Studies on Aging and Coprecipitation. XXVI. The Coprecipitation of Silver Chloride with Colloidal and Flocculated Silver Bromide

BY I. M. KOLTHOFF AND F. T. EGGERTSEN

When a slightly soluble compound BC (AgBr) is precipitated from a solution which contains the component A (Cl⁻), and the compound AC (AgCl) can form mixed crystals with BC, there will be a coprecipitation of AC with BC. This will happen even if AC does not separate under the experimental conditions in the absence of BC. Suppose the conditions during the precipitation of BC are such that there is distribution equilibrium

$$\text{BC} + \text{A} \rightleftarrows \text{AC} + \text{B}$$
$$\text{Solid} \quad \text{Solution} \quad \text{Solid} \quad \text{Solution}$$
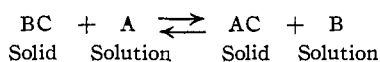
during the growth of BC. If the precipitate is not subject to aging, the distribution of A between solution and solid at any stage during the precipitation of BC will be determined by the logarithmic expression of Doerner and Hoskins[1]

$$\log \frac{y}{a} = K \log \frac{n}{b} \tag{1}$$

in which a and b are the initial amounts of A and B in the solution, y and n the final amounts in solution, and K a constant which is equal to the reciprocal of the distribution constant D in equation (2).

When the reagent C is added slowly to a well-stirred mixture of A and B, the distribution of A usually will occur according to the logarithmic expression. However, when the primary precipitate formed is subject to very rapid recrystallizations, the initial distribution of A (and of B) will change very rapidly. The primary precipitate which consists of heterogeneous mixed crystals of BC and AC will tend to become homogeneous. When the precipitate has come to thermodynamic equilibrium with the solution the distribution of A is determined by the expression

$$\frac{(\text{A}) \text{ solution}}{(\text{A}) \text{ solid}} = D \frac{(\text{B}) \text{ solution}}{(\text{B}) \text{ solid}} \tag{2}$$

This equilibrium has been found to be realized in the system silver bromide–silver chloride. When silver nitrate was added to a mixture of bromide and chloride under such conditions that the precipitate remained in colloidal solution during the precipitation, and the mother liquor was analyzed

immediately after the precipitation, the distribution of chloride between solid and solution was found to occur according to equation (2). On the other hand, if the precipitate was flocculated during the precipitation, the distribution of the chloride was found to approach expression (1). The results obtained are given in the experimental part of this study.

Experimental

Chemicals Used.—C. P. products of silver nitrate and of sodium chloride, tested for purity, were used. The sodium chloride was dried at 550°. Potassium bromide was prepared by thermal decomposition of recrystallized, chlorate-free, potassium bromate. One-tenth molar solutions of the bromide, chloride and silver nitrate were prepared. Potentiometric titrations showed that these solutions had exactly the same normality.

Experimental Procedure.—In general, 10 ml. of the 0.1 M silver nitrate solution was added to 20 ml. of a solution containing 10 ml. of 0.1 M bromide and 10 ml. of a chloride solution of varying molarity (either 0.01, 0.1 or 1 M). The solution was agitated vigorously with a mechanical stirrer during precipitation. The precipitate was formed both in the presence and the absence of 1 drop (0.04 ml.) of 1 M aluminum nitrate in the solution to which silver nitrate was being added. The 0.1 M silver solution was added at different rates. Precipitations carried out in fifteen seconds were made from a pipet. Marks were made on this pipet so that 1 and 2% deficiency and 1 and 2% excess of silver (referred to bromide) could be added. In experiments in which the silver nitrate was added more slowly a 10-ml. buret was used. The end of the buret was drawn out to a tip of such size that it would deliver the silver nitrate at the desired speed.

If desirable the precipitates were aged by shaking the suspensions at room temperature on a mechanical shaker in a dark room. The bromide content of the supernatant liquid was determined by adding (if necessary) one drop of 1 M aluminum nitrate to the suspension, shaking for three minutes by hand and filtering. The bromide analysis on 20 ml. of the clear filtrate was made by a procedure described previously.[2] Upon analysis of 10 to 30 ml. samples of 0.001 M bromide an accuracy of 0.5 ± 0.2% was obtained. The presence of aluminum nitrate did not affect the results.

When formed in the absence of aluminum nitrate the precipitate remained in colloidal solution except in the experiments with 1 M sodium chloride, in which case the electrolyte concentration was great enough to cause flocculation. Using a 0.1 M chloride solution the suspen-

(1) H. A. Doerner and W. M. Hoskins, THIS JOURNAL, **47**, 662 (1925).

