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THE EFFECT OF HYDROSTATIC PRESSURE ON THE
IONIC CONDUCTIVITY OF SILVER CHLORIDE

by
Albert E. Abey

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For the Degree of

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Albert Edward Abey
entitled The Effect of Hydrostatic Pressure on the
Ionic Conductivity of Silver Chloride.
be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

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To the memory of my father

ABSTRACT

The conductivity of AgCl was measured continuously at five different pressures up to 8 kbars while the temperature was varied from 300°K up to 680°K. From the pressure variation of the parameters involved the activation volume for Frenkel defect formation, ΔV_f , is found to be 16.7 cm³ per mole while the activation volume for interstitial motion, ΔV_{Im} , to be 3.25 cm³ per mole and the activation volume for vacancy motion, ΔV_{Vm} , to be 4.7 cm³ per mole. The activation volume for dissociation of vacancy-divalent impurity complexes, ΔV_a , is found to be 0.98 cm³ per mole. The enthalpies of association, vacancy motion, and interstitial motion are found to be 0.16 ev, 0.32 ev, and 0.151 ev, respectively, at a pressure of 1 bar. The ratio of interstitialcy mobility to vacancy mobility is found for a pressure of 1 bar at a temperature of 488°K and for a pressure of 6 kbars at a temperature of 527°K to be 8 and 10, respectively.

INTRODUCTION

The study of electrical conductivity in ionic crystals is, and has been for some time, the subject of study by a large number of investigators.¹ More recently the study of ionic conductivity has been expanded to include the effect of hydrostatic pressure upon the mechanisms involved.^{2,3} This interest is based not only on the desire to know the functional dependence of the conductivity on the external parameters, but to a greater degree on the desire to learn and understand the basic mechanisms which are responsible for the particular conductivity which a given type of ionic crystal displays.

The study of conductivity in ionic crystals enters into the region of point defects in solids. Seitz discusses Schottky defects, Frenkel defects, and substitutional foreign ions which are believed to exist in the different types of ionic crystals and which take part in the electrical conductivity of those crystals.⁴ In AgCl it has been established recently by Fouchaux and Simmons⁵ that Frenkel defects are the predominant type of intrinsic defects present over all temperatures up to the melting point. In general, Frenkel defects may exist in both the cation and anion sublattices.

However, the work of Tubandt⁶ on the transport numbers for AgCl, which shows the silver ion transport number to be unity, indicates that only the Frenkel defects in the cation sublattice contribute to the conductivity. This conclusion is substantiated by the work of Compton⁷ who found that the tracer mobility of the chlorine ion is considerably smaller than the mobility of the silver ion.

In order to fill the gap in the study of the properties of ionic crystals, it is considered necessary to measure accurately the ionic conductivity of pure AgCl crystals as a function of temperature and of pressure. To obtain a better overall picture a wide temperature range in measurement including the region in the vicinity of 300°K is required. To obtain a clear interpretation of the pressure dependence, the application of pure hydrostatic pressure is mandatory. In order to increase the reliability of the ionic conductivity measurement at high pressure, it is of utmost importance to devise a new method which would allow one to measure the ionic conductivity at different pressures over a large temperature range which has hitherto been impossible to cover by means of the techniques so far available. The present experiment is also undertaken to meet the need for a pressure study on the ionic conductivity of AgCl to complement the work of Compton⁷ by providing the activation volume for the diffusion process.

EXPERIMENTAL PROCEDURE

The AgCl crystals were received from the Harshaw Chemical Company and were prepared by the standard cutting, polishing, and etching techniques. The conduction samples are cylindrical in shape, approximately 0.4 cm-thick and 1 cm in diameter, and consist of about four or five large single crystals. Electrodes are applied to the flat surfaces of the samples by using several coats of Dag 154, a colloidal carbon paint, as suggested by Layer and Slifkin.⁸ Care is exercised to confine the paint to the end surfaces in order to avoid accidental electrical shorting. The Dag 154 is not affected in any visible way by the pressure fluid in any of the runs up to 680°K.

