reaction between carbon monoxide and oxygen at and above the upper explosion limit. The mechanism of the upper limit involves oxygen atoms and ozone as chain carriers. The mechanism of the reaction above the upper limit includes the mechanism of the upper limit and in addition a chain initiating mechanism that involves water.

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Studies on Aging of Precipitates. XV. The Mechanism of the Interaction between Dissolved Bromide and Solid Silver Chloride

BY I. M. KOLTHOFF AND H. C. YUTZY[1]

When silver chloride is shaken with a solution containing chloride and bromide of such a composition that no mass-action precipitation of pure silver bromide occurs, mixed crystals of silver chloride and bromide will be formed. In a previous study[2] indication has been obtained that the penetration of the bromide into the solid is not solely a result of recrystallization of the precipitate but that other factors mainly account for the relatively large speed of penetration of bromide into well aged silver chloride. The mechanism of the distribution of the bromide is further investigated in the present study.

Experimental

The materials and methods of analysis used were the same as described in previous papers.[2]

In the first place experiments were carried out with a silver chloride precipitate which had been aged drastically for thirty-five days in a 2 *M* sodium chloride solution at room temperature. After aging, the silver chloride was filtered on a sintered glass crucible, washed and made air dry. Weighed portions were shaken for various periods of time with 225 ml. of an aqueous solution being 0.0888 *M* in sodium chloride and 2.2×10^{-4} *M* in potassium bromide. The supernatant liquids obtained after centrifuging were analyzed for bromide and the final bromide concentrations plotted against the time of shaking. If it were assumed that the value obtained after extrapolation of the curve to a time of shaking of zero corresponded to the bromide concentration in the solution after exchange equilibrium in the surface had been attained, the amount of surface could be calculated from the known distribution coefficient of bromide between solution and silver chloride.[3] A detailed account of the experiments and the calculations is given in the thesis of the junior author.[1] The results indicated that 6.3% of the silver chloride used consisted of surface. Microscopically, the size-distribution curve of the same product was determined; from the average particle diameter it was calculated that 0.017% of the silver chloride consisted of surface. The value calculated from the exchange experiments is about 400 times greater than the microscopic one. It is hardly possible to attribute this large difference to a large internal surface as the silver chloride was very well aged. For the same reason the great speed of penetration of the bromide into the silver chloride hardly can be attributed to a rapid recrystallization of the solid. That this rapid disappearance of anomalously large amounts of bromide from the solution is not due to mass precipitation of silver bromide as a separate phase is easily shown. If such a precipitation occurs the ratio of the concentration of chloride ions to that of bromide ions in the solution must be equal to the ratio of the solubility products—about 300. In the case cited, the bromide concentration was found by analysis, after a week's shaking, to be 6×10^{-5}; the chloride concentration was 8.90×10^{-2}, corresponding to a ratio of chloride to bromide of 1450.

That the rapid penetration of bromide is not to be attributed to a large internal surface or a rapid recrystallization of the silver chloride was also shown by working with extremely coarse silver chloride which had been recrystallized from ammonia and with products which had been aged for a year at 27° as an equivalent body in water. Both were made air-dry before use. A systematic study was made with the year old precipitate varying widely experimental conditions, such as concentrations, volume of solutions, amount of precipitate, etc., in order to discover factors which determine the speed of penetration of the bromide into the solid. The results are given in a condensed form in Table I. As an indication of the speed of penetration of the bromide into the silver chloride the values of *K'* after eighty hours of shaking are given in the last

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[1] From a thesis submitted by H. C. Yutzy to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the Degree of Doctor of Philosophy (June, 1936).

[2] I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, 59, 1634 (1937).

[3] H. C. Yutzy and I. M. Kolthoff, *ibid.*, 59, 916 (1937).

column (as estimated from the curves in Fig. 1). The value was calculated from the expression

$$\frac{[\text{Cl}^-]_{\text{solution}}}{[\text{Cl}^-]_{\text{solid}}} = K' \frac{[\text{Br}^-]_{\text{solution}}}{[\text{Br}^-]_{\text{solid}}}$$

The values of K' vary with the time of shaking and become equal to the distribution coefficient[3] K when distribution equilibrium has been attained; in none of the experiments was the equilibrium value reached, even after one month of shaking.

