Interaction of Silver Molybdate and Mercuric Bromoiodide in Solid State

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The kinetics and the mechanism of the solid-state reaction between silver molybdate and mercuric bromoiodide were studied. Ag_2MoO_4 and $HgBrI$ react in an equimolar ratio at room temperature to give Ag_2HgI_4, $AgBr$, AgI, and $HgMoO_4$ whereas AgI, $AgBr$, and $HgMoO_4$ are the end products when the same mixture is heated at 100°C for 24 hr. The mechanism of the reaction has been established by X-ray diffraction analyses and thermal and electrical conductivity measurements. The kinetics have been studied by visual technique. The rate of product thickness follows the parabolic rate law, $x^2 = kt$, x being the thickness of product layer at time t and k the parabolic rate constant. This is multiple solid-state ionic reaction, controlled by diffusion of $HgBrI$ molecules and not by counter diffusion of cations. The diffusion coefficient of $HgBrI$ for vapor phase and surface migration were determined. © 1988 Academic Press, Inc.

Introduction

In a previous communication (*1*) we described the kinetics and the mechanism of diffusion controlled solid-state reaction between silver molybdate and mercuric iodide. The mercurate ion, HgI_4^{2-}, that appears as an intermediate plays the key role in this reaction. The present work was undertaken to investigate the interaction of silver molybdate with mercury(II) bromoiodide with a view toward checking the formation of HgI_4^{2-} ion and studying its role in this complex solid-state reaction and to provide information on the variation of electrical conductivity of solid electrolytes during the course of interaction.

This paper shows that Ag_2MoO_4 and HgBrI, at room temperature, react in an equimolar ratio to give Ag_2HgI_4, AgBr, AgI, and $HgMoO_4$ whereas the same mixture

maintained at 100°C for 24 hr yields AgBr, AgI, and $HgMoO_4$ as the final products with the intermediate appearance of Ag_2HgI_4. The reaction is diffusion controlled and proceeds predominantly via gaseous phase with a little contribution of surface migration.

Experimental

Ag_2MoO_4 was prepared by Ricci and Linke's (*2*) method by mixing hot aqueous solutions of $AgNO_3$ (Merck) and Na_2MoO_4 (Baker) in the dark as detailed earlier (*1*). Its X-ray diffractogram showed (*3*) it to be octahedral crystal of Ag_2MoO_4. HgBrI was prepared by Oppenheim's (*4*) method. Equimolar solutions of $HgBr_2$ (Merck) and HgI_2 (Merck) were mixed in acetone. On standing yellow crystals of HgBrI were ob-

Temperature ($°C \pm 0.5$)	k (cm/hr)	Mean deviation	n
60	2.29×10^{-5}	1.2×10^{-4}	
70	3.46×10^{-5}	1.14×10^{-4}	
80	5.49×10^{-5}	9.4×10^{-5}	
90	9.54×10^{-5}	5.3×10^{-5}	2
103	2.08×10^{-4}	5.9×10^{-5}	
120	4.78×10^{-4}	3.2×10^{-5}	

tained as determined by X-ray pattern and melting point measurements.

The kinetics of this reaction were studied using the visual technique described previously (1). HgBrI was placed over Ag_2MoO_4 in a glass capillary of uniform bore. The reaction capillary was kept in an air thermostat maintained to $\pm 0.5°C$. The progress of the reaction was followed by measuring the total thickness of the product layers formed at the interface by a calibrated traveling microscope. Each experiment was run in triplicate and the agreement between the corresponding values of different sets was quite satisfactory. The average values were used for calculating the rate constants given in Table I.

The diffraction patterns of powdered Ag_2 MoO_4 and HgBrI mixed in different molar ratio at 100°C and room temperature were recorded by Norelco geiger counter X-ray diffractometer (PW 1010 Philips) using $CuK\alpha$ radiation with a Ni filter applying 32 kV at 12 mA. Compounds present in different mixtures were identified by calculating their d values and comparing them with the standard values of expected compounds. Compounds identified in different mixtures are given in Table II.

