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The Determination of the Chemical Diffusion Coefficients for AgBr and α-AgI by Means of an Improved d.c. Polarization Cell

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In order to determine the chemical diffusion coefficients for AgBr and α-AgI, a new experimental technique was developed. A Pt probe was inserted into the middle of the AgX (X=Br or I) pellet in an improved d.c. polarization cell of the Ag/AgX/carbon type, and the applied potential difference between the Ag and carbon electrodes was changed abruptly. The accompanying change in $E(L/2)$, the EMF between the Ag electrode and the Pt probe, was followed, and the chemical diffusion coefficient, $\tilde{D}$, was determined by the analysis of the change in $E(L/2)$ with the time. In the temperature range from 325 to 400 °C, $\tilde{D}$ for AgBr with excess silver was found to be

$$\tilde{D} = 7.10 \times 10^{2} \exp\left(-\frac{1.96\times10^{4}\ \mathrm{cal\ mol^{-1}}}{RT}\right)\mathrm{cm^{2}\ s^{-1}}. \quad \text{(i)}$$

In the temperature range of 330 to 500 °C, $\tilde{D}$ for α-AgI was

$$\tilde{D} = 4.95 \times 10^{-1} \exp\left(-\frac{7.71\times10^{3}\ \mathrm{cal\ mol^{-1}}}{RT}\right)\mathrm{cm^{2}\ s^{-1}}. \quad \text{(ii)}$$

Using these chemical diffusion coefficients and the electronic conductivity data, the nonstoichiometry, and apparent mobility of electronic carriers of AgBr and α-AgI were determined.

Generally, the chemical diffusion coefficient for a solid compound is obtained from the measurement of the responding weight change or electrical conductivity change, both of which changes are caused by the sudden change in the chemical potential of its components. Gravimetric measurements are useful when the solid compound has a large nonstoichiometry, while the measurement of the electrical conductivity is effective when the conductivity of the sample is quite sensitive to the chemical potential of its components.

However, in the case of the silver halides, the nonstoichiometry is too small to be detected by the gravimetric method, and the electrical conductivity, which is essentially ionic, is constant, irrespective of the chemical potential of silver. Therefore, the chemical diffusion coefficients for silver halides cannot be determined by means of conventional techniques, and new techniques must be developed.

Weiss has carried out some pioneering work on the determination of the chemical diffusion coefficient for AgBr.[1,2] He employed a Hebb-Wagner d.c. polarization cell of the type:

(I) Ag/AgBr/carbon, inert atmosphere

and tried to determine the chemical diffusion coefficient by two methods. In the first method, a constant potential was applied to the cell until a stationary state was reached. Then, the potential was removed abruptly and the EMF decay was followed. From the decay constant, the chemical diffusion coefficient was then determined. In the second method, the current decay was followed after the step-like change in the potential difference applied between the electrodes. However, a large discrepancy was found between the results of these two measurements.

Recently, the present authors have investigated the cell of the (I) type. They have found that the electrical potential of the electrode attached to the surface of AgX pellet is quite sensitive to the activity of the halogen, X, in the atmosphere in contact with the AgX surface and does not show the activity of the X in the AgX.[3] Also, the ionic current due to the electrolysis of AgX was found not to be blocked completely in the cell of the (I) type, because the carbon electrode is exposed to an inert atmosphere and the halogen partial pressure around the electrode is considerably lower than that at the AgX/carbon interface.[4] These findings suggest problems with Weiss' experiments. In Weiss' first method, the carbon electrode was exposed to an inert atmosphere, so the EMF decay might have reflected the decomposition of AgBr at the AgBr/carbon interface. In his second method, an appreciable ionic current due to the decomposition of AgBr might have flowed in the cell.

The purpose of the present study is to present a new polarization technique, one which is free from the problems encountered in Weiss' experiments, and to report the results of measurements, made using a new technique, of the chemical diffusion coefficients for AgBr and α-AgI.

