m(\mathrm{OH})^- \qquad (8)$$

The activity of the water is involved in Equation 8 only as the fourth root. In our measurements the activity of the water does not differ from unity by more than 10% at the highest concentration investigated. Therefore, if we include the fourth root of the activity coefficient of the water in that of the complex base, the maximum error introduced is 2.5% and this only at the highest concentrations. The equilibrium at ionic strengths, 0.01 to 0.27, was determined in the same manner as in the case of the silver ammonia chloride.

Silver oxide was prepared by adding 0.5 *N* silver nitrate to an excess of 0.1 *N* barium hydroxide which had been found to be free from halides. The precipitate was washed thoroughly and heated to boiling in distilled water to decompose any silver carbonate. This method of preparation did not exclude small quantities of barium carbonate but the presence of that substance should have no effect on the measurements.

The silver was determined by the method of Volhard. In a few cases the equilibrium was approached from supersaturation by diluting mixtures which had already come to equilibrium and rotating for more than twenty-four hours in the thermostat.

In the more dilute solutions, the distribution experiments were omitted because of the difficulty of measuring accurately the concentration of ammonia in the toluene layer. The average value[3]

$$\mathrm{NH_4OH(aq.\ in\ Ag(NH_3)_2OH)};\ (\log \gamma')/\mu = 0.136 \qquad (9)$$

has been used in calculating the values of $1/K_m'^{1/2}$ from those of $1/K_m'^{1/2}$.

The results of our measurements are given in Table III. Col. 1 gives molality of the total base, Col. 2 that of the silver constituent which is also the ionic strength, Col. 3 the molality of the free ammonium hydroxide, equal to molality of total base less three times the molality of silver constituent, Col. 4 the value of $1/K_m^{1/2}$, Col. 5 the value of the same function after changing the molality of the $\mathrm{NH_4OH}$ to activity by means of Equation 9, and Cols. 6 and 7 have the same significance as the corresponding columns in Table I.

The values of Col. 6 are plotted against $\mu^{1/2}$ in Fig. 2. This plot also shows the values of $\log(1/K_c'^{1/2})$ calculated from the results of similar measurements (moles per liter) by Whitney and Melcher.[8,11c,d] Olmer[12] also studied this reaction at room temperature, and at ionic strengths from 0.1 to 1.4. His results are qualitatively in agreement with those of Fig. 2 and show that the activity coefficient of the silver ammonia hydroxide

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[12] Olmer, *Bull. soc. chim.*, **35**, 333 (1924).

rapidly increases in the more concentrated solutions, thus offering additional evidence that this substance is a strong base.

Table III

Solubility of Silver Oxide in Aqueous Ammonia at 25°

Total m base	$m(Ag(NH_3)_2^+)$	$m(NH_4OH)$	$1/K_m^{1/2}$	$1/K_m'^{1/2}$	Log $(1/K_m'^{1/2})$	$\mu^{1/2}$
0.05302	0.01155	0.01838	1.59	1.59	0.201	0.107
.05532	.01282	.01667	1.32	1.32	.119	.113
.05821	.01338	.01806	1.35	1.36	.133	.116
.06173	.01406	.01955	1.39	1.40	.146	.119
.1479	.03499	.04289	1.23	1.25	.097	.187
.1575	.03606	.04932	1.37	1.39	.143	.190
.2456	.05787	.07198	1.25	1.26	.100	.240
.3155	.07352	.09490	1.29	1.32	.120	.272
.3200	.07535	.09494	1.26	1.29	.111	.274
.3540	.07787	.1231	1.55	1.59	.201	.279
.6519	.1525	.1945	1.28	1.34	.127	.391
.6767	.1582	.2021	1.28	1.34	.127	.398
.6950	.1623	.2082	1.28	1.35	.130	.403
.8673	.2033	.2574	1.26	1.34	.127	.452
.9518	.2225	.2841	1.26	1.35	.130	.472
1.2304	.2888	.3642	1.26	1.38	.140	.538

