SOLID REACTION

Solid reactions, in which one or more of the reactants are solid substances, can be divided into different types, such as

1) Solid A + Solid B ———⟶ Solid AB

2) Solid A + gas B ———⟶ Solid AB

3) Solid A + liquid B ———⟶ Solid AB

4) Solid A + gas B ———⟶ gas AB

5) Various types of thermal decompositions, such as explosions of solids

A very considerable amount of work has been done on the kinetics of these reactions. The most important principles are referred to lattice imperfection which plays a very large role in the solid-state reaction. Many of the interesting properties of solids result from the presence of imperfections or defects in the solid. It may be intrinsic, or native to a crystal, if it is produced as a consequence from thermal motions of any crystal in equilibrium at the temperature above 0°K. Native imperfections may be present at any concentration, which differs from that expected in a pure crystal at equilibrium, as a result of the accidental or deliberate addition of other imperfections, because of interaction between imperfections or because nonequilibrium conditions prevail.

In many such reactions, the diffusion in solid state is rate

controlling and it is only possible by virtue of lattice defects of various types. Another factor that has an important effect on rate is lattice strain, which may arise from imperfections in the lattice, or from the existence of impurity atoms of such a nature as to disturb the regularity of the lattice.[12] The addition of impurity (foreign atom) with different valence from that of the corresponding host-crystal atoms, is an important method used to introduce vacancies into a crystal, for example in an-AgCl - $CdCl_2$ mixed crystal with only a small amount of $CdCl_2$ present, as shown in Fig. 2.1
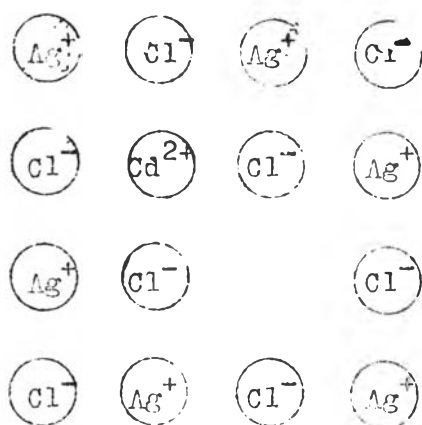

Fig. 2.1 Production of cation vacancies in AgCl by the addition of a divalent impurity.[1]

The Cd^{2+} ions occupy normal cation sites, but for every Cd^{2+} in the crystal there must be incorporated a cation vacancy (omission of an Ag^+) in order to maintain the charge neutrality in the crystal as a whole.[1] In principle at least, interstitials can be produced in an

entirely analogous fashion. The production of vacancies by the addition of foreign impurity can be easily demonstrated by density measurements. Any strain which is induced from what was stated above, may act as a source of energy, and support the chemical process, or it may increase the ease with which imperfections are formed and hence increase the rate of diffusion.

The mechanisms of solid-solid reactions could be elucidated by the identification of products, and they could be devided into two broad types, addition and double decomposition.[1]

1) Addition reaction (the simplest case of solid-solid reactions)

$$A + B \longrightarrow AB$$

A number of reactions are known including the numerous silicate reaction, spinel formation, for example,

$$ZnO + Fe_2O_3 \longrightarrow ZnFe_2O_4$$

In some cases of these reactions, only one kind of cation moves through the product at an appreciate rate, so the reaction site is the boundary between the product and the reactant consisted of the immobile cation. In such case the anion must be transported by solid-state diffusion or in the gas phase. The possibility of those two possibilities must be considered, such as, when the rate of reaction of a reacting carbonate is found to exceed the rate of evaporation of CO_2 it can safely be concluded that the reaction does not proceed via the vapour phase; on the other hand, if the evaporation rate is comparable, the liberated CO_2 may be involved.

In the addition reaction of

$$Ag_2S + Sb_2S_3 \longrightarrow 2AgSbS_2 ,$$

a product is formed not only at the interface between the reactants, a process of solid-state diffusion (of silver), but it also forms on new surface which is far apart from the initial interface as the result of vapour transport (of sulfur).

In another case both cations move, thus in the reaction

$$2AgI + HgI_2 \longrightarrow Ag_2HgI_4 ,$$

Ag^+ and Hg^{2+} diffused through the solid. Wagner[13] has given a quantitatively thermodynamic theory for a reaction of

$$AX + BX \longrightarrow ABX_2$$

which assumed that

1) the rate of reaction is determined by diffusion through the product phase (and not by surface effects)

2) there are two cases which stated about the kind of ions migrated in the reaction. In the first, only the cations (A,B) are mobile, the nonmetal ion (X) are fixed, the second, cations as well as anions are mobile.

3) the cations move with their normal valency.

4) the mobilities of the cations correspond to their transport fraction in an electrolysis experiment.

