Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1065–1072

Comparative Study of the Kinetics and Mechanism of Solid-Solid Reaction of HgClI with Cu_2HgI_4 and Ag_2HgI_4

AFAQ AHMAD, SABA BEG*, SARITA and POOJA VARSHNEY
Department of Chemistry, Aligarh Muslim University, Aligarh-202 002, India
E-mail: sababeg2003@yahoo.co.in

The reactions of HgClI with Cu_2HgI_4 and Ag_2HgI_4 in the solid state were studied by X-ray diffraction, chemical analysis and electrical resistivity measurements. The kinetics of the reactions has been studied by the moving boundary method. The data for the lateral diffusion best fit the equation $x^n = kt$. The activation energies for the reaction of HgClI with Cu_2HgI_4 and Ag_2HgI_4 is 64.38 ± 2.54 J/mol and 96.630 ± 0.183 J/mol, respectively. Both the reactions are diffusion controlled and proceed *via* vapour phase diffusion of the HgClI.

Key Words: Solid-solid reaction; Electrical resistivity; Diffusion.

INTRODUCTION

Cu_2HgI_4 and Ag_2HgI_4 are readily formed from the solid-solid reactions of HgI_2 with CuI and AgI respectively[1, 2]. In a series of reactions, involving silver(I), copper(I) halides and tungstate and molybdate of silver with mercury(II) halides in solid state[3–11], it was observed that the reactions proceed *via* the formation of tetra iodo mercurate(II) of copper(I) and silver(I), respectively. Therefore, it is concluded that the formation of silver(I) tetra iodo mercurate and copper(I) tetra iodo mercurate is the key to the understanding of these reactions. Moreover, these tetra iodo mercurates undergo phase transitions. Therefore it is considered pertinent to understand the effect of such transitions on the mechanism of solid state reaction.

This paper presents a comparative study of the kinetics and mechanism of the reaction of HgClI with Cu_2HgI_4 and Ag_2HgI_4. In the former, mixtures of different products and in the latter, same products are obtained.

EXPERIMENTAL

$HgCl_2$ (E. Merck) and HgI_2 (E. Merck) were used as such. HgClI was prepared by the method reported by Ansari and Mehdi[12]. CuI was prepared by the method of Berthemot[13] and Guichard[14]. Electrical resistivity measurements were made on samples compressed into pellets, (about 0.2×10^{-2} m thick and 0.31×10^{-4} m in surface area) in 1 : 3, 1 : 2, 1 : 1, 2 : 1 and 3 : 1 molar mixtures of HgClI with Cu_2HgI_4 and Ag_2HgI_4 by an RLC Digibridge (Gen Rad Model 1659 USA) at 80°C, using a teflon conductivity cell with platinum electrodes as described elsewhere[3]. Figs. 1 and 2 depict the variation in resistance with time, for the various molar mixtures. The kinetics was studied using the moving boundary technique described elsewhere[15]. The results are shown in Tables 1 and 2.

The X-ray diffractograms of powdered materials were recorded by Norelco Geiger X-ray diffractometer (PW 1010 Philips) using CuK_α radiation and Ni-filter. The reactants in different molar ratios were mixed in an agate mortar and heated in