Two different sample holders are used in obtaining the conductivity data. One is used in what will be referred to subsequently as the low temperature region of the experiment, from 300°K to 530°K; the other in what will be referred to subsequently as the high temperature region, from 530°K to 680°K. The sample holders, which differ only in the material used in their construction, are shown in Fig. 1. In the low temperature region the sample holder is constructed of Teflon. Teflon has a volume resistivity of 10^{15} ohm-cm at

room temperature. This large volume resistivity, which remains almost constant over the low temperature region, is the main reason for using Teflon. The sample is placed, as shown in Fig. 1, between two stainless steel electrodes. A copper wire is silver-soldered to each electrode and the wire passes through an alundum insulator out of the sample holder. For the high temperature region of the experiment the sample holder is the same as for the low temperature region except the Teflon is replaced by Lava A which has been baked at 1000°C.

For the low temperature portion of the experiment a new type of electrical lead-in through the apparatus was devised. These lead-ins, "cones," are the determining factor in the reliability of the low temperature data. The cones are made from Eccobond 76 epoxy and placed in the apparatus plug, which is fabricated from Carpenter 883 "red tough" steel which has been hardened to Rockwell 40 C, as shown in Fig. 2. The leakage resistance of these cones at room temperature is infinite as measured on a General Radio type 544B meg-ohm bridge and drops to 10^{11} ohms at 150°C. These epoxy cones are of particular use because of this high resistance. The cones are constructed by first placing a taut copper wire, which passes through the alundum insulator, up the middle of a hole in the apparatus plug. The apparatus plug is then heated by means of a heat gun so that

the epoxy can flow freely. The epoxy is then applied as shown making sure that no air pockets are left in the cone. After being allowed to cool to room temperature the plug is cured for three hours at 110°C and for three hours at 150°C. These cones have been used in a liquid pressure system at temperatures from 200°C to 230°C at pressures up to 8 kbars for up to 82 hours with very good results. Results indicate that the longevity of these cones is good as long as the wire is not fatigued by bending at the point where the wire leaves the epoxy. The repair of a damaged cone is quite simple as the old cone can be removed in a short time by using a coning tool and replaced in exactly the same manner as a new cone is made without touching any of the remaining undamaged cones. For the high temperature portion of the experiment the epoxy cones are replaced by the standard pipestone cones which have a leakage resistance of about 10^8 ohms at room temperature.

The pressure system used is of the standard hydrostatic type⁹ and is shown schematically in Fig. 3. The sample vessel was constructed from Carpenter 883 "red tough" steel which has been hardened to Rockwell 40 C. The sample vessel, which is 55 cm in length and 21 cm in diameter, is placed in an external air furnace which is 85 cm in length and 42 cm in diameter. This vessel-furnace combination appears to give very good temperature uniformity over the

central portion of the vessel in which the sample is placed.

Dow Corning 200 fluid (3 centistoke) is used as a pressure medium. This fluid has a volume resistivity of 10^{14} ohm-cm at room temperature and maintains a sufficiently high volume resistivity so that leakage current through the fluid can be neglected in this experiment. The pressure is measured by means of a manganin gauge which was calibrated using the freezing pressure of mercury at 0°C (7640 bars) and atmospheric pressure at room temperature.

For both the low and high temperature portions, the temperature is measured with a calibrated chromel-alumel thermocouple which is placed about 0.15 cm from the sample as shown in Fig. 1. The temperature measurements do not appear to depend in any way upon the exact distance of the thermocouple junction from the sample.

For the low temperature portion of the experiment, with the epoxy cones and Teflon sample holder, the leakage resistance is sufficiently large so that leakage current to ground can be neglected and the sample resistance can be measured directly by means of a General Radio 1615A impedance bridge using a 1442P decade resistor. For the high temperature portion of the experiment, with pipestone cones and Lava A sample holder, the sample resistance decreases to a value where the leakage current can again be neglected and the sample resistance can still be measured directly.

EXPERIMENTAL RESULTS

The sample resistance data were taken at constant pressure while the temperature was varied at a rate of less than one-half a degree per minute by means of the external furnace. The sample resistance measurements were taken every two degrees. After the data for each portion of the experiment were taken the sample was removed from the sample holder and measured with a micrometer and the conductivity determined from the dimensions.

The data were taken using two samples, both from the same ingot. One sample was used for the low temperature portion and the other for the high temperature portion. The low temperature portion ranged from 300°K to 530°K and the high temperature portion from 530°K to about 680°K. The two portions of the curves matched well and no artificial normalizing factor was needed in an effort to establish the semblance of continuity of these two portions. The conductivity was measured as a function of temperature at 1, 2000, 4000, 6000, and 8000 bars. The low temperature portion of the 2 kbar curve was the result of two partial runs as was the lower portion of the 8 kbar curve. A plot of $\ln \sigma$ vs $1/T$ is shown in Fig. 4 for the five pressures used in this work.