Electrical conductivity measurements were made on compressed polycrystalline samples using a Teflon conductivity cell as described earlier (1). Powdered Ag_2MoO_4 and HgBrI were mixed thoroughly in an agate mortar in different molar ratios. Each mixture was poured into a die and pressed into the form of a disk of about 0.2 cm thick and 0.31 cm^2 in surface area and held between platinum electrodes. The conductivity measurements were made at 100°C using a conductivity bridge (Cambridge Instruments, England) at 50 cycles per second at 100°C. The electrical conductivity of the individual components involved in the reac-

TABLE II

COMPOUNDS IDENTIFIED IN Ag_2MoO_4–HgBrI MIXTURE

Molar ratios of Ag_2MoO_4 and HgBrI in different mixtures	Compounds identified in different mixtures	
	Kept at room temperature for 15 days	Heated at 100°C for 24 hr and then cooled to room temperature
2:1	AgBr, AgI, Ag_2HgI_4, HgMoO$_4$, and Ag_2MoO_4	AgBr, AgI, HgMoO$_4$, and Ag_2MoO_4
1:1	AgBr, AgI, Ag_2HgI_4, and HgMoO$_4$	AgBr, AgI, and HgMoO$_4$
1:2	AgBr, AgI, Ag_2HgI_4, HgMoO$_4$, and HgBrI	AgBr, AgI, HgMoO$_4$, and HgBrI
1:3	AgBr, AgI, Ag_2HgI_4, HgMoO$_4$, and HgBrI	AgBr, AgI, HgMoO$_4$, and HgBrI

TABLE III

ELECTRICAL CONDUCTIVITY[a]
OF DIFFERENT COMPOUNDS
AT 100°C

Compounds	Conductivity (ohm^{-1} cm^{-1})
Ag$_2$MoO$_4$	8.7×10^{-6}
HgBrI	8.5×10^{-7}
HgMoO$_4$	4.5×10^{-6}
AgBr	9.2×10^{-6}
AgI	9.5×10^{-6}
Ag$_2$HgI$_4$	4.3×10^{-4}

[a] Conductivity of materials pressed in the form of disk of 0.2 cm thick and 0.31 cm^2 surface area was measured at 100°C.

tion was also measured for comparison and reported in Table III.

Thermal changes during the reaction were studied by mixing powdered Ag$_2$MoO$_4$ and HgBrI in a double-walled flask kept in a calorimeter. The rise in temperature was noted by a Beckman thermometer reading up to 0.01°C.

Diffusion coefficients of HgBrI in air and for surface migration have been determined as described by Rastogi and Dubey (5). Glass tubes of known diameter were filled with known amounts of HgBrI such that the distance of HgBrI surface from the open end of the tube was the same in each case. Tubes were kept in air thermostat maintained at 150 ± 0.5°C and the amount of HgBrI diffusing away was measured by weighing each tube at fixed time intervals. Vapor pressure of HgBrI was measured using a manometer.

Results and Discussion

For a complete understanding of the process, the points which must be considered are (i) the mechanism of chemical interaction and (ii) the mechanism of lateral diffusion when reactants were kept in contact and when they were separated by an air gap.

Mechanism of Chemical Interaction

The X-ray diffraction analysis (Table II) of an equimolar mixture of Ag$_2$MoO$_4$ and HgBrI heated at 100°C for 24 hr and then cooled to room temperature showed the presence of AgBr, AgI, and HgMoO$_4$. The reaction seems to follow a simple exchange mechanism:

$$Ag_2MoO_4 + HgBrI \rightarrow$$
$$AgBr + AgI + HgMoO_4. \quad (1)$$
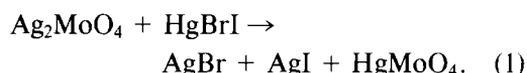
However, as shown in Table II, Ag$_2$HgI$_4$ was formed in addition to AgBr, AgI, and HgMoO$_4$ when the same mixture was kept at room temperature.

Electrical conductivity measurements (Fig. 1) made with disks prepared from a 1:1 molar mixture of Ag$_2$MoO$_4$ and HgBrI show a slow and then sharp rise followed by a fall. The steep rise in electrical conductivity and the X-ray analysis of the mixture kept at room temperature clearly indicates that the reaction represented by Eq. (1) passes through some intermediate steps where Ag$_2$HgI$_4$ is formed. This intermediate is completely consumed at higher temperature but only partly at room temperature. That the reaction at 100°C also passes through Ag$_2$HgI$_4$ is indicated by the following observations: The mixture kept at 100°C first turned red and thereafter, yellow. The red product on rapid cooling turned yellow (Ag$_2$HgI$_4$ is red above 50.7°C and yellow below it) (6) then again turned red on heating. This suggests that the reaction at higher temperature also may be proceeding through Ag$_2$HgI$_4$. Furthermore, as AgI is known to react (7) with HgBrI giving Ag$_2$HgI$_4$ and AgBr, it is presumed that the reaction proceeds through the following course:

$$3Ag_2MoO_4 + 3HgBrI \rightarrow$$
$$3AgBr + 3AgI + 3HgMoO_4 \quad (1a)$$
$$3AgI + HgBrI \rightarrow$$
$$Ag_2HgI_4 + AgBr \quad (1b)$$
$$Ag_2HgI_4 + Ag_2MoO_4 \rightarrow$$
$$\underline{\hspace{2cm} 4AgI + HgMoO_4 \quad (1c)}$$
$$4Ag_2MoO_4 + 4HgBrI \rightarrow$$
$$4AgBr + 4AgI + 4HgMoO_4.$$
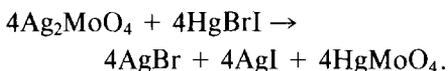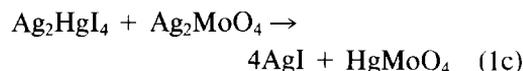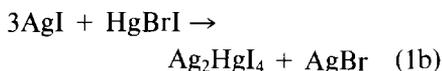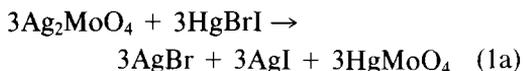
The small initial rise in electrical conductivity is due to the formation of AgBr and AgI through Reaction (1a), which are slightly more conducting than the reactants (Table III). The sharp rise thereafter and transitory appearance of red color seems to be due to the formation of the highly electrically conducting species Ag_2HgI_4 (8) through Reaction (1b) and its fall thereafter and attainment of permanent yellow color seems to be due to the disappearance of Ag_2HgI_4 through its reaction with remaining Ag_2MoO_4 (Reaction (1c)). Ag_2HgI_4 and Ag_2

MoO_4 react (1) rapidly when mixed in an equimolar ratio at high temperature, to give AgI and $HgMoO_4$ as products. At room temperature, however, Reaction (1c) does not seem to proceed to any significant extent, thereby showing the presence of Ag_2HgI_4 in addition to AgBr, AgI, and $HgMoO_4$.

The initial rise in temperature shown by thermal maxima (Fig. 2) which occurs about 25 min after mixing the reactants in an equimolar ratio at room temperature is due to the surface reaction which is fast. The fall in temperature thereafter is due to the fact that dissipation of heat dominates the evolution.