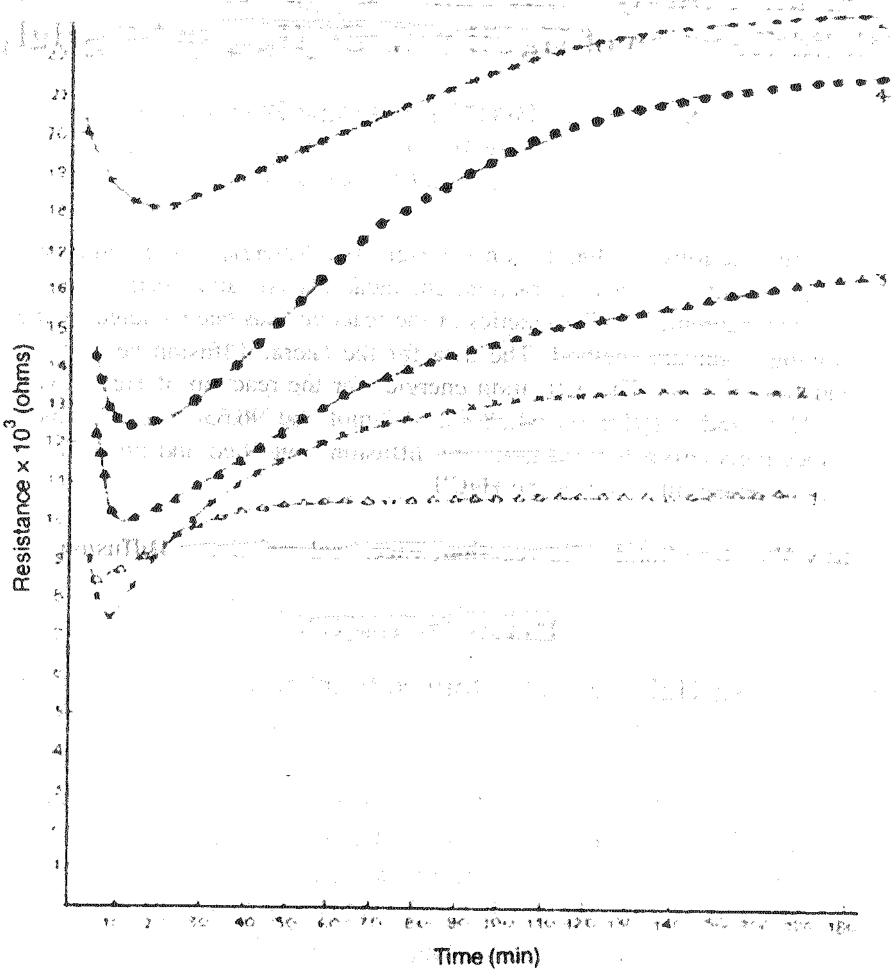

Fig. 1. Resistivity change as a function of time for HgCII and Cu_2HgI_4 in different molar ratios: (1) 3 : 1, (2) 2 : 1, (3) 1 : 1, (4) 1 : 2, (5) 1 : 3

an air thermostat maintained at 80°C for over 3 days to ensure complete reaction. The diffractograms of these mixtures were recorded at room temperature. Compounds present in different mixtures were identified by comparing the calculated d-values and intensities with the standard values of the expected compounds. The results are listed in Tables 3 and 4.

TABLE-1

DEPENDENCE OF PARAMETERS OF EQUATION $x^n = kt$ ON TEMPERATURE FOR THE REACTION BETWEEN HgCII AND Cu_2HgI_4

Temperature (°C ± 0.05)	k (cm/h)	Standard deviation	Relative standard deviation	n
70	2.55×10^{-4}	5.95×10^{-6}	1.908×10^{-2}	1.58
80	5.16×10^{-4}	1.20×10^{-5}	1.77×10^{-2}	1.58
90	6.30×10^{-4}	1.85×10^{-5}	2.47×10^{-2}	1.59
100	1.11×10^{-3}	2.46×10^{-5}	1.76×10^{-2}	1.59
110	1.24×10^{-3}	2.58×10^{-5}	1.45×10^{-2}	1.60