Noyes and Kohr and later Newton[13] have determined the ratio of potassium chloride and potassium hydroxide shaken with an excess of silver oxide and silver chloride. When their values of K_c and K_m are plotted against $\mu^{1/2}$ they appear to be in agreement. An extrapolation to $\mu^{1/2} = 0$ gives

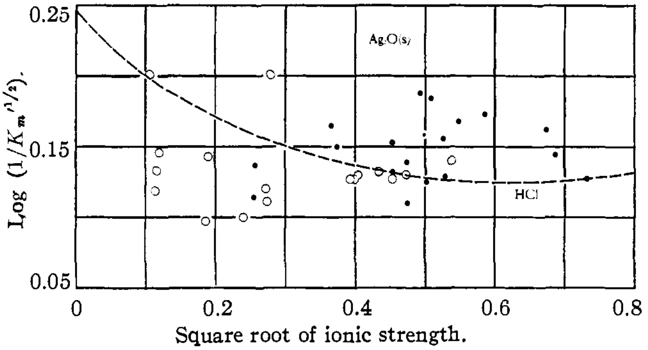

Fig. 2.—Solubility of silver oxide in aqueous ammonium hydroxide at 25°.

$$AgCl(s) + OH^- = \tfrac{1}{2}Ag_2O(s) + Cl^-;\ \log K_{298.1} = -2.050 \pm 0.003;\quad \Delta F^\circ_{298.1} = 2798 \pm 5 \text{ cal.} \qquad (10)$$

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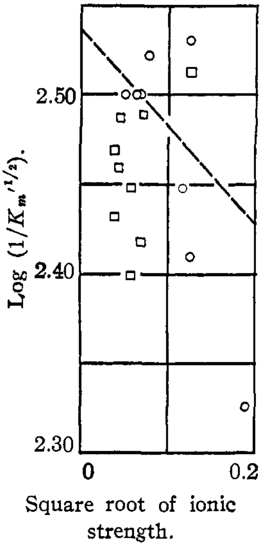
[13] (a) Noyes and Kohr, *Z. physik. Chem.*, **42**, 336 (1902); (b) Newton, This Journal, **50**, 3258 (1928).

and this value gives a reasonable ratio between the activity coefficients of OH^- and Cl^- in the more concentrated solutions.[14]

Combining Equations 5 and 10 we find

$$\tfrac{1}{2}Ag_2O(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + OH^- + \tfrac{3}{2}H_2O(l); \log K_{298\cdot1} = -0.494 \pm 0.005; \ \Delta F^\circ_{298\cdot1} = 674 \text{ cal.} \tag{11}$$

whence we find $\log (1/K^{1/2}) = 0.247$ and this point is shown on Fig. 2 as the intersection of the dotted curve with the ordinate $\mu^{1/2} = 0$. The dotted curve is that of the logarithm of activity coefficient of hydrochloric acid plus 0.247. In general, the activity coefficient of strong bases is slightly less than that of hydrochloric acid. Our results show agreement with the assumption that the complex hydroxide is an approximately normal strong base in the region of $\mu^{1/2}$ = about 0.4. If we were to attempt to superimpose Fig. 2 upon the plot of $\log \gamma$ for strong bases so as to pass through the points at about $\mu^{1/2} = 0.2$, then we should find the activity coefficient of silver ammonia hydroxide much higher than that of any other substance at 0.2 M, and we should need to explain a discrepancy between the free energy as given by Equation 10 and the difference between Equations 5 and 11. A possible explanation of the anomalous activity coefficient of the hydroxide of silver ammonia complex is a change in the fineness of subdivision of the solid phase with the concentration and nature of the electrolyte. The probable analytical errors are not of the right sign to explain the unusual results.



○, Bodländer and Fittig; □, Whitney and Welcher.

Fig. 3.—Solubility of silver bromide in aqueous ammonia.

