

CHAPTER 1
INTRODUCTION



In general, solid-state chemical reactions which are heterogeneous, differ markedly from homogeneous reaction according to lack of role of solvation. There are several factors, such as impurities, structural effects and irradiation which can affect solid-state chemical reactions.⁽¹⁾ Several possible bulk diffusion mechanism⁽¹⁾ by which the diffusion of atoms in solid might occur, are shown in Fig 1.1 .

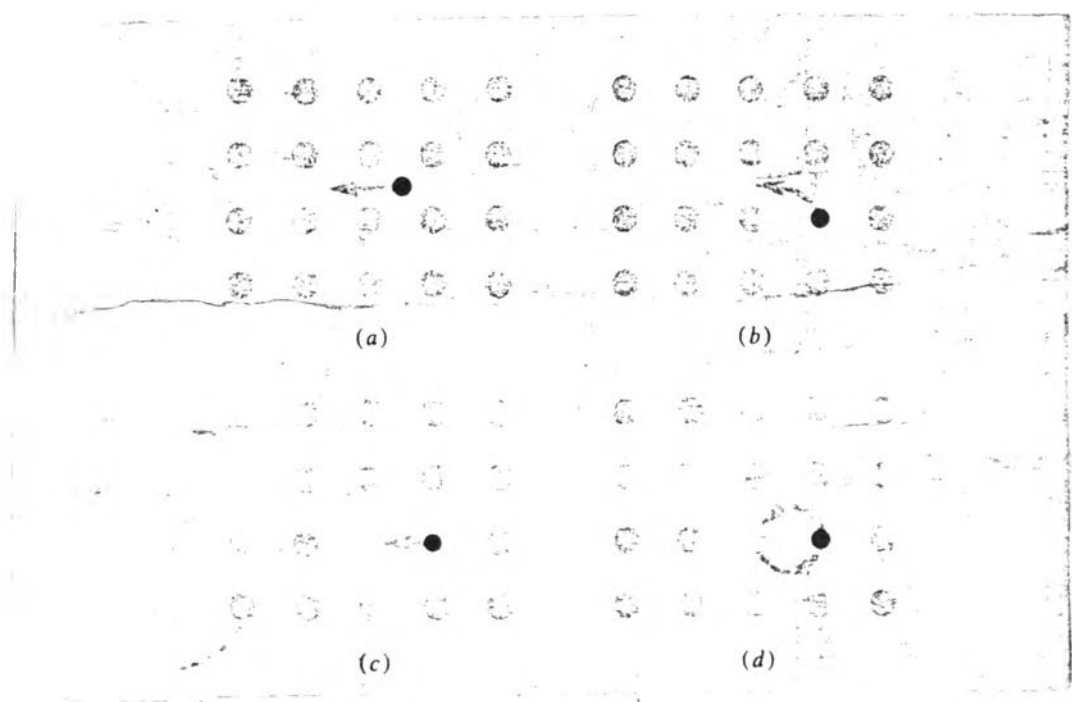


Fig. 1.1 Diffusion mechanism: (a) interstitial, (b) dissociative, (c) vacancy, (d) ring.

The vacancy (c) and interstitial (a) mechanisms are most important, in the latter case, an interstitial atom, whether it is an impurity atom or a displaced atom of the host crystal can move into an adjacent interstitial site. Successive moves result in atomic motions over many lattice distance. A variation of the interstitial mechanism for diffusion, shown in (b), is often called "dissociative diffusion". In this case foreign atoms present in normal substitutional lattice sites migrate via interstitial sites. Certain impurity systems, such as copper in germanium, show this behaviour, the copper can occupy both normal lattice sites and interstitial positions, with an equilibrium governing the distribution between the two kinds of sites. Another defect diffusion mechanism, shown in (c) depends upon the presence of vacancies in the crystal. An atom occupying a normal lattice position adjacent to a vacancy can move into the position of the vacancy, thus effectively interchanging position with it. Successive jumps of this kind result in motion of the vacancy over macroscopic distances. Both impurity and host lattice atoms can diffuse by the vacancy mechanism. In the case of impurities, migration is possible only when the vacancy is adjacent to the site of an impurity atom. Diffusion mechanisms also include another broad class involving atom rotations (d), the cooperative motion of two (or more) atoms can result in a net diffusive motion. The atoms simultaneously interchange their position, when they are alike or reasonably similar in chemical property as in metals or alloys. A simple exchange is possible because the resulting

structure is energetic as the structure before the exchange, and this holds true in these solids for diffusion of either an impurity or host lattice atom.