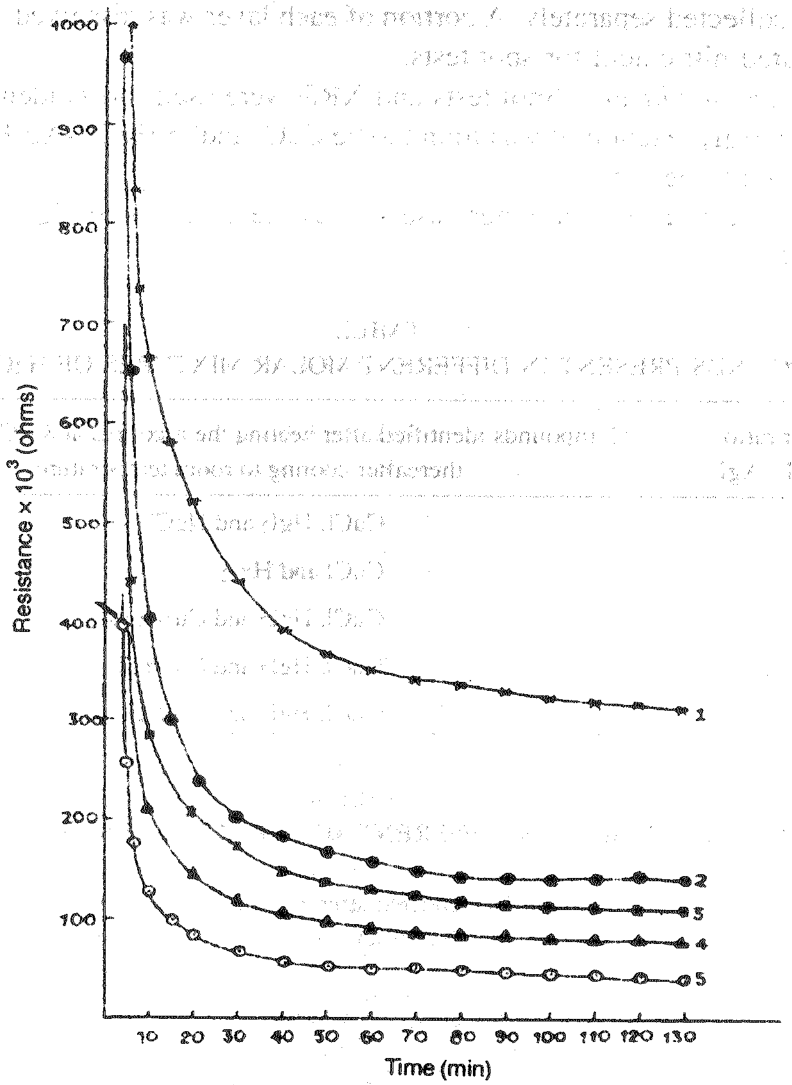

Fig. 2. Resistivity change as a function of time for the reaction between HgClI and Ag_2HgI_4 in different molar ratios: (1) 3 : 1, (2) 2 : 1, (3) 1 : 1, (4) 1 : 2, (5) 1 : 3

TABLE-2

DEPENDENCE OF PARAMETERS OF EQUATION $x^n = kt$ ON TEMPERATURE FOR THE REACTION BETWEEN HgClI AND Ag_2HgI_4

Temperature (°C ± 0.05)	k (cm/h)	Standard deviation	Relative standard deviation	n
70	1.003×10^{-4}	3.210×10^{-6}	3.199×10^{-2}	2.433
80	2.176×10^{-4}	4.305×10^{-5}	8.273×10^{-2}	2.439
90	4.800×10^{-4}	4.413×10^{-4}	8.282×10^{-4}	2.366
100	7.858×10^{-4}	3.456×10^{-5}	4.393×10^{-2}	2.377
110	1.574×10^{-3}	9.178×10^{-5}	5.815×10^{-2}	2.267

Analysis of the product layers

A reaction tube having distinct product layers was broken carefully and the products collected separately. A portion of each layer was dissolved separately in concentrated nitric acid for spot tests.

White product layer: Spot tests and XRD were used for its identification. In $HgClI$-Cu_2HgI_4 reaction, it was found to be CuCl and in $HgClI$-Ag_2HgI_4 reaction it was found to be AgCl.

Red product layer: In either case, it was identified to be HgI_2 by spot tests and XRD[16].

TABLE-3

COMPOUNDS PRESENT IN DIFFERENT MOLAR MIXTURES OF $HgClI$-Cu_2HgI_4

Molar ratio HgClI : AgI	Compounds identified after heating the mixtures at 80°C for 3 d and thereafter cooling to room temperature
3 : 1	CuCl, HgI_2 and $HgCl_2$
2 : 1	CuCl and HgI_2
1 : 1	CuCl, HgI_2 and Cu_2HgI_4
1 : 2	CuCl, HgI_2 and Cu_2HgI_4
1 : 3	CuCl, HgI_2 and Cu_2HgI_4

TABLE-4

COMPOUNDS PRESENT IN DIFFERENT MOLAR MIXTURES OF $HgClI$-Ag_2HgI_4

Molar ratio HgClI : AgI	Compounds identified after heating the mixtures at 80°C for 3 d and thereafter cooling to room temperature
3 : 1	AgCl, HgI_2 and $HgCl_2$
2 : 1	AgCl and HgI_2
1 : 1	AgCl, HgI_2 and Ag_2HgI_4
1 : 2	AgCl, HgI_2 and Ag_2HgI_4
1 : 3	AgCl, HgI_2 and Ag_2HgI_4

RESULTS AND DISCUSSION

For a comprehensive understanding of the solid-solid reaction in the two cases, the chemical interaction and the lateral diffusion, when the reactants were kept in contact and also when separated by an air gap, have been considered in detail.