$AgBr(s) + 2NH_4OH(aq.) = Ag(NH_3)^+ + Br^- + 2H_2O(l)$.—We show in Fig. 3 the values of $\log (1/K_m'^{1/2})$ and $\log (1/K_c'^{1/2})$ as calculated from the measurements of Bodländer and Fittig[11a,d] and of Whitney and Melcher[8, 11c,d] plotted against $\mu^{1/2}$ or $\mu_c^{1/2}$. Account was taken of the amount of NH_4^+ present. The limiting value, $\log (1/K^{1/2})$, was calculated from Equation 5 and the free energies of silver chloride, silver bromide, chloride and bromide ions,[15] and found to be 2.537. The experimental values are found to be in agreement with this value, and show that the activity coefficient of silver ammonia bromide is somewhat lower than that of the complex chloride. We thus write

$$AgBr(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Br^- + 2H_2O(l); \log K_{298\cdot1} = -5.074 \pm 0.005; \ \Delta F^\circ_{298\cdot1} = 6926 \text{ cal.} \tag{12}$$

Solubility of Silver Cyanide in Hydrocyanic Acid. $AgCN(s) + HCN(aq.) = H^+ + Ag(CN)_2^-$.—We have studied this reaction in solutions of

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[14] See Randall and Breckenridge, This Journal, 49, 1435 (1927).

[15] Randall and Spencer, unpublished calculations.

hydrocyanic acid from 0.1 to 0.5 *M*. When silver cyanide is allowed to come to equilibrium with aqueous hydrogen cyanide, a small concentration of a strong acid is produced. A measurement of this acid concentration and the concentration of hydrocyanic acid permits the calculation of the equilibrium constant. The fugacity of the hydrogen cyanide is proportional to its molality.[3]

Hydrocyanic acid was prepared by the method used by Perry and Porter,[16] who investigated the vapor pressures of solid and liquid hydrogen cyanide. A solution of 18 *N* sulfuric acid was added slowly to powdered potassium cyanide in a distilling flask and the vapors were collected in water. The production of cyanogen by oxidation is not probable because of the slow rate of oxidation exhibited by sulfuric acid of the strength used. Perry and Porter had no difficulty with the cyanogen impurity. Silver cyanide was precipitated in dilute solution by the addition of silver nitrate to a slight excess of potassium cyanide. Some of the experiments were carried out in glass stoppered bottles, others in sealed flasks.[2a] In a few cases equilibrium was approached from supersaturation by maintaining the mixtures at a temperature of about 35° for several hours before rotating in the thermostat. The mixtures of silver cyanide, benzene and aqueous hydrocyanic acid were rotated in the thermostat at 25° for several days. To prevent loss of hydrogen cyanide by evaporation, samples were forced by pressure from the reaction bottles. The acid concentration was determined by titration with 0.01 *N* sodium hydroxide. Samples for the determination of cyanide were received in excess of sodium hydroxide and titrated by the method of Liebig to an endpoint with potassium iodide.

In Table IV we have summarized the results of the solubility measurements. Column 1 gives the molality of hydrocyanic acid, Col. 2 that of the complex acid, Col. 3 the reciprocal square root of the stoichiometrical constant, Col. 4 its logarithm and Col. 5 the square root of the ionic strength. The acid concentration produced in these equilibria is so small that an accurate determination of the equilibrium constant is difficult. We have plotted, in Fig. 4, $1/K_m^{1/2}$ against the square root of the ionic strength and for the purpose of making the very slight extrapolation to zero molality have taken the point determined by the mean value of $1/K_m^{1/2}$ and the mean value of $\mu^{1/2}$. From this point we have extrapolated to zero ionic strength with the aid of the curve for hydrochloric acid and have obtained for log $(1/K^{1/2})$ the value 2.212.

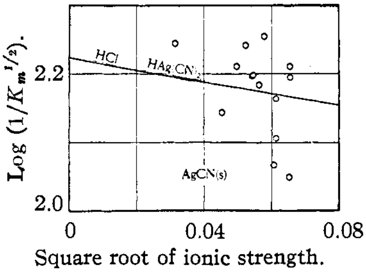

Fig. 4.—Solubility of silver cyanide in aqueous hydrogen cyanide at 25°.

$$AgCN(s) + HCN(aq.) = H^+ + Ag(CN)_2^-;\ K_{298.1} = 3.77 \times 10^{-5};\ \Delta F^\circ_{298.1} = 6038 \text{ cal.} \quad (13)$$

Solubility of Silver Chloride in Hydrocyanic Acid. $AgCl(s) + 2HCN(aq.) = 2H^+ + Ag(CN)_2^- + Cl^-$.—The solubility of silver chloride in

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[16] Perry and Porter, This Journal, **48**, 299 (1926).

