CHAPTER IV

REACTION OF \( \text{Ag}_2\text{MoO}_4 \) - \( \text{HgI}_2 \)
Easy formation of highly conducting iodomercurates of silver\textsuperscript{1} and copper\textsuperscript{2} in the solid state reactions of silver(I) halides and copper (I) halides with mercury (II) halides, is regarded to be due to proneness of silver ions to occupy interstitial positions rather than form vacancy pairs. AgHgCl\textsubscript{2}I and AgHgCl\textsubscript{2}I\textsubscript{3} are stable only in solid state and decompose when put in water or alcohol, were formed in this laboratory from the solid state state reaction of silver iodide with mercury (II) halides. Silver salts are important from the viewpoint of their microwave conductivity\textsuperscript{4}. Silver molybdate has been found electrically conducting and of the same order as that of silver iodide. This has prompted us to study the reaction of Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} with a view (1) to establish the mechanism of the reaction, (2) to study the effect of temperature on reaction rate. The mechanism of reaction has been explained by X-ray analysis, thermal and conductivity measurements. Kinetics of the reaction has been studied by visual technique. Diffusion coefficient of mercuric iodide has been determined experimentally.

On mixing Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} (powder above 300 mesh) the colour of mixture changed to orange from dark brown. This orange material on heating above 51°C turned red which again became orange on cooling below this temperature.
Rate measurements

Kinetics of the reaction in solid state were studied by placing HgI$_2$ over Ag$_2$MoO$_4$ (powdered above 300 mesh) in a pyrex glass tube of 0.5 cm internal diameter. An approximately 5 cm long tube of uniform bore was chosen and one end of the tube was sealed by fusion and known amount of Ag$_2$MoO$_4$ powder was introduced into the tube through its open end. The tube was vertically held and Ag$_2$MoO$_4$ powder was gently pressed with a glass rod of 0.5 cm diameter. The reaction tube containing Ag$_2$MoO$_4$ and a weighed amount of HgI$_2$ on a tissue paper were kept in an air oven controlled to ± 0.5°C. After 15 minutes HgI$_2$ was placed over Ag$_2$MoO$_4$ surface in the reaction tube. Same glass rod was used to press the HgI$_2$ over Ag$_2$MoO$_4$. As a change in reaction kinetics of powdered solids is likely to occur due to pressure changes, the same quantity of reactants were always used. The progress of reaction was followed by measuring the total thickness of product layer formed at the interface by a travelling microscope having a calibrated scale in its eye piece. Each experiment was run in triplicate and the agreement between the corresponding values of different sets is quite satisfactory. The average values were used for calculating the rate constants given in Table I.
Table - I

Temperature dependence of parameters of equation $x^n = kt$ for $Ag_2MoO_4 - HgI_2$ reaction.

<table>
<thead>
<tr>
<th>Temperature (± 0.5°C)</th>
<th>$k$ (cm/hr)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>$1.285 \times 10^{-6}$</td>
<td>2.30</td>
</tr>
<tr>
<td>92</td>
<td>$4.123 \times 10^{-6}$</td>
<td>2.40</td>
</tr>
<tr>
<td>105</td>
<td>$7.975 \times 10^{-6}$</td>
<td>2.50</td>
</tr>
<tr>
<td>120</td>
<td>$2.078 \times 10^{-5}$</td>
<td>2.70</td>
</tr>
<tr>
<td>128</td>
<td>$3.025 \times 10^{-5}$</td>
<td>2.75</td>
</tr>
<tr>
<td>135</td>
<td>$4.512 \times 10^{-5}$</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Soon after the placement of $HgI_2$ over $Ag_2MoO_4$ in the reaction tube, a yellow colour boundary formed at the interface and this grew with time on $Ag_2MoO_4$ side. After some time a red layer started to develop between yellow layer and $HgI_2$, and simultaneously a gap developed between red layer and $HgI_2$ (Fig. 1). On cooling to room temperature, the red layer turned yellow ($Ag_2HgI_4$ is red above 50.7°C and yellow below it)⁶. The kinetics were likewise studied at different temperatures. When lateral diffusion experiments were run keeping air-gap between the reactants at the start itself,
Fig. 1. Diagramatic representation of the sequence of products formed in lateral diffusion between Ag$_2$MoO$_4$ and HgI$_2$ in solid state.
reaction proceeded likewise giving the similar layers of product on Ag$_2$MoO$_4$ surface.

