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Analysis of Solid-Solid Reactions: A Review

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This paper reviews some important aspects of the analysis of solid-solid reactions which include: fundamental considerations, experimental techniques, analysis of pellet-pellet reactions, analysis of mixed powder reactions, role of the gas phase, and reactor design. Illustrations are given wherever necessary. Examples of industrial applications, important systems studied, and the models used are tabulated.

SCOPE

Solid-solid reactions have usually been the domain of physicists and physical chemists. Thus, considerable basic work on the theory of solid-solid interactions has been reported over the years, particularly in the sixties, as a result of the emergence of solid state devices in preference to the more conventional devices that were used earlier. Even in the chemical industries, solid-solid reactions are known to play an important part, such as in the cement industry, manufacture of ferrites, catalysts, etc. However, solid-solid reactor design has remained a totally empirical art.

Although in recent years a few significant studies have been reported in the literature on solid-solid reaction systems, no comprehensive article has yet appeared which seeks to cover the various aspects of solid-solid reactions, starting from fundamentals to applications, with particular emphasis on the analysis of such reactions. There seems to be little doubt that solid-solid reactions would become increasingly important in the years ahead. It was therefore considered opportune to present a concise picture of solid-solid reactions in the hope that more rational approaches to analysis and design may be thought of.

Accordingly, the present article has been structured to cover the following aspects of solid-solid reactions: fundamental considerations, experimental methods used, analysis of pellet-pellet system, analysis of mixed powder systems, the role of gas phase, and reactor development. A significant feature of the review is that comprehensive tables have been presented with examples to highlight the importance of solid-solid reactions, the types of models used, and the systems for which they have been successfully employed. Although the present state of art does not permit the rational design of reactors, some progress appears to have been made in the modeling and analysis of solid-solid reactions.

CONCLUSIONS AND SIGNIFICANCE

Numerous studies on solid-solid reactions have been reported, but emphasis has essentially been on the diffusional aspects of these reactions. Overall kinetics, whenever studied, have been based on expressions that either involve a number of assumptions or are empirical. Nevertheless, a few significant expressions have been developed, as will be evident from the comprehensive tables presented.

Interest in the thermodynamics of solid-solid reactions is increasing. Better methods have been devised for obtaining the ΔG, ΔH, and ΔS values of a reaction. These are useful in the a priori calculation of rate constants.

More sophisticated experimental techniques, like electron probe microanalysis, have emerged which provide a better and deeper understanding of the progress of a reaction.

In spite of improvements and sophistications in various other processing industries, those involving solid-solid reactions still remain an art. Though much is now known about the diffusional resistances involved, no rational methods of predicting reaction rates based on the simultaneous influence of diffusion and reaction are available. Also, many problems concerned with mixed and contact have remained unsolved. Some of the recent developments using sol-gel processes are significant in this respect.

It would appear from this review that little has been done on the a priori design of reactors for solid-solid reactions, which is an important consideration from the chemical engineering viewpoint. Progress has been made towards the understanding of the basic mechanisms in solid-solid reactions, but attempts to analyze and model these reactions are few. Thus there is need to apply chemical engineering knowledge to arrive at a more rational approach to solid-solid reactions along lines that have become common for other heterogeneous systems such as gas-solid, gas-liquid, etc.

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Solid-solid reactions have been carried out industrially for a long time. In fact, the manufacture of refractories and ceramics, one of the olden arts, utilizes solid-solid reactions extensively. The cement industry also employs solid-solid reactions. The manifold applications of these reactions in the now ever expanding electronics industry is well known. The various areas of application of solid-solid reactions, along with the modes of application, are summarized in Table 1 to highlight the broad spectrum of their utility.

Probably one of the first to realize the importance of solid-solid reactions was Pukall (1914) who prepared a number of compounds which could not be prepared earlier. His work was followed by that of Hedvall (1952). An extensive list of such compounds, along with the raw materials and reaction temperatures, has been presented by Singer and Singer (1971).

Though solid-solid reactions have been practiced for a long time, modeling of these reactions started only recently. Jander (1927) for the first time presented a mathematical analysis of solid-solid reactions. Though it involved a number of assumptions, it had the merit of being the first. Jander's model was modified and developed by a number of workers. A few review articles have also appeared in the literature from time to time (for example, Feigl et al., 1944; Cohn, 1948; Rose, 1961; Parravano, 1962; Yoganarsimhan, 1970; Rastogi, 1970). Some of them are relatively old and consequently do not include the more recent developments, while the others are rather specific and short. The present article is designed to cover most of the significant developments in the field, with its major emphasis on the analysis of these reactions.