TABLE IV

SOLUBILITY OF SILVER CYANIDE IN AQUEOUS HYDROCYANIC ACID AT 25°

m(HCN(aq.))	m(HAg(CN)$_2$)	Log $(1/K_m^{1/2})$	$\mu^{1/2}$	m(HCN(aq.))	m(HAg(CN)$_2$)	Log $(1/K_m^{1/2})$	$\mu^{1/2}$
0.0296	0.000983	2.244	0.0314	0.2275	0.00424	2.050	0.0652
.1016	.000204	2.144	.0452	.2325	.00316	2.184	.0562
.1596	.00245	2.211	.0496	.3000	.00375	2.164	.0612
.1780	.00366	2.067	.0606	.3625	.00331	2.254	.0576
.1825	.00246	2.198	.0544	.4230	.00400	2.210	.0653
.2124	.00292	2.197	.0541	.4260	.00511	2.106	.0612
.2245	.00272	2.241	.0523	.4465	.00427	2.195	.0654

aqueous hydrocyanic acid has been treated in the same manner as that of silver cyanide.

Our analysis determines only the molality of the strong acid and the molality of the hydrocyanic acid. In the simplest interpretation the complex cyanide and the chloride would have the same molality equal to half that of the acid. From the equilibrium constant of the solubility of silver cyanide in aqueous hydrogen cyanide, it is evident that if in our solutions the complex ion concentration were half that of the acid, the solutions would be supersaturated with respect to silver cyanide. Therefore, we must introduce a correction to account for the reaction

$$\mathrm{AgCl(s)} + \mathrm{HCN(aq.)} = \mathrm{AgCN(s)} + \mathrm{H}^+ + \mathrm{Cl}^- \qquad (14)$$

The chloride ion concentration is greater than that of the silver cyanide complex.

Columns 1 to 4 of Table V give the molality of the hydrogen cyanide, the hydrogen ion, the complex and of the chloride, Col. 5 the reciprocal fourth root of K_m, Col. 6 its logarithm and the last the square root of the ionic strength. To determine the equilibrium constant we have plotted log $(1/K_m^{1/4})$ against the square root of the ionic strength and have extrapolated to zero ionic strength with the aid of the curve for hydrochloric acid. This gives us log $K_m^{-0.25}$ = 2.180 and

$$\mathrm{AgCl(s)} + 2\mathrm{HCN(aq.)} = \mathrm{Ag(CN)_2}^- + 2\mathrm{H}^+ + \mathrm{Cl}^-;\ K_{298.1} = 1.9 \times 10^{-9};\ \Delta F^\circ_{298.1} = 11{,}902 \text{ cal.} \qquad (15)$$

TABLE V

SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS HYDROCYANIC ACID AT 25°

m(HCN(aq.))	m(Acid)	m(Complex)	m(Chloride)	Log $(1/K_m^{1/4})$	$\mu^{1/2}$
0.0938	0.00303	0.00132	0.00161	2.163	0.0552
.1831	.00430	.00182	.00258	2.146	.0652
.2292	.00493	.00199	.00294	2.141	.0702

Solubility of Silver Iodide in Potassium Cyanide. $\mathrm{AgI(s)} + 2\mathrm{CN}^- = \mathrm{Ag(CN)_2}^- + \mathrm{I}^-$.—Measurements were made with "precipitated" silver iodide and also with a crystalline form. The precipitated silver iodide was prepared by adding 0.5 N silver nitrate to an excess of 0.1 N potassium iodide. The precipitate was separated and dried at 100°. The preparation of hexagonal crystals of silver iodide involved a digestion of mercuric iodide with 0.1 M silver nitrate at the boiling point. This method does not exclude mercury salts but these should have no effect on the reaction other than to cause a slight increase of ionic strength.