5) there is no appreciable electronic conduction.

If only the cations move, the formation of the new phase occurs only at the interface $AX - ABX_2$ and $ABX_2 - BX$, e.g. for the formation of Ag_2HgI_4

$$4AgI + Hg^{2+} \dashrightarrow \qquad 2HgI_2 + 2Ag^+ \longrightarrow$$
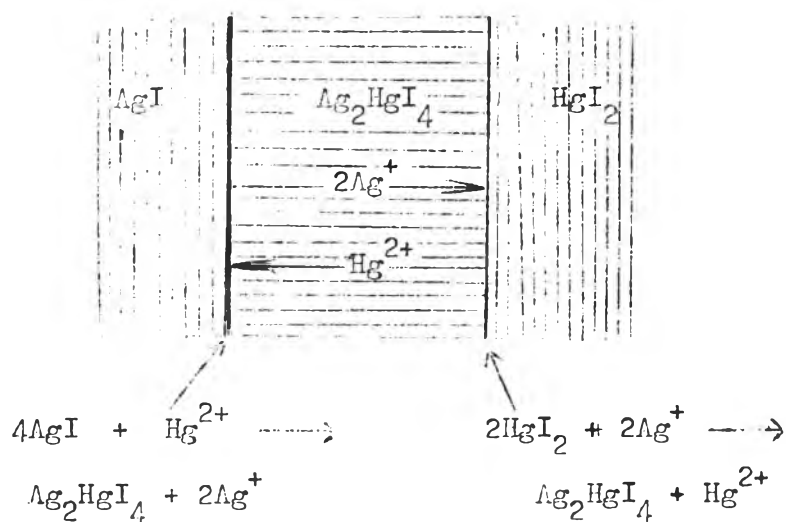$$Ag_2HgI_4 + 2Ag^+ \qquad\qquad Ag_2HgI_4 + Hg^{2+}$$

Fig 2.2   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.

Wagner's theory[13] has been extended to cover also cases in which cations as well as anions are mobile and there is a parallel migration of both cations and anion in the process. An interesting variant is found in reactions when one of reactants is in single crystal form, and the other is a powder; here the crystallinity acts as a marker, for example;

$$Al_2O_3 \text{ (single crystal)} + NiO \text{ (powder)} \longrightarrow NiAl_2O_4 \, .$$
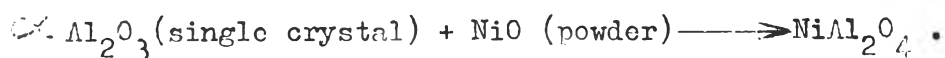
The product phase was formed between the interface of reactants; it was polycrystalline at the side of the powder but was a single crystal at the side of the Al_2O_3, the oxygen sublattices of $NiAl_2O_4$ and Al_2O_3 are different (cubic and hexagonal close packing respectively). Wagner proposed a mechanism for the neccessary rearrangement involving dislocation.

Solid reactions involving only one reactant, and the occurring products are gas and solid phase, are decomposition reactions, such as the decomposition of $CaCO_3(s)$ to $CaO(s)$ and $CO_2(g)$. In this case the reactant decompose thermally at least one gaseous product.
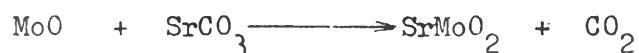
$$A(s) \longrightarrow B(s) + C(g)$$

Although in some cases, B is also a gas, the decomposition can be slow or rapid if in an explosion. In some decompositions the induction period is absent, and the rate is at its essentially maximum from the beginning. The decompositions of lead and silver azides show this behaviour. Induction periods can usually be shortened (or eliminated) by grinding or crushing the solid in order to increase the surface area and produce dislocation, and both factors facilitate nucleation.

More complicated addition reactions involving the decomposition of one reactant are shown in the reactions.

$$ZnO + BaCO_3 \longrightarrow BaZnO_2 + CO_2$$
$$TiO_2 + SrCO_3 \longrightarrow SrTiO_3 + CO_2$$

$$SiO_2 \quad + \quad 2MSO_4 \longrightarrow M_2SiO_4 \quad + \quad 2SO_3$$

$$(\quad M \quad = \quad Ba, \quad Sr \ or \ Ca \quad)$$

$$MoO \quad + \quad SrCO_3 \longrightarrow SrMoO_2 \quad + \quad CO_2$$

Addition reactions which lead to multiple product layers may indicate the stability of various products. For example it has been observed in the formation of Mg_2SiO_4 and $MgSiO_3$ from $MgO + SiO_2$, and Co_2TiO_4, $CoTiO_3$, $CoTi_2O_5$ from $CoO + TiO_2$. The thickness of the individual phase should be proportional to rate constant. In some cases kinetic rather than equilibrium consideration prevails, and expected phases do not occur, this happens upon reaction of CaO and SiO_2.