Theoretical

Distribution Profiles of Nonstoichiometry in a d.c. Polarization Cell. A schematic drawing of the d.c. polarization cell employed in the present study is shown in Fig. 1. It is constructed of an AgX pellet with the length, L, sandwiched between an Ag electrode and a so-called 'ion-blocking' electrode.[4] When an inactive electrode is inserted into AgX as a probe at a certain distance, x, from the Ag/AgX interface, and when a potential difference, $E(L)$, is then applied between the Ag electrode and the ion-blocking electrode, an electrical potential difference, $E(x)$, is observed between the Ag electrode and the probe. Denoting the electrochemical potential of electrons in AgX by η_e, we can express $E(x)$ by

$$E(x)F = -\{\eta_e(x)-\eta_e(0)\} \quad (1)$$

where $\eta_e(x)$ denotes η_e at the x position, $\eta_e(0)$ represents η_e at the Ag/AgX interface, and F denotes the Faraday constant. Expressing the chemical potential of silver in AgX by μ_{Ag}, and the electrochemical potential of silver ions in AgX by η_{Ag^+}, we obtain

$$\eta_e(x) = \mu_{Ag}(x) - \eta_{Ag^+}(x). \tag{2}$$

From Eqs. 1 and 2,

$$\begin{aligned} E(x)F &= -\{\mu_{Ag}(x)-\mu_{Ag}(0)\} + \{\eta_{Ag^+}(x)-\eta_{Ag^+}(0)\} \\ &= E'(x)F + E''(x)F, \end{aligned} \tag{3}$$

where

$$E'(x)F = -\{\mu_{Ag}(x) - \mu_{Ag}(0)\}, \tag{4}$$

and

$$E''(x)F = \eta_{Ag^+}(x) - \eta_{Ag^+}(0). \tag{5}$$

When the ionic current in the cell is completely blocked, η_{Ag^+} in the cell is constant throughout the AgX pellet. Thus,

$$E'' = 0. \tag{5$'$}$$

From Eqs. 3, 4, and 5′,

$$E(x)F = -\{\mu_{Ag}(x)-\mu_{Ag}(0)\}. \tag{6}$$

When the chemical potential of silver in AgBr is close to that of metallic silver, AgBr is known to show the n-type electronic conduction. In this case, the electronic conductivity, σ_e,[4] is expressed by

$$\sigma_e = \sigma_e{}^\circ \exp\{(\mu_{Ag}-\mu_{Ag}{}^\circ)/RT\}, \tag{7}$$

where $\mu_{Ag}{}^\circ$ and $\sigma_e{}^\circ$ are the μ_{Ag} and σ_e of AgBr in equilibrium with metallic silver, and where R is the gas constant, and T, the temperature. The n-type electronic conduction is caused by the conduction electrons released from the excess silver atoms. When we represent the nonstoichiometry of AgBr by δ, the metal-excess silver bromide is expressed by the chemical formula $Ag_{1+\delta}Br$ and the concentration of the conduction electrons and the conductivity, σ_e, of AgBr are both proportional to δ. Therefore,

$$\delta = \delta^\circ \exp\{(\mu_{Ag}-\mu_{Ag}{}^\circ)/RT\}, \tag{8}$$

where δ° is δ in AgBr in equilibrium with metallic silver. From Eqs. 6 and 8,

$$\delta(x) = \delta^\circ \exp\left\{-\frac{E(x)F}{RT}\right\}, \tag{9}$$

where $\delta(x)$ is δ at a ceretain distance, x, from the Ag/AgX interface. As α-AgI shows the p-type electronic conduction due to electron holes, the electronic conductivity, σ_h, can be expressed as[4]

$$\sigma_h = \sigma_h{}^\circ \exp\{(\mu_{Ag}{}^\circ-\mu_{Ag})/RT\}, \tag{10}$$

where $\sigma_h{}^\circ$ is the σ_h of AgI in equilibrium with metallic silver. The p-type conduction indicates that α-AgI is a metal-dificient compound with the chemical formula of $Ag_{1-\delta}I$. The hole concentration and electronic conductivity of α-AgI are proportional to δ. Thus,

$$\delta = \delta^\circ \exp\{(\mu_{Ag}{}^\circ-\mu_{Ag})/RT\}. \tag{11}$$

From Eqs. 6 and 11,

$$\delta = \delta^\circ \exp\left\{\frac{E(x)F}{RT}\right\}. \tag{12}$$

In a previous paper[3] the present authors have shown that, under ion-blocking conditions, $E(x)$ in the n-type region of AgBr shows a steady-state distribution