(2) I. M. Kolthoff and H. C. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

sions were partially flocculated after two and one-half hours and completely flocculated after twenty-four hours of aging. In the presence of one drop of 1 M aluminum nitrate the precipitate was flocculated as it was formed.

Experimental Results

The experiments reported in Table I show the effect of rate of precipitation on the distribution of chloride and bromide in the system. The distribution coefficient D in expression (2) for well aged mixed crystals with high mole fractions of silver bromide according to Yutzy and Kolthoff[3] is equal to about 450. We have confirmed this value, but found for colloidal precipitates a different value of 393. (K in expression (1) is equal to 1/393.)

<div style="text-align:center">TABLE I</div>

Ten ml. of 0.1 M Ag$^+$ added to mixture of 10 ml. 0.1 M Br$^-$ and 10 ml. 0.1 M Cl$^-$ in the absence and presence of 1 drop 1 M Al^{+++}.

Time of addn. of Ag$^+$, min.	0.25	3.7	6.7	10
Br$^-$ left in solution in %; no Al[a]	4.80	4.76		4.76
	4.82	4.76		4.76
Br$^-$ left in solution in %; with Al[b]	3.02	2.06	1.85	1.74
	3.08	2.12	1.92	1.77

[a] The temperature was 30 ± 1°. [b] The temperature was 25 ± 1°.

Using the latter value the calculated percentage of bromide left in the solution when homogeneous mixed crystals are formed is equal to 4.80 (and 4.50 with D = 450), and when heterogeneous mixed crystals are formed, the calculated percentage of bromide is 1.1.

In the experiments given in Table II the suspensions were aged for various periods of time after the addition of silver nitrate. The experiments of Table II were repeated, but the bromide-chloride mixture was diluted with 70 ml. of water before the addition of silver nitrate. In the pres-

<div style="text-align:center">TABLE II</div>

<div style="text-align:center">EFFECT OF AGING UPON DISTRIBUTION OF BROMIDE</div>

Composition of suspensions the same as in Table I; temperature 29–30°.

Time of aging, hours	0	0.5	2.5	24	48
Br left in solution in %; no Al[a]	4.80	4.74	4.63	4.46	4.51
	4.82	4.79	4.68	4.45	4.53
			4.69		
Br left in solution in %; with Al[b]	2.16	2.84	3.17	3.92	4.51
	2.18	2.91	3.40	4.22	4.55
			3.59	4.45	

[a] Silver nitrate added in fifteen seconds. [b] Silver nitrate added in three minutes and forty seconds.

ence of 2 drops of 1 M aluminum nitrate (flocculated state) the results were about the same as

(3) H. C. Yutzy and I. M. Kolthoff, THIS JOURNAL, **59**, 916 (1937).

those given in Table II; in the absence of aluminum the suspension was still largely colloidal after one day of aging. In the latter case the percentage of bromide in the solution was 4.60 immediately after the addition of silver, 4.72 after thirty minutes, 4.64 after two and one-half hours and 4.63 after twenty-four hours of aging. From these results one would infer that the distribution coefficient D is slightly smaller when the particles are very fine and in the colloidal state than when they are aged and cemented together in the form of irregular agglomerates. The difference cannot be explained by adsorption phenomena, as the amount of bromide in the solution upon aging of the colloidal suspension would be expected to increase as a result of desorption, whereas actually a decrease was found (Table II).

In the experiments reported in Table III the ratio of bromide to chloride was varied between 10 and 0.1. To 10 ml. of 0.1 M bromide were added 10 ml. of chloride of varying strengths and 10 ml. of 0.1 M silver nitrate.

<div style="text-align:center">TABLE III</div>

<div style="text-align:center">EFFECT OF VARYING RATIO OF Br$^-$ TO Cl$^-$ UPON DISTRIBUTION, TEMPERATURE 29–30°</div>

Ratio Br$^-$ to Cl$^-$	Amount of bromide in soln. in %[a] No Al^{+++} added			Amount of bromide in soln. in %[b] Al^{+++} added		
	Found	Calcd.[c]		Found	Calcd.[d]	
10:1	1.44	1.44	1.46	0.49	0.57	0.16
1:1	4.80	4.82	4.80	2.16	2.18	1.13
1:10	11.52	11.49	14.65	8.76	8.78	6.81

[a] Silver nitrate added in fifteen seconds. [b] Silver nitrate added in three minutes and forty seconds. [c] Calculated on the basis of homogeneous distribution (expression 2); D = 393. [d] Calculated on the basis of heterogeneous distribution (expression 1).

