

Studies on Aging of Precipitates and Coprecipitation XXXIX. Low Temperature Conductivity of Silver Bromide

I. Shapiro and I. M. Kolthoff

Citation: *J. Chem. Phys.* **15**, 41 (1947); doi: 10.1063/1.1746285

View online: <http://dx.doi.org/10.1063/1.1746285>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v15/i1>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast

www.goodfellowusa.com

Studies on Aging of Precipitates and Coprecipitation

XXXIX. Low Temperature Conductivity of Silver Bromide*

I. SHAPIRO AND I. M. KOLTHOFF

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

(Received October 4, 1946)

The following expression is proposed for the electrical conductivity of silver bromide

$$\chi = (Ae^{-W/2kT} + KS)e^{-U/kT},$$

in which S is the magnitude of the active surface. When $Ae^{-W/2kT} \gg KS$ the high temperature kind of conductivity predominates. In the opposite case the low temperature kind of conductance predominates. Conductivity-temperature curves of fresh (large S) and well-aged (small s) silver bromide have been determined. In agreement with theoretical expectations it is found that

$$\chi = 3.0 \times 10^5 e^{-18,000/RT} + A_i e^{-8300/RT}$$

in which A_i varies in proportion to the active surface of the product. A pellet prepared from freshly precipitated silver bromide was found to have about 500 times as large a conductance as a pellet prepared from the fused product. At a given temperature the following relation exists between χ and the pressure p applied to the pellet: $d \ln \chi / dp = -k$. The value of k increases with decreasing active surface and with increasing temperature. The temperature effect is accounted for by the contribution of the active surface.

INTRODUCTION

THE theory of the ionic conductivity in crystals based upon Frenkel¹ and Schottky² disorders has been reviewed by Mott and Gurney³ and by Barrer.⁴ The agreement of the theoretical considerations with experimental findings has been satisfactory in most cases; however in some salts at low temperatures certain discrepancies are found.

In general the experimental ionic conductivity-temperature curves for salts can be divided into two parts, a reversible high temperature curve obeying a law

$$\chi = Ae^{-E/kT} \quad (1)$$

and families of low temperature curves obeying analogous laws

$$\chi_1 = A_1 e^{-E_1/kT} \quad (E_1 < E). \quad (2)$$

The value of the constant A_1 in Eq. (2) depends

¹ J. Frenkel, *Zeits. f. Physik* **35**, 652 (1926).

² W. Schottky and C. Wagner, *Zeits. f. physik. Chemie* **B11**, 163 (1930).

³ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford Press, 1940), p. 42.

⁴ R. M. Barrer, *Diffusion in and through Solids* (Macmillan Company, New York, 1941), p. 239.

upon the previous history and treatment of the specimen.

The equation for the electrical conductivity in solids also can be expressed by

$$\chi = nev, \quad (3)$$

where n is the number of carriers (e.g., number of positions of disorder), e is the ionic charge, and v is the mobility of the carriers. Considering the case of a Frenkel disorder in a crystal (i.e., some cations occupying interstitial positions instead of normal positions) the number of carriers, n , in thermal equilibrium at temperature T is given by

$$n = Ne^{-W/2kT}, \quad (4)$$

where W is the work necessary to move an ion from a normal position to a distant interstitial position. The mobility of these carriers can be expressed by

$$v = Be^{-U/kT}, \quad (5)$$

where U is a potential barrier and B is a constant. Therefore Eq. (3) can be rewritten as

$$\chi = Ae^{-(\frac{1}{2}W+U)/kT}. \quad (6)$$

By comparing Eq. (6) with Eq. (1),

$$E = \frac{1}{2}W + U. \quad (7)$$

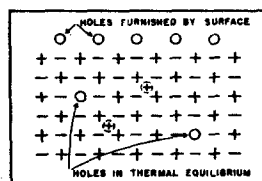


FIG. 1. Frenkel-type lattice disorder.

Several explanations for the break in the conductivity-temperature curves in ionic crystals have been given by workers in this field. Some workers hold the view that at the higher temperatures the exponential in the conductivity equation is governed by $(\frac{1}{2}W + U)$, but at the lower temperatures the positions of disorder are "frozen in" and only part of the exponential is used, namely U . Koch and Wagner⁵ carried out some unique experiments on mixed crystals of AgBr-PbBr₂ and have shown that small additions of lead bromide greatly increase the conductivity of silver bromide. On the basis of these mixed crystal measurements Koch and Wagner believe that the low temperature conductivity is governed primarily by impurities in the crystals.