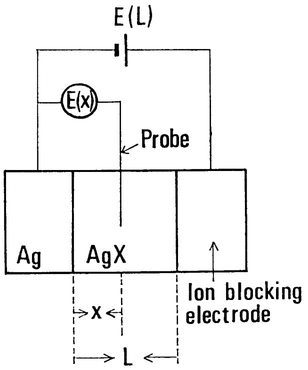


Fig. 1. Schematic diagram of experimental method.

$$\frac{x}{L} = \frac{1-\exp\left\{-\dfrac{E(x)F}{RT}\right\}}{1-\exp\left\{-\dfrac{E(L)F}{RT}\right\}}. \tag{13}$$

Similarly, for AgI with the p-type conduction,

$$\frac{x}{L} = \frac{\exp\left\{\dfrac{E(x)F}{RT}\right\}-1}{\exp\left\{\dfrac{E(L)F}{RT}\right\}-1}. \tag{14}$$

The combination of Eqs. 9 and 13 yields

$$\frac{x}{L} = \frac{\delta(x)-\delta^\circ}{\delta(L)-\delta^\circ}. \tag{15}$$

The combination of Eqs. 12 and 14 also results in the same equation. Equation 15 shows that when a steady state is reached under the ion-blocking conditions, the nonstoichiometry of AgBr and α-AgI is linearly distributed in the d.c. polarization cell.

Determination of the Chemical Diffusion Coefficient for AgBr and α-AgI. When a constant potential difference, $E_1(L)$, is applied between the electrodes of the cell in Fig. 1 for a time sufficient to attain the steady-state, and is then changed to $E_2(L)$ abruptly, the distribution of δ in AgX gradually changes with the time from one steady state to another steady state. This process is controlled by the chemical diffusion in AgX. If the molar amount of X in a unit volume of AgX is expressed by C, the amount of silver excess or silver deficit in a unit volume will be given by $C\delta$. Therefore, the diffusion equation is

$$\frac{\partial(C\delta)}{\partial t} = \tilde{D}\frac{\partial^2(C\delta)}{\partial x^2}, \tag{16}$$

where $\tilde{D}$ denotes the chemical diffusion coefficient, and t, the time. Because C is constant, Eq. 16 can be rewritten as

$$\frac{\partial\delta}{\partial t} = \tilde{D}\frac{\partial^2\delta}{\partial x^2}. \tag{17}$$

In the case of AgBr, the boundary conditions are

$$\frac{\delta(x,\,0)-\delta^\circ}{\delta(L,\,0)-\delta^\circ} = \frac{x}{L} \qquad \text{for } t=0 \tag{18}$$

$$\delta(L) = \delta^\circ \exp\left\{-\frac{E_1(L)F}{RT}\right\} \qquad \text{for } t<0 \tag{19}$$

$$\delta(L,\,t\geq 0) = \delta^\circ \exp\left\{-\frac{E_2(L)F}{RT}\right\} \qquad \text{for } t\geq 0 \tag{20}$$

$$\delta(0,\ t) = \delta^{\circ} \qquad \text{for } x=0. \tag{21}$$

Solving Eq. 17 under the condition of Eqs. 18—21, we obtain

$$\frac{\delta(L/2, t)-\delta(L/2, 0)}{\delta(L/2, \infty)-\delta(L/2, 0)} = \frac{4}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{2n-1}\exp\left\{-\frac{\tilde{D}\pi^2(2n-1)^2t}{L^2}\right\}, \tag{22}$$

where n is the integer. The same solution as Eq. 22 is obtained in the case of α-AgI. When t becomes large, the $n>2$ terms in the series of Eq. 22 become negligibly small. It follows that

$$\frac{\delta(L/2, \infty)-\delta(L/2, t)}{\delta(L/2, \infty)-\delta(L/2, 0)} = \frac{4}{\pi}\exp\left(-\frac{\tilde{D}\pi^2t}{L^2}\right). \tag{23}$$

The change in $\delta(L/2)$ with the time can be calculated from $E(L/2)$ by using Eqs. 9 and 13. From the slopes of the plots of $\log[\{\delta(L/2, \infty)-\delta(L/2, t)\}/\{\delta(L/2, \infty)-\delta(L/2,0)\}]$ *versus* t, we can determine the chemical diffusion coefficient, $\tilde{D}$.