The silver iodide was rotated in a thermostat in contact with a potassium cyanide solution of known strength for several days. Sufficient sodium hydroxide was added to repress the hydrolysis of the cyanide. To determine the silver content a sample was acidified with nitric acid and heated to remove hydrogen cyanide; this precipitated the silver iodide, which was collected on a filter, dried at 100° and weighed.

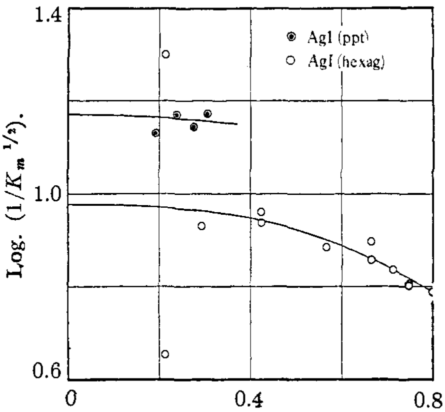

Fig. 5.—Solubility of silver iodide in aqueous potassium cyanide at 25°.

The measurements of the solubility of the precipitated and crystalline forms are summarized in Tables VI and VII and the results are plotted in Fig. 5. The limiting value of log $K^{1/2}$ in the case of precipitated silver iodide was calculated by combining Equation 15 with the free energy of ionization of aqueous hydrogen cyanide[17] and the standard free energies of the silver chloride[18] and silver iodide electrodes.[15] We thus find

$$\text{AgI(ppt.)} + 2\text{CN}^- = \text{Ag(CN)}_2{}^- + \text{I}^-;\ K_{298\cdot1} = 221;\ \Delta F^\circ_{298\cdot1} = -3201 \text{ cal.} \quad (16)$$

The greatest uncertainty is in the value for the free energy of ionization of the hydrogen cyanide. The value of log $K^{1/2} = 1.172$ is shown in Fig. 5 as the limit of the extrapolated curve. This extrapolation appears to be reasonable. In the extrapolation of the curve for the hexagonal silver iodide, it was made parallel to the curve for the precipitated variety, whence log $K^{1/2} = 0.978$, and

$$\text{AgI(hexag.)} + 2\text{CN}^- = \text{Ag(CN)}_2{}^- + \text{I}^-;\ K_{298\cdot1} = 90.4;\ \Delta F^\circ_{298\cdot1} = -2670 \text{ cal.} \quad (17)$$

From the difference of Equations 16 and 17

$$\text{AgI(ppt.)} = \text{AgI(hexag.)};\ \Delta F^\circ_{298\cdot1} = -531 \text{ cal.} \quad (18)$$

TABLE VI

SOLUBILITY OF PRECIPITATED SILVER IODIDE IN POTASSIUM CYANIDE AT 25°

Total $m(\text{CN}^-)$	m(AgI)	$m(\text{CN}^-\text{(free)})$	m(NaOH (added))	Log $(K_m{}^{1/2})$	$\mu^{1/2}$
0.01837	0.00866	0.00065	0.0197	1.131	0.192
.03676	.01778	.00120	.0200	1.170	.238
.05521	.02666	.00191	.0199	1.146	.275
.07337	.03549	.00239	.0196	1.173	.305

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[17] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[18] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

TABLE VII

SOLUBILITY OF HEXAGONAL SILVER IODIDE IN POTASSIUM CYANIDE AT 25°

Total $m(CN^-)$	$m(AgI)$	$m(CN^-(free))$	m(NaOH (added))	Log $(K_m^{1/2})$	$\mu^{1/2}$
0.0208	0.0102	0.00049	0.0244	1.301	0.212
.0208	.0093	.0021	.0244	.653	.212
.0405	.0191	.00224	.0444	.931	.292
.0836	.0386	.00456	.0946	.938	.423
.0836	.0396	.00434	.0946	.961	.423
.146	.0684	.00889	.1738	.886	.566
.195	.0911	.0126	.2433	.858	.663
.195	.0916	.0116	.2433	.897	.663
.261	.1217	.0177	.2448	.836	.712
.318	.1474	.0232	.2421	.802	.748
.318	.1475	.0230	.2421	.806	.748
.398	.1840	.0300	.2424	.788	.800

Solubility of Silver Thiocyanate, Silver Iodide and Silver Bromide in Potassium Thiocyanate.—Bodländer and Fittig[11a] have given the formula and free energy of the silver thiocyanate complex. Their data suggested that the free energies of silver bromide and silver iodide might be linked through their solubility in potassium thiocyanate. We have measured the solubility of silver thiocyanate, silver bromide and silver iodide in solutions of potassium thiocyanate.