Whenever the mechanism in the bulk single crystal is vacancy, interstitial or interchange, the high vacancy concentrations and larger-than-normal openings between atoms result in rapid diffusivities. (2)

From the discussions of diffusions in solids, it is clear that impurities can have an important influence on rates of diffusion. Such effects have been observed in the reaction,



The addition of Li to the ZnO reduces the activation energy thus increases the rate of reaction, whereas the addition of Ga raises the activation energy and decreases the rate of reactions. (3) In other similar cases, the effect of the impurities is presumed to be a change in the concentration of lattice defects.

A solid-state reaction system often deviates from idealized case of single-crystal solids. The reactants may be powders, in which the transport of reactants is limited by the contacts between particles or by the vapor phase transport in the regions between particles. In this case, vapor transport is important, and this possibility must be considered. Thus, 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 vapor phase.

On the other hand, if the evaporation is comparable, liberated CO_2 may be involved.

In the addition reaction



the product forms by migration of both cations in the solid product phase, in the absence of gaseous oxygen. When oxygen is present, Co^{2+} migrates through the solid and oxygen is transported through the vapour phase.

Structures also affect solid reactions when the structures of the reactants and/or products are highly imperfect ("active" solids), since the more rapid diffusion accelerates the rates.

Solid-state reactions can also be influenced by irradiation. The function of the radiation in many photochemical reactions is to provide the necessary activation energies to the reactants. However, the displacement of either electrons or atoms from their normal positions in solid leads to bond breaking and deformation. Thus, produces decomposition, degradation, cross-linking, polymerization, etc. Induced reactions in solids are those in polymers. The radiation produces free radicals (and ions), which then react with other monomer molecules to produce larger radicals, those in turn, react further with monomers and thus propagate the chain reaction. When the polymer itself is exposed to radiation, its molecular structure can be modified by further reactions, such as "cross-linking" and chain scission.

Irradiation of a solid may increase the number of vacancies and interstitials, and these influence diffusion rates. Both nucleation and diffusion which can be enhanced by the radiation-produced defects, accelerate a chemical reaction. The thermal decomposition of KMnO_4 is enhanced by pre-irradiation, and the proposed mechanism also involves the production of (cation) vacancies and interstitials.

Reactions and other transformations occurring in the interior of solids have been studied systematically during this recent years. Characteristics of processes of such reactions were first investigated for metals by Tammann.⁽⁴⁾ The diffusion of solid metals into one another was first recognized by Robert Austen⁽⁵⁾ for the interdiffusion of lead and gold. Bruni⁽⁴⁾ proved the occurrence of diffusion in metals; from the decrease in electrical conductivity with mixed crystal formation. The wider study of reactions between solids was first taken up by Hedvall⁽⁵⁾ for the case of non-metallic solids (oxides, salts, etc). Following Hedvall, the course and mechanism of reactions of this type had been investigated by Tammann⁽⁶⁾, W. Jander⁽⁴⁾, Fischbeck⁽⁴⁾. From the knowledge of the structures of solids derived from X-ray crystallography and an understanding of the forces acting between the constituents of the crystal lattice, Smekal⁽⁴⁾, Jost⁽⁷⁾, Wagner⁽⁴⁾ were able to find a rigorous physical basis of the interpretation of the phenomena observed in the reactions of solids. It also became clear that reactions and transformation occurring in

the solid state should pass through intermediate states characterized by high reactivity, such that many substances prepared by solid-state reactions can be obtained in forms of high energy content and high reactivity.⁽³⁾ This theoretical advance is due largely to Wagner.⁽⁴⁾

Processes of diffusion are of fundamental importance for reactions take place in solids. Diffusion causes the progress in solid-solid reaction, as a result of molecular motion without the operation of any external forces. A very general class of chemical processes in solids may be described as "diffusion controlled reactions" because the rate of change of concentrations of the reacting species, starting from some initial distribution of the species in the volume of the solid, is controlled by their rates of diffusion toward each other.

Diffusion is defined quantitatively by Fick's Law⁽¹⁾, which for diffusion along the X coordinate,

$$f = -D \frac{\partial N}{\partial X}$$

where f is the flux of the diffusing species (the number of flowing species across 1 cm^2 per unit time) and $\frac{\partial N}{\partial X}$ is its concentration gradient in the X direction. The proportionality constant D is called the diffusion coefficient, or diffusivity. D has the dimensions of square centimeters per second in c.g.s. unit. The temperature dependence of the diffusion coefficient is of great importance.