2) Double decomposition reaction, the other type of solid state reaction are

$$AB \quad + \quad CD \longrightarrow AD \quad + \quad CB.$$

This introduces the additional difficulty, that two instead of one product phase is formed. If it is again assumed that these products are formed between the reacting phases.

There are two possibilities,

2.1 The first one is mentioned by Jost.[9] . Both product phases form a coherent layer. In reaction, where the anions are virtually immobile, the phase with corresponding to anions will be adjacent to the starting one, i.e. it must expect the sequence as shown in Fig.2.3
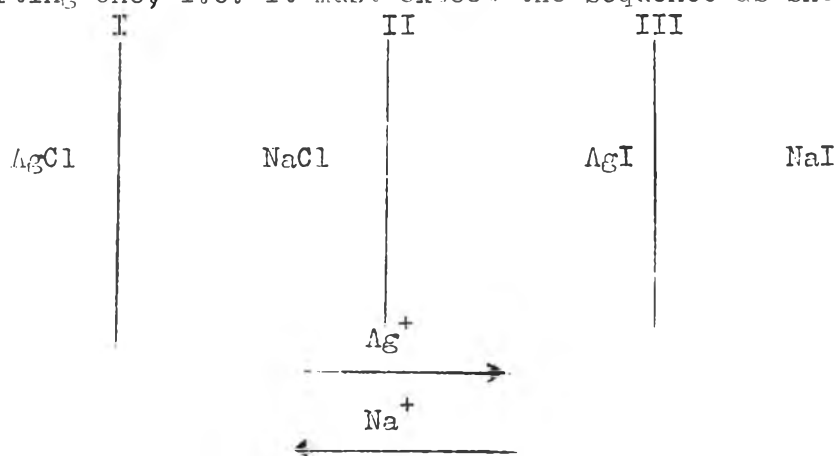

Fig.2.3 Schematic of layer structure for solid-solid reaction

of AgCl and NaI

The cations, moving in opposite directions, they have to migrate through both product phases, causing the prosucts grow at the boundaries I and III. This mechanism was also observed for

$$ZnS + CdO \longrightarrow ZnO + CdS$$

It was found that the layer sequence being ZnS/ CdS/ZnO/CdO.
It indicated that the cations are the mobile species.

2.2 In a second mechanism, proposed by Wagner[13], the two product phases form a mosaic.

$$AgCl + Na^+ \longrightarrow NaCl + Ag$$
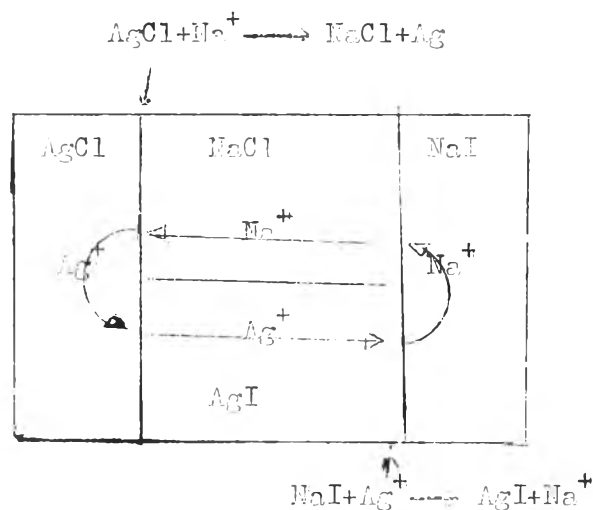

$$NaI + Ag^+ \longrightarrow AgI + Na^+$$

Fig.2.4 Schematic of a solid-state double decomposition reaction, showing ionic motions and reactions at the interfaces.[13]

Each ion has to diffuse through its own compound, i.e, Na^+ must migrate through both of NaI and one of its product, NaCl. In fact it shows the greater rate of this type of process with circular currents which will make it predominant over the multilayer mechanism. Mosaic are formed when the diffusion fronts in the two-layer mechanisms become unstable.