TABLE I

SPEED OF PENETRATION OF BROMIDE INTO ONE-YEAR OLD SILVER CHLORIDE UNDER VARYING CONDITIONS

No.	Volume of soln. shaken, ml.	Initial NaCl concn., M	Initial KBr concn., M	$\frac{\text{Initial }[\text{Cl}^-]}{\text{Initial }[\text{Br}^-]}$	AgCl taken, g.	$\frac{\text{Total }[\text{Br}^-]}{\text{Total }[\text{Ag}^+]}$	K' (80 hours)
1	200	1	5×10^{-3}	200	1	0.143	220
2	225	0.444	2.22×10^{-3}	200	1	.072	130
3	225	.888	2.22×10^{-3}	400	1	.072	130
4	225	.0888	2.22×10^{-4}	400	0.08	.090	130
5	225	.0888	2.22×10^{-4}	400	1	.0072	22
6	130	.0154	7.70×10^{-5}	200	1	.0014	5

In Fig. 1 the values of K' are plotted after different periods of shaking. Examination of the results in the table and, particularly, of the curves in Fig. 1 reveals the striking result that the rate of penetration of the bromide is determined solely by the ratio of moles of bromide to moles of silver in the system (see expts. 2, 3, 4 in Table I and corresponding curves). The concentration of chloride in the solution is not a determining factor as a ten-fold change in concentration (expts. 2, 3, 4) did not affect the rate of distribution. Neither does the concentration of bromide in solution nor the amount of silver chloride taken determine the rate of penetration of the bromide.

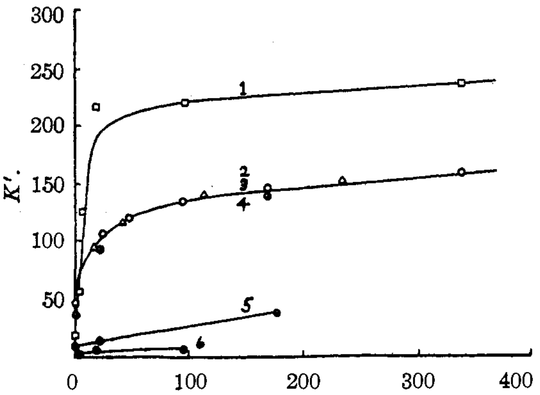

Fig. 1.—Rate of entrance of bromide into one year old precipitate: ratio of bromide to silver, 1 □ 0.143; 2, ○ 0.072; 3, △ 0.072; 4, ◑ 0.090; 5, ⊖ 0.0072; 6, ⦶ 0.0014.

In expt. 4 the amount of silver chloride taken was 12.5 times less than in expts. 2 and 3 and still the speed–penetration curve of the bromide was in all three cases nearly identical, and the ratio of total bromide to silver was the same. Evidently, the results cannot be interpreted by assuming an initial exchange between bromide and chloride on the surface of the silver chloride followed by a rapid recrystallization of the latter by way of the solution. There is no apparent reason why the rate of this recrystallization should increase so much with increasing ratio of bromide to silver. Only when this ratio becomes extremely small (experiment 6) does the speed of penetration of the bromide seem to be determined by the rate of recrystallization of the precipitate; then the curves become comparable to those obtained on shaking of aged lead sulfate with thorium B or of aged barium sulfate with lead and chromate, respectively.

The great speed of penetration of the bromide at higher mole ratios of bromide to silver can hardly be interpreted as being due to a rapid diffusion of the bromide through the solid lattice. As may be concluded from the work of Tubandt,[4] such a process must be extremely slow at ordinary temperatures.

It would seem that the only interpretation left, then, is that the first surface layer of silver chloride and bromide formed by exchange has dimensions such that it is impossible for it to remain in the position occupied by the pure silver chloride layer initially. Thus, the surface layer of the mixed crystals will be split off from the solid or develop a great number of cracks and crevices to relieve the strain. Either process would result in an exposure of fresh surface to the solution with subsequent repetition of the interaction. This will go on as long as the concentration of bromide in solution is such as to cause enough bromide to enter the surface to produce the required deformation and strain. The process is thus pictured as a direct attack of the structure of the original particles as a result of a disrupture of the lattice of the silver chloride by the layers of heterogeneous mixed crystals formed.

