



KINETICS AND MECHANISM OF SOLID STATE REACTIONS OF SILVER TUNGSTATE WITH MERCURIC BROMIDE AND MERCURIC CHLORIDE

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Abstract—The kinetics and mechanism of the $\text{Ag}_2\text{WO}_4\text{-HgBr}_2$ and $\text{Ag}_2\text{WO}_4\text{-HgCl}_2$ reactions have been studied in the solid state. The kinetics have been carried out by a visual technique. Both the reactions follow the parabolic rate law $X^2 = Kt$, where X is the thickness of product layer at time t and K is the parabolic rate constant. The kinetics have been studied at several temperatures, for different lengths of air-gap between the two reactants and for different particle sizes of the reactants. It has been demonstrated that diffusion in both the reactions is predominantly controlled by the vapour phase, but diffusion by surface migration is also significant. In order to understand the mechanism of the reactions, X-ray powder diffraction, chemical analysis, conductivity and thermal studies have been carried out. Silver tungstate reacts with mercuric bromide and mercuric chloride in the molar ratio 1:1 to give AgBr , HgWO_4 and AgCl , HgWO_4 , respectively, as the end products.

There has been an increasing interest in the study of solid state reactions due to industrial and technological applications. Although much research is being carried out on solid state reactions,¹⁻⁴ there is still a need to study a large number of solid-solid systems in order to have a better and deeper understanding of the precise mechanism in solid state reactions. The interactions of mercury(II) halides with sodium tungstate and silver molybdate in the solid state have been reported by Sharma and Batra⁵ and Beg and Rafiuudin.⁶ The authors have recently reported⁷ the interaction of silver tungstate with mixed halides of mercury(II) in the solid state. In the present work, reactions of silver tungstate with mercuric bromide and mercuric chloride have been studied with a view to understanding the mode

of propagation in the solid state and to characterize the reaction products. The reactions are diffusion controlled and proceed mostly via the vapour phase, but diffusion by surface migration is also significant.

EXPERIMENTAL

Materials and methods

Silver nitrate (E. Merck), sodium tungstate (E. Merck), mercuric bromide (B.D.H.) and mercuric chloride (B.D.H.) were used without further purification. Silver monotungstate, being photo-sensitive, was prepared fresh for each set of experiments, as reported earlier.⁸

Kinetic studies

The kinetics of the reactions between silver tungstate and mercury(II) halides were carried out using

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a visual technique.⁹ The mercury(II) halides were placed over silver tungstate in a Pyrex glass tube of 0.5 cm internal diameter which had one end sealed, and the tube was kept in an air thermostat controlled to $\pm 0.5^\circ\text{C}$. The progress of the reaction was followed by measuring the total thickness of the product layer formed at the interface by a travelling microscope having a calibrated scale in its eyepiece at different intervals. The kinetics were likewise conducted at different temperatures, for different particle sizes of the reactants and for different lengths of air-gap between the reactants. Each experiment was run in triplicate and the average values were used for calculating the rate constants (Tables 1 and 2).

X-ray studies

Different molar mixtures of the reactants were mixed thoroughly in an agate mortar. One part of each mixture was heated in an air thermostat at $150 \pm 0.5^\circ\text{C}$ while the other was kept at room temperature. The mixtures were analysed using a Nor-elco Geiger counter X-ray diffractometer (PW 1010 Phillips) using Cu-K_α radiation and a nickel filter applying 32 kV at 12 mA. The compounds identified

in different reaction mixtures are given in Tables 3 and 4.

Analysis of product layers

Sufficient amounts of product layers of the reactions $\text{Ag}_2\text{WO}_4\text{-HgBr}_2$ (a) and $\text{Ag}_2\text{WO}_4\text{-HgCl}_2$ (b) were collected separately by breaking the reaction tubes. X-ray and chemical analyses of the material showed the presence of AgBr and HgWO_4 (a) and AgCl and HgWO_4 (b).

Thermal measurements

Ag_2WO_4 and mercury(II) halides in different molar ratios were mixed in a Dewar flask calorimeter and the change in temperature was noted with a Beckmann thermometer at different time intervals.

Conductivity measurements

Electrical conductivity measurements were carried out for both the reactions using discs prepared from different molar ratio mixtures of reactants. A disc 0.2 cm in thickness and 0.31 cm^2 in surface area was held between platinum electrodes and the electrical conductivity was measured using a Gen Rad Model 1657 RLC Dibrige (120 Hz).