Solid state reactions, in general, include reactions in which at least one of the reactants is a solid. Thus, a variety of reactions, gas-solid, solid-solid, decomposition, transformation, etc., are grouped under the title of solid state reactions. Of these, solid-solid reactions include three types of reactions: simple addition, wherein the solid reactants react to give a solid product, for example, formation of ferrites, chromites, aluminates, etc., from the respective parent oxides; addition by elimination where, in addition to the solid product, a gaseous product is involved; and exchange, wherein cations and anions of the reactants are exchanged to give products.

TABLE 1. EXAMPLES OF INDUSTRIAL APPLICATIONS OF SOLID-SOLID REACTIONS

No. 1	Field of application 2	Nature of application/reaction 3	Reference(s) 4
1	Ceramics	Manufacture of ceramic and refractory materials; also small quantities of certain compounds, added to improve the properties, react in the solid state.	Kingery (1967) Singer and Singer (1971)
2	Oxide semiconductors and ferrites	Manufacture (and doping).	Sittig (1970)
3	Cement production	In the dry manufacturing process the components react in the solid state. Typically, in the MO-SiO_2 and MO-Al_2O_3 systems ($M = Ca$, Mg, etc.) a number of product phases are formed and proper conditions are to be chosen to get desired compositions.	Lea (1970)
4	Catalyst preparation	Mixed oxide catalysts, which are known to be very selective, are some times prepared in the solid state.	Naidu et al. (1973) Bleijenberg et al. (1965) Stork and Pott (1974)
5	Metallurgy	(i) Preparation of solid solutions and alloys (ii) Reduction of ores, e.g. iron ore (hematite) by coke.	Ray (1974)
6	Polymer chemistry	(i) Polymerization in the solid state (ii) Preparation of large polymer single crystals.	Voigt-Martin (1974) Baughman (1974)
7	Fertilizers	The compounds react in the solid state during processing, as well as when fed to the soil.	Adhya et al. (1974) Srinivasa et al. (1973) Kutty and Murthy (1974)
8	Drugs	If the adjuvents present in the drugs react with the active ingredients, stability of the drug is affected leading to storage problems.	Tarjanyi et al. (1971)
9	Spacecraft thermal control	Heat sources required in spacecraft most conveniently use solid-solid exothermic reactions.	Riebling (1969)
10	Organic chemistry	Useful in controlling the rate, isomer distribution and steriochemistry of organic compounds, e.g. (i) transcinnamic acid dimerises only in the solid state, (ii) disproportionation reactions (terephthalic acid synthesis)	Pimentel (1958) Cohen and Schmidt (1964) Gokhale et al. (1975)
11	Inorganic pigments	A number of inorganic pigments, such as basic silicate, white lead, lead zinc oxides etc. are prepared by solid-solid reaction. The partial conversions desired in certain cases can be achieved by solid-solid reaction only.	Kirk and Othmer (1968)
12	Inorganic complexes	Preparation of some inorganic complexes, which could not otherwise be prepared.	Gentile and Mao (1965) Gentile and Campisi (1965) Gentile and Shankoff (1965) Gentile et al. (1967) Rastogi and Dube (1967)

The present treatment is restricted mainly to solid-solid addition reactions. We start with fundamental considerations like thermodynamics and diffusion, proceed to analysis, and finally refer to reactor development.

FUNDAMENTAL CONSIDERATIONS

Two approaches can be employed towards the understanding of solid-solid reactions: based on the thermodynamic behavior of the systems, which is more or less a gross approach; and based on molecular energy levels, which has received relatively little attention. Also, a fundamental factor to be considered is diffusion. In a solid-solid reaction, the immobile product layer formed may offer a barrier to the progress of the reaction. It is essential that either or both the reactants should diffuse through this layer as well as through the other reactant and react.

THERMODYNAMIC CONSIDERATIONS

In this section, we shall make a brief reference to certain important aspects of the main thermodynamic parameters as they apply to solid-solid reactions. The use of these parameters in formulating the kinetics will be brought out later.

The free energy change ΔG is expressed as

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

It has been observed that for many solid-solid reaction systems, the entropy contribution to the free energy change of reaction is very small. This is because most of the reactions consist essentially of lattice rearrangements. Obviously, order-disorder changes contribute little to the reaction, so that

$$\Delta G \approx \Delta H \tag{2}$$

This has been conceptually explained by Duncan and Stewart (1967) who applied statistical mechanics to correlate the disorder entropy with the occurrence of the most probable lattice rearrangement. Their calculations of the values of ΔG, ΔH, and ΔS from the experimentally observed rate constants also support this.