**Analysis of product layers**

A reaction tube having thick product layer was broken and product collected separately. X-ray diffraction analysis of the yellow layer (red layer, Ag$_2$HgI$_4$, also turned yellow at room temperature) revealed the yellow layer to be a mixture of AgI, HgMoO$_4$, and Ag$_2$HgI$_4$. Chemical analysis of the yellow layer also gave the same products.

**X-ray studies**

Powdered Ag$_2$MoO$_4$ and HgI$_2$ (both above 300 mesh) were mixed in different molar ratios in an agate mortar. One part of each mixture was heated at 100°C for 24 hr and then cooled to room temperature. Mixtures were analyzed by Norelco Geiger counter X-ray diffractometer (PW 1010 Philips) using CuKα radiation with Ni filter applying 32 kv at 12 mA.

The compounds were identified by calculating their d values and corresponding intensities and comparing them with the standard values of expected compounds. Compounds identified in different molar ratio mixtures of Ag$_2$MoO$_4$ and HgI$_2$ are given in Table II. The X-ray diffraction pattern
obtained for different molar mixtures of $\text{Ag}_2\text{MoC}_4$ and $\text{HgI}_2$
are given in Tables III to VII.

Table - II

<table>
<thead>
<tr>
<th>Molar ratios of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ 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 and then cooled to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>$\text{AgI}, \text{Ag}_2\text{HgI}_4$, $\text{Ag}_2\text{MoO}_4$ and $\text{HgMoO}_4$</td>
<td>$\text{AgI, HgMoO}_4$</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>$\text{Ag}_2\text{HgI}_4$, $\text{HgMoO}_4$</td>
<td>$\text{Ag}_2\text{HgI}_4$, $\text{HgMoO}_4$</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>$\text{Ag}_2\text{HgI}_4$, $\text{HgMoO}_4$ and $\text{HgI}_2$</td>
<td>$\text{Ag}_2\text{HgI}_4$, $\text{HgMoO}_4$ and $\text{HgI}_2$</td>
<td></td>
</tr>
</tbody>
</table>
### Table - III

X-ray diffraction data for 1:1 molar mixture of Ag\textsubscript{2}HCO\textsubscript{4} and HgI\textsubscript{2} heated at 100\textdegree C then cooled to room temperature.

<table>
<thead>
<tr>
<th>d in Å (\text{°} )</th>
<th>( I/I_0 )</th>
<th>d in Å (\text{°} )</th>
<th>( I/I_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.288\textsuperscript{++}</td>
<td>28</td>
<td>2.293\textsuperscript{+}</td>
<td>73</td>
</tr>
<tr>
<td>3.240\textsuperscript{++}</td>
<td>76</td>
<td>1.960\textsuperscript{++}</td>
<td>59</td>
</tr>
<tr>
<td>3.051\textsuperscript{++}</td>
<td>100</td>
<td>1.764\textsuperscript{++}</td>
<td>19</td>
</tr>
<tr>
<td>2.731\textsuperscript{+}</td>
<td>22</td>
<td>1.620\textsuperscript{++}</td>
<td>23</td>
</tr>
<tr>
<td>2.578\textsuperscript{++}</td>
<td>28</td>
<td>1.47\textsuperscript{+}</td>
<td>7</td>
</tr>
</tbody>
</table>

\textsuperscript{+} Lines for AgI\textsuperscript{7}; \textsuperscript{++} Lines for Hg\textsubscript{2}CO\textsubscript{4}\textsuperscript{3}

### Table - IV

X-ray diffraction data for 1:1 molar mixture of Ag\textsubscript{2}HCO\textsubscript{4} and Ag\textsubscript{2}HgI\textsubscript{4} heated at 100\textdegree C then cooled to room temperature.