Mechanism and Chemical Interaction

$HgClI$-Cu_2HgI_4 reaction: X-ray diffraction measurements (Table-3) reveal that HgClI reacts with Cu_2HgI_4 in 2 : 1 molar ratio in solid state giving CuCl and HgI_2. X-ray analysis of 2 : 1 molar mixture shows the presence of CuCl and HgI_2 as end products. The resistivity measurements further suggest it to be a two-step process (Fig. 1) as the resistance initially decreases sharply with time and thereafter increases gradually to attain a maximum. The initial decrease in resistance is due to reaction (1a) as CuI and CuCl produced in this step have lower resistance as compared to those of reactants[17].

$$HgClI + Cu_2HgI_4 \rightarrow CuI + CuCl + 2HgI_2 \qquad (1a)$$

The subsequent rise in resistance is due to conversion of poorly resisting CuI and HgI_2 to more resisting Cu_2HgI_4.[6]

$$2CuI + HgI_2 \rightarrow Cu_2HgI_4 \qquad (1b)$$

The overall reaction mechanism can be represented as

$$\begin{array}{c} 2HgClI + 2Cu_2HgI_4 \rightarrow 2CuI + 2CuCl + 4HgI_2 \\ 2CuI + HgI_2 \rightarrow Cu_2HgI_4 \\ \hline 2HgClI + Cu_2HgI_4 \rightarrow 2CuCl + 3HgI_2 \end{array}$$

X-ray measurements show the presence of CuCl, HgI_2 and Cu_2HgI_4 as end products in 1 : 1, 1 : 2 and 1 : 3 molar mixtures of the reactants. Since the resistivity behaviour of these mixtures is also the same as that of 2 : 1 molar mixture, it is concluded that they all follow the same reaction mechanism and the presence of Cu_2HgI_4 as one of the end products in these cases is due to the Cu_2HgI_4 present in excess over the stoichiometric ratio of 2 : 1.

The initial gradual decrease in resistance (in 1 : 3, 1 : 2 and 1 : 1 molar mixture) for lesser and lesser time is an interesting exposition of the law of mass action. This decrease does not show up in the 3 : 1 molar mixture, as HgClI is much in excess in this molar mixture. As HgClI decomposes to HgI_2 and $HgCl_2$ at room temperature[18], $HgCl_2$ appears in XRD analysis along with CuCl and HgI_2 and not HgClI as expected.

HgClI-Ag_2HgI_4 reaction: X-ray diffraction studies (Table-4) show that HgClI and Ag_2HgI_4 react in the molar ratio 2 : 1 giving AgCl and HgI_2 as end products.

$$2HgClI + Ag_2HgI_4 \rightarrow 2AgCl + 3HgI_2$$

The time resistivity curves (Fig. 2) show a sharp decrease in resistance before finally becoming constant. The decrease in resistivity can be explained by steps (2a) and (2b) where poorly resisting products AgCl, AgI and Ag_2HgI_4 19 are formed. The overall reaction mechanism can be represented as:

$$\begin{array}{cr} 2HgClI + 2Ag_2HgI_4 \rightarrow 2AgCl + 2AgI + 4HgI_2 & (2a) \\ 2AgI + HgI_2 \rightarrow Ag_2HgI_4 & (2b) \\ \hline 2HgClI + Ag_2HgI_4 \rightarrow 2AgCl + 3HgI_2 & (2) \end{array}$$

Resistivity measurement with pellets of 1 : 3, 1 : 2 and 1 : 1 molar mixture of HgClI and Ag_2HgI_4 show them to be following the pattern of 2 : 1 molar mixture. However, the presence of Ag_2HgI_4 in addition to AgCl and HgI_2 in X-ray analysis of these molar mixtures is due to the excess amount of Ag_2HgI_4 in the reaction mixture.

The time resistivity curve of 3 : 1 molar mixture is the same as that of 2 : 1, but its XRD analysis shows the presence of $HgCl_2$ in addition to AgCl and HgI_2. In this molar mixture, HgClI is in excess and is left unreacted. As HgClI decomposes to HgI_2 and $HgCl_2$ 18 on standing at room temperature, $HgCl_2$ and HgI_2 appear in XRD analysis and not HgClI.