Chemical Diffusion Coefficient and Electronic Conductivity. According to Wagner's theory of metal oxidation,[5] the diffusion through the oxide layer is generally interpreted as consisting of migration processes of ions and electrons, and, in the case of diffusion-controlled oxidation, the chemical diffusion coefficient, $\tilde{D}$, is given by

$$\tilde{D} = \frac{V_m}{Z_1F^2}\,\frac{(\sigma_1+\sigma_2)\sigma_3}{\sigma_1+\sigma_2+\sigma_3}\,\frac{\partial\mu_M}{\partial\delta}, \tag{24}$$

where σ_1, σ_2, and σ_3 are the conductivities of cations, anions, and electrons respectively, and where Z_1 is the number of the charge of the cations, μ_M is the chemical potential of metal, and V_M is the molar volume.

The same diffusion situation as in the metal oxidation is set up in the present experiment, except for the initial several seconds, where the transient current flows to charge or discharge the cell. For AgBr with the n-type conduction, the diffusion of Ag^+ ions and electrons contributes most to the chemical diffusion. Therefore,

$$\tilde{D} = \frac{\sigma_{Ag^+}\sigma_e V_m}{(\sigma_{Ag^+}+\sigma_e)F^2}\,\frac{\partial\mu_{Ag}}{\partial\delta}. \tag{25}$$

Since σ_{Ag^+} is much larger than σ_e, Eq. 25 becomes

$$\tilde{D} = \frac{\sigma_e V_m}{F^2}RT\frac{1}{\delta}. \tag{26}$$

Here Eq. 8 is used. Equation 26 indicates that the nonstoichiometry can be determined by chemical diffusion measurements and electronic conductivity measurements.

Similarly, the diffusion of Ag^+ ions and positive holes occurs during the chemical-relaxation process in α-AgI.

From Eq. 24,

$$\tilde{D} = \frac{\sigma_{Ag^+}\sigma_h V_m}{(\sigma_{Ag^+}+\sigma_h)F^2}\,\frac{\partial\mu_{Ag}}{\partial\delta}. \tag{27}$$

Since $\sigma_{Ag^+}\gg\sigma_h$, using Eq. 10 we obtain

$$\tilde{D} = \frac{\sigma_h V_m}{F^2}RT\frac{1}{\delta}. \tag{28}$$

Experimental

Cells and Samples. Figure 2 shows the cell structure and the block-diagram of the circuit used for the measurement. The samples were prepared in the way described elsewhere.[3] The cell construction was essentially the same as that of the improved d.c. polarization cell,[4] except that in the present work the platinum probe was placed in the middle of the AgX pellet. A hole, 0.8 mm in diameter, was drilled along the axis of the silver electrode to the middle of the AgX pellet. In this hole, a platinum wire 0.2 mm in diameter, protected by an alumina tube (0.8 mm in outer diameter and 0.4 mm in inner diameter), was buried as a probe so that only the tip of the wire was in contact with the AgX pellet.

Measurement Procedure. The cell was set in an electrical furnace, the temperature of which was controlled within ±1 °C. Then a constant potential difference, $E_1(L)$, was created between the silver and carbon electrodes by means of a potentiostat. The potential difference, $E(L/2)$, between the silver electrode and the platinum probe was recorded by means of high-input-impedance voltage follower and a recorder. After $E(L/2)$ had reached a steady value, $E_1(L)$ was changed abruptly to $E_2(L)$ by means of a function generator and the time change of $E(L/2)$ was recorded. In several runs, the time change in the current passing through the cell was also recorded. The chemical diffusion coefficient was determined by the analysis of the recorded curve of $E(L/2)$ *versus* the time.

The measurement for AgBr was performed in the temperature range from 325 to 400 °C, with $E(L)$ values of from 10 to 200 mV. Under these conditions, AgBr showed the n-type electronic conduction. The measurements for α-AgI were performed in the temperature range from 330 to 500 °C, with $E(L)$ values of from 300 to 550 mV.

Results and Discussions

Several examples of the time change of $E(L/2)$ for AgBr (L=6.0 mm) are shown in Figs. 3(a) and 3(b).