Silver bromide was made by precipitating potassium bromide in dilute solution with silver nitrate in the presence of dilute nitric acid; silver thiocyanate was prepared in an analogous manner. Potassium thiocyanate of known strength was rotated in bottles in the thermostat in contact with the solid phase at 25° for several days. The silver content of the sample selected for analysis was determined gravimetrically by precipitating the dissolved solid and weighing. The thiocyanate was oxidized by heating with 2 *N* nitric acid, the solid precipitating during the oxidation. When the solid phase was silver thiocyanate, a small concentration of potassium thiocyanate was added to the solution before filtering to replace any silver thiocyanate which had been oxidized.

In the silver bromide equilibria agreement was obtained in two sets of experiments in which rotation was continued respectively for two days and three weeks. This eliminates the time factor in the explanation of the results. In the silver thiocyanate equilibria a few rough measurements were made in which the equilibrium was approached from supersaturation. They were consistent with the others.

Table VIII gives the results of the solubilities of silver bromide. The first column gives the total molality of potassium thiocyanate, the second of the dissolved silver bromide, the third the free thiocyanate if the formula of the complex is $Ag(CNS)_2^-$, and the fourth a function of the equilibrium constant.

Table IX gives similar results for the solubility of precipitated silver iodide in potassium thiocyanate, while Table X summarizes the silver thiocyanate equilibria.

TABLE VIII

SOLUBILITY OF SILVER BROMIDE IN POTASSIUM THIOCYANATE AT 25°

$AgBr(s) + 2CNS^- = Ag(CNS)_2^- + Br^-$

Total m(KCNS)	m(AgBr)	m(KCNS (free))	Log ($K_m^{1/2}$)
0.2510	0.0011	0.249	−2.340
.2702	.0012	.267	−2.340
.5205	.0095	.501	−1.722
.5819	.0085	.564	−1.824
.7577	.0285	.701	−1.390
.7762	.0307	.715	−1.367
1.0089	.0663	.875	−1.122
1.0089	.0668	.875	−1.118

TABLE IX

SOLUBILITY OF PRECIPITATED SILVER IODIDE IN POTASSIUM THIOCYANATE AT 25°

$AgI(amorp.) + 2CNS^- = Ag(CNS)_2^- + I^-$

Total m(KCNS)	$m \times 10^4$ (AgI)	m(KCNS (free))	Log ($K_m^{1/2}$)
0.202	0.20	0.202	−4.00
.315	.14	.315	−4.30
.425	.67	.425	−3.91
.500	.51	.500	−4.00
.608	.40	.608	−4.18
.710	.97	.710	−3.85
.765	1.46	.765	−3.72
1.009	1.63	1.008	−3.80

TABLE X

SOLUBILITY OF SILVER THIOCYANATE IN POTASSIUM THIOCYANATE AT 25°

$AgCNS(s) + CNS^- = Ag(CNS)_2^-$

Original m(KCNS)	m(AgCNS)	m(KCNS(free))	Log (K_m)
0.312	0.00202	0.310	−2.187
.564	.0121	.512	−1.627
.870	.0458	.824	−1.255
1.124	.0985	1.026	−1.018

Evidently we cannot account for the solubility of these solids in potassium thiocyanate by the formation of a single complex ion $Ag(CNS)_2^-$ Attempts to interpret these results by other simple assumptions have been unsuccessful. The reactions here studied are analogous to those of the silver halides in halide ion solutions. By assuming a sufficient number of complexes, and determining the equilibrium constants among these by the method of approximations, one should be able to satisfy the experimental data, but it is doubtful if such a calculation would be of more than academic interest.