This has been found experimentally to be exponential according to the equation

$$D = D_0 e^{-\Delta H/RT}$$

Where ΔH is the "activation energy" for the process, D_0 and R are constants. For the diffusion of carbon in iron, an equation of this form fits well the experimental data as in Fig. 1.2, $\log D$ is plotted against $10^3/T$, a straight line is obtained.

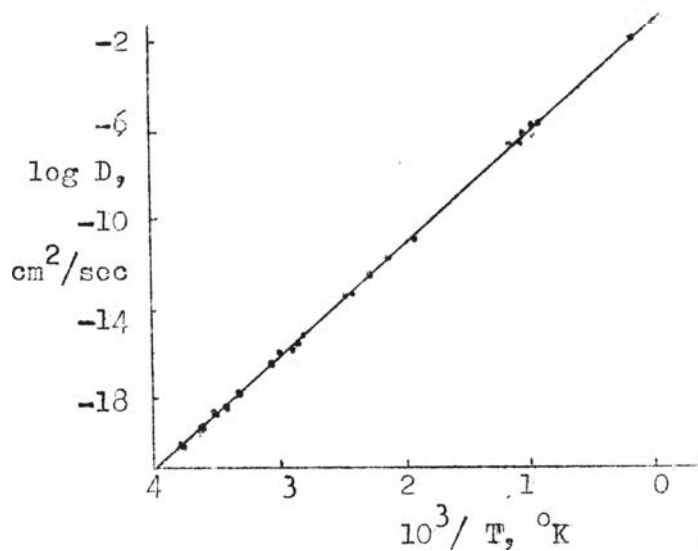


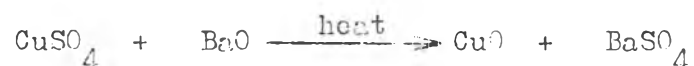
Figure 1.2 Diffusion coefficient of carbon in α -iron ⁽¹⁾

The basis for temperature dependence will now be indicated, by consideration of the atomic motions leading to diffusion.

Diffusion measurements in solids are not easy to perform. Values of D are low in many cases, particularly in the lower range of temperatures, then the experimental methods are tedious. A preferred method is to use radioisotopes as tracer, for either impurity or

self diffusion.

In the reaction,



a mixture of BaO and CuSO_4 was heated, a strongly exothermic process set in at 355 degree Celcius. A rise of the heating curve was obtained by plotting the temperature of the mixture against the time (Fig 1.3), in doing this the mixture was heated steadily.

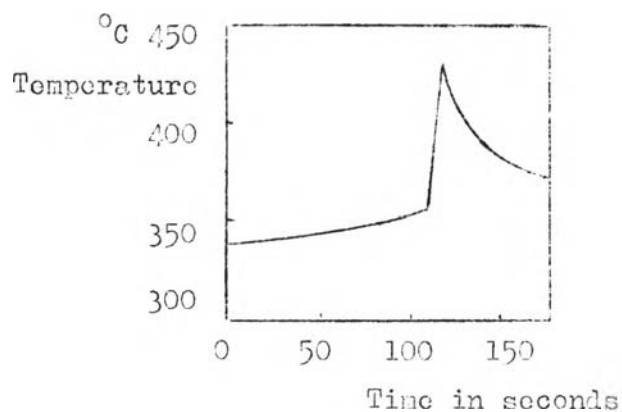


Fig 1.3 Heating curve for $\text{BaO} + \text{CuSO}_4$ (according to Hedvall).⁽⁴⁾

The evolution of heat, which may take place at temperature far below the melting point or decomposition temperature of the constituents of the mixture, represents the heat of reaction. Analytical result after heating proves that reaction has, infact, taken place. It has been proved that reaction is independent upon the