Table 1. Dependence of parabolic rate constant on temperature for the reaction of Ag_2WO_4 and HgBr_2

Temperature ($\pm 0.5^\circ\text{C}$)	K (cm h^{-1})	Mean deviation
120	1.10×10^{-4}	0.015×10^{-4}
130	1.90×10^{-4}	0.011×10^{-4}
140	2.88×10^{-4}	0.009×10^{-4}
150	4.37×10^{-4}	0.010×10^{-4}
160	6.61×10^{-4}	0.013×10^{-4}
170	9.75×10^{-4}	0.010×10^{-4}

Table 2. Dependence of parabolic rate constant on temperature for the reaction of Ag_2WO_4 and HgCl_2

Temperature ($\pm 0.5^\circ\text{C}$)	K (cm h^{-1})	Mean deviation
145	2.29×10^{-4}	0.010×10^{-4}
154	3.16×10^{-4}	0.014×10^{-4}
161	4.57×10^{-4}	0.019×10^{-4}
169	6.60×10^{-4}	0.011×10^{-4}
179	1.00×10^{-3}	0.012×10^{-3}
188	1.51×10^{-3}	0.010×10^{-3}

Table 3. Compounds present in different molar ratio mixtures of Ag_2WO_4 and HgBr_2

Molar ratios of Ag_2WO_4 and HgBr_2	Compounds present in mixtures heated at 150°C and then cooled to room temperature
1:1	AgBr and HgWO_4
1:2	AgBr, HgWO_4 and HgBr_2
2:1	AgBr, HgWO_4 and Ag_2WO_4
1:3	AgBr, HgWO_4 and HgBr_2

Table 4. Compounds present in different molar ratio mixtures of Ag_2WO_4 and HgCl_2

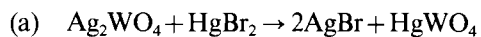
Molar ratios of Ag_2WO_4 and HgCl_2	Compounds present in mixtures heated at 150°C and then cooled to room temperature
1:1	AgCl, HgWO_4
1:2	AgCl, HgWO_4 and HgCl_2
2:1	AgCl, HgWO_4 and AgWO_4
1:3	AgCl, HgWO_4 and HgCl_2

Diffusion coefficient measurements

The diffusion coefficients of HgBr_2 and HgCl_2 have been determined by the method described elsewhere.¹⁰ Four glass tubes of different diameter were filled with known amounts of mercury(II) halides in such a way that the distance of the mercury(II) halides' surface from the open end of the tube was the same in all the tubes. These tubes were then placed in an air thermostat maintained at $150 \pm 0.5^\circ\text{C}$ and the amount of mercury(II) halides diffusing away was noted at different times by weighing.

RESULTS AND DISCUSSION*Mechanism of chemical interaction*

X-ray diffraction analyses (Tables 3 and 4) reveal that Ag_2WO_4 reacts with mercuric bromide and mercuric chloride in 1:1 molar ratio giving AgBr , HgWO_4 and AgCl , HgWO_4 respectively. Both the reactions seem to follow a simple exchange mechanism:



Thermal measurements (Figs 1 and 3) made with different molar ratios of Ag_2WO_4 and mercury(II) halides show one peak, indicating the reactions to be a single step process. The maxima were obtained up to 40 min after mixing the reactants and the continuous fall thereafter seems to be due to the dominance of dissipation of heat over the evolution rate. Electrical conductivity measurements (Figs 2 and 4) made for different molar mixtures of Ag_2WO_4 and mercury(II) halides show a gradual rise in con-

ductivity and constancy thereafter. The increase in the conductivity of different molar mixtures of Ag_2WO_4 and mercury(II) halides may be attributed to the formation of silver halides as final products, which have higher conductivities than that of silver tungstate. Here, polymorphic phase transition¹¹ of Ag_2WO_4 may also contribute to the enhancement of conductivities of the mixtures. All these measurements indicate the reactions to be single step processes. However, it was observed that at 150°C a 1:2 molar mixture of HgBr_2 - AgBr and HgCl_2 - AgCl showed a change in conductivity from 1.0×10^{-6} to 4.4×10^{-6} and from 8.2×10^{-7} to $3.0 \times 10^{-6} \text{ S cm}^{-1}$, whereas no change in conductivity was noted for a 1:1 molar mixture of the reactants in both cases. In analogy with the formation of highly conducting Ag_2Hgl_4 from AgI and HgI_2 , the increase in the conductivity in both the systems may be assumed to be due to the formation of Ag_2HgBr_4 and Ag_2HgCl_4 .¹² If this presumption is true, the reaction of equimolar mixtures of Ag_2WO_4 - HgBr_2 and Ag_2WO_4 - HgCl_2 may be taking place in a similar way as reported elsewhere.⁸