A mosaic mechanism may also occur if one of the product phases is an electronic conductor, i.e, in the reaction between CuCl and AgCl. Now the circular current is made up of ionic current in the CuCl and the AgCl, and an electronic current in the Ag and the Cu.
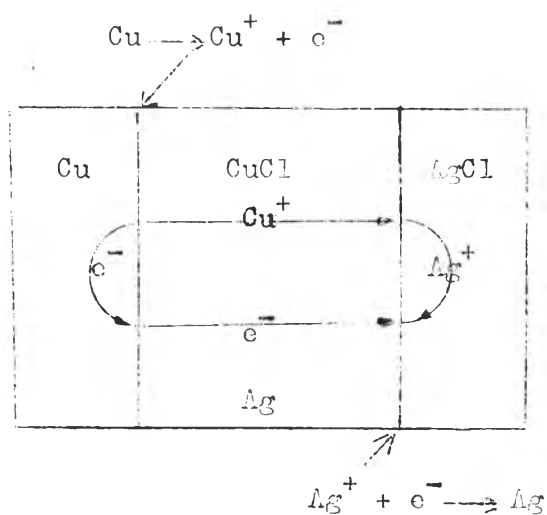
$$Cu \longrightarrow Cu^+ + e^-$$

Cu	CuCl	AgCl

Cu^+

e^-

Ag^+

e

Ag

$$Ag^+ + e^- \longrightarrow Ag$$

Fig 2.5 Schematic of solid-state reaction requiring
flow of electrons through product phases.[14]

The reaction of

$$PbS + CdTe \longrightarrow PbTe + CdS,$$

represented a mixed case, coherent layer and mosaic mechanisms.[15]
The layer-model applying in the initial stage of the reaction, a later
stage giving a mosaic of PbTe + CdS close to the PbS, separated from
the CdTe by a layer of PbTe as shown below

| PbS	CdS + PbTe	PbTe	CdTe
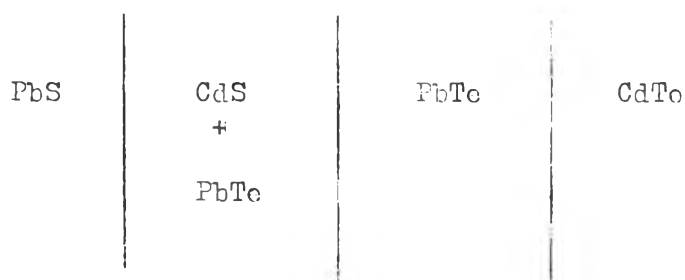
Reaction between solids involving the gas phase

Reaction between solids need not proceed entirely in the
solid phase, the gas phase may play an essential role. It was proved
by Borchardt[16] from calculating the maximum rate of evaporation of
the required reactant e.g. CO_2 from a reacting carbonate, used the
kinetic gas theory and compared with the reaction rate actually
observed.

A mechanism in solid state diffusion as well as vapour
transport plays a part is also possible. Such a mechanism has been
found for reactions

$$Ag_2S + Sb_2S_3 \longrightarrow 2AgSbS_2$$

and

$$Ag_3SbS_3 + Sb_2S_3 \longrightarrow 3AgSbS_2 \ .$$
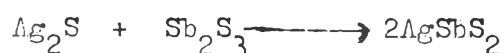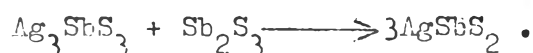
Here the product phase is formed not only between the reacting phases, but also on the other side of the Sb_2S_3 surface not facing to Ag_2S or Ag_3SbS_3. This can be explained by assuming that transport of silver atoms by solid-state diffusion had combined with transport of sulphur through the vapour, it is probable that the transport of silver involves the migration of ions and electrons rather than of atoms. Duckwitz and Schmalzried[13] carried out addition reactions between a single crystal oxide and a volatile oxide which react by the process of a solid spinel phase, when the product layer is still very thin, the reactions are limited by surface effects, in later stage they are diffusion controlled.

If the involving solid phases are not volatile, transport of the anion species via the gas phase will only be appreciable when this species has been added to the gas phase. In that case the reaction mechanism will be dependent on the atmosphere. Schmalzried has observed such an effect for the formation of Co_2TiO_4 from the separated oxides.[13] In an oxygen free atmosphere the product phase grew by migration of the two cation species

$$2CoO + TiO_2 \longrightarrow Co_2TiO_4 \quad (\text{in } N_2)$$
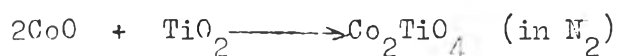
which there was a counter diffusion between Co^{2+} and Ti^{4+}. In the presence of oxygen, parallel diffusion occurred to cobalt, electron through the crystal and oxygen as $O_2(g)$ through the vapour.

$$2CoO + TiO_2 \longrightarrow Co_2TiO_4 \quad (\text{in air}).$$
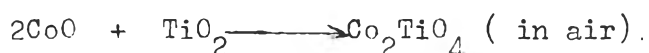
In the mechanism involving two cation species, the
slower one will determine the growth rate. If cation, electron
and gaseous oxygen are involved, the electron transport or the
oxygen transport is not the rate determining, but the slowest
"neccessary" cation diffusion is the rate determining, therefore
the slowest process limits the rate.