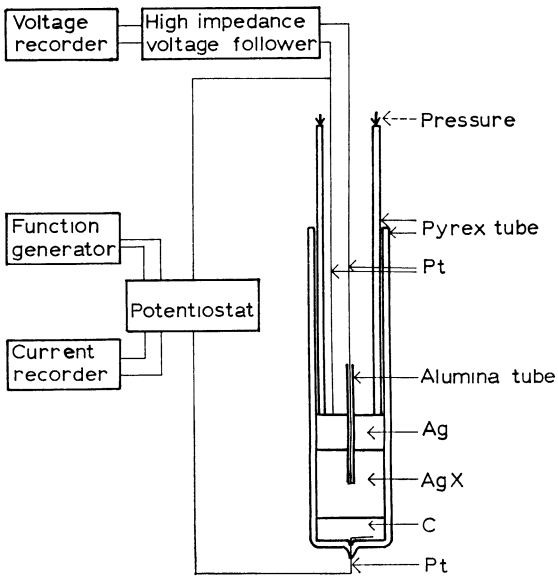


Fig. 2. Construction of cell and block-diagram of circuit.

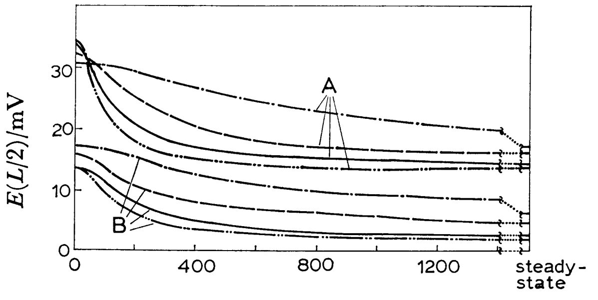


Fig. 3(a). Time change of $E(L/2)$ for AgBr, $L=6.0$ mm. —·—·—; 325 °C, — — —; 350 °C, ——; 375 °C, —··—··—; 400 °C.
Curves A; Results for the step of $E(L)$ from 200 mV to 40 mV. Curves B; Results for the step of $E(L)$ from 40 mV to 10 mV.

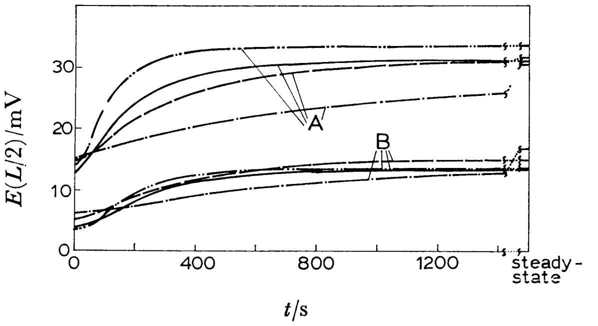
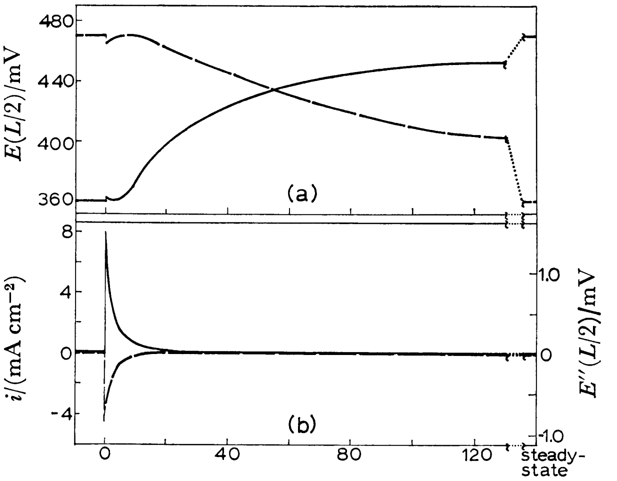


Fig. 3(b). Time change of $E(L/2)$ for AgBr, $L=6.0$ mm. —·—·—; 325 °C, — — —; 350 °C, ——; 375 °C, —··—··—; 400 °C.
Curves A; Results for the step of $E(L)$ from 40 mV to 200 mV. Curves B; Results for the step of $E(L)$ from 10 mV to 40 mV.



Figs. 4(a), 4(b). Time change of $E(L/2)$, i, and $E''(L/2)$ for α-AgI at 330 °C, $L=7.0$ mm.
——; Step of $E(L)$ from 400 mV to 500 mV.
— — —; Step of $E(L)$ from 500 mV to 400 mV.

