[Contribution from the Chemical Laboratory of Harvard University]

The Influence of Halides upon the Extinction Coefficients, and its Bearing upon the Constitution, of Silver Halides in Fusion

By George S. Forbes and Hervey B. Elkins

During experiments on fused salts, recounted elsewhere,[3] it was noted that a relatively small addition of an alkali chloride nearly discharged the color of silver chloride. Extinction coefficients were thereupon measured to test some of the current theories regarding constitution and color of fused salts.

The apparatus (Fig. 1) is illuminated at the slit S, by the mercury arc Q having a horizontal constriction 2 cm. long.[1] The rays enter a Fuess quartz monochromator, supported so that both telescopes are in a vertical plane. The drum, graduated in wave lengths, rotated the prism table and collimated both lenses. Beyond the exit slit S_2 was fastened a tube with a third lens which made the emergent light nearly parallel. The strong green line, $\lambda = 5460$ Å., used in all the measurements was imperfectly separated from yellow and blue. The cell C stood on a steel frame E, 7.5 × 5 cm. in an oven made of a rectangular crystolon tube 17 cm. long and maintained at 500° by a winding of heavy Chromel A ribbon. Pyrex rings 30 mm. in diameter and of several heights were ground to make opposite edges parallel. Each ring was cemented to a Pyrex plate with alundum cement. The desired mixture was introduced, fused, and then a smaller Pyrex plate was slid over the ring, making contact with the salt over all its surface except at two sides. When extinctions were very high, a ring of silver wire between Pyrex plates formed a cell. The thinnest layers were formed by fusing a small weighed sample between two Pyrex plates which were then pressed together. The thickness was found from the area, weight and density of the sample.

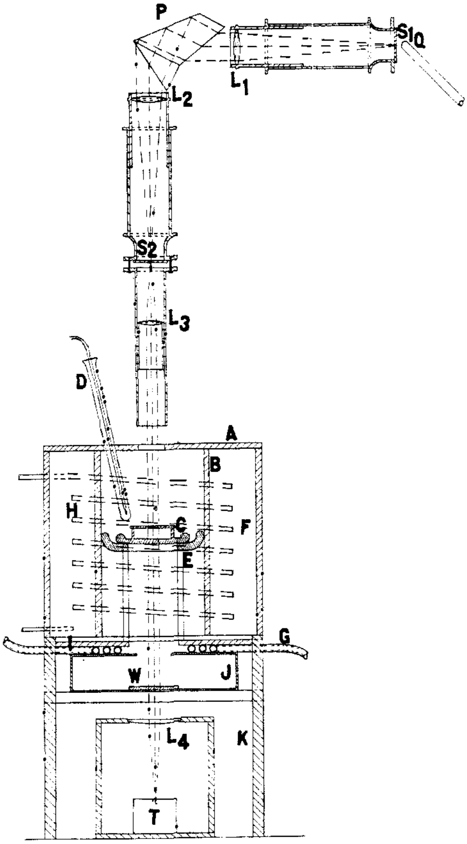

Fig. 1.

Under the furnace was set a rectangular brass box B having suitable rectangular openings cut in top and bottom. A glass window W was cemented over the opening in the bottom. The box was filled with a suitable solution of neodymium nitrate

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[1] *Cf.* Forbes and Harrison, *J. Opt. Soc. Am.*, **11**, 99 (1925).

and nickel nitrate which very effectively absorbed yellow and blue as well as infra-red. The coil G, of small copper pipe, containing circulating cold water absorbed part of the heat of the oven. The parallel filtered light, brought to convergence by the lens L_4, of 14 cm. focal length, was focused upon the slit of a Hilger thermopile T. A Leeds and Northrup galvanometer of sensitivity 15 mm./microvolt on a Julius suspension was read through a telescope, using a millimeter scale at 5 meters distance. The thermopile was moved back and forth in all cases until maximum deflections resulted, but errors due to distortion of the image were not wholly eliminated. Extinction coefficients, *i. e.*—$(\log L/L_0)d$, where d is in centimeters, varied about 5% when half the incident light was transmitted by the mixture, and up to 20% when transmission or absorption fell to 10% or so. As a test for the purity of the light, nineteen mixtures containing silver chloride were measured in two thicknesses, $d_2 = 2d_1$, and K_{d_1}/K_{d_2} averaged 1.09. In a somewhat similar series involving bromides, the ratio came out 1.21.