<table>
<thead>
<tr>
<th>d in Å (\text{°} )</th>
<th>( I/I_0 )</th>
<th>d in Å (\text{°} )</th>
<th>( I/I_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.76\textsuperscript{+}</td>
<td>56</td>
<td>1.96\textsuperscript{+}</td>
<td>26</td>
</tr>
<tr>
<td>3.156\textsuperscript{++}</td>
<td>82</td>
<td>1.93\textsuperscript{++}</td>
<td>56</td>
</tr>
<tr>
<td>3.076\textsuperscript{++}</td>
<td>23</td>
<td>1.608\textsuperscript{++}</td>
<td>26</td>
</tr>
<tr>
<td>2.561\textsuperscript{++}</td>
<td>36</td>
<td>1.540\textsuperscript{++}</td>
<td>26</td>
</tr>
<tr>
<td>2.28\textsuperscript{+}</td>
<td>72</td>
<td>1.240\textsuperscript{+}</td>
<td>23</td>
</tr>
</tbody>
</table>

\textsuperscript{+} Lines for AgI\textsuperscript{7}; \textsuperscript{++} Lines for Hg\textsubscript{2}CO\textsubscript{4}\textsuperscript{3}
Table - V

X-ray diffraction data for 1:1 molar mixture of \( \text{Ag}_2\text{I}_4 \) and \( \text{HgI}_2 \) kept at room temperature for 15 days.

<table>
<thead>
<tr>
<th>( d ) in ( \text{Å} )</th>
<th>( \frac{I}{I_0} )</th>
<th>( d ) in ( \text{Å} )</th>
<th>( \frac{I}{I_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.35*</td>
<td>26</td>
<td>2.561**,**</td>
<td>25</td>
</tr>
<tr>
<td>3.62*</td>
<td>70</td>
<td>2.301*</td>
<td>50</td>
</tr>
<tr>
<td>3.25*,**</td>
<td>70</td>
<td>1.951**,**</td>
<td>25</td>
</tr>
<tr>
<td>3.22**</td>
<td>80</td>
<td>1.91*</td>
<td>40</td>
</tr>
<tr>
<td>2.785**</td>
<td>100</td>
<td>1.75**,**</td>
<td>35</td>
</tr>
</tbody>
</table>

* Lines for \( \text{AgI} \); ** Lines for \( \text{Hg}_2\text{I}_4 \);

Table - VI

X-ray diffraction data for 1:2 molar mixture of \( \text{Ag}_2\text{I}_4 \) and \( \text{HgI}_2 \) heated at 100°C then cooled to room temperature.

<table>
<thead>
<tr>
<th>( d ) in ( \text{Å} )</th>
<th>( \frac{I}{I_0} )</th>
<th>( d ) in ( \text{Å} )</th>
<th>( \frac{I}{I_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.66*</td>
<td>100</td>
<td>2.100**</td>
<td>11</td>
</tr>
<tr>
<td>3.211*,**</td>
<td>21</td>
<td>1.981**</td>
<td>11</td>
</tr>
<tr>
<td>2.97**</td>
<td>32</td>
<td>1.960**</td>
<td>12</td>
</tr>
<tr>
<td>2.578**</td>
<td>17</td>
<td>1.748**</td>
<td>9</td>
</tr>
<tr>
<td>2.238*</td>
<td>100</td>
<td>1.534**</td>
<td>9</td>
</tr>
</tbody>
</table>

** Lines for \( \text{Hg}_2\text{I}_4 \); * Lines for \( \text{Ag}_2\text{HgI}_4 \)
Table - VII

X-ray diffraction data for 1:3 molar mixture of Ag$_2$MoO$_4$ and Hgl$_2$ heated at 100°C then cooled to room temperature.