Results of X-ray diffraction analyses (Table II), electrical conductivity, and thermal measurements (Figs. 1 and 2) with 1:2, 1:3, and 2:1 molar ratio mixtures of Ag_2MoO_4 and HgBrI, suggest that the reaction in these cases follow the same mechanism as explained for equimolar ratio mixture both at room temperature and at 100°C.
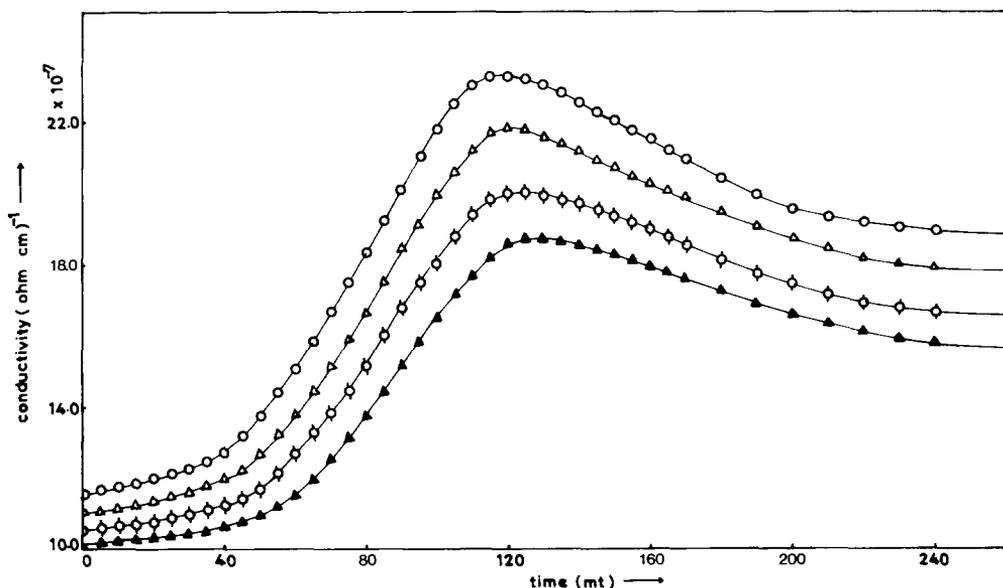
FIG. 1. Change in conductivity with time for the reaction between Ag_2MoO_4 and HgBrI at 100°C. Molar ratios are (○) 2:1, (△) 1:1, (◇) 1:2, and (▲) 1:3.
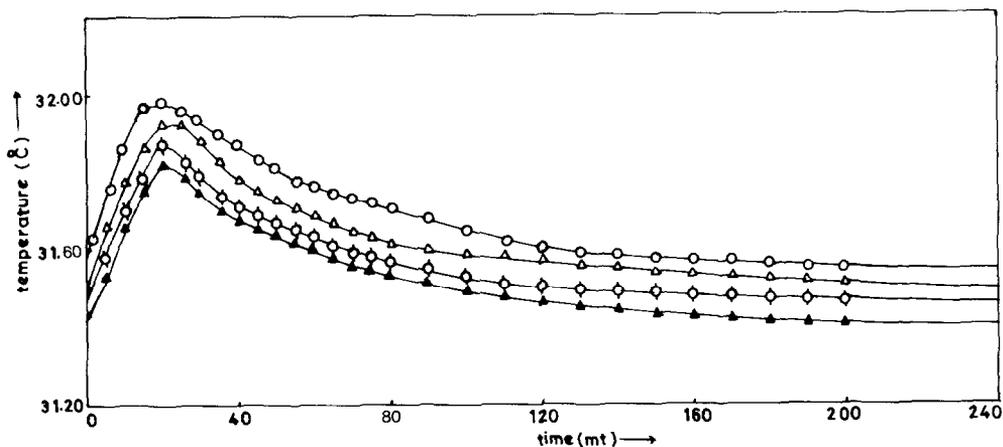
FIG. 2. Temperature rise as a function of time for the reaction between Ag$_2$MoO$_4$ and HgBrI. Molar ratios are (O) 2 : 1, (△) 1 : 1, (◇) 1 : 2, and (▲) 1 : 3.

