

they found that the reaction constant,

$$k = 2.1 \times 10^{-11} \text{ equivalent. cm}^{-1} \cdot \text{sec}^{-1}$$

when  $k$  was the number of equivalents of newly formed compound per  $\text{cm}^2$  per second. The new complex salt,  $\text{Ag}_2\text{HgI}_4$ , was nucleated at the interface and the reaction still carried on by diffusion of reactants species through the newly formed layer.

Wagner's mechanism for the diffusion-chemical processes of this reaction was that both cations,  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ , diffuse through the solid in opposite directions as shown in Fig 3.2 (30).

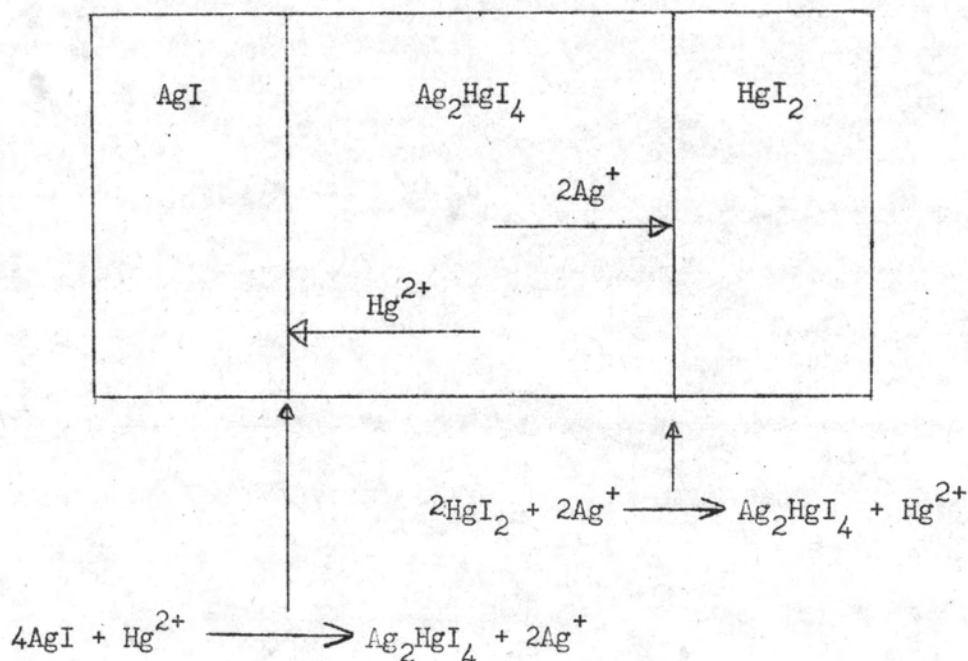


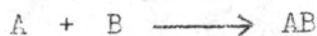
Fig 3.2 Schematic of a solid-state addition reaction, showing ionic motions and reactions at the interfaces with the assumption that both cations are mobile in the product phase.

In contrast to chemical reaction in solution in which water was used as a single solvent and reaction was homogeneous, the complex salt of  $\text{Ag}_2\text{HgI}_4$  was prepared by adding potassium iodide solution to mercury nitrate solution until the precipitate of mercury iodide,  $\text{HgI}_2$ , was dissolved into  $\text{HgI}_4^{2-}$  in excess potassium iodide and then treated with silver nitrate solution, the yellow precipitate of silver tetraiodo mercurate (II),  $\text{Ag}_2\text{HgI}_4$ , was obtained (31).

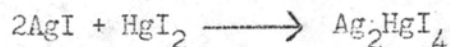
It showed that in some cases solid reactions were preferable to preparation reactions in solution.

The mechanism of solid-solid reactions could be elucidated from the identification of products and these reactions could be divided into two broad types--addition and double decomposition (32).

