Department of Chemistry

Aligarh Muslim University Aligarh

For M.Sc. III Semester

Paper: Solid State Chemistry

Chapter: Solid State Reactions

Solid State Reactions

Solid state reactions are the reactions which occur among solids. Classically it is defined as the reaction where the product is solid and the two reactants must be solid but practically many reactions are categorised as solid state reactions even though both the reactants are not solid. For example, in the rusting of iron which is classified as solid state reaction, it has one of the reactant as solid and the other is gaseous. The study of solid-state reactions has become very significant because many polycrystalline solids can be prepared only by this method. Reaction among solid is not simple and it involves different conditions for the progress of the reaction. The structural studies of the product also involve different techniques.

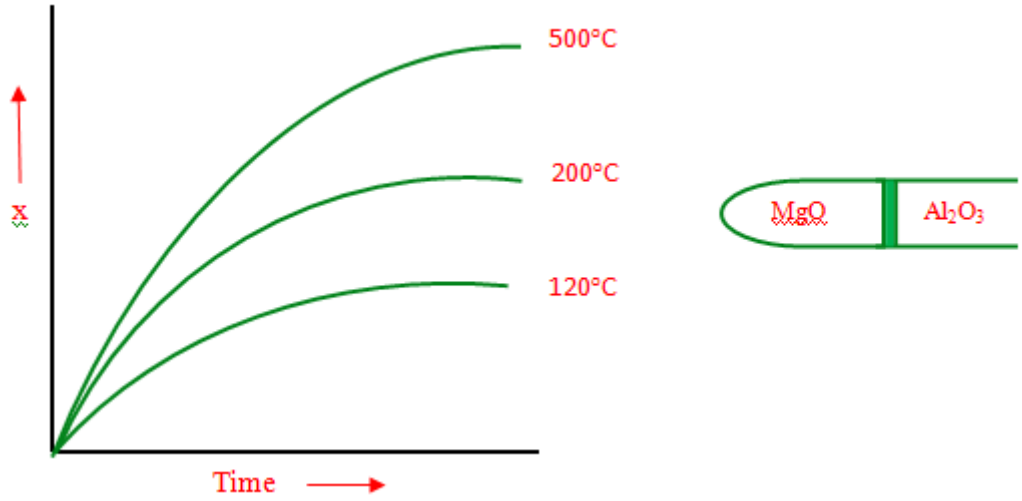
General principle of solid state reactions

Reaction among solids is not very common phenomenon but certain reactions have been found to occur among solids. The study of solid-state reaction has gained importance because of the reason that this is one important procedure for the synthesis of polycrystalline solids. Polycrystalline solids are important for technological advances in material science. Materials of number of properties can be prepared by using solid state reaction method.

Solid state reactions are usually difficult to occur. The reason is that it has a well-defined geometrical spinel structure. So usually these reactions can occur only at high temperature normally above 1000^{o}C. In some cases the reaction can occur also at room temperature but progress of reaction in such cases cannot be monitored unless the temperature is raised to certain optimum value. Like other reactions, the study of solid-state reaction also can be done in terms of thermodynamics and kinetics. In thermodynamics, the spontaneity of solid-state reactions is studied in terms of energy changes whereas in kinetics, the growth of the product is studied with time.

In doing Kinetics, the formation and the growth of the product is monitored with the help of microscope and the growth is plotted against time at different constant temperature. In most of the cases the rate equation is found to follow parabolic Rate Law and applying this rate equation one can determine the rate constant for the reaction and from rate constant, by

plotting against inverse temperature using Arrhenius expression, one can determine the activation energy of the reaction. With the value of activation energy one can understand the rate of reaction as well as the medium of the reaction.



Why solid state reactions are difficult?

Solid state reactions are difficult because of the two important factors

1) Migration of the two species from the two reactants to the interface is difficult process as it has to move across the spinel structure, In this case, MgO and Al_2O_3

2) Further growth of the product at nucleation point become more difficult as now the reactant moving species has to cross the product spinel, in this case $MgAl_2O_4$ which has different spinel structure than both MgO and Al_2O_3

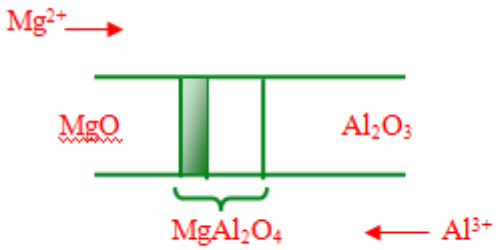
In this reaction, the mobile species are Mg and Al. Mg in MgO is Octahedrally arranged with the oxide ions whereas in Aluminium oxide, it is tetrahedrally structured and in $MgAl_2O_4$ the evidence of both type appear in the spinel and therefore the migration of two mobile species become very difficult and it can occur to substantial level only at very high temperature.

Wagner reaction mechanism

Counter diffusion of cations in solid state reactions and the formation of product at the interface as a result of migration of the magnesium ions and Aluminium ions is popularly known as Wagner reaction mechanism. This is most common reaction mechanism among solid state reactions. For example, in the reaction between MgO and Al_2O_3 in solid state, the magnesium ions move to right side and Aluminium ions move to left side as a result of this migration of counterions, product is formed at the interface between these two reactants.

With the progress of the reaction more and more product is formed at the interface between the two and also two interfaces developed at the right side.

1) Interface between $MgO/ MgAl_2O_4$



$$2Al^{3+} - 3Mg^{2+} + 4MgO \longrightarrow MgAl_2O_4$$

2) At interface of $MgAl_2O_4/ Al_2O_3$

$$3Mg^{2+} - 2Al^{3+} + 4Al_2O_3 \longrightarrow 3MgAl_2O_4$$

Overall rxn

$$4MgO + 4Al_2O_3 \longrightarrow 4MgAl_2O_4$$

By this reaction mechanism the electrochemistry or the electrovalency during the course of the reaction is maintained as for every 3 magnesium ions which are moving to right side, 2 aluminium ions are moving to left hand side. So the charges and mass during the course of reaction is being maintained. This mechanism also explain the observance of product at the interface between the two reactants in the ratio of 1:3 as 1/3 product is formed on one side whereas the 3 proportions is formed on the other side because of the migration of relative amount of magnesium and aluminium to the reaction side. The formation of the product and the growth of product at the interface can be monitored in many solid-state reactions by keeping a marker of the radioactive material or fluorescent material and this is popularly known as Kirkendell effect.