The Solubility of Silver Chloride in Sulfite Solutions.—From the measurements of Luther and Leubner,[19] the details of which are found in another place,[11d] we find on extrapolation to infinite dilution

$$AgCl(s) + 2SO_3^{--} = Ag(SO_3)_2^{---} + Cl^-;\ K_{298.1} = 0.0578;\ \Delta F^\circ_{298.1} = 1690 \text{ cal.} \quad (19)$$

The Solubility of Silver Bromide in Sulfite Solutions.—Likewise from the solubility measurements of Luther and Leubner,[11d,19] we find on extrap-

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[19] Luther and Leubner, *Z. anorg. Chem.*, **74**, 393 (1911).

olating to zero ionic strength along a line parallel to the curve of log K_c against $\mu_c^{1/2}$ for Reaction 19, the value log K = 3.754, whence

$$AgBr(s) + 2SO_3^{--} = Ag(SO_3)_2^{---} + Br^-;\ K_{298.1} = 1.76 \times 10^{-4};\ \Delta F^\circ_{298.1} = 5124 \text{ cal.} \quad (20)$$

The difference in the values of the free energy from Equations 19 and 20 is −3434 cal. while the corresponding difference between Equations 5 and 12 is −3454 cal. which is a very satisfactory check upon the accuracy of the measurements and the assumptions made in the various extrapolations.

The Equilibrium of Silver Chloride and Silver Bromide with Silver Thiocyanate.—From the measurements of Hill,[20,11d] we find by extrapolation

$$AgCl(s) + CNS^- = AgCNS(s) + Cl^-;\ K_{298.1} = 161;\ \Delta F^\circ_{298.1} = -3012 \text{ cal.} \quad (21)$$

$$AgBr(s) + CNS^- = AgCNS(s) + Br^-;\ K_{298.1} = 0.505;\ \Delta F^\circ_{298.1} = 404 \text{ cal.} \quad (22)$$

The difference between Equations 21 and 22 is −3416 cal., which is also in satisfactory agreement with the difference between Equations 5 and 12.

The Free Energy of Some Silver Complexes

Silver Ammonia Complex.—The free energy of the silver ammonia complex ion is best calculated from Equation 5, which is based upon the solubility of silver chloride. We have already shown that the results based upon the solubility of silver oxide (Equation 11) and of silver bromide (Equation 12) in aqueous ammonia are in agreement with Equation 5. Hence combining with the values for the free energy of formation of silver chloride,[15] aqueous ammonia,[11d,17] chloride ion,[18] and liquid water,[11d,17] we find

$$Ag(s) + N_2(g) + 3H_2(g) = Ag(NH_3)_2^+ + E^-;\ \Delta F^\circ_{298.1} = -4003 \text{ cal.} \quad (23)$$

Dissociation Constant of Silver Ammonia Complex.—By combination of Equation 23 with the free energy of silver ion,[11d,17] liquid water and ammonia we find

$$Ag(NH_3)_2^+ + 2H_2O(l) = Ag^+ + 2NH_4OH(aq.);\ \Delta F^\circ_{298.1} = 9851 \text{ cal.};\ K_{298.1} = 7.86 \times 10^{-8} \quad (24)$$

Silver Cyanide Complex.—We calculate the free energy of formation of silver cyanide complex from Equation 15 and the free energies of silver chloride,[15] aqueous hydrogen cyanide[11d,17] (27,510) and chloride ion,[18] whence

$$Ag(s) + 2C(graph.) + N_2(g) + E^- = Ag(CN)_2^-;\ \Delta F^\circ_{298.1} = 72{,}047 \text{ cal.} \quad (25)$$

As in the case of the silver ammonia complex, this value has already been shown to be in agreement with that calculated from other reactions. (Equation 16.)

Silver Cyanide.—From Equations 13 and 25 with the free energy of aqueous hydrogen cyanide we find for the free energy of formation of silver cyanide.

$$Ag(s) + C(graph.) + \tfrac{1}{2}N_2(g) = AgCN(s);\ \Delta F^\circ_{298.1} = 38{,}499 \text{ cal.} \quad (26)$$

Dissociation Constant of Silver Cyandie Complex.—From Equation

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[20] Hill, This Journal, 30, 68 (1908).