presence of lower-melting and thermal dissociation.⁽⁴⁾ The involved processes are true solid-phase reactions. Reactions occurring in the same way as that cited include those between basic and acidic oxides to form salts or double oxides, reactions between non-volatile acidic oxides and carbonates, the substitution of metals in salts, oxides or sulphides by baser metals, double decompositions between salts (e.g., $\text{BaCO}_3 + \text{CaSO}_4 \longrightarrow \text{BaSO}_4 + \text{CaCO}_3$); and double decompositions between metal oxides and metal sulphides, phosphides, carbides, or silicides. To explain these reactions, it is assumed that, with a rise in temperature the atoms or ions in crystal execute vibrations of continually increasing amplitude about their mean positions. When the amplitudes of these vibrations become great enough, they result in a more or less frequent exchange of positions in the crystal lattice. The place-exchange occurs especially readily in "loosened" or "defective" crystal. Even in completely homogeneous crystals, the lattice defects (interstitial atoms and vacant lattice positions), which are always present to some extent in a state of thermodynamic equilibrium, make it possible for place-exchange to occur. At points where different crystals are in contact, atoms or ions can pass from one crystal to another by place-exchange.⁽⁹⁾ In a powder mixture, place-exchange at the points of contact of chemically dissimilar particles, results in a chemical change, which is then propagated into the interior of the crystal by a continuation of the process from the interface. The propagation of chemical change is necessarily dependent upon the rate at which atoms or ions can migrate into the crystal by place-exchange processes i.e;

on their diffusion rate in the crystal.⁽¹⁰⁾

The rates of reactions in solids are dependent upon the speed of diffusion of atoms or ions through the crystalline particles, therefore, rates of reactions in solids are strongly dependent on the particle size of the powders, the more finely grounded a powder mixture, the more rapidly do reactions proceed.⁽¹¹⁾

In reactions between solids, it is possible for several compounds to be formed between two substances, these products depend not only on the composition of the reactants, but also on the rates of diffusion through the various phases of the ions undergoing exchange, for example in the reaction of CaO and SiO_2 , four compounds with the compositions $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot 2\text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$ can be formed by crystallization. It was shown by W. Jander⁽⁴⁾ that in the solid state the primary product is always the orthosilicate, $2\text{CaO} \cdot \text{SiO}_2$, whatever the mixture is composed of. If SiO_2 is present in excess, the orthosilicate is subsequently converted into the silicate corresponding to their compositions. In a mixture of 1:1 molar ratio, the orthosilicate is first converted to the silicate $3\text{CaO} \cdot 2\text{SiO}_2$ and then the meta-silicate $\text{CaO} \cdot \text{SiO}_2$ is formed, the process of the reaction is described as shown in Fig 1.4

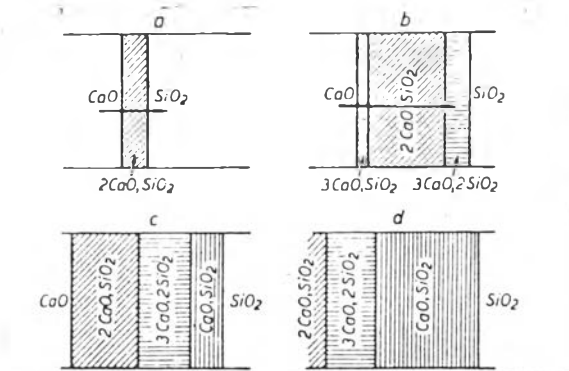


Fig. 1.4 Schematic representation of the course of the reaction between CaO and SiO₂ in the solid state (4)

The present work was interested in solid-solid reactions of the first transition elements, such as, chromium, iron, cobalt and copper compounds at various temperatures, from room temperature up to 150^o C, using colour change during the progressive period as indicator. The starting materials were taken from the laboratory store where these compounds were provided for many analytical purposes of undergraduate study in the Chemistry Department, therefore this work does intend to study solid-solid reactions of these materials for displaying their behaviours when they are mixed together in solid phase, sometimes the chemical or physical properties may be changed in this way. For some interesting reactions as many experimental methods as possible were set up to gain more detail.

From all details which obtained by observing the processes and the number of occurring products, the solid-solid reactions could be divided into one product and more than one product formations. Both types showed one direction growth and two direction growth of progressive products. The second and following products may occur at the interface between the former and one of the reactants, or between two of products interface. The products were collected to further study on their chemistry.

Some pairs of the reactants which do not react at room temperature will be selected to carry out at higher temperatures.

The interesting reactions were selected to obtain the chemically information, such as, mechanism or process of chemical change, the composition of products, the structural change between products and reactants, the conductivity of reactant comparable with product and the conductivity change during progressive period of the reaction.

The mechanism of colour change was carefully studied by taking photograph consecutively through microscope at 100-400 times magnification. The compositions of products were analysed by atomic absorption, X-ray fluorescence techniques and other suitable methods. The structural changes between products and reactants were compared by X-ray powder diffraction patterns and infrared spectra.