SUMMARY

The easy formation of the highly conducting iodo-mercurate of silver from the solid state reaction of silver (I) iodide with mercury (II) iodide is regarded to be due to the proneness of silver ions to occupy interstitial positions rather than to form vacancy pairs. Silver molybdate is electrically conducting and its conductivity is of the same order as that of silver iodide. The growing importance of silver salts from the viewpoint of their microwave conductivity prompted us to study the reactions of silver molybdate with mercuric halides in solid state.

In the present investigation following reactions have been studied in solid state:

(1) Silver molybdate and mercuric iodide,
(2) Silver molybdate and mercuric bromide,
(3) Silver molybdate and mercuric chloride,
(4) Silver molybdate and mercuric bromoiodide, and
(5) Silver molybdate and mercuric chlorobromide.

Mechanism of these reactions were studied in solid state by X-ray diffractometry, chemical analysis, thermal and conductivity measurements. Individual steps involved in each reactions were confirmed separately. The kinetics of these reactions were studied by visual technique.
(1) $\text{Ag}_2\text{MoO}_4 - \text{HgI}_2$ reaction

$\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ react in an equimolar ratio at $100^\circ\text{C}$ giving $\text{AgI}$ and $\text{HgMoO}_4$ as products. The steep rise and fall in conductivity curve and the appearance of transitory red colour during the progress of reaction suggest the intermediate formation of $\text{Ag}_2\text{HgI}_4$ which is highly conducting. This proceeds as given below.

$$\text{Ag}_2\text{MoO}_4 + \text{HgI}_2 \rightarrow 2\text{AgI} + \text{HgMoO}_4 \quad (1a)$$

$$2\text{AgI} + \text{HgI}_2 \rightarrow \text{Ag}_2\text{HgI}_4 \quad (1b)$$

$$\text{Ag}_2\text{HgI}_4 + \text{Ag}_2\text{MoO}_4 \rightarrow 4\text{AgI} + \text{HgMoO}_4 \quad (1c)$$

$$2\text{Ag}_2\text{MoO}_4 + 2\text{HgI}_2 \rightarrow 4\text{AgI} + \text{HgMoO}_4$$

Each step was confirmed separately. Thermal measurement with 1:1 molar mixture of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ at room temperature give one inflection only, thereby suggesting the reaction to be single step. At room temperature reaction (1c) does not proceed to any significant extent, and reaction (1b) is much faster than reaction (1a) even at room temperature.

In higher molar mixtures (1:2, 1:3 etc.) of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ the same mechanism, as explained for equimolar ratio follows. In 1:3 molar mixture, the excess of $\text{HgI}_2$ is left
unreacted, but in 1:2 mixture the excess HgI₂ is removed by the product AgI giving Ag₂HgI₄. Hence no HgI₂ was detected in the final X-ray analysis of 1:2 molar mixture. Compounds identified in different molar ratio mixtures of Ag₂MoO₄ and HgI₂ by X-ray analysis are given in Table I.

Table - I

<table>
<thead>
<tr>
<th>Molar ratios of Ag₂MoO₄ and HgI₂ in different mixtures</th>
<th>Compounds identified in mixtures kept at room temperature for 15 days Maintained at 100°C for 24 hr then cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>AgI, Ag₂HgI₄, HgMoO₄ and Ag₂MoO₄ AgI and HgMoO₄</td>
</tr>
<tr>
<td>1:2</td>
<td>Ag₂HgI₄ and HgMoO₄ Ag₂HgI₄ and HgMoO₄</td>
</tr>
<tr>
<td>1:3</td>
<td>Ag₂HgI₄, HgMoO₄, Ag₂HgI₄, HgMoO₄ and HgI₂ HgI₂</td>
</tr>
</tbody>
</table>

In lateral diffusion experiment, the sequence of product observed is,

\[
\text{Ag}_2\text{MoO}_4 \rightleftharpoons \text{HgMoO}_4 \rightleftharpoons \text{AgI} \rightleftharpoons \text{Ag}_2\text{HgI}_4 \rightleftharpoons \text{HgI}_2
\]

From the observed sequence of product and molecular nature of HgI₂ it is suggested that in lateral diffusion HgI₂
diffuse as such and not through the counter diffusion of cations. The lateral diffusion data fitted the equation,

$$X^n = kt$$

where $X$ is thickness of product at time $t$, and $k$ and $n$ are constants. $k$ is related to diffusion and follow the Arrhenius equation. The activation energy evaluated from log $k$ versus inverse temperature plot was 95.93 kJ/mol. The higher value of $n$ in this reaction, which otherwise should have 2, had the reaction followed the parabolic rate law, rises further with the rise in temperature from 80-135°C, suggest an additional resistance to the reaction rate, like sintering which rises further with rise in temperature. To see the initial difference in reaction rate at two temperature ranges, the activation energy was determined at zero time by plotting zero time growth curve and taking logarithm of that. The activation energy value of 20.90 kJ/mol in lower temperature range and 90.49 kJ/mol in higher temperature range suggest that the process is grain boundary or surface diffusion controlled in lower temperature range while in the higher temperature range the process is bulk diffusion controlled right from the start.