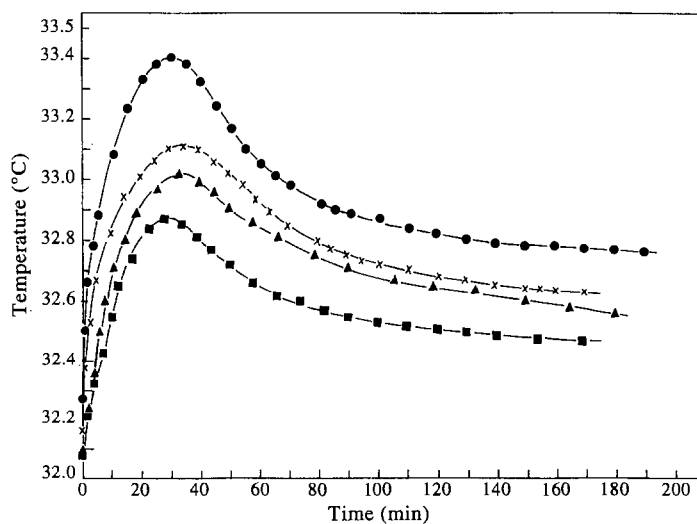
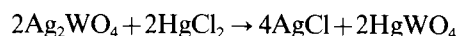
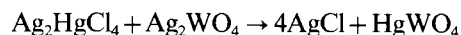
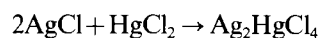
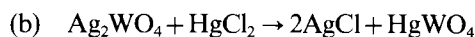
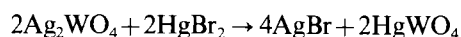
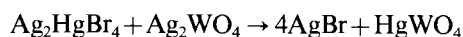
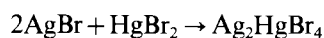
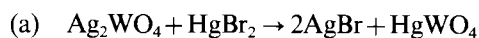


Fig. 1. Temperature rise as a function of time for the reaction between Ag_2WO_4 and HgBr_2 . Molar ratios are: (●) 1:1; (×) 1:2; (▲) 2:1; (■) 1:3.

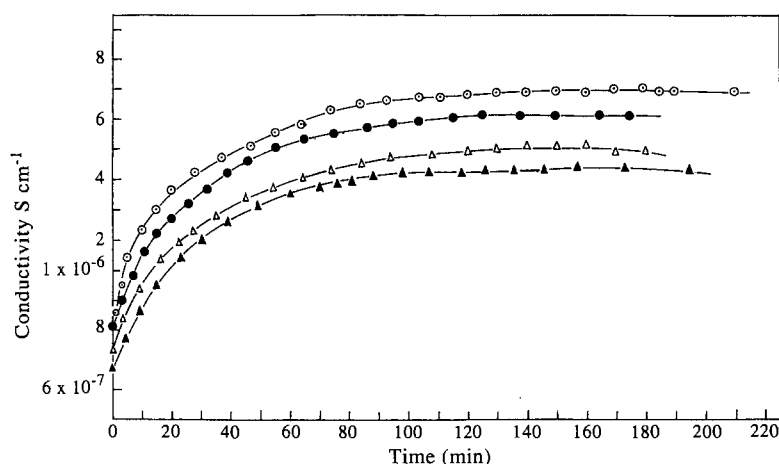


Fig. 2. Variation of electrical conductivity with time for the reaction between Ag_2WO_4 and HgBr_2 at 150°C . Molar ratios are: (\odot) 1:1; (\bullet) 1:2; (\triangle) 2:1; (\blacktriangle) 1:3.