As melting points of single alkali halides are inconveniently high when pure or when containing moderate admixtures of silver chloride, a eutectic mixture of lithium chloride and potassium chloride was substituted.[2]

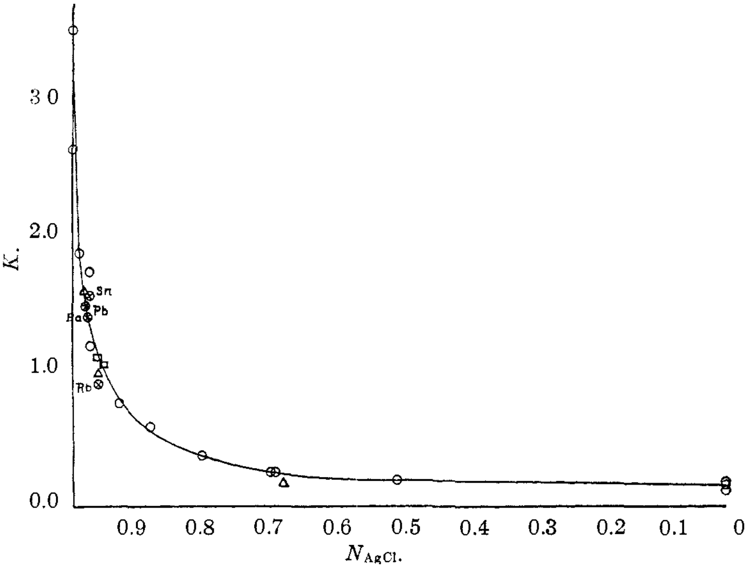

Fig. 2.—Absorption coefficients ($K = -(1/d) \log L/L_0$) for solutions of fused silver chloride in other chlorides: ○, LiKCl; △, LiCl; □, KCl.

Figure 2 plots extinction coefficients K_{5460} against mole fraction of silver chloride N_{AgCl}. Three series of measurements were made with silver chloride, free from alkali chloride, one of which was unexpectedly low. Averaging all three, $L/L_0 = 10^{-3.30d}$, so 3.30 was the starting point of the curve. Observations were also made on the eutectic, without silver chloride, which was not quite optically clear. The averaged correction for reflection, absorption and scattering by solvent was 0.14. Mixtures containing silver chloride and *one* other chloride such as LiCl, KCl, RbCl, $BaCl_2$, $SrCl_2$ and $PbCl_2$ remained in fusion if only $N_{AgCl} > 0.9$, and all the points lie close to the curve determined for AgCl + the constant eutectic. In the case of the bivalent chlorides coincidence occurs only if moles, not equivalents, are plotted, suggesting that if Cl^- is the

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(2) Richards and Meldrum, THIS JOURNAL, **39**, 1816 (1917).

decolorizer bivalent chlorides are only half dissociated under these conditions, perhaps as $BaCl^+ + Cl^-$, etc. Figure 2 makes it clear at once that there is no linear relation between K and N_{AgCl}. The same holds for activity of silver chloride, for it has been shown elsewhere that with a small concentration of a foreign salt $a_{AgCl} = kN_{AgCl}$.[3]

Fused silver chloride might contain Ag^+, Cl^-, AgCl, complex anions as $AgCl_2^-$, complex cations as Ag_2Cl^+, associated molecules, and even Ag, Cl or Cl_2. Of these, undeformed Ag^+ and Cl^- are eliminated, as many other salts containing these separately are colorless. Of the others, only complex cations should be strongly suppressed upon adding small amounts of dissociated chlorides.