DISCUSSION OF EXPERIMENTAL ERRORS

Although no complete runs were repeated, it was necessary to repeat a portion of several runs in order to complete these runs after an equipment breakdown. These reproduced runs varied by less than one percent from the original data over the region repeated. The data for the low temperature portions of the experiment connected with the data from the high temperature within one percent for each of the five pressures. The error in the sample resistance measurements due to imbalance of the bridge was always less than one percent. The error in measuring the dimensions of the sample was about three-fourths of one percent. The temperature was measured with an error of $\pm 1^{\circ}\text{C}$ while temperature differences were determined with an error of $\pm 0.1^{\circ}\text{C}$. The pressure was held constant to ± 10 bars on all runs except for the 8 kbar run where the pressure was held constant to ± 50 bars.

No corrections were made for the temperature or pressure dependence of the crystal dimensions in the calculations of the conductivity from the sample resistance. Calculations show that the error caused by neglecting these two effects is less than one percent. Also, no corrections were

made for the anomalous resistance caused by the polarization¹⁰ of the crystal. However, a frequency of 10^4 cycles per second was used to minimize this blocking effect of the electrodes. This did not appear to be a serious error as no change in sample resistance was noted when the measuring frequency was lowered to 10^3 cycles per second.

DISCUSSION OF EXPERIMENTAL RESULTS

In general, the electrical conductivity, σ , of a substance is given by

$$\sigma = \sum_{ij} q_i n_{ij} \mu_{ij}, \quad (1)$$

where n_{ij} is the number of type i charge carriers which take part in type j conduction, q_i is the electrical charge of type i carriers, and μ_{ij} is the mobility of type i carriers when transported by a mechanism of the j^{th} type. Using Tubandt's⁶ results and assuming the prevalence of Frenkel defects in the cation sublattice of AgCl, Equation (1) can be written

$$\sigma = q \sum_j n_I \mu_{Ij} + q n_V \mu_V, \quad (2)$$

where n_I is the number of interstitial silver ions, μ_{Ij} is the mobility of the different possible mechanisms for interstitial motion, n_V is the number of silver vacancies, and μ_V is the silver vacancy mobility. It has been shown by Friauf¹¹ that in AgBr two types of motion are predominant for silver interstitial ions. Both of these mechanisms are of the types which have been called interstitialcy by Seitz.^{12,13} These two mechanisms, collinear and non-collinear,

have different energies of motion and therefore different mobilities. Because of this evidence and of the work of McCombie and Lidiard¹³ and of Teltow¹⁴ on AgCl it will be assumed that the same two types of interstitial motion are present in AgCl as in AgBr. Hence, Equation (2) can be written

$$\sigma = qn_I(\mu_{Ic} + \mu_{In}) + qn_V\mu_V, \quad (3)$$

where μ_{Ic} is the mobility for the collinear interstitialcy mechanism and μ_{In} is the mobility for the non-collinear interstitialcy mechanism.

The mobility, μ_{ij} , can be shown¹ to be of the form

$$\mu_{ij} = (\mu_{oij}/T) \exp(-G_{ij}/kT). \quad (4)$$

In the above relation, μ_{oij} is a function of pressure P and temperature T . μ_{oij} can be assumed to a good approximation to have a constant value. In Equation (4), G_{ij} is the Gibbs free energy required for a type i charge carrier to move by mechanism j from an equilibrium position to a saddle point between two equilibrium positions.

If one considers a perfectly pure AgCl crystal, the equilibrium concentration of silver interstitials and that of silver vacancies are related by¹⁵

$$(x_V)(x_I) = \exp(-G_f/kT) = x_o^2, \quad (5)$$

where x_o is a solubility constant which is a function of temperature and pressure, x_v is the concentration of vacancies, x_I is the concentration of interstitials, and G_f is the Gibbs free energy of formation for Frenkel defects. The relation given by Equation (5) is a solubility product and holds even when the crystal contains some impurities which gives size to the inequality of x_v and x_I .