Navrotsky and Kleppa (1968) have, in fact, found a constant value of $\Delta H \approx -10$ kcal/mole for all the spinel formation reactions on the basis of the experimental investigations on a variety of systems. Since most of the spinel formation reactions are lattice rearrangements, the difference in lattice energies of the products and reactants should also give the enthalpy of formation. Here again a value of $\Delta H \approx -10$ kcal/mole was obtained by Miller (Navrotsky and Kleppa, 1968). There are also instances where ΔH is considerably different from this value. This has been attributed to the structural differences and the site preference characteristics of cations. These differences also affect the reactivity of compounds (Stone and Tilley, 1965).

Values of different thermodynamic parameters have also been reported by Rastogi et al. (1963) in their studies on a number of organic solid-solid reactions.

An interesting method of calculating thermodynamic parameters, particularly the free energy of formation, is from the emf measurements of a solid cell consisting of the reactants and a solid electrolyte in the form of pellets (Kröger, 1974; Toropov and Barazakovskii, 1966). This method is now widely used for obtaining the free energy values of reactions.

ENERGETICS

The energetics of solid-solid reactions has not so far been studied, a notable exception being the work of Melton (1971) who developed a theory to describe the initiation of chemical reactions in solids.

It is well known that of the four modes of energy, namely, translational, rotational, vibrational, and electronic, a solid (being a rigid body) possesses mainly the vibrational energy. Obviously, the initiation of a reaction in a solid is via the excitation of the vibrational energy levels of the individual molecules. Melton has assumed that lattice vibrations in a solid can be treated as pseudo collisions between the individual molecules in the lattice. Thus, the solid is treated as an ordered dense gas. Chemical reactions in solids are then explained by the collision theory developed for gases. The treatment finally results in the following expression for the rate constant:

$$k = \frac{P_{i \mapsto f}\,\overline{v}}{\sqrt{2}\,bN} \tag{3}$$

As the calculation of the reaction transition probabilities is not possible, the results are of qualitative interest only.

Since in solid-solid reactions the basic problem is that of energy transfer between different modes of vibrations, it may be interesting to study the problem from statistical thermodynamic considerations, wherein vibrational energy and partition functions are defined based on the fundamental properties of the molecules, and the equilibrium constant for a reaction is then defined in terms of partition functions.

DIFFUSION

Diffusion is an important phenomenon in solid-solid reactions. Being slow, it often controls the rates of such reactions. Thus, most of the studies in this area have been centered around the role of diffusion.

In a solid-solid reacting system, two solids react to form a product which separates them. Further reaction progresses through three steps in series: self-diffusion of the reactant species, its diffusion through the product layer, and finally its diffusion and reaction in the other reactant. Thus, three different diffusivities are involved. Again, one-way diffusion or counterdiffusion may be involved in the process.

Often these diffusivities are determined independently of reaction. However, diffusivities under reaction conditions can be quite different owing to differences in structure, defect characteristics, impurity concentrations, etc. An example illustrating this fact is the difference in the diffusivity values reported by Tomás et al. (1969) and by Arrowsmith and Smith (1966) for the system phthalic anhydride + sulphathiazole. The values reported by Arrowsmith and Smith from independent diffusion experiments are of the order of 10^{-7} to 10^{-8} cm^2/s, whereas those reported by Tomás et al. from in situ evaluation during reaction and analyzed by the Serin-Ellickson expression are of the order of 10^{-10} to 10^{-11} cm^2/s. Another factor to be considered is that the product formed between reactant phases may exhibit different structural features on its two different sides. An example of this is provided by the studies of Schmalzried and Rogalla (1963) on the system

$$Al_2O_3 \text{ (single crystal)} + NiO \text{ (powder)} \rightarrow NiAl_2O_4$$

The product phase formed between the reactants was polycrystalline on the nickel oxide side but single crystal on the aluminum oxide side.

In single crystals, the only mode of diffusion is volume or bulk diffusion, predominantly via vacancy mechanism (that is, ionic vacancy gradient acts as a driving force for diffusion). In polycrystalline materials, in addition, other modes of diffusion may also contribute, such as surface diffusion, grain boundary diffusion, etc. Moreover, several other factors affect the diffusion process, for example, sintering of particles on heating, the so-called Kirkendall effect in oxide systems (that is, movement of boundaries due to transport of oxygen in the gas phase), and the electroneutrality condition for ionic diffusion (according to which the charges should always be balanced, (that is, for every positive ion diffusing in one direction, a positive ion should diffuse in the opposite direction or a negative ion in the same direction). The important vacancy mechanism for bulk diffusion depends to a large extent on the particular defect structure and impurity concentration. These various aspects of the phenomenon of diffusion in solids are discussed in detail in a number of books and monographs (for example, Shewmon, 1963; Schmalzried, 1965; Kröger, 1974; Frischat, 1974). Here we present only the salient features germane to our purpose.