Values of diffusion coefficient of HgI$_2$ in air and for surface migration suggest that reaction mostly proceeds via vapour phase, with a small contribution of surface migration.
Ag₂MoO₄ and HgBr₂ react when mixed in an equimolar ratio both at room temperature and at 100°C, giving AgBr and HgMoO₄ as products. Reaction follows the exchange mechanism.

\[
\text{Ag}_2\text{MoO}_4 + \text{HgBr}_2 \rightarrow 2\text{AgBr} + \text{HgMoO}_4
\]  

The initial white mixture of Ag₂MoO₄ and HgBr₂ changed to yellow gradually at room temperature and sharply at 100°C. Thermal and conductivity measurements also suggest the reaction to be single step. On heating the equimolar mixture of Ag₂MoO₄ and HgBr₂ at 200°C, the transitory appearance of orange colour suggest the formation of Ag₂HgBr₄, which seems stable only at high temperature and breaks into AgBr and HgBr₂ at low temperature.

In high molar ratios, Ag₂MoO₄ and HgBr₂ react in the same way as in the case of 1:1 molar ratio, and excess of either of the reactants left unreacted.

Compounds identified in different molar ratio mixtures of Ag₂MoO₄ and HgBr₂ are given in Table II.

In lateral diffusion experiment, the sequence of product observed is,

\[
\text{Ag}_2\text{MoO}_4 | \text{HgMoO}_4 | \text{AgBr} | \text{HgBr}_2
\]
Table - II

Compounds identified in different molar ratio mixtures of Ag$_2$MoO$_4$ and HgBr$_2$.

<table>
<thead>
<tr>
<th>Molar ratios of Ag$_2$MoO$_4$ and HgBr$_2$ in different mixtures</th>
<th>Compounds identified in mixtures kept at room temperature for 15 days</th>
<th>Maintained at 100°C and cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>AgBr, HgMoO$_4$ and Ag$_2$MoO$_4$</td>
<td>AgBr, HgMoO$_4$ and Ag$_2$MoO$_4$</td>
</tr>
<tr>
<td>1:1</td>
<td>AgBr, HgMoO$_4$, Ag$_2$MoO$_4$ and HgBr$_2$</td>
<td>AgBr and HgMoO$_4$</td>
</tr>
<tr>
<td>1:2</td>
<td>AgBr, HgMoO$_4$, Ag$_2$MoO$_4$ and HgBr$_2$</td>
<td>AgBr, HgMoO$_4$ and HgBr$_2$</td>
</tr>
<tr>
<td>1:3</td>
<td>AgBr, HgMoO$_4$, Ag$_2$MoO$_4$ and HgBr$_2$</td>
<td>AgBr, HgMoO$_4$ and HgBr$_2$</td>
</tr>
</tbody>
</table>

Solid HgBr$_2$ being molecular in nature, diffuse as such in the vapour form giving the observed sequence of products. Lateral diffusion data best fit parabolic rate equation,

\[ \chi^2 = kt \]

The activation energy evaluated from log k versus inverse of temperature plot was 78.16 kJ/mol.
Kinetics were also studied by keeping air gaps of different lengths between the reactants at the start itself. The value of rate constant was found to depend on the length of air gap between the reactants according to equation,

\[ k' = A e^{-bd} \]

where \( d \) is the length of air-gap and \( A \) and \( b \) are constants. The linear plot of \( \log k' \) versus \( d \) indicate that as the length of air gap increases, the reaction rate decreased.

Values of diffusion coefficient of \( \text{HgBr}_2 \) in air and on surface determined experimentally suggest the reaction to proceed via vapour phase with slight contribution of surface migration.

(3) \( \text{Ag}_2\text{MoO}_4 - \text{HgCl}_2 \) reaction

\( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgCl}_2 \) react in 1:1 molar ratio both at room temperature and 100\(^\circ\)C giving \( \text{AgCl} \) and \( \text{HgMoO}_4 \) as products. The initial white mixture changed to yellow. The reaction seems to follow the simple exchange mechanism.

\[ \text{Ag}_2\text{MoO}_4 + \text{HgCl}_2 \rightarrow 2\text{AgCl} + \text{HgMoO}_4 \] (3)

Thermal and conductivity measurements made with 1:1 molar mixture of \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgCl}_2 \) give only one inflection suggesting thereby the reaction to be single step.
In mixtures of other higher molar ratio, $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$ react in the same way as in the case of an equimolar ratio and the reactants in excess is left unreacted. Compounds identified in different molar ratio mixtures of $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$ are given in Table - III.