In view of the work carried out by Smekal⁶ and other workers, it seems that the break in the curves is more regular than a mere dependence upon impurities or the "freezing of the positions of disorder" at some temperature. In any real crystal there exist cracks and imperfections which may be considered as internal surface. Any surface, internal or external, should be capable of furnishing a high concentration of "holes" to the crystal since an ion near the surface can migrate to a vacant lattice position (of which there are many) on the surface just as well as to a vacant lattice position in the interior of the crystal (see Fig. 1). Therefore at any temperature the total concentration of holes (note: a "hole" can be considered as a "carrier") will be dependent upon the active surface present and the normal concentration of holes existing in thermal equilibrium. The temperature function of the holes (or carriers) in the lattice in thermal equilibrium is given by Eq. (4) while the concentration of holes in the surface practically is independent of the temperature (as long as no aging occurs in the material). Hence Eq.

⁵ E. Koch and C. Wagner, *Zeits. f. physik. Chemie* **B38**, 295 (1937).

⁶ A. Smekal, *Handbuch der Physik* (1933), Vol. 24, Part 2, page 881.

(6) should be rewritten as

$$\chi = (Ae^{-W/2kT} + KS)e^{-U/kT}, \quad (8)$$

where S is magnitude of active surface and K is a proportionality factor. When the temperature T is such that

$$Ae^{-W/2kT} \gg KS, \quad (9)$$

then the high temperature form of the conductivity equation becomes predominant and Eq. (8) reduces to Eqs. (1) or (6). On the other hand when the temperature T is such that

$$Ae^{-W/2kT} \ll KS, \quad (10)$$

then the low temperature curve becomes the more important and Eq. (8) reduces to Eq. (2). This reasoning explains why compressed pellets of powdered silver bromide have a higher conductivity than those of the fused salt at low temperatures but that the conductivity of the former becomes equal to that of the latter at higher temperatures.⁶ Also the increase in conductivity with addition of lead bromide to silver bromide⁵ can be explained in the light of the above discussion because each molecule of lead bromide added creates a cation hole in the crystal lattice. These created holes behave identically with the surface holes of the crystals.

The validity of Eq. (8) can be checked indirectly by measuring the pressure effect on conductivity. Jost and Nehlep⁷ have shown that in the high temperature range

$$d \ln \chi / dp = -\beta \ln C / \alpha T = \text{a constant} \quad (11)$$

where β is the coefficient of compressibility, α is the coefficient of expansion, T is the absolute temperature, and C is a constant which is determined by

$$\exp(-(\alpha V_0/k) \cdot (dE/dV)).$$

It is obvious from Eq. (11) that the slope of the conductivity-pressure curve numerically will decrease with increasing temperature. However, in the low temperature range, Eq. (11) need not apply. The pressure effect at low temperatures will be considered in more detail after the experimental data are given.

⁷ W. Jost and G. Nehlep, *Zeits. f. physik. Chemie* **B34**, 348 (1936).

The experiments on the effects of temperature and pressure upon ionic conductivity of silver bromide powders have been carried out in conjunction with a study on the "aging" phenomena of powders.⁸ The effect of the change in surface of the powder upon ionic conductivity could be followed by conductance measurements.

EXPERIMENTAL PROCEDURE

Preparation of Samples

The preparation of the silver bromide samples and the subsequent measurements of the electrical conductivity at various temperatures and pressures are given in detail in the thesis of the Junior author. All of the silver bromide used in these experiments were prepared by a precipitation method using analytical grade reagents and conductivity water. Solutions of 0.4*N* silver nitrate were added to equivalent amounts of potassium bromide solutions with vigorous stirring. The precipitates were washed five times with large volumes of water, then five times with acetone, and finally five times with thiophene-free benzene. Dry air was passed through the precipitate on a Büchner funnel until the odor of benzene no longer was detectable. All precipitations and treatment of the silver bromide were carried out in photographically inactive red light.

Portions of the silver bromide powder were thermally aged by heating the powder to various temperatures (measured with a nichrome-constantan thermocouple) for definite periods of time in a Pyrex tube placed in a well of a copper block furnace. To prevent loss of bromine from the silver bromide at the elevated temperatures (above 100°C) a stream of bromine vapor was maintained over the powder in the furnace. The temperature and heating time of the "aged" powders are given with the experimental data.