The time changes of $E(L/2)$ and the current for AgI ($L=7.0$ mm) at 330 °C are shown in Figs. 4(a) and 4(b).

Table 1. Comparison of calculated and observed values of $E(L/2)$ in a steady state (AgBr)

Temp °C	$E(L)$ mV	$E(L/2)$/mV Calcd	$E(L/2)$/mV Obsd $L=4.7$ mm	$E(L/2)$/mV Obsd $L=6.0$ mm
325	10	4.8	7.2	6.4
	40	16.2	17.4	16.0
	200	34.6	33.5	31.0
400	10	4.8	6.5	3.3
	40	16.6	17.8	14.0
	200	38.4	40.7	34.3

Table 2. Comparison of calculated and observed values of $E(L/2)$ in a steady state (α-AgI)

Temp °C	$E(L)$ mV	$E(L/2)$/mV Calcd	$E(L/2)$/mV Obsd $L=7.0$ mm	$E(L/2)$/mV Obsd $L=10.0$ mm
330	375	339	345	—
	400	364	364	375
	430	394	—	405
	500	464	470	—
	530	494	—	504
500	300	254	256	—
	400	354	363	345
	500	454	452	450

In Tables 1 and 2, the observed steady-state values are compared with those calculated by using Eqs. 13 and 14. Both agree within the limits of experimental error; this error can be attributed to the inaccuracy in the positioning of the platinum probe, because the platinum wire itself has a diameter of 0.2 mm and a slight plastic deformation of pellets prior to the experiments may also result in a small displacement of the probe.

As is shown in Fig. 4(b), the cell exhibits a transient current for several seconds after the sudden change of $E(L)$. It appears to be an ionic one which flows to charge or discharge the improved d.c. polarization cell.[4] The ionic current, i_{ion}, can be expressed by

$$i_{\text{ion}} = \frac{\sigma_{\text{Ag}^+}}{F}\frac{\partial \eta_{\text{Ag}^+}}{\partial x} = \sigma_{\text{Ag}^+}\frac{E''(x)}{x} = \sigma_{\text{Ag}^+}\frac{E''(L/2)}{L/2}. \tag{29}$$

Using the values of σ_{Ag^+} given by Biermann and Jost,[6] we can calculate the $E''(L/2)$ values, which are shown by the subscale in Fig. 4(b). Obviously $E''(L/2)$ decays to 0 ± 1 mV within 2 s after the sudden change in $E(L)$. When $E''(L/2)$ actually vanishes,

$$E(L/2)F = -\{\mu_{\text{Ag}}(L/2)-\mu_{\text{Ag}}(0)\}. \tag{30}$$

In the case of AgBr, Eq. 30 is found to hold within 0.5 s after the sudden change in $E(L)$.

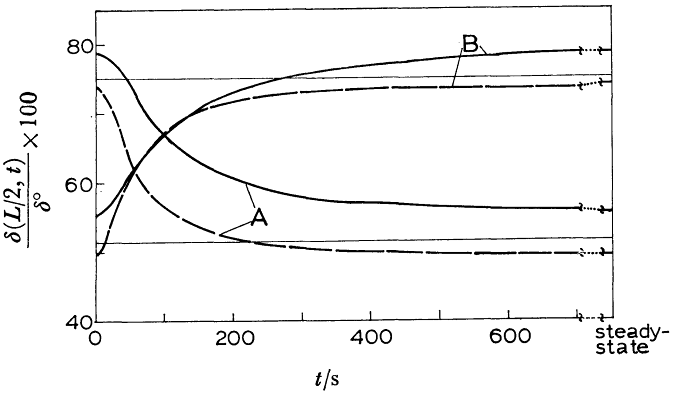


Fig. 5. Plots of $\delta(L/2,t)/\delta^\circ$ *versus* t for AgBr at 400 °C. ——; L=6.0 mm. — — —; L=4.7 mm.
Curves A; Step of $E(L)$ from 40 mV to 200 mV.
Curves B; Step of $E(L)$ from 200 mV to 40 mV.