At low temperatures silver ion vacancies can occur in numbers far larger than that predicted by Equation (5) for a perfectly pure crystal where $x_I = x_v$. These silver ion vacancies arise from the addition of aliovalent impurity ions into the cation sublattice. Only divalent impurity cations which go into the sublattice substitutionally will be considered in this paper. In order to maintain electrical neutrality each divalent impurity ion in the crystal introduces one silver ion vacancy. One therefore has

$$x_v = x_I + c, \quad (6)$$

where c is the concentration of divalent cation impurities. Equations (5) and (6) yield the vacancy concentration as

$$x_v = \frac{c}{2} \left\{ 1 + \left(1 + \frac{4x_o^2}{c^2} \right)^{\frac{1}{2}} \right\}. \quad (7)$$

Combining these expressions, one obtains the following expression for the conductivity:

$$\sigma = Nq \exp(-G_f/2kT) [(\mu_{oIc}/T) \exp(-G_{Ic}/kT) + (\mu_{oIn}/T) \exp(-G_{In}/kT) + (\mu_{oV}/T) \exp(-G_V/kT)] \times \left\{ \left[\frac{c^2}{4} \exp(G_f/kT) + 1 \right]^{\frac{1}{2}} - \frac{c}{2} \exp(G_f/2kT) \left[\frac{\varphi - 1}{\varphi + 1} \right] \right\}, (8)$$

where $\varphi = (\mu_{Ic} + \mu_{In})/\mu_V$. The first half of the right hand side of Equation (8), i.e.,

$$Nq \exp(-G_f/2kT) [(\mu_{oIc}/T) \exp(-G_{Ic}/kT) + (\mu_{oIn}/T) \exp(-G_{In}/kT) + \mu_{oV}/T \exp(-G_V/kT)] ,$$

is the value of the conductivity, σ_o , of a pure crystal as a function of temperature.

At low temperatures the interaction between vacancies and divalent impurity ions will result in neutrally charged complexes (i.e., an associated divalent impurity ion-vacancy pair) which will lower the conductivity for a given temperature. The degree of association p is given in a relation found by Lidiard¹⁶ as

$$\frac{p}{(1-p)^2} = zc \exp(G_a/kT), \quad (9)$$

where c is the concentration of divalent impurities, z is the number of distinct orientations of the complex, and G_a is the Gibbs free energy of association. In deriving this relation Lidiard treated the case where only nearest neighbor

vacancy-impurity ions are considered as associated.

The curves of temperature dependence $\ln(\sigma)$ vs $(1/T)$ for the different pressures, as shown in Fig. 4, have essentially the same shape. These curves consist of three distinct regions. These regions are shown for a typical $\ln(\sigma)$ vs $(1/T)$ curve in Fig. 5. At the lower temperatures (region I) a plot of $\ln(\sigma)$ vs $(1/T)$ has a slope which is a slowly varying function of temperature. In this region the slope decreases as the temperature is decreased. In region II the $\ln(\sigma)$ vs $(1/T)$ curve has a constant slope. At the higher temperatures (region III) the slope decreases sharply and then increases slowly, finally becoming a straight line at the high temperature portion of region III.

The constant slope of the $\ln(\sigma)$ vs $(1/T)$ curve in region II is predicted by Equation (8) when $c \gg \exp(-G_f/2kT)$. In this region the conductivity, σ , is given by

$$\sigma = N_c q \mu_{OV} / T \exp(-G_{Vm}/kT). \quad (10)$$

Here N_c is the number of silver vacancies which are present in region II. These vacancies are those which arise from the substitutional addition of divalent cations and their number remains essentially constant throughout this region. The enthalpy of motion for silver vacancies, H_{Vm} , is given by

$$H_{Vm} = -K \left(\frac{\partial \ln(\sigma T)}{\partial \frac{1}{T}} \right)_P \quad (11)$$

The slope in region II gives a value of H_{Vm} of .32ev.

As the temperature is decreased and the $\ln \sigma$ curve enters region I the slope of the $\ln(\sigma)$ vs $1/T$ curve decreases slightly. This is interpreted as the association portion of the $\ln(\sigma)$ curve where the formation of complexes begins to affect the conductivity. The possibility of this change in slope arising from surface conduction is ruled out as the slope increases in going from region I to region II. Because of this association, Equation (10) must be changed to read

$$\sigma = Nq\mu_{oV}/T \exp(-G_V/kT)(1-p) \quad (12)$$

in the temperature range where association takes place.