In most cases the electrical conductivity measurements were made on pellets prepared from compressed powders but in several instances the pellets were formed by fusing the silver bromide and machining the congealed melt to the correct size on a lathe. The pellets formed from the powders were compressed under 3000 atmos-

pheres pressure. Previous work on the pressure effect of silver bromide powders indicate that under these conditions the apparent density of the powders is within one percent of the true density of silver bromide. Therefore the data on compressed powder and fused-cut pellets should be comparable.

Electrical Conductivity Measurements

A sketch of the conductivity cell is shown in Fig. 2. In this cell the electrical conductivity of the silver bromide could be measured under various conditions of temperature and pressure. The pistons which served as electrodes were silver plated and a lamina of Bakelite served as an insulator between the pistons and die. The pressures on the silver bromide pellets were measured with a calibrated gage on the hydraulic press, and the temperatures were measured with a copper-constantan thermocouple connected to a type-*K* potentiometer. An electric heater and stirrer in an oil bath were used to obtain the various high temperatures while freezing mixtures, e.g., dry ice and acetone, were used for the low temperatures.

A direct current was used for measuring the conductivity of the pellets. The current flowing through a pellet under a given voltage was read on a three-range combination micro-milliammeter. For the source of voltage nine 1½v dry cells and three 45v "B" batteries were wired in such a manner that various voltages in the range of 1½v to 135v could be applied by turning the

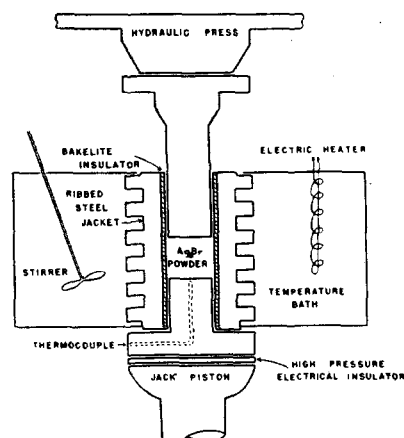


FIG. 2. High pressure conductivity cell.

⁸ I. M. Kolthoff, *Tekniska Samfundets Handlingar* **3**, 119 (1939).

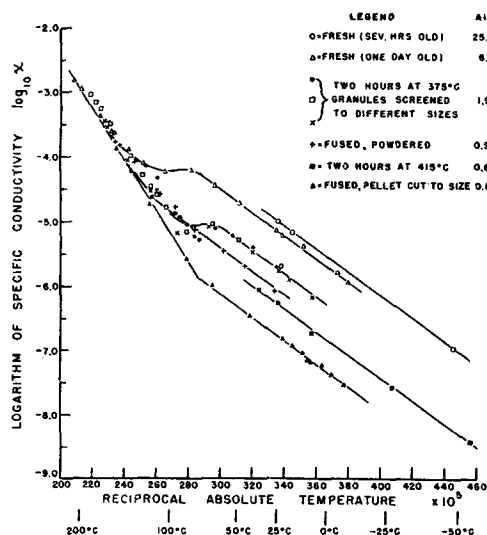


FIG. 3. Electrical conductivity of silver bromide as a function of temperature.

knob of a double gang switch. The actual voltage used depended upon the resistance of the pellet so that the current always was within a definite range. A voltmeter was used to measure accurately the various voltages. The dimensions of the pellets were measured with a micrometer at the conclusion of the experiments. All electrical and mechanical measurements were reproducible to within 1 percent.

A continuous direct current must not be allowed to flow through a pellet otherwise dendritic silver bridges will form across the electrodes and will cause a short-circuit through the pellet. For that reason the actual current was kept to a minimum and was allowed to flow through the pellet just long enough (few seconds for each reading) to obtain the necessary data. Since the total quantity of electricity passing through a pellet during the course of the experiment was negligibly small compared to the quantity of electricity necessary to produce the silver "bridges," the error introduced by the transport of ions can be disregarded.

RESULTS AND DISCUSSION

Conductivity of Fresh Silver Bromide

Fused silver bromide is an ionic conductor in which only the silver ions are migrating.⁹ Since

⁹ C. Tubandt, *Handbuch der experimental Physik* (Leipzig, 1932), Vol. 12, p. 389, 397.

fresh silver bromide at room temperature has a conductivity that may be more than 10^4 times as great as the conductivity of the fused product under similar conditions, the possibility of a change in mode of conductivity with age was investigated. Transference experiments of fresh silver bromide (to be published) show that there is no change in mode and that the fresh silver bromide is an ionic conductor in which only the silver ions are migrating through the silver bromide crystals.