Consider the possible equilibrium

$$Ag_nCl^{(n-1)+} + (n-1)Cl^- \rightleftharpoons n\,AgCl \rightleftharpoons \frac{n}{2}\,Ag^+ + \frac{n}{2}\,AgCl_2^-$$

Let us suppose that the third configuration is by far the most stable, recalling the $Ag_2(CN)_2 \rightleftharpoons Ag^+ + Ag(CN)_2^-$ in water solution. Then all the other reactants will be present in minimal concentration. If a highly dissociated chloride is added, $2\,M^+Cl^- + Ag^+ = 2\,M^+ + AgCl_2^-$. Provided that $N_{AgCl} > 0.5$, nearly half the ions present will be $AgCl^-{}_2$ and $[Ag^+] = N_{AgCl} - 0.5$. Thereupon

$$[Ag_nCl]^{(n-1)+} = K_1\,\frac{[Ag^+]^{n/2}\,[AgCl_2^-]^{n/2}}{[Cl^-]^{(n-1)}} = K_2\,[Ag^+]^{(n-1/2)} \tag{1}$$

since $[AgCl_2^-]$ is constant and $[Cl^-] = K_3\,[AgCl_2]^{1/2}/[Ag^+]^{1/2}$. A corresponding equation, under equivalent assumptions, would apply equally well to silver bromide in alkali bromides.

Figure 3, Curves I and II, shows how the concentrations of complexes should vary with changes in N_{AgCl} provided that $n = 4$ and 8, respectively, and the dissociation of $Ag^-\cdot AgX_2^-$ very small. The curves do not closely follow those for the observed extinction coefficients. The system K_{AgBr} in potassium bromide is reduced to a comparable basis by multiplying K by 3.30/140.

Suppose, however, that silver chloride is the most stable state. Then

$$[Ag_nCl]^{(n-1)+} = K[AgCl]^n/[Cl^-]^{(n-1)} \text{ and } [Cl^-] = (1-N)_{AgCl} + [Ag^+]$$

since the complex ion if unstable requires little chloride ion for its formation.

Curves III and IV show how the concentrations of the cations Ag_2Cl^+ and Ag_3Cl^{++} should vary with mole fraction of silver chloride, the corresponding dissociation constants of the silver chloride being 3×10^{-4} and 3×10^{-3}. The agreement of curve III with the two observed curves is perhaps within the experimental error.

The assumption that fused silver halides are largely undissociated is consistent with the conclusion of Hildebrand and Salstrom that fused silver bromide is not a strictly polar compound.[4] Moreover, it has been shown that the vapors of the silver halides do not consist of silver and halide ions.[5,6]

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(3) Elkins and Forbes, THIS JOURNAL, **55**, 3250 (1933).

(4) Hildebrand and Salstrom, *ibid.*, **54**, 4257 (1932).

(5) Franck and Kuhn, *Z. Physik*, **43**, 164 (1927); **44**, 607 (1927).

(6) Brice, *Phys. Rev.*, **35**, 960 (1930).

While electromotive force data indicate that the activities of fused silver chloride and bromide in solution in alkali halides are nearly proportional to the mole fractions, they apparently tell us nothing about the activity of the silver *ion* and constitute no objection to the above assumption.[3,7]