#### Addition reactions



An example of this type was



The mechanism of this reaction had described above and because of the two species of cations moved apart in opposite directions, then no electric motions are required. Ionic diffusion rates were very high in these particular compounds. The identification of this complex salt was such that there just three cations for every four cation sites and the unusually high density of cation vacancies was responsible for the high ionic diffusion rates. The relatively small cations would diffuse (ionic radii  $\text{Ag}^+$  1.26 Å,  $\text{Hg}^{++}$  1.10 Å), while the

iodine ions (ionic radii  $2.16 \text{ \AA}$ ) hardly expected to move (36).

The experiment was set-up (29), the thin sections of the components AgI and  $\text{HgI}_2$ , and the compound  $\text{Ag}_2\text{HgI}_4$ , were placed according to the scheme.

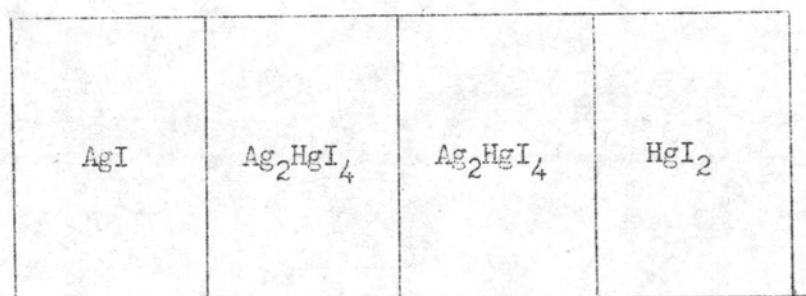
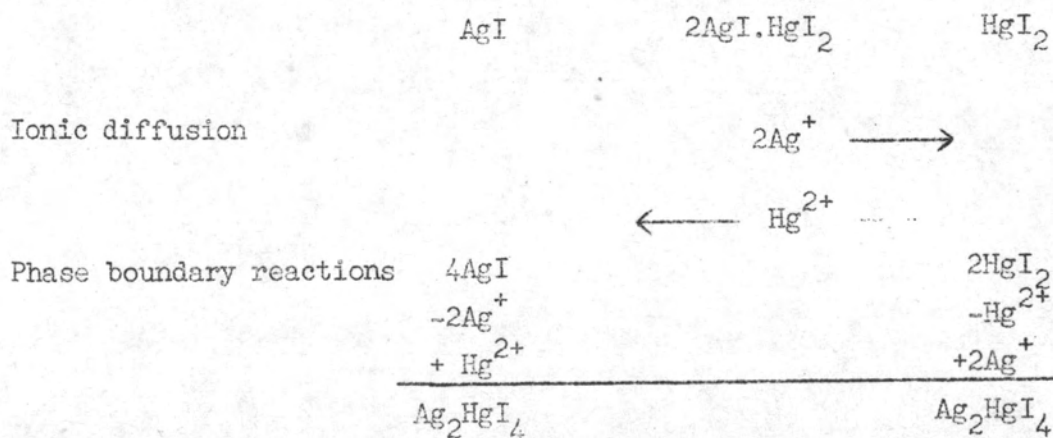


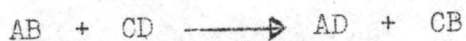
Fig 3.3 Schematic of layer structure for the experiment of solid-solid reaction, AgI and  $\text{HgI}_2$ .

The weight of each section and the content of silver and mercury were determined before and after the experiment. The result showed that the amount of AgI used was two times of  $\text{HgI}_2$ . The scheme for mechanism of the formation of  $\text{Ag}_2\text{HgI}_4$  was expected as follow (33).

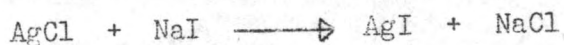


In this case both cations diffused through the complex product while in some cases only one cation moved through the product and the reaction site was the boundary between the product and the reactant with the immobile cation. The anion must also be transported by solid-state diffusion.