Conductivity as a Function of Voltage

Since it has been found convenient to vary the voltage dependent upon the resistance of the silver bromide samples (resistance varies greatly with "age" and temperature) so that the current always will be within a definite range, the validity of the application of Ohm's law to the data was checked. It was found that Ohm's law is applicable for the entire range of voltages used in these experiments and is not affected by variation of temperature and/or pressure.

Conductivity as a Function of Temperature

The dependence of conductivity upon temperature for the various aged silver bromide samples is shown in Fig. 3. All temperature experiments were carried out under a constant pressure of 925 atmos. after the pellets had been subjected to pressures of 3000 atmos. From pressure-conductivity experiments it was found that one could obtain reproducible results at the high pressures whereas the measurements at low pressures might be influenced by poor contact between electrodes and pellet.

An inspection of the curves in Fig. 3 reveals three outstanding features: (1) The slopes of the curves for all samples are approximately the same at low temperatures; (2) At high temperatures all curves merge into one straight line whose slope is greater than that at the low temperature; and (3) At any one low temperature the conductivity is strongly dependent upon the "age" (including thermal treatment) of the samples of silver bromide. Empirically all the curves in Fig. 3 can be expressed by the following equation:

$$\chi = 3.0 \times 10^5 e^{-18,000/RT} + A e^{-3300/RT},$$

where the values of A_i depend upon the previous history of the particular samples. The values of A_i are listed in the legend of Fig. 3. The Q -values of 18,000 cal. (high temperature) and 8300 cal. (low temperature) are in excellent agreement with the values obtained by Koch and Wagner⁵ on mixed crystals of AgBr-PbBr₂.

The slight dip in the curves for the comparatively fresh powders shown in Fig. 3 is due to thermal aging as the specimens are heated. The actual shape of the dip in the curves depends upon experimental conditions (e.g., rate of heating, etc.). As long as the temperature is sufficiently low, the low temperature curves are reversible, but as soon as appreciable aging occurs, the curves follow a line of correspondingly lower conductivity. Of course, the high temperature curve is reversible regardless of the age of the specimen.

Conductivity as Function of Age of Powder

The total surface of the unpressed powders of the various aged samples of silver bromide were measured by the dye adsorption method¹⁰ by using wool violet and a Cenco photometer. Direct measurements of the surface after the powder once is compressed are unobtainable. However, experiments on the change of conductivity with pressure as the powders are compressed afford an approximate method for evaluating the change in surface with pressure. (The data on the electrical conductivity during the compaction of silver bromide powders will be

TABLE I. Effect of pressure on conductivity of silver bromide pellets at room temperature.

Sample no. (corresponds to curve no. in Fig. 4)	"Age," heat treatment of silver bromide	Conductivity at zero pressure (extrapolated) $\chi_{p=0}$, $\Omega^{-1} \text{ cm}^{-1}$	$k/\text{atmos.}$ $\times 10^4$
1	Fresh (less than 1 day old)	2.20×10^{-5}	0.644
2	Fresh (one day old)	1.03×10^{-5}	1.25
3	Unheated (20 days old)	7.9×10^{-6}	1.27
4	Heated 4 hours at 110°C	4.0×10^{-6}	1.63
5	Heated 2 hours at 375°C	2.4×10^{-6}	1.59
6	Heated 2 hours at 375°C	2.1×10^{-6}	1.53
7	Fused, quenched, powdered	1.4×10^{-6}	1.45
8	Fused, powdered, { 14-20 mesh	1.1×10^{-6}	1.65
9	Fused, powdered, { mixed size	1.1×10^{-6}	1.73
10	Fused, powdered, { 10-14 mesh	9.8×10^{-7}	1.68
11	Fused, powdered, { 8-10 mesh	9.0×10^{-7}	1.64
12	Fused, cooled slowly, powdered	3.0×10^{-7}	2.11
13	Fused pellet, cut to size	1.9×10^{-7}	2.22
14	Fused pellet, cooled slowly, annealed, cut to size	6.9×10^{-8}	2.50

¹⁰ I. M. Kolthoff and A. S. O'Brien, J. Am. Chem. Soc. 61, 3409 (1939).