Of the different types of diffusivities involved, self-diffusion is unimportant from the viewpoint of solid-solid addition type of reactions. Hence we are concerned with one-way or counterdiffusion of reactant species through the product layer and in the other reactant. The kind of diffusion processes occurring in these are generally referred to as chemical diffusion. Since at least two components are always involved in such cases, two diffusion equations have to be considered. However, often it is sufficient to follow the concentration of only one component explicitly.

For a one-dimensional case, Fick's second law provides the necessary differential equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial l}\left(D\frac{\partial C}{\partial l}\right) \tag{4}$$

For constant D, this reduces to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial l^2} \tag{5}$$

Solutions to Equations (4) and (5) with different boundary conditions have been provided by Crank (1975). In a typical case of diffusion between two solids kept in contact with each other, the initial and boundary conditions are

$$\left.\begin{array}{llll} C(l,t) = 0 & \text{for} \quad l > 0 & \text{and} & t = 0 \\ C(l,t) = C^* & \text{for} \quad l < 0 & \text{and} & t \geq 0 \\ \text{and} \\ \dfrac{dC}{dl} = 0 & \text{for} \quad l \to \pm\infty & \text{and} & t > 0 \end{array}\right\} \tag{6}$$

The solution to Equation (5) with the above initial and boundary conditions is given by

$$C(l,t) = \frac{C^*}{2}\left[l - \text{erf}\left(\frac{1}{2\sqrt{Dt}}\right)\right] \tag{7}$$

If D is concentration dependent, Equation (4) has to be solved. An important method of solution in this case is the Boltzmann-Matano method (see Shewmon, 1963). Accordingly, Equation (4) is transformed into an ordinary differential equation by defining a new variable $\eta = l/\sqrt{t}$ to obtain

$$-\frac{\eta}{2}\frac{dC}{d\eta} = \frac{d}{d\eta}\left(D\frac{dC}{d\eta}\right) \tag{8}$$

Equation (8) can then be solved for appropriate boundary conditions. Thus, for example, boundary conditions (6) will now be

$$\left.\begin{array}{l} C = C^*, \quad \eta = -\infty \\ C = 0\ , \quad \eta = +\infty \end{array}\right\} \tag{9}$$

Integration of Equation (8), substitution for η, and rearrangement of the resulting expression gives

$$D(C) = -\frac{1}{2t}\left(\frac{1}{dC/dl}\right)\int_0^C l\,dC \tag{10}$$

Equation (10) can be used to obtain $D(C)$ by graphical integration and differentiation of the concentration profile $C(l)$. Apple and Pask (1971) have applied this method to the systems nickel oxide-magnesium oxide and nickel oxide-calcium oxide.

Wagner (1969) considered counterdiffusion of cations in the binary systems of the type AX-BX, AX-BX_2, and AO-B_2O_3 and based his analysis on a single component. Thus, in the system AO-B_2O_3, for the counterdiffusion of A^{2+} and B^{3+}, he defined an interdiffusion coefficient $\tilde{D}$ as

$$\tilde{D} = \frac{N_1N_2(v_1 - v_2)}{\partial N_2/\partial l} \tag{11}$$

Considering the ionic fluxes and the molar volumes of respective cations, he arrived at an expression for the interdiffusion coefficient $\tilde{D}$:

$$\tilde{D}(N_2^*) = \frac{(N_2^+ - N_2^-)V_m(N_2^*)}{2t(\partial N_2/\partial l)_{l=l^*}}\left[(1 - Y^*)\int_{-\infty}^{l^*}\frac{Y}{V_m}dl + Y\int_{l^*}^{\infty}\frac{1-Y}{V_m}dl\right] \tag{12}$$

where N_2^* = mole fraction of B^{3+} on the concentration profile at the particular distance l^*; $V_m(N_2^*)$ = molar volume of cations at the particular mole fraction of interest, that is, N_2^*; t = time; $(\partial N_2/\partial l)_{l=l^*}$ = tangent to the profile curve at the particular distance l^*; Y = $(N_2 - N_2^-)$, an auxiliary variable of composition; Y^* = value of Y at $N_2 = N_2^*$; N_2^+ and N_2^- = mole fractions of B^{3+} in B_2O_3 and in AO, respectively. Equation (12) can be used to calculate $\tilde{D}(N_2^*)$ by evaluation of integrals by graphical integration, if concentration profile is plotted in terms of Y/V_m.

Further simplification of Equation (12) is achieved by considering V_m independent of N_2, so that it cancels out, and also using the fact that normally we start with pure components, so that $N_2^- = 0$ and $N_2^+ = 1$, resulting in $Y = N_2$.

This method has been applied to the system MgO-$MgAl_2O_4$ by Whitney II and Stubican (1971) who also correlated the $\tilde{D}$ values thus calculated to the individual self-diffusivities.