Further Evidence of Disrupture of the Original Particles.—The following experiments give further evidence that the rapid penetration of the

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(4) C. Tubandt, *Z. anorg. allgem. Chem.*, **115**, 105 (1921); Tubandt, H. Reinhold and W. Jost, *Z. physik. Chem.*, **129**, 69 (1927); *Z. anorg. allgem. Chem.*, **177**, 253 (1928); *Z. physik. Chem.*, Bodenstein Festband, 874 (1931).

bromide cannot be attributed to a recrystallization of the silver chloride by way of the solution.

a. One-gram samples of the one-year old product[2] were shaken with 175 ml. of 0.57 *M* sodium chloride for one hour, twenty-four hours, and eight days, respectively. After these periods 50 ml. of 0.01 *M* potassium bromide was added and the shaking continued for one hour and twenty-four hours, after which the supernatant liquids were analyzed for bromide. The calculated values of K' are given in Table II.

TABLE II

EFFECT OF SHAKING SILVER CHLORIDE WITH STRONG SODIUM CHLORIDE PREVIOUS TO BROMIDE DISTRIBUTION

Time of shaking with 0.57 *M* NaCl	0	1 hour	1 day	8 days
K' after 1 hour	47	51	49	38
K' after 24 hours	106	107	105	91

The solubility of the silver chloride in 0.57 molar sodium chloride is approximately 2 to 3 times larger than in water.[5] Hence a further aging of the one-year old product might be expected to take place upon shaking with 0.57 *M* chloride solution. If the speed of entrance of bromide were determined mainly by the rate of recrystallization of the silver chloride, the further aging in the concentrated sodium chloride solution should decrease the speed of entrance materially. Actually, it was found that the rate of entrance was unchanged after one day of aging in the sodium chloride solution; after a week of aging the speed had decreased slightly due to a decrease of the specific surface of the silver chloride.

b. The rate of distribution of bromide was determined in alcoholic medium. As the solubility of silver chloride is much less in alcoholic than in aqueous medium, it would be expected that the rate of entrance of bromide should decrease materially going from water to ethanol as a solvent, if the rate of distribution would be determined by the rate of recrystallization of the solid by way of the solution. Experiments were made in 42% ethanol and in 100% ethanol. One-gram samples of the one-year old precipitate were shaken for various periods of time with 225 ml. of a solution 0.435 *M* in sodium chloride and 2.18×10^{-3} *M* in potassium bromide in 42% ethanol. With 100% ethanol as a solvent the latter was 0.4656 *M* in lithium chloride and 2.37×10^{-3} *M* in sodium bromide. Some of the results are given in Table III.

TABLE III

SPEED OF DISTRIBUTION OF BROMIDE FROM ALCOHOLIC MEDIUM

Time of shaking	1 hr.	2.5 hrs.	24 hrs.	3 days	6 days	13 days
K' (42% ethanol)	22		67	81	86	95
K' (100% ethanol)	1.9	4.5	15.6		23	

Comparison with experiments conducted in water containing the same amounts of chloride and bromide as used in the above experiments does not reveal the exact effect of the solvent, as the distribution coefficient of the bromide from alcoholic medium is about one-third that from aqueous medium.[3] However, from the results in Table III it is apparent that the rate of entrance of the bromide from alcoholic media is much greater than can be accounted for by a recrystallization by way of the solution.

The following experiments lend support to the interpretation as a disruptive attack upon the structure of the original particles. If aged silver chloride is shaken with an aqueous solution containing chloride and bromide, the first rapid entrance of the bromide is attributed to a disrupture of the silver chloride lattice. When the concentration of bromide in the solution has been greatly depleted the further entrance is determined by the rate of recrystallization by way of the solution. This rate is very small when dealing with a well aged precipitate. If fresh bromide be added to the solution after most of the first supply of it has been removed by the precipitate, one would expect a rapid decrease in concentration again, upon further shaking, until it has become very small. Upon addition of still more bromide a similar rapid decrease should be noticeable, if the interpretation of the mechanism is correct.

The experiments were performed in the following way: one-gram portions of the one-year old precipitate were added to two bottles, (A) containing 225 ml. of a solution 0.444 *M* in sodium chloride and 0.00221 *M* in potassium bromide; (B) the same as (A) but containing twice as much chloride. After shaking for twenty-four hours, all except 5 ml. of the supernatant liquid was removed and analyzed for bromide. The original volume of fresh solution was added, the mixture shaken again for twenty-four hours, etc. After the fourth period of shaking, only 50 ml. of the solution was removed, 5.00 ml. of 0.01 *M* bromide was added and the mixture shaken again for twenty-four hours. After this time a 50-ml. sample was removed from each bottle and the shaking continued for three weeks (to see whether equilibrium could be reached).