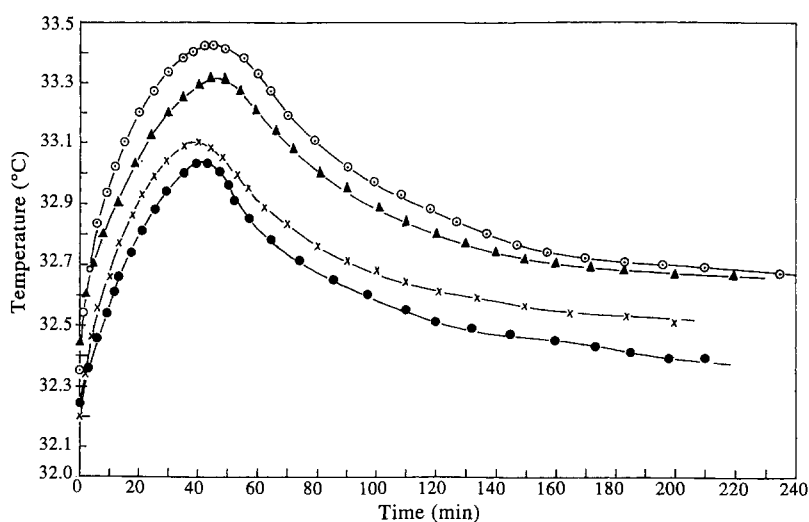


Fig. 3. Temperature rise as a function of time for the reaction between Ag_2WO_4 and HgCl_2 . Molar ratios are: (\odot) 1:1; (\blacktriangle) 1:2; (\times) 2:1; (\bullet) 1:3.

However, the X-ray diffraction patterns taken at room temperature for 1:2 molar mixtures of HgBr_2 – AgBr and HgCl_2 – AgCl did not show the presence of any new lines. On the basis of conductivity measurements, the authors assume the formation of Ag_2HgBr_4 and Ag_2HgCl_4 at the experimental temperature (150°C) as the intermediate products during the course of the reaction, which react with Ag_2WO_4 to give silver halides and HgWO_4 . Unfortunately, analysis could not be done at higher temperatures due to the non-availability of a high temperature facility in the diffractometer. X-ray powder diffraction analyses, electrical conductivity and thermal measurements of other molar mixtures, namely 1:2, 2:1 and 1:3 of Ag_2WO_4 and mercury(II) halides, show that the reaction sequences follow the same pattern as that of the

1:1 molar mixture and the excess of either reactant remained unreacted.

Mechanism of lateral diffusion

In the kinetic experiments of the Ag_2WO_4 – HgBr_2 system, soon after the placement of HgBr_2 over Ag_2WO_4 in the reaction tube, a greenish yellow layer appeared at the interface which proceeded towards the Ag_2WO_4 side with time and later separated into yellow and green layers. A gap also developed between mercuric bromide and the product layers. The analyses of the green and yellow product layers at room temperature identified them to be AgBr and HgWO_4 . In the Ag_2WO_4 – HgCl_2 system, a yellowish-white layer appeared at the interface which increased

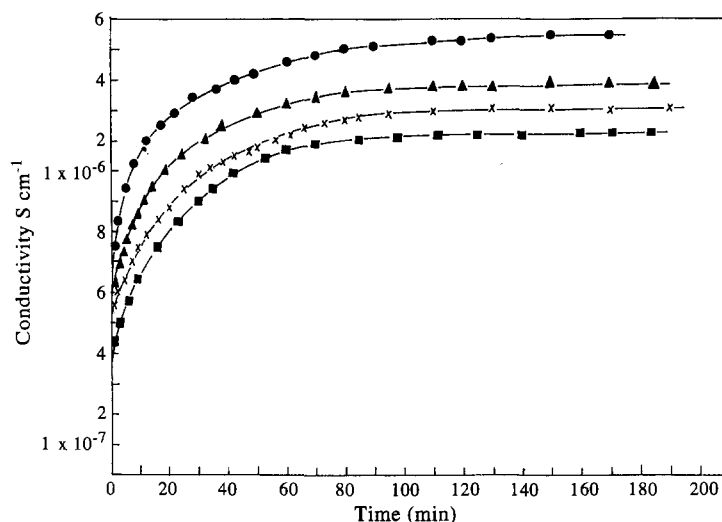


Fig. 4. Variation of electrical conductivity with time for the reaction between Ag_2WO_4 and HgCl_2 at 150°C . Molar ratios are: (●) 1:1; (▲) 1:2; (×) 2:1; (■) 1:3.

on the Ag_2WO_4 side and later separated into white and yellow layers. The analyses revealed them to be AgCl and HgWO_4 .

The kinetic data for lateral diffusion in either case at different temperatures best fit the parabolic rate equation

$$X^2 = Kt, \quad (1)$$

where X is the product thickness at time t and K is a constant. The value of the rate constant in both reactions was found to increase with temperature in accordance with the Arrhenius equation (Tables 1 and 2). The activation energies evaluated from Arrhenius plots (Fig. 5) were 71.5 and 79.3 kJ mol^{-1} respectively.