Figure 5 shows some typical examples of the plot of $\delta(L/2)$ *versus* t. The plots of $\log[\{\delta(L/2,\infty)-\delta(L/2,t)\}/\{\delta(L/2,\infty)-\delta(L/2,0)\}]$ *versus* t are shown in Fig. 6. Clearly, the plots in Fig. 6 fall on a straight line. Thus, the chemical diffusion coefficient, $\tilde{D}$, is calculated from the slope of the plots. Figure 7 shows the $\tilde{D}$ values obtained in the present work. The $\tilde{D}$ values show a good linearity in the figure. $\tilde{D}$ for AgBr can be expressed by this equation

$$\tilde{D} = 7.10 \times 10^2 \exp\left(-\frac{1.96\times10^4 \text{ cal mol}^{-1}}{RT}\right) \text{cm}^2 \text{ s}^{-1}, \quad (31)$$

and $\tilde{D}$ for α-AgI can be given by

$$\tilde{D} = 4.95 \times 10^{-1} \exp\left(-\frac{7.71\times10^3 \text{ cal mol}^{-1}}{RT}\right) \text{cm}^2 \text{ s}^{-1}. \quad (32)$$

Using Eq. 26, the nonstoichiometry of AgBr in equilibrium with metallic silver can be calculated from the $\sigma_e{}^\circ$ obtained by Ilschner.[7] The plot A in Fig. 8 shows δ° of AgBr. From the intercept of the plot at the ordinate and the slope of the plot, the molar entropy, $\Delta\overline{S}$, and the molar enthalpy, $\Delta\overline{H}$, of the dissolution of silver can be calculated. The results are $\Delta\overline{S}$= 2.87eu and $\Delta\overline{H}$=−21.4 kcal mol^{-1} respectively. Since the dissolution of silver into AgBr consists of the transfer of atoms between two solid phases, the entropy change is close to zero.

In a previous paper,[4] the present authors have determined $\sigma_h{}^*$, the hole conductivity of α-AgI in equilibrium with 1 atm of iodine gas. We can calculate δ^*, the nonstoichiometry of α-AgI in equilibrium with 1 atm of iodine gas, by using Eq. 28 and $\sigma_h{}^*$. The calculated results are shown as the B plot in Fig. 8. The entropy and enthalpy of the dissolution of iodine into α-AgI in equilibrium with 1 atm of iodine gas are $\Delta\overline{S}$=−21.8 eu and $\Delta\overline{H}$=1.51 kcal mol^{-1} respectively. As iodine atoms are transferred from the gas phase to the solid phase, $\Delta\overline{S}$ takes a large negative value.

The apparent mobility of electrons in AgBr, m_e, and that of holes in α-AgI, m_h, are calculated by means of the following equations:

$$\sigma_e{}^\circ = \left(\frac{N\delta^\circ}{V_m}\right) m_e e, \quad (33)$$

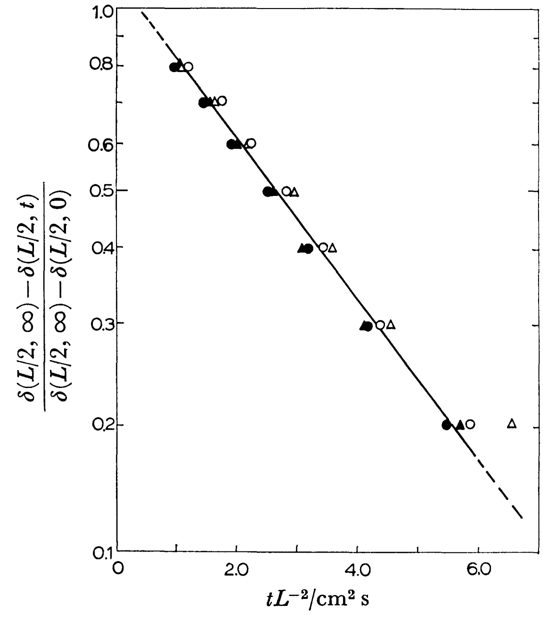


Fig. 6. Plots of $\{\delta(L/2,\infty)-\delta(L/2,t)\}/\{\delta(L/2,\infty)-\delta(L/2,0)\}$ *vs.* tL^{-2} for AgBr at 400 °C.
○; L=6.0 mm, step of $E(L)$ from 200 mV to 40 mV.
△; L=6.0 mm, step of $E(L)$ from 40 mV to 200 mV.
●; L=4.7 mm, step of $E(L)$ from 200 mV to 40 mV.
▲; L=4.7 mm, step of $E(L)$ from 40 mV to 200 mV.