Greskovich and Stubican (1970) compared the methods of Boltzmann-Matano and Wagner using the system MgO-Cr_2O_3 and concluded that the latter analysis yields more correct values. This is so because the experimentally observed change in molar volume is not accounted for in the Boltzmann-Matano analysis. Some of the more pertinent results of diffusion studies are discussed later.

EXPERIMENTAL TECHNIQUES

Before we proceed to the analysis of solid-solid reactions, it would be desirable to outline briefly the experimental techniques commonly used in these studies and enumerate the others. Since a number of phases, crystalline or amorphous, may be present simultaneously in such a system, analyzing the extent of reaction and the choice of experimental technique becomes critical.

Chemical Analysis

Chemical methods are most convenient and quick. Hence, whenever possible, such methods are used. The particular method of analysis to be used depends on the system under study, but usually a simple titration is good enough for the purpose (Krishnamurthy et al., 1974; Hlavac, 1961; Tomas et al., 1969; Ramachandran et al., 1974).

Thermal Analysis

In solid-solid addition reactions, no weight changes are involved, but the reactions are normally exothermic; hence differential thermal analysis (DTA) is a possible method (Ishii et al., 1977). The drawbacks of solid systems are low heat conductivity of solids, possibility thereby of presence of temperature gradients, difference in heat capacities, and heat transfer coefficients of reference and sample, etc., which could partly be rectified by choosing small sample size, dynamic atmosphere, and product of reaction itself for the reference. (For details of thermal analysis techniques see Wendlandt, 1974.)

For reactions involving weight changes, thermogravimetric analysis (TGA) offers a useful tool, particularly for addition by elimination type of reactions where one of the products is a gas (Hulbert and Klawitter, 1967).

Pressure/Volume Measurements

When gaseous products are formed in the reaction, the kinetics can be followed by measuring volume or pressure changes as a function of time. Typical examples of such studies are:

$$Ag_2SO_4 + CaO \rightarrow CaSO_4 + 2\,Ag + \frac{1}{2}O_2$$

(McCartney et al., 1961)

$$BaCO_3 + BaTiO_3 \rightarrow Ba_2TiO_4 + CO_2$$

(Rieman and Daniels, 1957)

However, when reaction involves more than one step (consecutive reactions), this procedure would not be useful for obvious reasons.

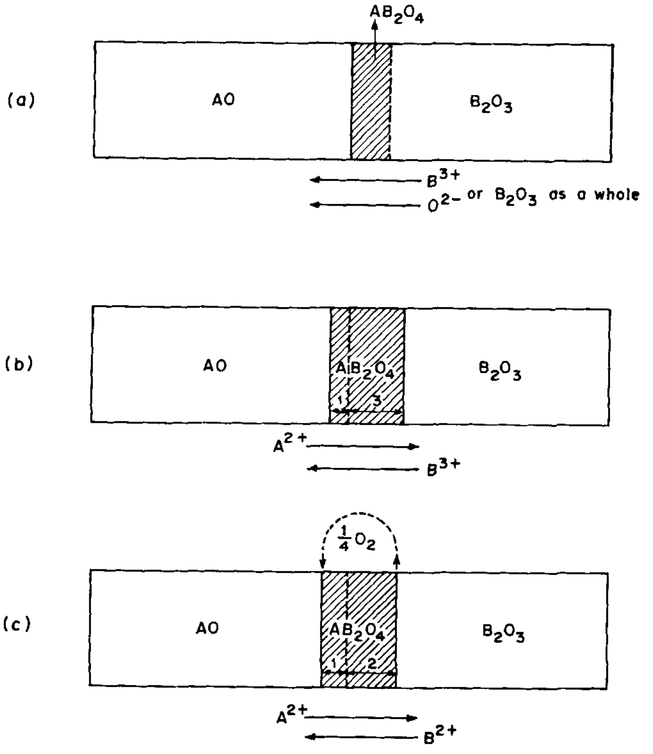


Fig. 1. Different modes of diffusion.

Visual Techniques

When a colored product is formed, the course of reaction can be followed by measuring the product layer thickness by optical methods (Rastogi et al., 1962). But certain factors restrict its use, for example, owing to surface or vapor phase diffusion, product might form only on the surface, and the measurement of total reaction would be erroneous. Also, in systems in which thicknesses are of the order of a few hundred microns, visual or microscopic measurements would not be possible.

Electron Microprobe Analysis (EPMA)

The relatively recent EPMA technique is very precise and probably the most useful in solid-solid reaction studies. So far small concentrations were difficult to analyze; also, concentration changes over a very small length were impossible to determine. Both these problems have been overcome by this method. The details of the technique are described in analytical monographs (for example, Birks, 1963).