The other type of solid state reaction was



Since two products were formed it was a double decomposition reaction and there might be as many as four solid phases involved. The example was



This possesses a substantial problem in material transport through two product phases and a layer structure for the separate phases developed. Several proposals had been tried to express the convincing mechanism of this reaction.

If the layer structure was as shown in Fig 3.4,

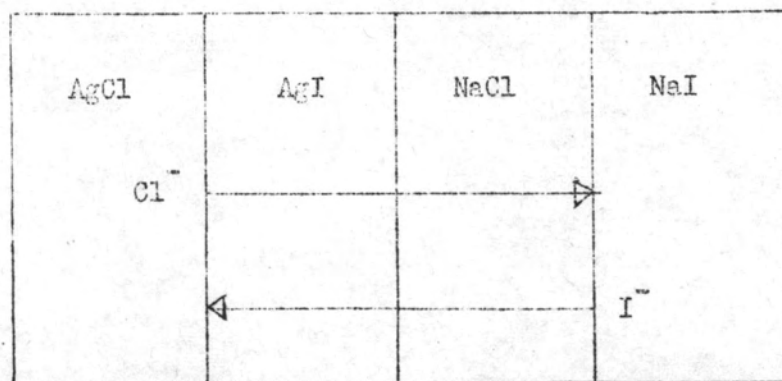


Fig 2.4 Schematic of layer structure for solid-solid reaction of AgCl and NaI, after motion of anion.

The mechanism corresponded to motion of anion (33). Chloride ion moved through AgI and NaCl to react at the NaCl/NaI interface and anion iodide moved through NaCl and AgI to react at the AgCl/AgI interface.

But Wagner (34) gave the schematic of the electrical circuit to represent the reaction which corresponded to cation mobility.

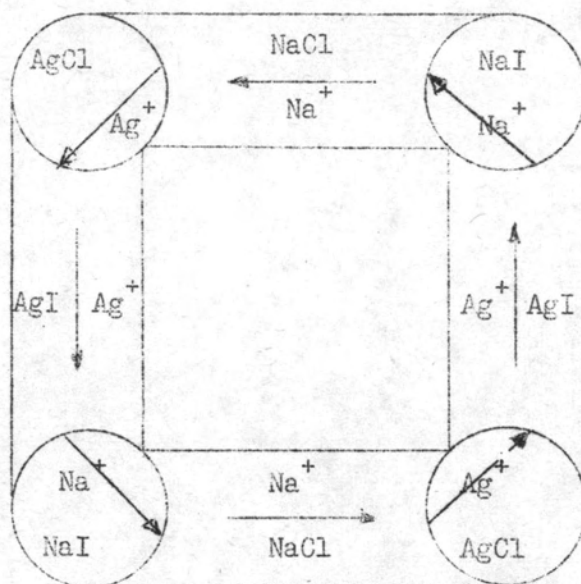


Fig 3.5 Powder reaction of  $\text{AgCl} + \text{NaI}$  after Wagner.

This circuit was composed partly of the products and reactants, the conductivity of the reactants might play a role in these reactions. This powder reactions were often observed at comparatively low temperatures so that ionic conduction due to irreversible disorder in the lattice or minute impurities might become the importance.

The modern mechanism (30) of this reaction was that the  $\text{Ag}^+$  and  $\text{Na}^+$  ions might diffuse through both product layers, as Wagners' mechanism but the products may form a parallel mosaic structure so that each ion has only to diffuse through its own compound as shown in Fig 3.6