<table>
<thead>
<tr>
<th>d in Å</th>
<th>I/I$_0$</th>
<th>d in Å</th>
<th>I/I$_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.12**</td>
<td>22</td>
<td>2.578*</td>
<td>16</td>
</tr>
<tr>
<td>3.66*</td>
<td>100</td>
<td>2.22</td>
<td>71</td>
</tr>
<tr>
<td>3.59**</td>
<td>31</td>
<td>2.187*</td>
<td>33</td>
</tr>
<tr>
<td>3.240*</td>
<td>26</td>
<td>1.97*</td>
<td>13</td>
</tr>
<tr>
<td>3.004+</td>
<td>33</td>
<td>1.582+</td>
<td>13</td>
</tr>
<tr>
<td>2.772**</td>
<td>22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ Lines for HgMoO$_4$; * Lines for Ag$_2$Hgl$_4$; ** Lines for Hgl$_2$.

Thermal studies

Weighed amounts of Ag$_2$MoO$_4$ and Hgl$_2$ (both powdered above 300 mesh) were taken in a Dewar flask, 20 cm long and 2 cm wide, kept in a wooden case packed with cotton. The mixture was stirred thoroughly and the rise in temperature with time was noted by Beckman thermometer reading upto 0.01°C for different molar mixtures. The results are given in Figure 2.
Fig. 2. Temperature rise as a function of time for the reaction between Ag₂MoO₄ and HgI₂. Molar ratios are: (O) 1:1, (●) 1:2, and (●) 1:3.
Conductivity measurements

Ag$_2$MoO$_4$ and HgI$_2$ were thoroughly mixed with each other in an equimolar ratio and the mixture was immediately poured into a die and pressed into a disc of about 0.2 cm thick and 0.31 cm$^2$ surface area. The disc was then placed between platinum electrodes of same surface area and change in conductivity with time was noted by conductivity bridge (Cambridge Instrument Co., England) at 50 c/s. Similarly conductivity variation for other molar ratio mixtures of Ag$_2$MoO$_4$ and HgI$_2$ were measured. Results are given in Figure 3. Conductivities of compounds involved in the Ag$_2$MoO$_4$ and HgI$_2$ reaction were measured at 100°C and given in Table VIII.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (Ohm Cm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$MoO$_4$</td>
<td>8.7 x 10$^{-6}$</td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>0.6 x 10$^{-6}$</td>
</tr>
<tr>
<td>HgMoO$_4$</td>
<td>4.5 x 10$^{-6}$</td>
</tr>
<tr>
<td>AgI</td>
<td>9.5 x 10$^{-6}$</td>
</tr>
<tr>
<td>Ag$_2$HgI$_4$</td>
<td>4.3 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

Conductivity of materials, pressed in the form of pellets of 0.2 cm thick and 0.31 cm$^2$ surface area were measured at 100°C.
Fig. 3. Change in conductivity as a function of time for the reaction between $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$. Molar ratios are: (○) 1:1, (●) 1:2, and (●) 1:3.
Diffusion study of HgI₂

Diffusion coefficients of HgI₂ were determined by the method as described by Rastogi and Dubey. Three glass tubes of different radii were taken and known amount of HgI₂ was filled in each tube in such a way that the distance of HgI₂ surface from open end of tube was same in all the cases. The amount of HgI₂ diffusing into atmosphere was determined by weighing each tubes at different times. Results are given in figures 8 and 9.