Table - III

Compounds identified in different molar ratio mixtures of $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$

<table>
<thead>
<tr>
<th>Molar ratios of $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$ in different mixtures</th>
<th>Compounds identified in different mixtures</th>
<th>Kept at room temperature for 15 days</th>
<th>Maintained at 100°C for 24 hr then cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>$\text{AgCl}, \text{HgMoO}_4$, $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{Ag}_2\text{MoO}_4$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{Ag}_2\text{MoO}_4$</td>
</tr>
<tr>
<td>1:1</td>
<td>$\text{AgCl}, \text{HgMoO}_4$, $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}$ and $\text{HgMoO}_4$</td>
<td>$\text{AgCl}$ and $\text{HgMoO}_4$</td>
</tr>
<tr>
<td>1:2</td>
<td>$\text{AgCl}, \text{HgMoO}_4$, $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{HgCl}_2$</td>
</tr>
<tr>
<td>1:3</td>
<td>$\text{AgCl}, \text{HgMoO}_4$, $\text{Ag}_2\text{MoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{HgCl}_2$</td>
<td>$\text{AgCl}, \text{HgMoO}_4$ and $\text{HgCl}_2$</td>
</tr>
</tbody>
</table>

Initially the rate of product growth is fast but the rate falls with the increase in thickness of the product layer suggesting the reaction to be diffusion con-
trolled. Lateral diffusion data best fit the parabolic rate equation,

$$X^2 = kt$$

The activation energy evaluated from log k versus inverse temperature plot was 74.06 kJ/mol. Reaction proceeded well even when the reactants were placed with an air gap between them at the start itself. Kinetics were studied also by keeping air gaps of different lengths between the reactants. Reaction rate decreased with increase in length of air gap.

Values of diffusion coefficient of HgCl₂ in air and for surface migration suggest that solid HgCl₂ react here in gaseous form. Surface migration of HgCl₂ also contribute to the overall vapour phase diffusion controlled reaction of Ag₂MoO₄ and HgCl₂.

(4) Ag₂MoO₄ - HgBrI reaction

On mixing powdered Ag₂MoO₄ and HgBrI in an equimolar ratio, the initial light yellow mixture changed to pale yellow. On heating this mixture to 100°C a red colour appeared which again changed to yellow on cooling below this temperature. Conductivity curve shows a sharp rise and a subsequent fall in conductance of the reaction mixture with time. This reaction is multistep and passes through the intermediate
formation of Ag₂HgI₄ (Ag₂HgI₄ is red above 50.7°C and yellow below it). The reaction probably proceeds through the following course,

\[
3\text{Ag}_2\text{MoO}_4 + 3\text{HgBrI} \rightarrow 3\text{AgBr} + 3\text{AgI} + 3\text{HgMoO}_4 \quad (4a)
\]

\[
3\text{AgI} + \text{HgBrI} \rightarrow \text{Ag}_2\text{HgI}_4 + \text{AgBr} \quad (4b)
\]

\[
\text{Ag}_2\text{HgI}_4 + \text{Ag}_2\text{MoO}_4 \rightarrow 4\text{AgI} + \text{HgMoO}_4 \quad (4c)
\]

\[
4\text{Ag}_2\text{MoO}_4 + 4\text{HgBrI} \rightarrow 4\text{AgBr} + 4\text{AgI} + 4\text{HgMoO}_4
\]

results of X-ray analysis of reaction mixture maintained at room temperature and at 100°C support this mechanism.

X-ray analysis of higher molar ratio mixtures of Ag₂MoO₄ and HgBrI is in conformity with the proposed mechanism. Compounds identified in different molar ratio mixtures are given in Table IV.

**Table - IV**

Compounds identified in different molar ratio mixtures of Ag₂MoO₄ and HgBrI.