15, the free energy of chloride ion, silver chloride and the free energy of dissociation of aqueous hydrogen cyanide,[11d,17] we find

$$\mathrm{Ag(CN)_2^-} = \mathrm{Ag^+} + \mathrm{2CN^-};\ \Delta F^\circ_{298.1} = 25{,}141\ \text{cal.};\ K_{298.1} = 3.81 \times 10^{-19} \quad (27)$$

Solubility Product of Silver Cyanide.—From Equations 13 and 27 we find

$$\mathrm{AgCN(s)} = \mathrm{Ag^+} + \mathrm{CN^-};\ \Delta F^\circ_{298.1} = 19{,}319\ \text{cal.};\ K_{298.1} = 7 \times 10^{-15} \quad (28)$$

Hydrogen Silver Cyanide.—Since the results of Table IV and Fig. 4 show the hydrogen silver cyanide to be a strong acid, we may write from Equation 25

$$\mathrm{Ag(s)} + \mathrm{2C(graph.)} + \mathrm{N_2(g)} + {}^1/_2\mathrm{H_2(g)} = \mathrm{HAg(CN)_2};\ \Delta F^\circ_{298.1} = 72{,}047\ \text{cal.} \quad (29)$$

Silver Sulfite Complex.—From Equation 19 and the free energy of silver chloride,[15] chloride ion[18] and sulfite ion,[11d,17] we find

$$\mathrm{Ag(s)} + \mathrm{2S(rhomb.)} + \mathrm{3O_2(g)} + \mathrm{3E^-} = \mathrm{Ag(SO_3)_2^{---}};\ \Delta F^\circ_{298.1} = -226{,}545\ \text{cal.} \quad (30)$$

We may consider this result verified by Equation 20. The largest uncertainty in the value lies in the uncertainty in the free energy of sulfite ion.

Dissociation Constant of Silver Sulfite Complex.—From Equation 30 and the free energies of silver and sulfite ion,[11d,17] we find

$$\mathrm{Ag(SO_3)_2^{---}} = \mathrm{Ag^+} + \mathrm{2SO_3^{--}};\ \Delta F^\circ_{298.1} = 11{,}633\ \text{cal.};\ K_{298.1} = 3.00 \times 10^{-9} \quad (31)$$

Summary

A method has been presented for the treatment of equilibria involving the solution of difficultly soluble compounds in weak acids or bases to form complex ions. The method has been applied to new data for the solubility of silver chloride and silver oxide in ammonium hydroxide and of silver chloride and silver cyanide in aqueous hydrogen cyanide.

The solubility of precipitated and crystalline silver iodide in potassium cyanide, and the solubility of silver bromide, silver iodide and silver thiocyanate in potassium thiocyanate has been determined.

The activity coefficient of silver ammonia chloride, of silver ammonia bromide, of silver ammonia hydroxide and of complex silver cyanide acid has been determined.

The data for the solubility of silver salts in weak acids have been reviewed and the free energy of several complex ions calculated.

The data for the free energy of several silver salts have been considered and the free energies of some of the silver compounds are presented in the following table.

TABLE XI

FREE ENERGY OF SOME SILVER COMPOUNDS

Substance	$\Delta F^\circ_{298.1}$, cal.	Equation	Substance	$\Delta F^\circ_{298.1}$, cal.	Equation
Ag(s)	0		$\mathrm{Ag(SO_3)_2^{---}}$	−226,545	35
AgCl(s)	−26,220	Ref. 18	$\mathrm{Ag(NH_3)_2^+}$	− 4,003	34
AgBr(s)	−22,910	Ref. 15	$\mathrm{HAg(CN)_2}$	72,047	29
AgI(hexag.)	−16,356	Ref. 18	AgCN(s)	38,499	26
AgI(ppt.)	−15,825	Ref. 15	$\mathrm{Ag(CN)_2^-}$	72,047	25

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