In the absence of flocculating agent the distribution was found again to be homogeneous, except when the ratio of bromide to chloride was 0.1. In the latter case, the concentration of electrolyte was very great, as 10 ml. of 0.1 M bromide was mixed with 10 ml. of 1 M chloride. Consequently, flocculation occurred during the addition of silver nitrate.

In the following experiments a mixture of 10 ml. of 0.1 M bromide and of 0.1 M chloride was used, but the amounts of silver nitrate added were slightly in deficiency and in excess to the amount of bromide present. The results are given in Table IV.

As the distribution coefficient increases with decreasing temperature it is to be expected that the coprecipitation of chloride with silver bromide

TABLE IV

EFFECT OF A SLIGHT DEFICIENCY AND EXCESS OF SILVER
NITRATE IN THE NEIGHBORHOOD OF THE FIRST EQUIVA-
LENCE POINT, TEMPERATURE 29–30°, $D = 393$

Excess of $AgNO_3$, %	Amount of bromide in soln. in %[a] No Al added Found		Calcd.[d]	Amount of bromide in soln. in %[b] Al present Found		Calcd.[e]	Amount of bromide in soln. in %[c] Al present Found		Calcd.
−2	5.80	5.83	5.90						
−1	5.28	5.32	5.33						
0	4.80	4.82	4.80	2.16	2.17 2.22	1.1		1.85	1.1
+1	4.24	4.29	4.33	1.50	1.54	0.40	1.33	1.42	0.40
+2	3.87	3.87	3.90	1.17 1.20	1.18 1.21	0.03	0.95	0.97	0.03

[a] Silver nitrate added in fifteen seconds. [b] In three
minutes and forty seconds. [c] In ten minutes. [d] Homo-
geneous distribution. [e] Heterogeneous distribution.

will decrease with decreasing temperature. In
the following experiments the equimolecular mix-
ture of bromide and chloride was cooled in an
ice-bath and kept there during the precipitation
with silver nitrate. The observed temperature at
the end of the precipitation (which required three
and one-half minutes) varied between 8 and 12°.
After addition of an amount of silver nitrate
equivalent to the amount of bromide in the ab-
sence of aluminum, the percentage of bromide
left in the solution was found to vary between
2.8 and 3.0, while at 30° 4.80% was left in the
solution. Precipitation in the presence of alumi-
num in three and one-half minutes yielded a super-
natant liquid which contained 1.55% of the bro-
mide (2.09% at 30°). When 1% excess of silver
was added in the presence of the flocculating
agent the supernatant liquid contained 1.0, and
with 2% excess 0.70% of the bromide (at 30°,
1.52 and 1.20, respectively).

In order to decrease the speed of interaction be-
tween the precipitate and the solution experi-
ments were made in which 0.1 to 1 ml. of nitro-
benzene was added to the bromide–chloride mix-
ture before precipitation. Caldwell[4] has found
that nitrobenzene is very effective in inhibiting
the reaction between silver chloride and dissolved
thiocyanate. It was thought, therefore, that the
distribution might approach the Doerner and
Hoskins expression more closely if the precipita-
tion were carried out with vigorous stirring in the
presence of nitrobenzene. It was found that the
presence of nitrobenzene had no appreciable ef-
fect upon the results. Even the speed of trans-
formation of the flocculated precipitate into homo-
geneous mixed crystals was not greatly affected
by the presence of 1 ml. of nitrobenzene. When

(4) J. R. Caldwell, Ind. Eng. Chem., Anal. Ed., 7, 38 (1935).

the precipitate was prepared in the presence of
aluminum and 1 ml. of nitrobenzene, the super-
natant liquid contained 2.02% of the bromide
immediately after addition of silver nitrate, 2.46%
after thirty minutes of shaking, 2.88 after two and
one-half hours and 3.68 after twenty-four hours.
The corresponding figures in the absence of ni-
trobenzene were 2.17, 2.88, 3.4 and 4.1.