$(1-p)$ is the number of dissociated vacancies. In the case where p is almost equal to unity Equation (12) gives

$$H_{Vm} + H_a/2 = -k \left(\frac{\partial \ln(\sigma T)}{\partial 1/T} \right)_P \quad (13)$$

where $(1-p) \approx (12c)^{-\frac{1}{2}} \exp(-G_a/2kT)$ is used. Using the value of H_{Vm} given above, H_a is found to be 0.16ev. In finding this value of H_a the slope at the lowest temperature in region I is used. This value is in reasonable agreement with the value found by Ebert and Teltow.¹⁷

In order to find G_a the simplest case is considered where S_a , the entropy of association, is assumed to be zero and thus $H_a = G_a$. Using this value of G_a the impurity concentration is obtained by using Equation (9) where p is found by comparing the projected conductivity from region II with the actual conductivity in region I. Using this method c is found to be 5×10^{-5} . Unfortunately, no independent method for determining c or for determining the type of impurity ion is available. However, this value of c which is found by using $H_a = G_a$ gives reasonable and consistent agreement with the experimental data obtained at higher temperatures.

In passing from region II to the lower temperature portion of region III, $\exp(-G_f/2kT)$ increases until it becomes comparable to c . At the high temperature portion of region III, $\exp(-G_f/2kT)$ increases until it is large compared to c . In the lower temperature portion of the conductivity, to the right of the knee between region II and region III, the conductivity of an impure crystal is greater than that of a pure crystal. On the other hand, in the higher temperature portion, to the left of the knee, the conductivity is less than that for a pure crystal. Since the number of interstitials is suppressed in this latter portion of the conductivity curve by the excess vacancies this reduction in conduction indicates a low mobility for the vacancies. The

difference between σ_o and σ in the region to the left of the knee increases rapidly to a maximum value as the temperature increases and then decreases rapidly approaching zero. When $c \ll \exp(-G_f/2kT)$, Equation (8) may be written as

$$\sigma = (\mu_{oI}/T) Nq \exp(-G_f/2kT) \exp(-G_{Im}/kT)(1 + 1/\phi), \quad (14)$$

where

$$\begin{aligned} 1/\phi &= \mu_{oV}/\mu_{oI} \exp(-G_{Vm}/kT) \exp(G_{Im}/kT) \\ &= A \exp(-\Delta/kT), \end{aligned} \quad (15)$$

where $A = \mu_{oV}/\mu_{oI}$ and $\Delta = G_{Vm} - G_{Im}$. In Equations (14) and (15) it has been assumed that one of the mobilities of interstitialcy motion is sufficiently large so that to a good approximation the combined interstitialcy mobility can be written as $\mu_I/T = \mu_{oI}/T \exp(-G_{Im}/kT)$. Using the data of Ebert and Teltow¹⁷ one gets reasonable values for A and Δ to give $1/\phi$ as

$$1/\phi = 4.5 \exp(-.165/kT). \quad (16)$$

Using Equation (16), Equation (14) can be written as

$$\begin{aligned} \ln(\sigma T) &\approx \ln[\mu_{oI} Nq \exp(-G_f/2kT) \exp(-G_{Im}/kT)] \\ &\quad + 4.5 \exp(-\Delta/kT), \end{aligned} \quad (17)$$

since $\exp(-.165/kT) < .035$ in the temperature range which is under consideration. Neglecting the temperature dependence of the first term one gets

$$-k[\partial \ln(\sigma T)/\partial(1/T)]_p = H_f/2 + H_{Im} + 4.5(H_{Vm} - H_{Im}) \exp(-\Delta/kT). \quad (18)$$

In the high temperature portion of region III Equation (18) gives a value of 0.151 ev for H_{Im} when a value of $H_f = 1.43$ ev found by Ebert and Teltow¹⁷ is combined with the value of H_{Vm} found above. This value of H_{Im} is in good agreement with the value of 0.148 found by Ebert and Teltow.¹⁷ These values of H_{Im} and H_{Vm} found above give an enthalpy difference, $(H_{Vm} - H_{Im})$, of 0.169 ev. This value is very close to the value of $(G_{Vm} - G_{Im})$ obtained from the values of ϕ of Ebert and Teltow. The closeness of these values indicates that the entropy change for motion of a vacancy is approximately the same as that for an interstitial. The slope at three different temperatures of the $\ln \sigma$ vs $1/T$ curve is shown in Table I for pressures of 1 bar and 6 kbars.