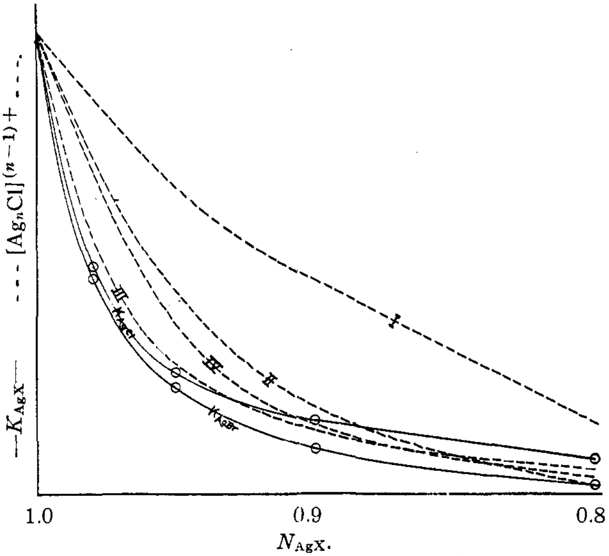

Fig. 3.—I, $[Ag_4Cl^{+++}]$, and II, $[Ag_8Cl^{7+}]$, if the dissociation of $AgCl_2^-$ is very small; III, $[Ag_2Cl^+]$ if the dissociation constant of AgCl is 3×10^{-4}; IV, $[Ag_3Cl^{++}]$ if the dissociation constant of AgCl is 3×10^{-3}.

Fajans' hypothesis[8] of ion deformation, if applied to the case under consideration, would picture Cl^- deformed by Ag^+. Alkali cations, having small deforming power, would reduce the cases of large deformation. But since K_{AgCl} is halved by adding 0.04 mole of eutectic, the influence of the added cations, if decisive, would have to be exerted over considerable distances. This theory is, of course, only qualitative in application.

The decision between the chemical and the physical theory might be reached by further experiments involving wide variation of wave length. For if a single individual were responsible for the whole absorption band, our curves would be independent of wave length if K_{AgCl} was always reduced to a fixed standard. On the basis of the physical theory the curves might readily differ. Unfortunately the absorption coefficients at higher frequencies are too great to study with our apparatus.

In Fig. 4 curves for logarithms of extinction coefficients of mixtures of silver halides in other mixtures are given. Linear relations are approached more nearly for log K than for K. In contrast to Fig. 2 concentration,

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[7] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930).

[8] Fajans, *Z. Krist.*, **66**, Bd. 3, 4 Heft (1928).

and absorption of solvent, are corrected for, so that only a line of zero slope would describe a system obeying Beer's law. K_{5560} for pure silver bromide can now be estimated by linear extrapolation as shown. The mean value for the two systems is 128. This method of extrapolation might prove of service in estimating K for silver halides, or other salts having excessive absorptions at certain wave lengths.

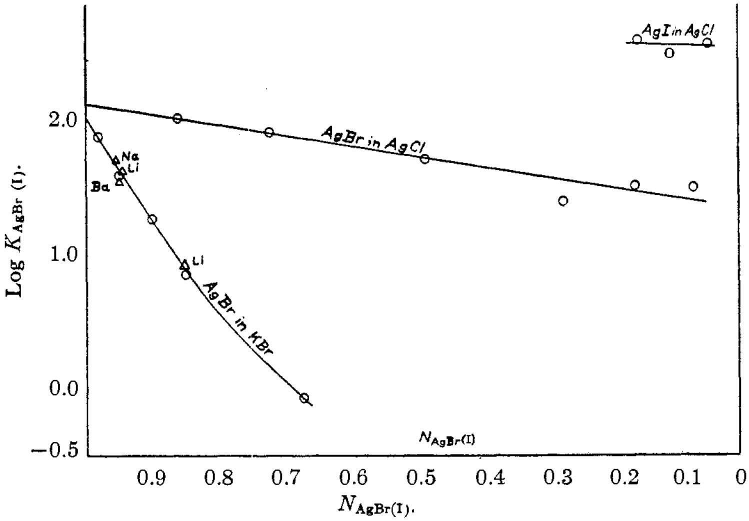

Fig. 4.

Summary

Extinction coefficients K for $\lambda = 5460$ Å. have been measured with an average uncertainty of ten per cent. for systems containing silver halides and alkali halides.

Addition of 0.04 mole of alkali halide to silver halide cuts K in half. One mole cuts K to about one per cent. of its initial value.

Of several possible chemical configurations considered, that postulating the complex cation Ag_2X^+ in equilibrium with silver chloride having a dissociation constant of 3×10^{-4} entails the smallest disagreement with the optical measurements.

If silver halides are mixed, log K is very nearly a linear function of N_{AgX}. The plots are of service in estimating by extrapolation the extinction coefficients of pure salts.

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