Experiments were also carried out in which the
precipitate was formed in the presence of wool
violet and of methylene blue. It has been shown
that these dyes almost completely prevent the
aging of silver chloride and of silver bromide.[5]
Hence, even in the absence of aluminum a distri-
bution approaching the logarithmic expression
was anticipated. However, the experimental
results were contrary to the expectation, the
amounts of bromide found in the supernatant
liquids being much greater than corresponded to
homogeneous distribution. This is explained
mainly by the fact that the silver nitrate dropping
into the solution is in local excess when the pre-
cipitate is formed. Particularly in the vicinity of
the first equivalence point the primary precipitate
will contain much more chloride than would cor-
respond to homogeneous distribution. As the
primary particles are covered immediately with
dye, which prevents their interaction with the
solution, they do not have an opportunity to come
to equilibrium with the liquid phase. In this
connection it may be added that practically all
of the dye added was coprecipitated with the
mixed silver halides.

As the rate of interaction of the uncoated silver
halide particles in the colloidal state with the
solution was found to be so great it was decided
to investigate whether this speed decreased ma-
terially, when the suspensions were aged in the
colloidal state. The experiments were carried
out in the following way. To a mixture of 10
ml. of 0.1 M bromide and 10 ml. of 0.01 M
chloride was added from a pipet in fifteen seconds
10 ml. of 0.1 M silver nitrate (temperature 27 ±
1°). When the suspension was flocculated with
aluminum, the supernatant liquid was found to
contain 1.40% of the bromide, corresponding to
homogeneous distribution. The above colloidal
suspension was aged in the absence of aluminum
for various periods of time, then 10 ml. of 0.09 M
sodium chloride was added with rapid stirring.

(5) (a) I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, 59, 1634
(1937); (b) A. S. O'Brien, Thesis, University of Minnesota, 1938.

TABLE V
EFFECT OF AGING IN THE COLLOIDAL STATE UPON THE SPEED OF EXCHANGE

Time of aging before adding 0.09 M chloride, min.		1	1	4	10	1 hour		5 hours	
Time of stirring with 0.09 M chloride, min.		1	5	1	1	1		1	
Bromide in solution, %	4.56	4.65	4.53	4.58	4.63	4.65	4.63	4.65	4.53	4.57

After stirring for one or five minutes the colloid was flocculated with aluminum, shaken for three minutes, and the supernatant liquid analyzed for bromide. Homogeneous distribution of the bromide throughout the system would now correspond to 4.6 to 4.7% of bromide in the mother liquor. The results are given in Table V.

Until aluminum was added all of the suspensions appeared to be completely colloidal with the exception of the one which had been aged for five hours, in which case a slight precipitate on the bottom of the bottle was noticed. A few experiments were made in which the original suspension was stirred for one-half minute. Aluminum was then added and after one-half minute of stirring 10 ml. of 0.09 M chloride. The suspensions were stirred one minute and shaken by hand four and eight minutes; the percentages of bromide in the supernatant liquids were 3.08 and 3.42, respectively. Evidently, the colloidal precipitate comes to equilibrium with the solution within one minute even after five hours of aging. However, even when flocculated fresh, the precipitate was not in equilibrium with the liquid phase after eight minutes of shaking.

Discussion

When silver nitrate is added to a mixture of bromide and chloride under such conditions that the precipitate remains in colloidal solution, the solid comes to equilibrium with the liquid phase almost instantaneously (Tables II and IV). A similar conclusion was inferred by Flood and Bruun[6] from their work on the potentiometric titration of bromide in the presence of chloride. However, these authors did not analyze their systems chemically. When the silver nitrate is added under such conditions that the silver halide flocculates immediately, heterogeneous mixed crystals are formed. With decreasing speed of addition of precipitant the distribution approaches the logarithmic expression (1); but does not become equal to it, as Flood and Bruun assume. Thus when the silver was added in a period of ten minutes in the presence of aluminum the percent-

(6) H. Flood and B. Bruun, Z. anorg. allgem. Chem., 229, 85 (1936).

age of bromide left in the supernatant liquid was found to be 1.8; if the distribution would have occurred according to the Doerner and Hoskins[1] expression 1.1% would have been found, and 4.8% if the distribution would have been homogeneous. The distribution cannot be found exactly equal to that calculated from the logarithmic expression, as the precipitate ages during the slow precipitation and tends to be transformed into homogeneous mixed crystals. This is quite evident from the experiments reported in Table II. As a result of the decrease of the specific surface by a cementing together of the particles homogeneous equilibrium was not reached until after a period of shaking of twenty-four hours or more. It is evident from Table IV that when the precipitate is flocculated during the addition of reagent and the amount of silver added is slightly in excess of the amount of bromide, the last fractions of the precipitate formed contain much less bromide than calculated on the basis of the logarithmic distribution expression (1). This is explained by the fact that, upon addition of silver nitrate to a solution nearly exhausted in bromide, the primary precipitate is very rich in chloride due to the local excess of silver and to the relatively slow aging of the precipitate in the flocculated state.