The pressure derivative of $\ln \sigma$ at constant temperature will contain terms of the type $(\partial \mu_{OI}/\partial P)_T$. It is of interest to examine the magnitude of terms of this type. One can write

$$\begin{aligned}
 (\partial \ln \mu_{OI} / \partial P)_T &= (\partial [\ln q a^2 \nu] / \partial P)_T \\
 &= (\partial [2 \ln a + \ln \nu] / \partial P)_T,
 \end{aligned}
 \quad (19)$$

where a is the lattice parameter and ν is a frequency factor which is related to the ionic vibrational frequency and which we shall assume to be equal to the Debye frequency, ν_D .

Equation (19) can be written as

$$RT(\partial \ln \mu_{OI} / \partial P)_T = |RT\gamma K| - 2/3 |RTK|, \quad (20)$$

where γ is the Grüneisen constant and K is the isothermal compressibility. Using available values for γ and K ¹⁸ we find $|RT\gamma K| \ll 0.1 \text{ cm}^3$ and $2/3 |RTK| \ll 0.1 \text{ cm}^3$. These values are small when compared with the pressure derivatives of $\ln \sigma$ at constant temperature, as given in Table II, and can therefore be neglected in the calculations of the activation volume which follow.

In region II the conductivity is given by Equation (10) and one can write

$$RT(\partial \ln \sigma / \partial P)_T = -(\partial G_{Vm} / \partial P)_T = \Delta V_{Vm}, \quad (21)$$

where ΔV_{Vm} is the activation volume for vacancy motion.

Using Equation (21) and the experimental plot of $\ln \sigma$ vs P at

constant temperature for region II which is shown in Fig. 6, a value for ΔV_{Vm} of $0.182 V_M$ is found where V_M is the molar volume. This value is somewhat smaller than the value of $.255 V_M$ which Kurnick² found for AgBr.

Using the assumptions incorporated in arriving at Equation (13) one can derive the pressure dependence of σ as

$$\begin{aligned} RT(\partial \ln \sigma / \partial P)_T &= -(\partial G_{Vm} / \partial P)_T - (\partial G_a / \partial P)_T / 2 \\ &= \Delta V_{Vm} + \Delta V_a / 2 \end{aligned} \quad (22)$$

for the portion of the $\ln \sigma$ curve falling in the lower temperature part of region I. ΔV_a is interpreted as the activation volume for dissociation, i.e., $(\partial G_a / \partial P)_T$. From Equation (22) ΔV_a is found to be $0.038 V_M$. Although this value is rather small it is significantly different from zero beyond the range of experimental errors.

In order to find ΔV_f , the activation volume for the formation of Frenkel defects, G_f is found from the ratio σ / σ_0 for the 1 bar and the 6 kbar conductivity curves in the manner described below. The ratio σ / σ_0 is minimized with respect to $1/T$ using the assumption that $(\varphi + 1) / (\varphi - 1)$ is a slowly varying function of $1/T$.¹⁵ From this minimizing one can obtain the relation

$$\exp(G_f / kT) = 4 / [c^2 \{ (\varphi + 1)^2 / (\varphi - 1)^2 - 1 \}] \quad (23)$$

as the condition for a minimum of the σ/σ_0 vs $1/T$ curve.

Using Equation (23) one can derive a quadratic equation for $(\sigma/\sigma_0)_{\min}$ as

$$\begin{aligned} & [1 - (\sigma/\sigma_0)_{\min}^2](\varphi + 1)^4/(\varphi - 1)^4 + (\sigma/\sigma_0)_{\min}^2(\varphi + 1)^2/(\varphi - 1)^2 \\ & - 2(\sigma/\sigma_0)_{\min}(\varphi + 1)^2/(\varphi - 1)^2 \\ & \times [(\varphi + 1)^2/(\varphi - 1)^2 - 1]^{\frac{1}{2}} - 1 = 0. \end{aligned} \quad (24)$$