Discussion

X-ray analysis (Table II) of an equimolar mixture of Ag₂MoO₄ and HgI₂ heated at 100°C for 24 hr and then cooled to room temperature showed the presence of AgI and HgMoO₄ only. This points to simple double decomposition represented by equation (1) which is in conformity with the principle of larger cations going well with larger anions and smaller cations with smaller anions.

\[
Ag₂MoO₄ + HgI₂ \rightarrow 2AgI + HgMoO₄ \quad (1)
\]

AgI is known to react fast with HgI₂ to give Ag₂HgI₄, but X-ray analysis (Table III) of final reaction mixture does not show the presence of Ag₂HgI₄. However, the following
observation does indicate its transitory formation in the reaction of \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgI}_2 \) when mixed in equimolar ratio. The initial dark brown mixture, on heating at 100\(^\circ\)C become yellow (AgI and HgMoO\(_4\) are yellow) and remained as such on cooling to room temperature. However another portion of this mixture kept at room temperature slowly turned orange. This orange material on heating above 50.7\(^\circ\)C turned red which again became orange on cooling below this temperature without allowing sufficient time to reach completion (Ag\(_2\)HgI\(_4\) is red above 50.7\(^\circ\)C and yellow below it\(^6\)). An equimolar mixture of \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgI}_2 \) heated at 100\(^\circ\)C for 24 hr react completely and give AgI and HgMoO\(_4\) as products (Table III).

The plot of conductivity versus time (Fig. 3,1) for 1:1 molar ratio mixture of \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgI}_2 \) clearly shows that the reaction represented by equation (1) is not simple and it comprises of atleast three steps. The reaction mechanism may be given as,

\[
\begin{align*}
\text{Ag}_2\text{MoO}_4 + \text{HgI}_2 &\rightarrow 2\text{AgI} + \text{HgMoO}_4 \quad (1a) \\
2\text{AgI} + \text{HgI}_2 &\rightarrow \text{Ag}_2\text{HgI}_4 \quad (1b) \\
\text{Ag}_2\text{HgI}_4 + \text{Ag}_2\text{MoO}_4 &\rightarrow 4\text{AgI} + \text{HgMoO}_4 \quad (1c) \\
2\text{Ag}_2\text{MoO}_4 + 2\text{HgI}_2 &\rightarrow 4\text{AgI} + 2\text{HgMoO}_4
\end{align*}
\]
At the start of the reaction, the very small change in conductivity is probably due to the occurrence of slow reaction represented by equation (1a). The rapid increase thereafter, is due to the formation of highly conducting $\text{Ag}_2\text{Hgl}_4^{14}$ through reaction (1b). The final fall in conductivity is due to predominance of disappearance reaction (1c). To confirm reaction (1c), $\text{Ag}_2\text{MoO}_4$ and $\text{Ag}_2\text{Hgl}_4$ were mixed in equimolar ratio and heated at $100^\circ\text{C}$ for 24 hr then cooled to room temperature. The X-ray analysis (Table IV) of the mixture indicated complete conversion into AgI and HgMoO$_4$. Strangely enough the stoichiometry of the initial step represented by equation (1a) also turns out to be the overall stoichiometry of the reaction represented by equation (1). As the conductivity of reactants and products is much lower than that of $\text{Ag}_2\text{Hgl}_4$ (Table VIII), the conductivity curve (Fig. 3,1) essentially monitors the concentration of $\text{Ag}_2\text{Hgl}_4$, and resembles the curve that represents the concentration of transient species in a consecutive reactions $^{15}$. It confirms the formation of $\text{Ag}_2\text{Hgl}_4$ and its subsequent consumption during the reaction.