Mechanism of lateral diffusion

Soon after placing HgClI over Cu_2HgI_4 (and Ag_2HgI_4) in the reaction capillary at 70°C, a red colour layer developed at the interface. The product layer grew with time towards the Cu_2HgI_4 (and Ag_2HgI_4) side, which later separated into red and white layers. A gap developed between the white layer and HgClI. When the experiment was repeated with an air gap of varying dimensions between the two reactants, the reaction proceeded in similar way giving the same kind of layers on Cu_2HgI_4 (Ag_2HgI_4) side, as was the case when the reactants were in contact. The dimension of the air gap did not affect the sequence of the layers. This shows that the mobile component is HgClI.

The X-ray and chemical analysis of different product layers of the reaction between HgClI and Cu_2HgI_4 thus formed, showed the following sequence of products in the reaction capillary.

$$Cu_2HgI_4 \mid HgI_2, CuCl \mid HgClI$$

The sequence of products, in the reaction capillary of HgClI and Ag_2HgI_4 was found to be

$$Ag_2HgI_4 \mid HgI_2, AgCl \mid HgClI$$

The rate of growth of product layers decreased with time. Initially, the process is fast and reaction controlled. As the thickness of the product layers became significant, HgClI took greater time to diffuse through the product layers. The process now becomes diffusion controlled and the rate of the reaction thus falls regularly with the growth of the product layers. The lateral diffusion data best fit (Figs. 3 and 5) the rate equation,

$$x^n = kt$$

where x is the total thickness of the product layers (in cm) at time t (in h) and k and n are constants. k follows the Arrhenius equation,

$$k = A \exp(-E/RT)$$

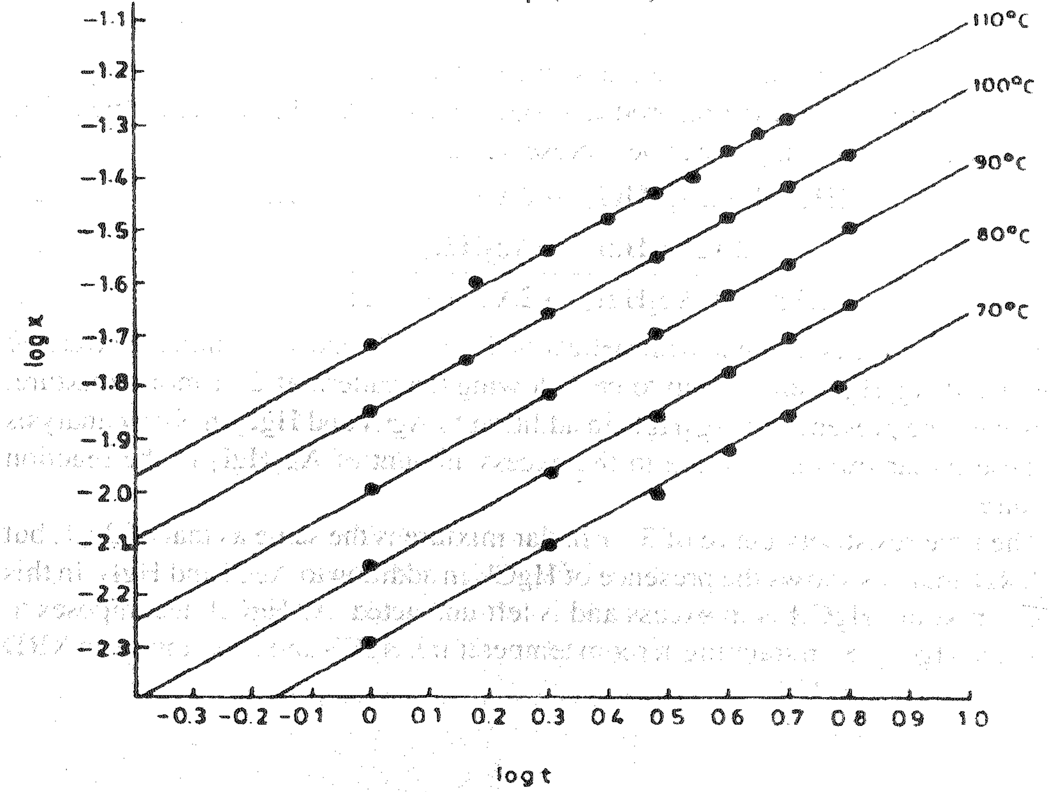

Fig. 3. Kinetic data for lateral diffusion and test for equation $x^n = kt$ for $HgClI$-Cu_2HgI_4 reaction