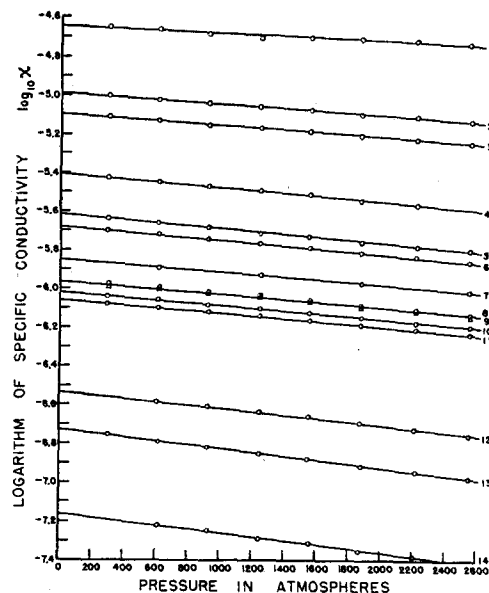


FIG. 4. Conductivity of pellets of silver bromide as function of recompression pressure 25°C (reversible).

published in a subsequent article.) Calculations of the surface in the compressed powder at room temperature give values which are approximately proportional to the (low temperature) conductivity of the pellets. This proportionality between surface and conductivity at a fixed (low) temperature bears the view that the low temperature conductivity is predominantly a "surface" conductivity (Eq. (10)). Further evidence substantiating this theory is given in the next section.

Conductivity as a Function of Recompression Pressure

The effect of recompression upon the conductivity of silver bromide pellets at room temperature is shown in Fig. 4. It is observed that each curve can be expressed by

$$d \ln \chi / dp = -k, \quad (12)$$

where k is a constant. The "age" or heat treatment of the various samples before compaction, the extrapolated conductivity at zero pressure ($\chi_{p=0}$), and the k -values for the samples are listed in Table I. The proportionality between surface and conductivity can be seen by comparing the "age" of the powder with its conductivity at room temperature. Of course, the

TABLE II. Effect of temperature upon the conductivity-pressure function

Age of sample	Temp. of press. exp. t°C	k/atmos. ×10 ⁴
Fresh (1 day old)	-10.5	0.284
	4.0	0.621
	25.8	1.30
	205.0*	1.86
Heated 2 hr. at 375°C	25.5	1.49
	38.6	1.58
	51.5	1.62
	64.1	1.73
	93.2	2.90
Fused-powdered	25°	1.68
	112°	1.77
	151*	2.28

* In high temperature region.

"fresh" powders had "aged" somewhat as a result of the pressure effect, nevertheless the trend still can be recognized clearly from the data of Table I.

From an inspection of Fig. 3 it is obvious that room temperature (25°C) is in the low temperature conductivity range hence only part of Eq. (8) need be considered here, so

$$\chi = KSe^{-U/RT}. \quad (13)$$

Thus at a fixed temperature the exponential of Eq. (13) is constant and the conductivity is proportional to the active surface in accordance with experimental facts.

The slight increase in the value of k (Table I) with age of the sample can be explained on the basis of a surface conductivity. The low temperature conductivity is proportional to the number of "continuous paths of surface" between the electrodes. Since isolated surfaces, especially if oriented perpendicular to the line of direction between electrodes, do not contribute materially

to an increase in conductivity, these so-called "paths of surface" refer to "active" surface and not necessarily "total" surface. As pressure is applied to a pellet, the number of "paths of surface" decreases. Since there are more "paths" in a pellet formed from a fresh powder than from a well-aged or fused powder, the relative decrease in number of paths will be less for the fresh powder pellet and therefore its conductivity will be less sensitive to pressure.

The effect of temperature upon the conductivity-pressure function is given in Table II. Regardless of the age of the sample the value of k increases with the temperature of the experiment. However from Eq. (11) one finds that the value of k should decrease with increasing temperature were only the mobility of the ions affected by pressure. By considering the influence of surface this anomaly can be reconciled. By taking the logarithm of Eq. (13) and differentiating with respect to pressure, we get

$$d \ln \chi / dp = d \ln S / dp - (1/RT)(dU/dp). \quad (14)$$

Experiments on the compressibility of silver bromide powders (in press) show that the change in the logarithm of porosity (related to surface) of a powder with pressure is a constant, and that the numerical value of the constant increases with temperature and/or age of the powder. By assuming that a similar function exists between surface and pressure for compressed pellets, then the value of k from Eq. (12) will depend more upon the surface term in Eq. (14) than upon the energy term. Indeed calculations based upon known data show that the energy term of Eq. (14) is much smaller than the experimentally determined values so that the assumption seems justified.