X-ray analysis (Table II) of an equimolar mixture of $\text{Ag}_2\text{MoO}_4$ and Hgl$_2$ kept at room temperature show the presence of $\text{Ag}_2\text{Hgl}_4$ along with AgI, HgMoO$_4$ and $\text{Ag}_2\text{MoC}_4$. 
Thermal measurements (Fig. 2,1) made with an equimolar mixture of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ at room temperature show only one inflection, thus offers no evidence of multiplicity of the reaction. This is understandable because step (1b) is much faster than step (1a). Although exchange reactions are usually fast, step (1a) will be slow because the ionic size of $\text{Ag}^+$ and $\text{Hg}^{2+}$ are very close to each other. Step (1b) is known to be fast even at low temperature. This explains why thermal measurement fails to provide evidence for steps involved in reaction. At room temperature reaction (1c) does not seem to proceed and if at all not to any significant extent. The X-ray diffraction data for 1:1 molar ratio mixture of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ kept at room temperature is given in table V.

X-ray analysis (Table II) of 1:2 molar mixture of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ heated at 100°C for 24 hr, show the presence of $\text{Ag}_2\text{HgI}_4$ and $\text{HgMoO}_4$ only. The colour of mixture when kept at room temperature changed to yellow from red. On heating this yellow mixture above 51°C the mixture turned red and changed to yellow if cooled below this temperature. The conductivity (Fig. 3,2) of 1:2 molar mixture of $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$ maintained at 100°C, first rises very slowly and then steeply to a constant value. The constancy in conductivity, after the sharp rise, suggest that
the highly conducting species Ag\textsubscript{2}HgI\textsubscript{4} formed through reaction (1b) is not consumed in other reaction and remains as such. On mixing Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} in 1:2 molar ratio both at 100°C and room temperature, reaction seems to follow same sequence, as in the case of equimolar mixture of Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} heated at 100°C, but reaction (1c) does not proceed in this case, and if at all not to any significant extent. Moreover if reaction (1c) occurs to some extent, AgI formed in reaction (1c) is changed into Ag\textsubscript{2}HgI\textsubscript{4} through reaction (1b). The X-ray diffraction analysis of 1:2 molar mixture of Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} heated at 100°C for 24 hr is given in table VI. The sequence of reaction involving 1:2 molar mixture of Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} may be written as,

\[
\begin{align*}
\text{Ag}_2\text{MoO}_4 + \text{HgI}_2 & \rightarrow 2\text{AgI} + \text{HgMoO}_4 \quad (2a) \\
2\text{AgI} + \text{HgI}_2 & \rightarrow \text{Ag}_2\text{HgI}_4 \quad (2b) \\
\text{Ag}_2\text{MoO}_4 + 2\text{HgI}_2 & \rightarrow \text{Ag}_2\text{HgI}_4 + \text{HgMoO}_4
\end{align*}
\]

X-ray analysis (Table II) of 1:3 molar ratio mixture of Ag\textsubscript{2}MoO\textsubscript{4} and HgI\textsubscript{2} heated at 100°C for 24 hr show the presence of HgMoC\textsubscript{4}, Ag\textsubscript{2}HgI\textsubscript{4} and HgI\textsubscript{2}. The overall reaction taking place in this ratio is in no way different from that which occurs in 1:2 molar ratio mixture. However the conductivity curve (Fig. 3,3) is this case is different from others. The second rise in conductivity in this case is a
unique feature and points to second time predominance of
the formation of Ag₂HgI₄ through reaction (3d) and the
complete reaction sequence in 1:3 molar mixture can be pre­
sumed as follows:

\[
\begin{align*}
\text{Ag}_2\text{MoO}_4 + \text{HgI}_2 & \rightarrow 2\text{AgI} + \text{HgMoO}_4 \quad (3a) \\
2\text{AgI} + \text{HgI}_2 & \rightarrow \text{Ag}_2\text{HgI}_4 \quad (3b) \\
\text{Ag}_2\text{HgI}_4 + \text{Ag}_2\text{MoO}_4 & \rightarrow 4\text{AgI} + \text{HgMoO}_4 \quad (3c) \\
4\text{AgI} + 4\text{HgI}_2 & \rightarrow 2\text{Ag}_2\text{HgI}_4 + 2\text{HgI}_2 \quad (3d) \\
2\text{Ag}_2\text{MoO}_4 + 6\text{HgI}_2 & \rightarrow 2\text{Ag}_2\text{HgI}_4 + 2\text{HgMoO}_4 + 2\text{HgI}_2 
\end{align*}
\]