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[5] G. S. Forbes and H. I. Cole, THIS JOURNAL, **43**, 2492 (1921).

After that time, all but 5 ml. of the solution was removed, and replaced by the 225 ml. of the original solution, the mixture shaken for twenty-four hours, the supernatant liquid removed and the process repeated once more. Knowing the volumes used and the bromide concentrations in the supernatant liquids, the amounts of bromide in the precipitate could be calculated. The results are given in Table IV.

TABLE IV

REPEATED ADDITION OF BROMIDE TO A YEAR OLD AgCl

Step	Period of shaking	$Br^- \times 10^4$ A	$Br^- \times 10^4$ B	Millimoles Br^- in precipitate A	Millimoles Br^- in precipitate B	K' A	K' B
1	24 hrs.	2.72	4.97	0.439	0.39	110	107
2	24 hrs.	3.58	6.46	.858	.74	175	164
3	24 hrs.	5.15	8.98	1.24	1.04	187	173
4	24 hrs.	6.42	10.92	1.60	1.29	205	185
5	24 hrs.	7.58	12.85	2.07	1.75	249	233
6	3 weeks	6.33	10.95	2.13	1.84	310	292
7	24 hrs.	10.37		2.39		212	
8	24 hrs.	11.03		2.64		247	

The values of K' obtained after each successive step of shaking for twenty-four hours increase gradually, showing that the kinetics of the reaction after each new addition of bromide are of the same order. The values obtained after three weeks of shaking are higher as the system tends to approach equilibrium.

Summary

The rapid formation of mixed crystals upon shaking of a solution containing chloride and bromide with well aged silver chloride cannot be attributed to a normal recrystallization of the solid by way of the solution. Experimentally, it has been shown that the rate of distribution increases with increasing ratio of bromide in solution to silver in the precipitate. When this ratio is very small the rate of distribution of bromide is determined by the speed of recrystallization of the silver chloride by way of the solution. The great initial speed of distribution found when the ratio of bromide to silver is larger is attributed to a direct attack upon the structure of the original particles. It is assumed that the bromide rapidly taken up in the surface layer by exchange causes a disrupture of the silver chloride lattice, exposing fresh surface to attack.

MINNEAPOLIS, MINN. RECEIVED JUNE 14, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionic Activity Coefficient Product and Ionization of Water in Barium Chloride Solutions from 0 to 50°

BY HERBERT S. HARNED AND CHARLES G. GEARY[1]

Electromotive forces of the cells

H_2 | $Ba(OH)_2$ (0.005), $BaCl_2$ (m_2) | AgCl-Ag (A)

H_2 | HCl (0.01), $BaCl_2$ (m_1) | AgCl-Ag (B)

have been obtained over the range 0 to 50°, and 0.03 to 3μ. Following the methods employed in this Laboratory,[2-6] we have computed: (1) the standard potential of the silver-silver chloride electrode from 0 to 50°; (2) the ionization constant of water from 0 to 50°; (3) the activity coefficient of hydrochloric acid in barium chloride solutions; (4) the ionic activity coefficient of water in barium chloride solutions; (5) the ionization of water in barium chloride solutions; (6) the relative partial molal heat content of hydrochloric acid in barium chloride solutions; (7) the heat of ionization of water in aqueous solution and barium chloride solutions.

Experimental Results

The cells were run in triplicate and in two series at 5° intervals, from 0 to 25°, and from 25 to 50°, so that at 25°, there were six checks of the electrodes used, and two on the composition of each solution. Reproducibility was in general better than ±0.05 mv., while the maximum deviation was about ±0.1 mv.

The measurements were corrected to one atmosphere of hydrogen by means of a special table prepared for this purpose. The vapor pressures of the solutions were determined (assuming the effects of 0.01 M hydrochloric acid and 0.005 M

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(1) This contribution contains material from a dissertation presented by Charles G. Geary to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

(2) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); *ibid.*, **55**, 4496 (1933).

(3) Harned and Copson, *ibid.*, **55**, 4496 (1933).

(4) Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

(5) Harned and Donelson, *ibid.*, **59**, 1280 (1937).

(6) Harned and Mason, *ibid.*, **54**, 3112 (1932).