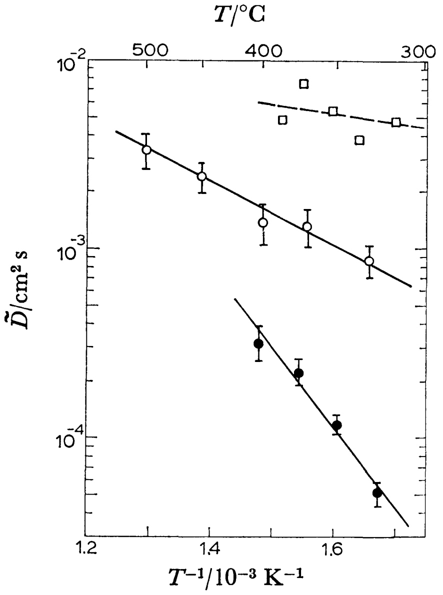


Fig. 7. Arrhenius plot of $\tilde{D}$. ○; α-AgI. ●; AgBr by this work. □; AgBr by Weiss.[1]

$$\sigma_h{}^* = \left(\frac{N\delta^*}{V_m}\right) m_h e, \quad (34)$$

where N denotes Avogadro's constant and where e denotes the charge of an electron. At 400 °C, m_e= 5.5×10^{-3} cm^2 V^{-1} s^{-1} for AgBr and m_h=2.5×10^{-2} cm^2 V^{-1} s^{-1} for α-AgI.

In Fig. 7, the $\tilde{D}$ values obtained by Weiss in his first work[1] are also plotted. His results showed larger $\tilde{D}$ values than those obtained in the present work, and the Arrehnius plot was not linear. When the applied potential difference is removed in Weiss'

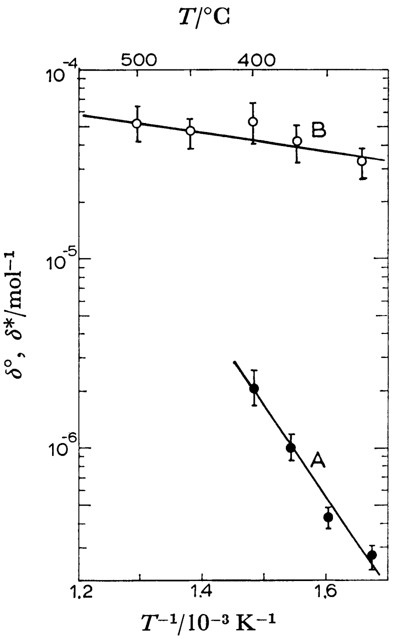


Fig. 8. Plots of $\delta°$ and δ^* *vs.* T^{-1}. A; $\delta°$ of AgBr. B; δ^* of α-AgI.

cell, the activity of the silver at the AgBr/carbon interface rises as a result of the diffusion of silver atoms toward the interface from the interior of AgBr, and also as a result of bromine gas be being released and silver atoms leaving at the interface due to the decomposition. This decomposition causes a faster decay of EMF, whcih results in the apparent $\tilde{D}$ values being larger than the real values. Because the decomposition rate is often controlled by the flow rate of the inert gas around the carbon electrode, the reproducibility may not be good. Figure 7 suggests the high probability that the measurements in Weiss' first work were disturbted by the decomposition of AgBr.

The $\tilde{D}$ values in Weiss' second work[2)] were ten times or more larger than those in his first work. We can see in Fig. 4(b) that the decay in the current occurs much faster than the chemical relaxation of the sample. This fact can explain why Weiss' second work resulted in such extraordinarily large $\tilde{D}$ values.

Weiss' first method can be useful when the chemical relaxation due to the chemical diffusion in the sample occurs faster than the relaxation by other effects, while the second method can be applied to a sample in which the transient ionic current is small enough. However, it seems AgBr was not a sample suitable for either of these measuring methods.

Summary

1) A new technique for the detemination of the chemical diffusion coefficients in ionic crystals was devised and applied to AgBr and α-AgI. The chemical diffusion coefficient for AgBr was found to be much smaller than that reported by a previous investigator.
2) Using the chemical diffusion coefficient and electronic conductivity of AgX, the nonstoichiometry, electron and hole mobilities, and entropy and enthalpy of the dissolution of elements into AgX were calculated.

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