The activation energy evaluated from the log k *vs.* 1/T plot (Figs. 4 and 6) made by least square fit method was found to be 64.38 ± 2.54 J/mol for the reaction between HgClI and Cu_2HgI_4, and 96.630 ± 0.183 J/mol for the reaction of HgClI with Ag_2HgI_4. The reaction rate constant measured with an initial air gap between the reactants decreased with an increase in the length of the air gap. The energy of activation suggests that the reactions are diffusion controlled, taking place *via* vapour phase diffusion.

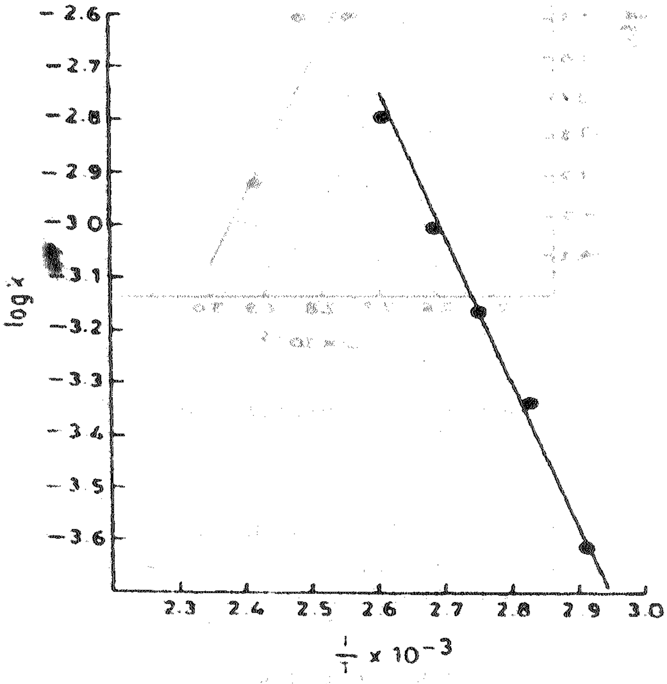

Fig. 4. Dependence of k on temperature for the reaction between HgClI and Cu_2HgI_4

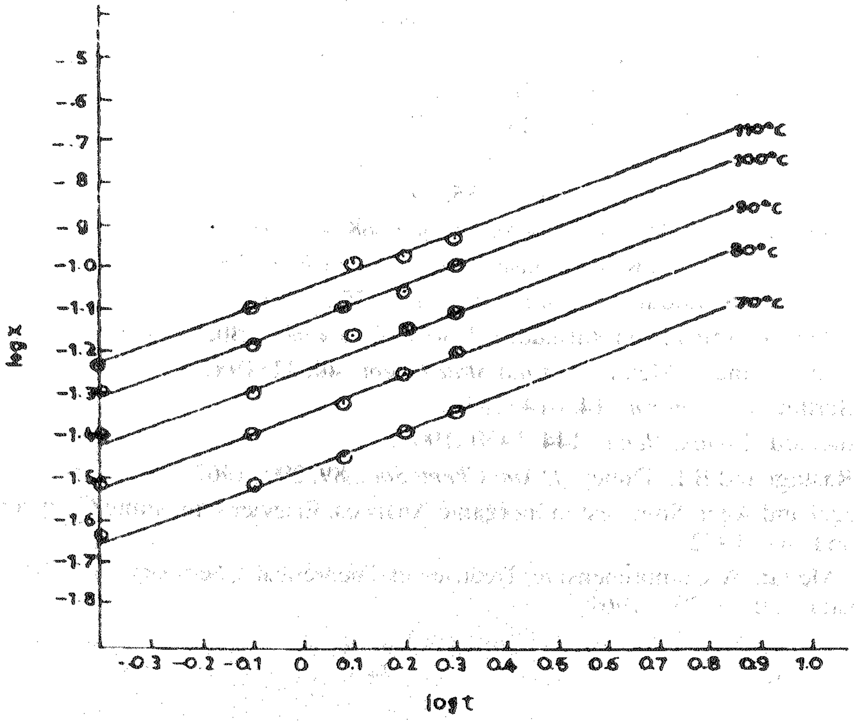

Fig. 5. Kinetic data for lateral diffusion and test for equation $x^n = kt$ for HgClI-Ag_2HgI_4