Mechanism of Lateral Diffusion

Soon after placing HgBrI over Ag$_2$MoO$_4$ in the reaction capillary, a yellow layer developed at the interface which progressed toward the Ag$_2$MoO$_4$ side. This yellow layer later separated into yellow and red layers. A gap developed between the red layer and HgBrI. When the experiment was repeated, keeping an air gap between the reactants from the beginning, it proceeded likewise to form similar layers on the Ag$_2$
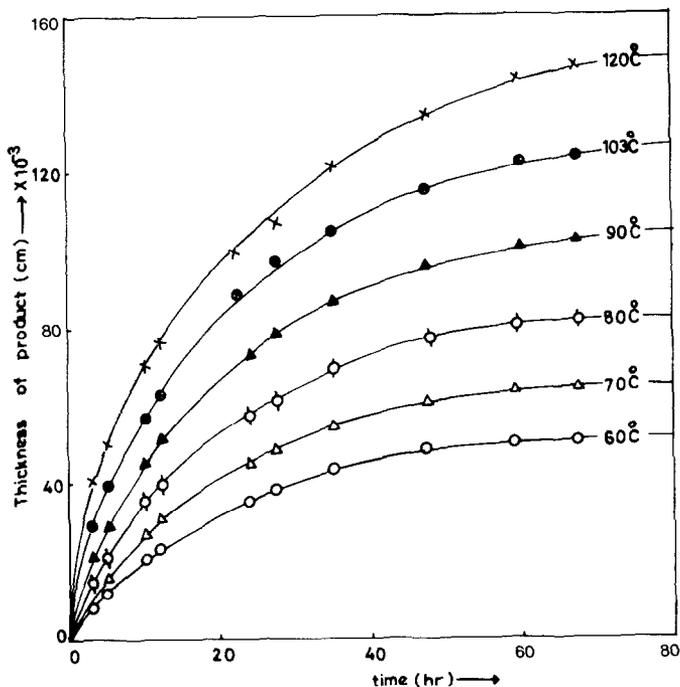
FIG. 3. Kinetic data for the reaction between Ag$_2$MoO$_4$ and HgBrI at various temperatures.
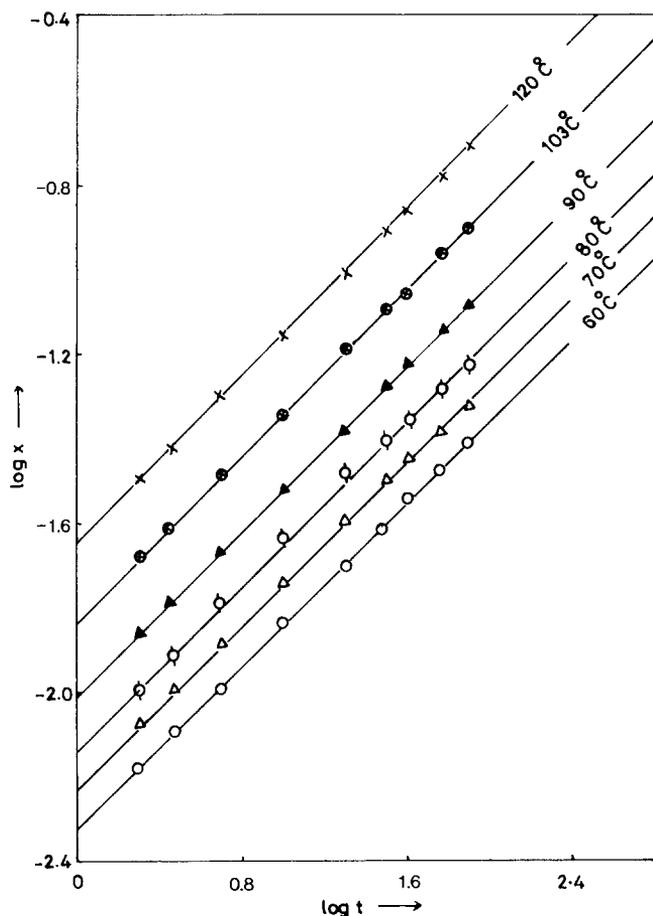
FIG. 4. Kinetic data for lateral diffusion and test of equation $x^n = kt$ for the reaction between Ag_2Mo O_4 and $HgBrI$.

MoO$_4$ surface. This clearly demonstrates that HgBrI is the mobile species. Gaseous HgBrI molecules react with Ag_2MoO_4 to yield $HgMoO_4$, AgBr, and AgI. AgI in turn reacts with the incoming HgBrI to form Ag_2 HgI_4. Some of the AgI, which was formed in the later stages, escaped conversion into Ag_2HgI_4 and was detected along with AgBr in the yellow layer. The X-ray and chemical analyses of the colored layers showed the following sequence of products in the reaction capillary:

$$Ag_2MoO_4 \mid HgMoO_4, AgBr,$$
$$AgI \mid Ag_2HgI_4 \mid HgBrI.$$
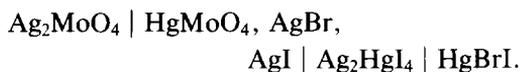
The rate of growth of product layer decreased with time as shown in Fig. 3. Initially the process is fast and reaction controlled. With the formation of product layers between the two reactants, the reagents take more and more time to diffuse through the barrier; the process becomes diffusion controlled and the rate thus falls continuously with the growth of product layers. The lateral diffusion data are best fit (Fig. 4) by the parabolic rate equation,