<table>
<thead>
<tr>
<th>Molar ratios of Ag₂MoO₄ and HgBrI in different mixtures</th>
<th>Compounds identified in different mixtures kept at room temperature for 15 days</th>
<th>Maintained at 100°C for 24 hr then cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 AgI,AgBr,Ag₂HgI₄, HgMoO₄ and Ag₂MoO₄ AgI,AgBr,Ag₂MoO₄</td>
<td>2:1 AgI,AgBr,Ag₂HgI₄, HgMoO₄ and Ag₂MoO₄ AgI,AgBr,Ag₂MoO₄</td>
<td>2:1 AgI,AgBr,Ag₂HgI₄, HgMoO₄ and Ag₂MoO₄ AgI,AgBr,Ag₂MoO₄</td>
</tr>
<tr>
<td>1:1 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and Ag₂MoO₄ AgI,AgBr and HgMoO₄</td>
<td>1:1 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and Ag₂MoO₄ AgI,AgBr and HgMoO₄</td>
<td>1:1 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and Ag₂MoO₄ AgI,AgBr and HgMoO₄</td>
</tr>
<tr>
<td>1:2 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
<td>1:2 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
<td>1:2 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
</tr>
<tr>
<td>1:3 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
<td>1:3 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
<td>1:3 AgI,AgBr,HgMoO₄, Ag₂HgI₄ and HgBrI AgI,AgBr,HgMoO₄ and HgBrI</td>
</tr>
</tbody>
</table>
The sequence of products observed in reaction tube is:

\[ \text{Ag}_2\text{MoO}_4 \rightarrow \text{HgMoO}_4 \rightarrow \text{AgBr, AgI} \rightarrow \text{Ag}_2\text{HgI}_4 \rightarrow \text{HgBrI} \]

Sequence of products obtained suggest that HgBrI diffuse as such. Lateral diffusion data best fit the parabolic rate equation,

\[ x^2 = kt \]

k is related with diffusion and shows the Arrhenius temperature dependence. Activation energy evaluated from log k versus inverse temperature plot was 72.18 kJ/mol. Kinetics of the reaction were studied also by keeping air gap of different lengths between the reactants. Reaction rate was found to decrease with the increase in length of air gap.

Values of diffusion coefficient of HgBrI in air and for surface migration suggest that solid HgBrI react here in gaseous form and reaction is vapour phase diffusion controlled.

(5) \text{Ag}_2\text{MoO}_4 - \text{HgClBr reaction}

Like HgBrI, HgClBr react with Ag$_2$MoO$_4$ in 1:1 molar ratio to give the same end products (AgCl, AgBr and HgMoO$_4$) both at room temperature and 100°C. The initial white mix-
ture turned to yellow colour. The mechanism of the reaction is given as,

\[ \text{Ag}_2\text{MoO}_4 + \text{HgClBr} \rightarrow \text{AgCl} + \text{AgBr} + \text{HgMoO}_4 \]  

(5)

This is in line with the larger cations going well with the larger anions and smaller cations with smaller anions. Thermal and conductivity measurements also support this view. In other higher molar ratios, reaction follow the same mechanism. Compounds identified in different molar ratio mixtures of Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr are given in Table V.

Table - V

Compounds identified in different molar ratio mixtures of Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr.

<table>
<thead>
<tr>
<th>Molar ratios of Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr in different mixtures</th>
<th>Compounds identified in different mixtures</th>
<th>Mixtures kept at room temperature for 15 days.</th>
<th>Mixtures maintained at 100°C for 24 hr and cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4} and Ag\textsubscript{2}MoO\textsubscript{4}</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4} and Ag\textsubscript{2}MoO\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4}, Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr</td>
<td>AgCl, AgBr and HgMoO\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4}, Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4} and HgClBr</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4}, Ag\textsubscript{2}MoO\textsubscript{4} and HgClBr</td>
<td>AgCl, AgBr, HgMoO\textsubscript{4} and HgClBr</td>
<td></td>
</tr>
</tbody>
</table>
In lateral diffusion the sequence of product observed is as follows:

\[ \text{Ag}_2\text{MoO}_4 \quad \text{HgMoO}_4 \quad \text{AgCl,AgBr} \quad \text{HgClBr} \]

The reaction proceeded smoothly with the formation of product layer on \( \text{Ag}_2\text{MoO}_4 \) side, even when the reactants were placed with an air gap between the reactants at the start itself. This suggest that \( \text{HgClBr} \) moves as such and once inside the reaction zone, reacts with \( \text{Ag}_2\text{MoO}_4 \) to give observed sequence of products in reaction tube. Lateral diffusion data best fit the equation,

\[ x^n = kt \]

The value of \( n \) varies from 2.60 to 2.11 in the temperature range 65-108°C and registers a constant value of 2 in the temperature range 118-140°C. The activation energy evaluated at lower and higher temperature ranges were 180 kJ/mol and 66 kJ/mol respectively. This suggest that in lower temperature range the process is reaction controlled, but as temperature increases a situation is reached where the process becomes diffusion controlled and \( n \) decreased gradually and attained a constant value 2. Kinetics of the reaction were studied also by keeping air gap between the reactants. Reaction rate was found to decrease with increase in length of air gap.
Values of diffusion coefficient of HgClBr in air and for surface migration suggest that the solid HgClBr react mostly in gaseous form.