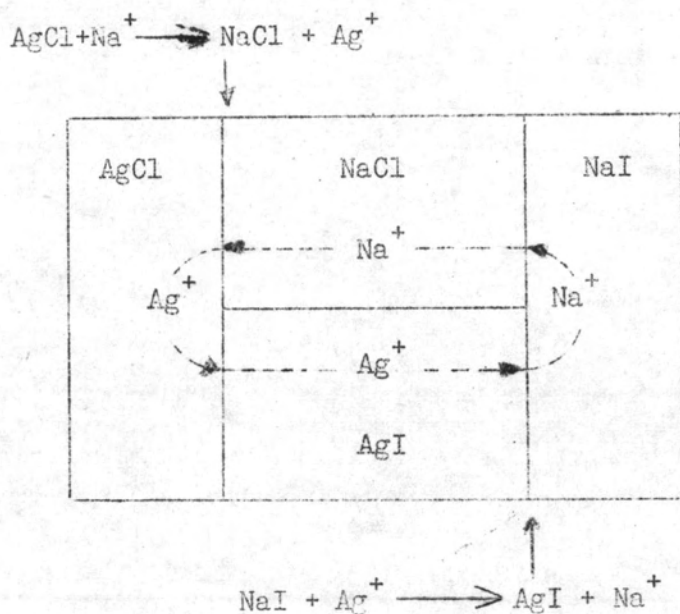
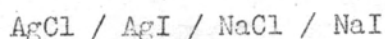


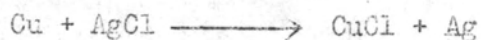
Fig 3.6 Schematic of a solid-state double decomposition reaction, showing ionic motions and reactions at the interfaces.

These three different schematic mechanism depended upon the type (anion or cation) and size (ionic radii) of diffused ion. The ionic diffusion seemed to relate directly to ionic size. The small cations (ionic radii  $\text{Ag}^+$  1.26 Å,  $\text{Na}^+$  0.95 Å) could diffuse while the bigger anion ( $\text{Cl}^-$  1.81 Å,  $\text{I}^-$  2.16 Å) would hardly be expected to move. This showed that the arrangement of the reaction products is not according to the following diagram



but corresponds to the pattern shown in Fig 3.5 and Fig 3.6

In some cases electron transfer might be required such as in the reaction



in which ionic conduction in one product is balanced by electronic conduction in the other as in Fig 3.7

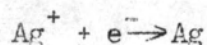
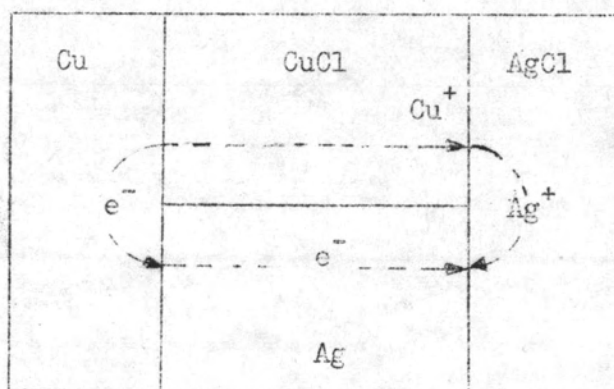


Fig 3.7 Schematic of solid-state reaction requiring flow of electrons through product phases.

It is believed that the fundamental of chemical processes in solid state was the motion of atoms or ions in crystals. Migration of atoms or ions in crystals involves point defects, either single ones such as interstitials or vacancies, or association. There are two phenomena involving migration over long distances (35).

1. Migration due to a concentration gradient, i.e. diffusion.
2. Migration in an electric field, ionic conduction.



The simplest approach is that in which the movement of atoms is described as a movement of the various types of imperfections.

Diffusion may occur in principle through both with neutral and charged imperfections. Ionic conduction requires an effective charge and occurs therefore only with charged imperfections.

It should be emphasized that it is only the effective charge that counts. Since imperfections with an effective charge might occur in any solid, it is independent of the type of binding, and thus independent of whether the crystal consists of ions as well as non-ionic (e.g. covalent) crystals. It may be, however, that the mobility with which charged imperfections move was such greater in an ionic than in a covalent crystal, so that in many cases in which an appreciable 'ionic' current is observed, the conclusion that the crystal contains ions might still be correct.