Our results show that (1) the reactions under study are diffusion controlled, (2) the diffusing species are mercury(II) halides and (3) the diffusion of mercury(II) halides in silver tungstate is controlled by both vapour phase and surface migration. Evidence is now given to substantiate the above conclusions.

The applicability of the parabolic equation for kinetic data clearly indicates that the reaction is diffusion controlled. As the reaction proceeds, the thickness of the product layer increases and the reactants take more time to diffuse through the product layer, leading to a fall in the reaction rate.

In another lateral diffusion experiment, when the reactants were placed in a glass tube with an air-gap between them at the start, the product layers were formed only on the silver tungstate side. This clearly indicates that it is only mercury(II) halides that move towards the silver tungstate side.

The formation of products on the silver tungstate

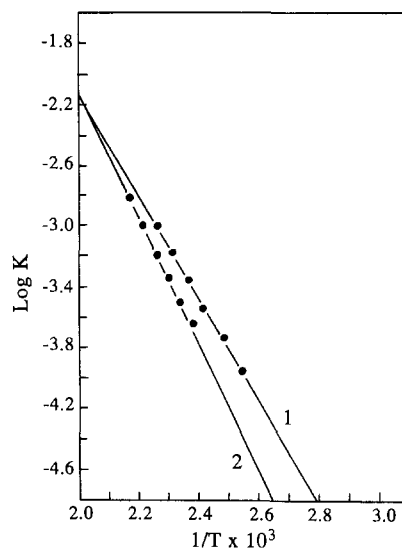


Fig. 5. Dependence of reaction rate on temperature for silver tungstate-mercuric bromide reaction (1) and silver tungstate-mercuric chloride reaction (2).

side when the reactants were kept with an initial air-gap between the high vapour densities of mercuric bromide and mercuric chloride indicates the possibility of vapour phase diffusion. However, in a set of lateral diffusion experiments with an initial air-gap between the reactants, the rate constants were found to depend on the length of air-gap, according to the equation:

$$K' = Ae^{-bd}, \quad (2)$$

where d is the length of air-gap, and A and b are constants. The linearity of the plots of $\log K'$ versus

d (Fig. 6) indicates that as the length of air-gap increased, the reaction rate decreased in both systems. Kinetics were also studied for different particle sizes of the reactants and it was observed that the rate constants for both reactions vary with particle size of the reactants, according to the following equation:

$$K'' = \theta r^2, \quad (3)$$

where θ is a constant and r is the radius of reactant particles. A plot of K'' versus r^2 (Fig. 7) gave a straight line, showing that the reaction rate increases with increase in particle size. These two experiments suggest that the surface migration of these mercury(II) halides also plays some part in

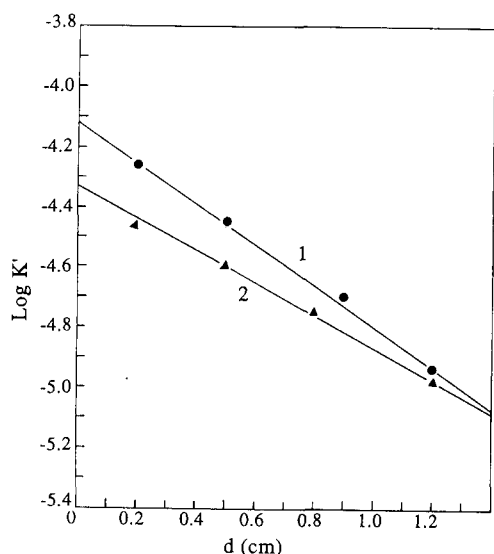


Fig. 6. Dependence of rate constant on the length of air-gap for silver tungstate-mercuric bromide (1) and silver tungstate-mercuric chloride (2) reactions at 150°C.

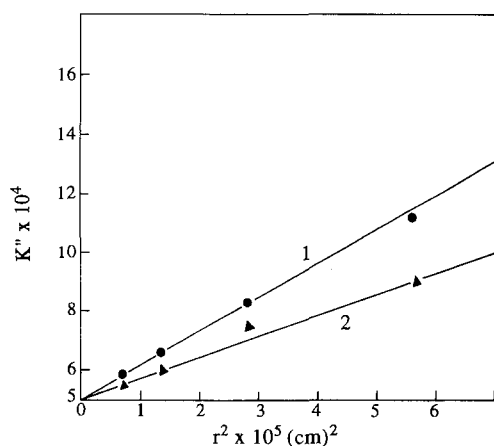


Fig. 7. Dependence of reaction rate on the particle size for silver tungstate-mercuric bromide (1) and silver tungstate-mercuric chloride (2) reactions at 150°C.