To find the curve for σ/σ_0 at the two different pressures it is necessary to extrapolate σ_0 to the knee between regions II and III from the higher temperature portion of region III where the plot of $\ln(\sigma)$ vs $1/T$ is essentially a straight line. Obviously this procedure is subject to question. However, the following method is used to draw a set of consistent lines for the two pressures. The point of intersection between the extrapolated σ_0 curve and the σ curve, where σ/σ_0 is unity, is checked by requiring the value of φ found at this point from Equation (8) to be the same as that of φ found at $(\sigma/\sigma_0)_{\min}$. This criterion showed a shift of 40°C in the temperature corresponding to the minimum value of (σ/σ_0) . The curves for σ/σ_0 are shown in Figs. 7 and 8. Equation (23) gives $G_f(P = 1 \text{ bar}, T = 488^\circ\text{K})$ and $G_f(P = 6 \text{ kbars}, T = 527^\circ\text{K})$ as 0.91 eV and 0.99 eV, respectively, when the values of $(\varphi + 1)/(\varphi - 1)$ obtained from Equation (24) are used.

$G_f(P = 1 \text{ bar}, T = 527^\circ\text{K})$ is obtained by using the value of the enthalpy of formation $H_f = 1.43 \text{ ev}$ found by Ebert and Teltow.¹⁷ The corrected value of G_f is 0.89 ev . ΔV_f was found from $(\partial G_f / \partial P)_T$ to be $0.65 V_M$. This value is slightly larger than Kurnick's² value of $0.55 V_M$ for ΔV_f for AgBr.

By using a method similar to the method used to find H_{Im} , ΔV_{Im} is found to be $0.129 V_M$. This value is again somewhat larger than the value of ΔV_{Im} found by Kurnick² for AgBr. The different values found for the parameters in this experiment are shown in Table III where they are compared with the values found by other authors on similar substances.

CONCLUSION AND SUMMARY

The ionic conductivity of a sample of AgCl is measured between 300°K and 680°K at five pressures up to 8 kbars. The divalent impurity concentration is found to be 5×10^{-5} . These impurities go into the cation sublattice substitutionally. The vacancies generated by these impurities decrease the conductivity in the intrinsic range and increase it in the extrinsic range.

The ratio of the mobilities, ϕ , at 1 atm (~ 1 bar) and at $T = 488^\circ\text{K}$ is found to be 8, while ϕ at 6 kbars and at $T = 527^\circ\text{K}$ is found to be 10. G_f at 1 bar and at $T = 488^\circ\text{K}$ is found to be 0.91 ev and G_f at 6 kbars and at $T = 527^\circ\text{K}$ to be 0.99 ev. At the low concentrations of impurities of specimens employed in this work the conductivity of AgCl is predicted well by Equations (8) and (9).

In all cases the enthalpy of the process under consideration increases as the pressure increases. By finding $(\partial \ln \sigma / \partial P)_T$, one finds that the activation volumes for dissociation of complexes, motion of vacancies, Frenkel defect formation, and interstitialcy motion are 0.98 cm^3 , 4.7 cm^3 , 16.7 cm^3 , and 3.25 cm^3 per mole, respectively.

The present work suggests several topics which would be of significance for investigation in the future. The extension of the measurement to the melting point is needed to examine the ionic conductivity of AgCl in the high temperature portion of region III. The study of the conductivity of AgCl containing a controlled amount of known impurities would allow one to find the Gibbs free energy of association for the different types of divalent impurities. Further, this study would allow one to find the effect of impurity concentration on the mobility of silver vacancies and the effect of impurity concentration on the enthalpies of motion for the silver vacancy. It would be of considerable significance to compare the pressure dependence of the diffusion rates in silver halides obtained by the radioactive tracer method and those by the ionic conductivity measurement with the help of the Einstein relation. This could best be done using the method of Friauf¹¹ at different pressures. Such a study is being initiated currently for AgCl as an extension of the present investigation.

TABLE I

Slope of $\ln \sigma$ versus $1/T$ for 1 bar and 6 kbars

Temperature region °K	Slope	
	1 bar	6 kbar
300	^{eV} 0.4	^{eV} 0.410
383	0.32	0.328
600	0.89	0.91

TABLE II

Relative pressure derivatives of $\ln \sigma$
at four different temperatures

Temperature °K	$(\frac{\partial \ln \sigma}{\partial P})_T / V_M$
300	0.201
417	0.182
555	0.475
606	0.465