Apart from the methods described above, a variety of other methods can be used, depending on the particular system under investigation. These include magnetic susceptibility (Szabo et al., 1961), electrical conductivity (Copp et al., 1966; Brandley and Green, 1967; Deren and Haber, 1966), X-ray analysis (Klug and Alexander, 1974), IR, NMR, mass spectroscopy, reflectance spectroscopy, etc. Newer techniques like low energy electron diffraction (LEED), electron spectrometric chemical analysis (ESCA), and X-ray electron photospectroscopy are coming up.

ANALYSIS OF PELLET-PELLET REACTIONS

In practice, most solid-solid reaction systems involve mixed powders. As such, it is important to elucidate the role of various factors in a mixed powder system. However, the processes occurring in a mixed powder system are often complex owing to factors like undefined geometry, particle size distribution, sintering, etc. Hence, it is logical first to isolate the various factors to the extent possible, study them independently, and then investigate the combined effects of these in an actual mixed powder system.

The first step towards this is to study reactions among pellets by which some of the complicating factors are eliminated, and the rest can be clearly identified and studied (namely, diffusion, sintering). Studies in pellet-pellet systems are mainly aimed at elucidating the transport mechanisms in detail and gaining insight into the phenomenon of coupled diffusion and reaction. The second aspect, which is essentially concerned with reaction modeling and is important from the engineering point of view, has received relatively little attention. The treatment of pellet-pellet reactions will therefore include the following: role of diffusion, reaction modeling, and sintering. In addition, multiphase product formation in such systems will be discussed.

The Role of Diffusion

In a pellet-pellet system, once the product layer has formed by the phase boundary processes, for the reaction to proceed one or both of the reactants must diffuse through this product layer and react. Depending on whether the diffusion is one sided or counterdiffusion is involved, product growth will occur on only one side or both sides of the original interface. In systems in which ionic diffusion occurs, the condition of electroneutrality restricts the diffusion process and consequently the product growth on the two sides of the original interface. For example, in oxide systems which are often encountered in practice, different situations can be encountered as represented in Figure 1. Consequently, the

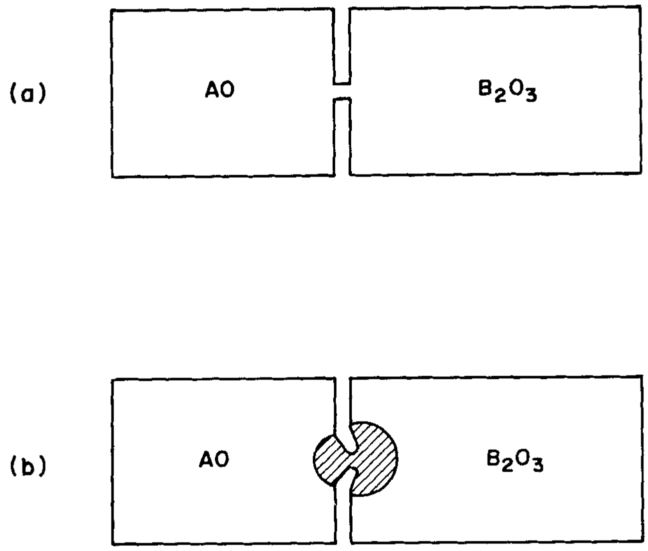


Fig. 2. Uneven swelling due to counter diffusion (Kooy, 1965). Reproduced from *Proceedings Fifth International Symposium Reactivity of Solids, Munich, 1964,* Elsevier Scientific Publishing Co., New York, p. 21 (1965).

product growth on the two sides of the original interface will be in the ratio 1:3 in case (b) and 1:2 in case (c).

A number of systems have been studied to investigate the mode of diffusion. Most of them make use of the marker experiments to follow the interface movement. The markers used are normally inert platinum wires which are originally placed at the interface. But, as pointed out correctly by Pettit et al. (1966), these markers may not be really inert in high temperature studies. Also, slippage and breakage of markers may take place owing to the uneven stresses developed at the interface. Hence, it has been suggested (Yamaguchi and Tokuda, 1967) that texture composition, which is found to be different in the two parts in case of counterdiffusion, can serve as a natural marker. Further, because of faster diffusion of one of the cations, vacancies are created which are visible under a microscope as pores. This layer of pores can be treated as a marker (Carter, 1961*a*; Hardel, 1972). Kooy (1965) has suggested a method of restricted contact so that, depending on diffusion rates, uneven product growth as well as swelling and contraction on two sides can be observed (see Figure 2). The procedure is useful in examining the Kirkendall effect.

Reaction Models

A system in the pellet-pellet form is also attractive from the viewpoint of mathematical analysis of coupled diffusion and reaction, more so because it retains the structures and concentration profiles in a clearly distinguishable pattern after the reaction is quenched.