When no flocculation occurs, the speed of addition and the amount of silver added are of no consequence with regard to the distribution, as the latter is found to become homogeneous almost instantaneously. The most striking result of this study is that the speed of exchange between the colloidal particles and the solution is extremely great and is not affected by aging of the solid in the colloidal state. Undoubtedly, the colloidal particles perfect themselves on aging but this has no apparent effect upon the speed of interaction between the solid and the solution. We believe that this very great speed of exchange is not typical of the colloidal state in general but is specific for silver bromide and possibly other silver halides. It is attributed by us to a great thermal mobility of the silver and bromide ions in the tiny colloidal particles of silver bromide. In a subse-

quent paper with A. S. O'Brien[5b] it will be shown that the speed of exchange between freshly precipitated, air-dried silver bromide and gaseous radioactive bromine is very great as a result of this thermal mobility. This thermal mobility should also be great when dealing with a freshly flocculated precipitate, but the speed of exchange with the solution decreases rapidly as a result of the decrease of the specific surface.

The coprecipitation of chloride with silver bromide decreases with decreasing temperature during the precipitation, as the distribution coefficient of the bromide between solid and solution decreases. This fact can be made use of to analytical advantage in the potentiometric titration of bromide in the presence of chloride with silver nitrate. It is expected that the errors will be smaller when the titration is carried out at the temperature of melting ice than at room temperature.

Acknowledgment.—We express our appreciation to the Graduate School of the University of Minnesota for the assignment of a grant which enabled us to carry out the present study.

Summary

1. Upon addition of silver nitrate to a mixture of bromide and chloride under such conditions that the particles remain in colloidal solution, a homogeneous distribution of the halides between solid and solution has been found. The presence of nitrobenzene during precipitation did not affect the time of attainment of equilibrium in a measurable way.

2. When the precipitant is added under such conditions that the precipitate is flocculated instantaneously, heterogeneous mixed crystals are formed. Upon very slow addition of silver the distribution approaches that calculated on the basis of the Doerner and Hoskins equation, but does not equal it as a result of aging and of the effect of a local excess of precipitant. Homogeneous equilibrium is attained only after long periods of shaking of the precipitate with the supernatant liquid.

3. When the particles are aged in the colloidal state for several hours and the composition of the liquid phase is changed after this time, the solid comes to equilibrium with the liquid almost instantaneously. This great speed of exchange has been attributed to a great thermal mobility of the silver and bromide ions in the colloidal particles.

4. The coprecipitation of chloride with silver bromide decreases with decreasing temperature during the precipitation.
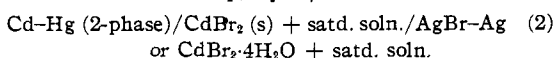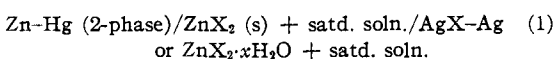

The Thermodynamics of Bi-univalent Electrolytes. V. The Heats of Formation and Entropies of Certain Zinc and Cadmium Halides

BY ROGER G. BATES[1]

The free energy of a given chemical system and its change with change of temperature, as measured by the electromotive forces of suitable reversible cells, have been used successfully to obtain heats of reaction with accuracy comparable with that of the direct calorimetric method used in the classical researches of Thomsen.[2] This indirect procedure is limited in its application to those cases in which the cell reaction is known to be free from side reactions. Unfortunately, the difficulties attendant upon the use of halogen electrodes prevent the application of the electromotive force method to the study of the reac-

(1) Sterling Fellow in Chemistry, 1937–1939.
(2) J. Thomsen, "Thermochemische Untersuchungen," Vols. I–IV, Barth, Leipzig, 1882, 1882, 1883, 1886.

tion in which halide salts are formed directly from their elements. A survey of the literature, however, shows many instances of poor agreement between the results of calorimetry and electromotive force, even when a pure cell reaction may reasonably be assumed.

In this investigation measurements were made of the cells

Zn–Hg (2-phase)/ZnX₂ (s) + satd. soln./AgX–Ag   (1)
                 or ZnX₂·xH₂O + satd. soln.

Cd–Hg (2-phase)/CdBr₂ (s) + satd. soln./AgBr–Ag   (2)
                 or CdBr₂·4H₂O + satd. soln.

where X represents Cl, Br or I, over the temperature range, 10–45°, except as limited by the stability of the particular solid phase present.