TABLE III

Parameters found in this work and other works on similar substances

Parameter	Present Work AgCl	Kurnick AgBr	Ebert and Teltow AgCl
ΔV_f	16.7 cm ³	16.0 cm ³	
ΔV_{VM}	4.7 cm ³	7.4 cm ³	
ΔV_{IM}	3.25 cm ³	2.6 cm ³	
ΔV_a	0.98 cm ³		
H_f		1.2 eV	1.43 eV
H_{VM}	0.32 eV	0.36 eV	0.334 eV
H_{IM}	0.151 eV	0.148 eV	0.148 eV
H_a	0.16 eV		0.18 eV
$G_f(1 \text{ bar}, T = 488^\circ\text{K})$	0.91 eV		
$G_f(6 \text{ kbar}, T = 527^\circ\text{K})$	0.99 eV		
$\phi(1 \text{ bar}, T = 488^\circ\text{K})$	8	≈ 8	≈ 8
$\phi(6 \text{ kbar}, T = 527^\circ\text{K})$	10	≈ 8	

Figure 1. Sample holder assembly for the measurement of ionic conductivity of ionic crystals at high pressure.

1— Teflon	4— Stainless Steel
2— Thermocoupling	5— Sample
3— Copper	6— Spring

Figure 2. Epoxy cone for the electrical lead-in. The left-hand hole (5) shows the geometry of the hole as machined.

The right-hand assembly is the epoxy lead-in as completed.

- 1— Copper Wire
- 2— Epoxy
- 3— Apparatus Plug
- 4— Alumina Insulator
- 5— $1/16$ " Hole Countersunk
16° To About .165 Dia.

Figure 3. Block diagram of the liquid pressure system.

Figure 4. Plots of $\ln \sigma$ versus $1/T^{\circ}\text{K} \times 10^3$ for 1 bar, 2, 4, 6 and 8 kbars.

Figure 5. Typical $\ln \sigma$ versus $1/T^{\circ}\text{K} \times 10^3$ curve showing the three temperature regions.

Figure 6. Plot of $\ln \sigma$ versus pressure for four different temperatures. Scaling factor x for $\ln \sigma$ is indicated by x .

(Solid circles: $T = 417^\circ\text{K}$, $x = 5$; solid triangles: $T = 555^\circ\text{K}$, $x = 3$; solid squares: $T = 606^\circ\text{K}$, $x = 2$; crosses: $T = 300^\circ\text{K}$, $x = 6$.)

Figure 7. Plot of σ/σ_0 versus $1/T^{\circ}\text{K} \times 10^3$ for a pressure of one bar.

Figure 8. Plot of σ/σ_0 versus $1/T^{\circ}\text{K} \times 10^3$ for a pressure of 6 kbars.

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APPENDIX A

Sample Preparation

The samples are cut from an ingot with a sharp razor blade. The samples are then etched in hypo solution. The flat surfaces of the samples are then squared with silicon carbide paper (Grit No. 320A). Then the samples are again etched in hypo solution. The flat surfaces are next polished with microcut paper (Grit No. 600) on a lap. Then the samples are again etched. After this the samples are polished with high purity alumina abrasive (0.3 micron) on microcloth, etched, and then polished with high purity alumina abrasive (0.05 micron) on microcloth. They are then etched, washed with trichlorethylene and washed with distilled water. After this preparation the samples are placed in a platinum boat and annealed in a vacuum of 10^{-5} mm at 430°C for five hours. After annealing the samples are cooled very slowly to room temperature.

The samples are then etched in hypo, washed in trichlorethylene, and washed in distilled water. Dag 154 paint is then applied to the sample faces. Annealing and all the operations thereafter are carried out either in the dark or under safety light. The following proportions are

employed for the hypo etch:

Hypo Etch

Sodium Thiosulphate	100 gm
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Distilled Water	375 cm ³
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APPENDIX B

Electrical System

To connect a General Radio 1615A bridge and a General Radio 1432 P decade resistor to the sample so that the sample resistance can be measured directly the following method is used:

1. Connect the low side of the decade box to the low side of the 3 TERM UNKNOWN.
2. Connect the high side of the decade box to the high side of the UNKNOWN.
3. Connect one side of the sample electrode to the EXT STANDARD high and the other to the EXT STANDARD low.
4. Set MULTIPLY switch at non-zero value.
5. Set D MAX switch to 0.01 or 0.1.
6. Set all D knife switches to zero.
7. Set method switch (located directly below 3 TERM connections) to 3 Term.
8. Balance Bridge using decade box and capacitance knife switches.

Resistance of sample is the decade box reading times M times the Multiply switch.

Electrical System