$$x^2 = kt, \qquad (2)$$

where x is the thickness of product layers at time t, and k, the parabolic rate constant,
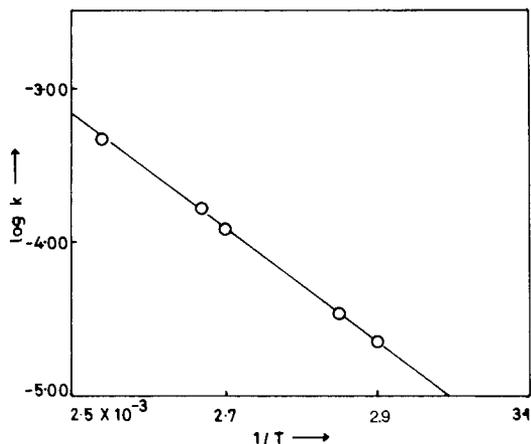
FIG. 5. Dependence of k on temperature for the reaction between Ag_2MoO_4 and $HgBrI$ in solid state.
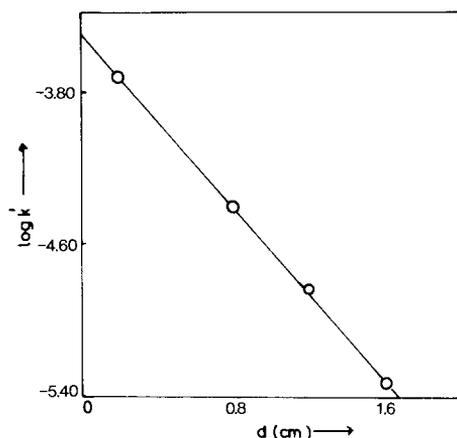
FIG. 6. Dependence of reaction rate on the length of air gap for the reaction between Ag_2MoO_4 and $HgBrI$.

follows the Arrhenius equation,

$$k = A_e^{-E_a/RT}. \qquad (3)$$

The activation energy evaluated from the log k versus inverse temperature plot (Fig. 5) was found to be 72.18 kJ/mole.

The rate constants measured with an initial air gap between the reactants were found to depend on the length of the air gap according to the equation,

$$k' = A_e^{-bd}, \qquad (4)$$

where d is the length of the air gap and A and b are constants. The linearity of plots of log k' versus d (Fig. 6) indicate that as the length of the air gap increased, the reaction rate decreased.

The vapor phase and surface diffusion coefficients of HgBrI were determined experimentally to ascertain their relative contributions in this diffusion-controlled solid-state reaction of Ag_2MoO_4 and HgBrI. The weight loss data best fit the relation

$$\Delta W = K_1 t, \qquad (5)$$

where ΔW is the amount of HgBrI diffused in the air, t the time, and K_1 a constant. The value of K_1 depends on the diameter of the

tube according to

$$K_1/r = \alpha r + \beta. \qquad (6)$$

The test of Eq. (6) has been made by plotting K_1/r against r in Fig. 7, where α and β are parameters (5) given by the equations

$$\alpha = \pi C_e D_v / l \qquad (7)$$

$$\beta = 2\pi C_e D_s, \qquad (8)$$

where r is the radius of the tube, l is the
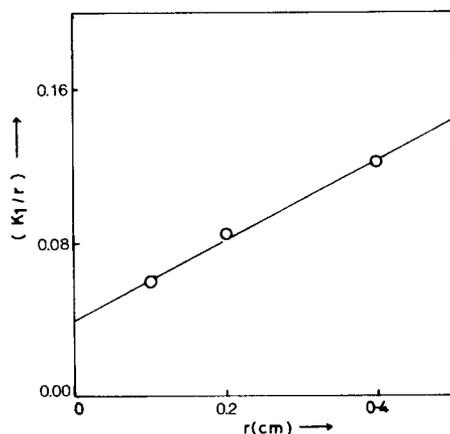
FIG. 7. Estimation of diffusion coefficient of HgBrI in air and on glass surface.

distance of HgBrI surface from open end of the tube, C_e is the equilibrium concentration of HgBrI just above the surface and related to the vapor pressure obeying the perfect gas law, D_v is the vapor phase diffusion coefficient, and D_s is the diffusion coefficient for surface migration. The values of diffusion coefficients were calculated first by evaluating α and β from the plot of K_1/r against r (Fig. 7), then finding out the equilibrium concentration C_e of HgBrI from the vapor pressure of HgBrI which was experimentally found to be an average of the vapor pressures of the individual species $HgBr_2$ and HgI_2. However, since the measured values of vapor pressures of $HgBr_2$ and HgI_2 do not compare well with the reported values (9) we have taken reported values for all our calculations and drawn conclusions from those. The values of diffusion coefficients for vapor phase and surface migration were calculated to be 1.21×10^{-2} and 2.35×10^{-4} cm²/sec, respectively, at 150°C. This suggests that the contribution of surface migration is also significant in the overall vapor-phase-dominated diffusion-controlled reaction of Ag_2MoO_4 and HgBrI in the solid state.

In light of reaction sequence (1a), (1b), and (1c) and Fig. 1, it is evident that in complex solid-state reactions where a solid electrolyte is formed, consumed, or consumed after formation, conductivity measurements can provide considerable insight into the reaction mechanism.

Acknowledgment

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