the diffusion process. The vapour phase and surface diffusion coefficients of mercuric bromide and mercuric chloride were determined to ascertain their relative contributions in both the diffusion-controlled solid state reactions. The weight loss data best fit (Figs 8 and 9) the empirical equation:

$$\Delta W = K_1 t, \quad (4)$$

where ΔW is the amount of mercuric bromide or mercuric chloride diffused in air, t is the time and K_1 is a constant. The value of K_1 depends on the

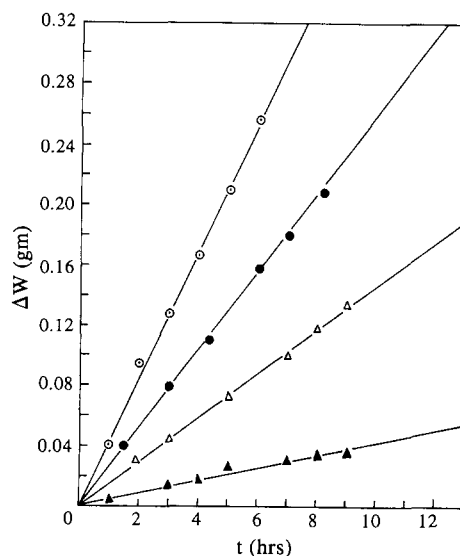


Fig. 8. Kinetic data for the study of diffusion of mercuric bromide. (▲) $r = 0.1$ cm; (△) $r = 0.2$ cm; (●) $r = 0.3$ cm; (⊙) $r = 0.4$ cm.

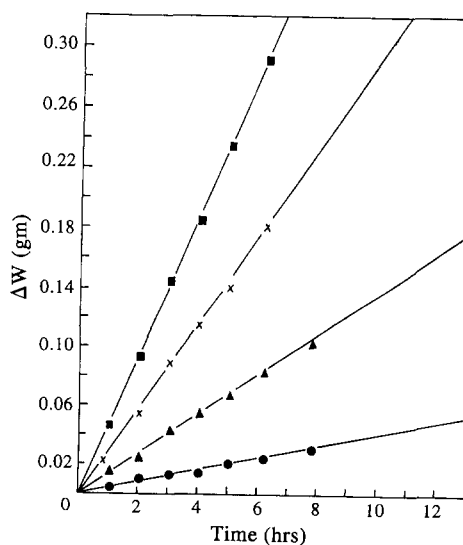


Fig. 9. Kinetic data for the study of diffusion of mercuric chloride. (●) $r = 0.1$ cm; (▲) $r = 0.2$ cm; (×) $r = 0.3$ cm; (■) $r = 0.4$ cm.

diameter of the tube, according to the following equation :

$$K_1/r = \alpha r + \beta, \quad (5)$$

where r is the radius of the tube; α and β are given by $\alpha = \pi C_e D_v / l$ and $\beta = 2\pi C_e D_s$; l is the distance of the mercury(II) halide surface from the open end of the tube; C_e is the equilibrium concentration of mercury(II) halides just above the surface and is related to the vapour pressure obeying the perfect gas law; D_v is the vapour phase diffusion coefficient; and D_s is the diffusion coefficient for surface migration.

A test of eq. (5) has been made by plotting K_1/r against r (Fig. 10). The values of D_s and D_v were calculated by evaluation and from the plot of K_1/r

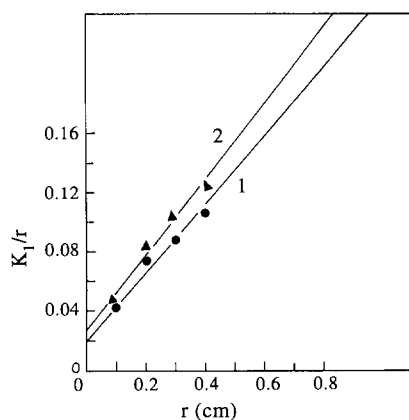


Fig. 10. Estimation of diffusion coefficients of mercuric bromide (1) and mercuric chloride (2) in air and for surface migration.

versus r , and were found to be 7.55×10^{-4} and $2.20 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ for mercuric bromide and 5.57×10^{-4} and $2.1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ for mercuric chloride respectively.

This suggests that the contribution of surface migration is also significant in the overall vapour phase-dominated diffusion-controlled reactions of Ag_2WO_4 and mercury(II) halides in the solid state.

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