Several approaches to the modeling of pellet-pellet reactions have been reported, starting from considerations of such purely fundamental properties of ions as charge, mobility, chemical potential of ions, etc., to a mathematical approach similar to that employed in other heterogeneous systems in chemical engineering. In view of their importance in solid-solid reactions, they are briefly discussed below.

Models Based on Diffusion in the Product Zone

Parabolic rate law model. Earlier studies mainly used the parabolic law of Tammann (1920) to follow the overall rate of reaction. According to this law, the square of the product zone thickness is directly proportional to time:

$$(\Delta l)^2 = kt \tag{13}$$

The expression is essentially an empirical one and is based on the assumption that diffusion of the reacting species through the product layer is the controlling step, so that

$$\frac{d(\Delta l)}{dt} = \frac{KD}{\Delta l} \tag{14}$$

Integration of the above expression yields Equation (13), the parabolic rate law, where k is the overall rate constant.

Because of the simplicity of the expression, and the easily obtainable product layer thickness (PLT) values, the parabolic rate law has been in use for a long time. In a number of studies, parabolic rate constants have been obtained and hence the activation energies and the thermodynamic parameters. Typical examples of PLT studies are presented in Table 2.

Rastogi et al. (1970), in their studies on a number of organic solid-solid reactions, used the modified form of the parabolic rate law given by

$$(\Delta l)^2 = 2k_i t \exp(-q\Delta l) \tag{15}$$

TABLE 2. EXAMPLES OF SYSTEMS FOR WHICH THE KINETICS HAVE BEEN STUDIED BY PELLET-PELLET EXPERIMENTS

No.	System	Rate law	Reference
1	2	3	4
1	$NiO\text{-}Al_2O_3$	$(\Delta l)^2 = kt$	Pettit et al. (1966)
2	$NiO\text{-}Al_2O_3$	$(\Delta l)^2 = kt$	Minford and Stubican (1974)
3	$NiO\text{-}Cr_2O_3$	$(\Delta l)^2 = kt$	Greskovich (1970)
4	$MgO\text{-}Cr_2O_3$	$(\Delta l)^2 = kt$	Greskovich and Stubican (1969, 1970)
5	$MgO\text{-}Al_2O_3$	$(\Delta l)^2 = kt$	Whitney and Stubican (1971)
6	AgI-TlI	$(\Delta l)^2 = kt$	Flor et al. (1975)
7	AgI-[K, Rb]I Initial: Later:	$\Delta l = kt$ $(\Delta l)^2 = kt$	Brandley and Greene (1967)
8	$Hg_2Cl_2\text{-}I_2$ $Hg_2Br_2\text{-}I_2$ $Hg_2I_2\text{-}I_2$	$(\Delta l)^2 = 2\,kt \exp[-q\,\Delta l]$ $(\Delta l)^2 = kt$	Rastogi and Dube (1967)
9	Picric acid with hydrocarbons	$(\Delta l)^2 = 2\,kt \exp[-q\,\Delta l]$	Rastogi et al. (1963)
10	Picric acid with naphthols	$(\Delta l)^2 = 2\,kt \exp[-q\,\Delta l]$	Rastogi and Singh (1966)
11	p-dimethylaminobenzaldehyde-diphenylamine hydrochloride	$(\Delta l)^3 = kt$	Qureshi et al. (1975)

As such, the expression is an empirical one, but theoretical justification based on probabilistic considerations has been provided by Rastogi and Singh (1966). This equation was first reported by Cohn (1948), who modified the parabolic rate law considering the effect of exothermicity on the reaction rate.

Wagner model. A rigorous model, considering diffusion in the product layer as the controlling step, is due to Wagner (1936). In his treatment, Wagner considered only the counterdiffusion of cations in the product layer. The rate of consumption of reactants was equated to the diffusional flux, the expression for which was derived considering the fundamental properties of ions, such as charge, mobility, chemical potential, etc. Thus, for the reaction scheme

$$\mathrm{AX} + \mathrm{BX} \rightarrow \mathrm{ABX_2}$$

the diffusional flux is given by

$$j_{\mathrm{total}} = -\int_{I}^{II} \frac{C_A + C_B}{1 + \dfrac{z'_B C_B v_B}{z'_A C_A v_A}} \frac{z'_B}{\Delta l} v_B C_B d\mu_o(AX) \tag{16}$$

where $\mu_o(AX)$ is the chemical potential, and I and II indicate the boundaries of the product layer. Koch and Wagner (1936) applied this theory to obtain the reaction rate constant k using the expression

$$k = j_{\mathrm{total}} \Delta l \tag{17}$$

This value of k was found to be in good agreement with the experimental value. However, certain observations were not explained by the theory.