The X-ray analysis (Table VII) of 1:3 molar mixture of
Ag₂MoO₄ and HgI₂ heated at 100°C for 24 hr also show the
presence of Ag₂HgI₄, HgMoO₄ and HgI₂. In this case the re­
action follow the same sequence as in 1:2 molar mixture
except that excess of HgI₂ is left unreacted.

**Mechanism of lateral diffusion**

In lateral diffusion experiments it was observed
that immediately after the placement of HgI₂ over Ag₂MoO₄
in the reaction tube, a yellow boundary formed at the inter­
face, which grew with time on Ag₂MoO₄ side and soon a red
layer formed between yellow layer and HgI₂. Simultaneously
a gap developed between red product layer and HgI₂. Later, when the experiments were run keeping an air-gap between the reactants at the start itself, the reaction proceeded likewise. This demonstrates that HgI₂ is the mobile species and reacts here via vapour phase.

If this reaction proceeds through the usually accepted mechanism of counter diffusion of cations, the product layers in reaction tube are expected to have the following sequence.

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

According to counter diffusion, AgI should not be detected in the product and if it is at all detected, it should be found with Ag₂HgI₄ and not with HgMoO₄. As this is different from the observed sequence in the product layer (Fig. 1), it is suggested that this reaction proceeds through the diffusion of HgI₂ as such and not through the counter diffusion of cations. From this the observed sequence of products in the reaction capillary follows all right. Once HgI₂ enters the reaction zone, (into Ag₂MoO₄ grain) AgI and HgMoO₄ are formed. AgI then reacts with the incoming HgI₂ to give Ag₂HgI₄, giving the observed product sequence. AgI formed in the initial stages is completely converted into Ag₂HgI₄. As Ag₂HgI₄ layer is formed
in between HgI₂ and HgMoO₄, some of the AgI formed in later stages escapes conversion into Ag₂HgI₄ and is detected in the yellow layer along with HgMoO₄. Silver molybdate has a MoO₄²⁻ framework, i.e. sublattice MoO₄²⁻ units, where highly mobile Ag⁺ prefers an interstitial site over a Schottky disorder. HgI₂ penetrates into the open anionic framework, yielding HgMoO₄ and AgI. Further interaction of AgI with incoming HgI₂ produces Ag₂HgI₄ germ nuclei the growth of which results in a kind of collapse of the earlier Ag₂MoO₄ lattice yielding HgMoO₄ and Ag₂HgI₄ crystallites.

The rate of reaction decreases (Fig. 4) with the increase in thickness of the product layer. Initially the chemical reaction is fast, but the process being diffusion controlled, reactant takes more and more time to diffuse through and reaction rate thus falls continuously with the increase in thickness of product layers.

Lateral diffusion data best the equation (Fig. 5)

\[ x^n = kt \]  \hspace{1cm} (4)

where \( x \) is the product thickness at time \( t \), \( k \) and \( n \) are constants. The observed higher value of \( n \) (Table I), which otherwise should have 2, had the reaction followed the parabolic rate law. The value of \( n \) rises further with the rise in temperature from 80-135°C, and this suggests an additional resistance to the rate of reaction, like sintering which
Fig. 4. Kinetic data for the reaction between $\text{Ag}_2\text{MoO}_4$ and $\text{Hgl}_2$ at various temperatures.
Fig. 5. Kinetic data for lateral diffusion and test of equation $x^n = kt$ for the reaction between $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$. 