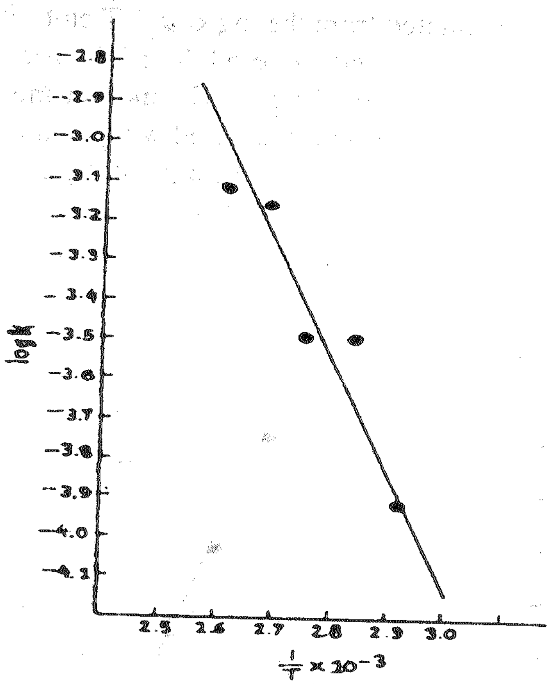

Fig. 6. Dependence of k on temperature for the reaction between HgClI and Ag_2HgI_4

Conclusion

Though the reactions HgClI-Cu_2HgI_4 and HgClI-Ag_2HgI_4 follow the same mechanism; their time resistivity pattern during the course of reaction is different as Cu_2HgI_4 is highly resisting and Ag_2HgI_4 is highly conducting.

REFERENCES

1. C. Wagner and E. Koch, *Z. Physik. Chem.*, **1334**, 1167 (1935).
2. E. Koch and C. Wagner, *Z. Physik Chem.*, **34B**, 317 (1936).
3. M.A. Beg and S.M. Ansari, *J. Solid State Chem.*, **18**, 57 (1976).
4. ———, *J. Solid State Chem.*, **20**, 103 (1977).
5. ———, *J. Solid State Chem.*, **23**, 23 (1978).
6. M.A. Beg and A. Ahmad, *Bull. Chem. Soc.(Japan)*, **55**, 3607 (1982).
7. ———, *Bull. Chem. Soc. (Japan)*, **55**, 297 (1982).
8. M.A. Beg and Rafiuddin, *J. Solid State Chem.* **68**, 45 (1987).
9. M.A. Beg, A. Jain and K.M.Ghouse, *J. Solid State Chem.*, **75**, 1 (1988).
10. M.A. Beg and Rafiuddin, *J. Solid State Chem.*, **75**, 7 (1988).
11. M.A. Beg, A. Ahmad and Rafiuddin, *J. Solid State Chem.*, **80**, 94 (1989).
12. S.M. Ansari and S. Mehdi, *J. Solid State Chem.*, **40**, 22 (1981).
13. J.B. Berthmot, *J. Pharm.*, **14**, 614 (1830).
14. M.Guichard, *Compt. Rend.*, **144**, 1430 (1907).
15. R.P. Rastogi and B.L. Dubey, *J. Am. Chem. Soc.*, **89**, 200 (1967).
16. F. Fiegel and Ager, Spot Test in Inorganic Analysis, Elsevier Publishing Company, pp. 203, 145 and 147 (1972).
17. H.W. Mellar, A Comprehensive Treatise on Theoretical Chemistry, Vol. III, Longmans (Canada) Ltd., p. 203 (1961).
18. R.P. Rastogi, B.L. Dubey and N.D. Agarwal, *J. Inorg. Nucl. Chem.*, **37**, 1167 (1975).
19. E. Koch and C.Z. Wagner, *Z.Physik. Chem.*, **34B**, 317 (1936).

(*Received*: 15 April 2005; *Accepted*: 12 December 2005) AJC-4533