\text{Fig. 5: Kinetic data for lateral diffusion and test of equation $x^n = kt$ for the reaction between $\text{Ag}_2\text{MoO}_4$ and $\text{HgI}_2$.}
rises further with the rise in temperature. \( k \) related to the diffusion constant, follows the Arrhenius equation (Fig.6). The activation energy, measured from \( \log k \) versus inverse temperature plot was 95.931 kJ/mol.

To see if there is any initial difference in the processes occurring in two temperature ranges, the slope of product-growth-curve that measures the reaction rate was determined at zero time and its logarithm was plotted against inverse temperature (Fig.7). The activation energy of 20.90 kJ/mol in lower temperature range in this case indicates that the process is grain boundary or surface diffusion controlled, whereas the activation energy of 90.49 kJ/mol for the second temperature range shows that in the higher temperature range process is bulk diffusion controlled right from the start.

Diffusion coefficient of \( \text{HgI}_2 \) was calculated to confirm whether surface migration also contribute in addition to vapour phase to the overall diffusion controlled reaction of \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgI}_2 \) in solid state. The data fit best the equation.

\[
\Delta W = K_1 t \quad (5)
\]

where \( \Delta W \) is the amount of \( \text{HgI}_2 \) diffused in air in time \( t \) and \( K_1 \) is a constant. \( \Delta W \) was plotted against time \( t \) (Fig.8) and \( K_1 \) calculated for glass tubes of various radius. The value of \( K_1 \) were found to depend on the radius of glass tube, according to the equation

\[
K_1/r = \alpha r + \beta \quad (6)
\]
Fig. 6. Dependence of $k$ on temperature for the reaction between Ag$_2$MoO$_4$ and HgI$_2$. 

\[ 1/T \]

\[ \log k \]

\[ 2.5 \times 10^{-3} \quad 2.7 \quad 2.9 \quad 3.1 \]
Fig. 7. Temperature dependence of initial rate constant \( k \) for the reaction between \( \text{Ag}_2\text{MoO}_4 \) and \( \text{HgI}_2 \).
Fig. 8. Kinetic data for the study of diffusion of HgI$_2$. Radius of glass tubes are: (O) 0.4 cm, (⊗) 0.2 cm, and (●) 0.1 cm.
where $r$ is the radius of tube and $\alpha$ and $\beta$ are given by

$$\alpha = \pi Ce Dv/l$$  \hspace{1cm} (7)$$

$$\beta = 2\pi Ce Ds$$ \hspace{1cm} (8)$$

where $l$ is the distance of HgI$_2$ surface from the open end of tube, $Dv$ the diffusion coefficient for vapour phase and $Ds$, the diffusion coefficient for surface migration of HgI$_2$. $Ce$, the equilibrium concentration of HgI$_2$ just above the HgI$_2$ surface was calculated from vapour pressure using the equation,

$$P = CRT$$ \hspace{1cm} (9)$$

$P$ is the vapour pressure of HgI$_2$ was obtained in the desired temperature range by using the equation,

$$\log_{10} P = \frac{0.052323}{T} + b$$ \hspace{1cm} (10)$$

where $T$ is the absolute temperature and $a$ & $b$ are constants and whose value for a particular temperature range is given. The vapour pressure of HgI$_2$ was obtained as 9.25 mm of mercury.

The test of equation (6) was made by plotting $k_1/r$ against radius (Fig. 9) and $\alpha$ and $\beta$ evaluated from the plot.
Fig. 9. Estimation of diffusion coefficient of HgI$_2$ in air and surface.
The values of diffusion coefficients of HgI$_2$ evaluated from equation 7 and 8 were found to be $1.17 \times 10^{-2}$ Cm$^2$/sec and $2.98 \times 10^{-4}$ Cm/sec for vapour phase and surface migration respectively. These values of diffusion coefficients of HgI$_2$ suggests that surface migration also contribute in addition to the vapour phase diffusion controlled solid state reaction of Ag$_2$MoO$_4$ and HgI$_2$. 
References


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9. ASTM, X-ray powder diffraction file No. 3-0949.

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