Schmalzried model. Schmalzried (1962, 1965) further developed Wagner's theory, considering all the three possible mechanisms of diffusion for the reaction

$$AO + B_2O_3 \rightarrow AB_2O_4$$

He defined the flux for an i^{th} species as

$$j_i = -\frac{C_i D_i}{RT} \operatorname{grad} \eta_i \tag{18}$$

Integrating the flux equation over the product layer thickness and assuming parabolic rate law, we obtain an expression for the rate constant k:

$$k = \frac{\nu z'_i C_i D_i}{m_o \Delta G^o{}_{AB_2O_4}} \left[1 - \exp \frac{m_o \Delta G^o{}_{AB_2O_4}}{RT} \right] \Delta V \tag{19}$$

where $\Delta G^o{}_{AB_2O_4}$ is the Gibbs energy of formation for AB_2O_4.

Models Based on the Reaction Zone Concept

Schmalzried model. As can be inferred from the above discussion, much attention has been given so far to diffusion in the product zone. The interactions taking place at the phase boundaries have been relatively neglected. Schmalzried first recognized this fact and in a recent article (1974) has considered the phase boundary reactions in some detail. Accordingly, in the reaction $AO + B_2O_3 \rightarrow AB_2O_4$, a zone is expected to form within AO near the boundary, which is supersaturated with respect to B_2O_3. The product AB_2O_4 is formed in this zone by a cation rearrangement. The relaxation time τ, that is, the time necessary for the cation to rearrange into product phases, can be measured by optical spectroscopy.

The advancement of the phase boundary is then a function of the mobility of B ions in AO and τ. Thus,

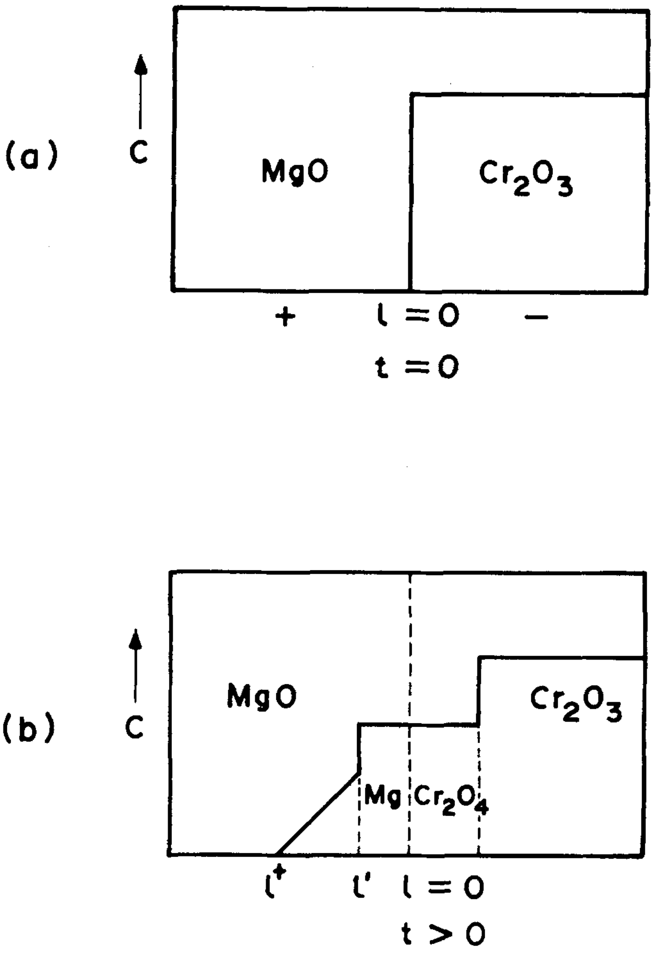


Fig. 3. Schematic representation of concentration profiles (Greskovich and Stubican, 1969). Reproduced from *J., Phys. Chem. Solids,* 30, 909 (1969).

$$\frac{d(\Delta l)}{dt} = f[D_B{}^{(AO)}, \tau] \tag{20}$$

As zero$^{\mathrm{th}}$ approximation, it is set to be

$$\frac{d(\Delta l)}{dt} = \frac{\bar{x} \Delta l_r}{\tau} \tag{21}$$

where Δl_r, the reaction zone thickness, is given by

$$\Delta l_r = [2 D_B{}^{(AO)} \tau]^{1/2} \tag{22}$$

$\bar{x}$ is a numerical factor indicating the fraction transformed into the product in time τ.

Greskovich-Stubican model. The existence of a reaction zone has been experimentally observed using EPMA technique in a number of studies. Thus, Grekovich and Stubican (1969) studied the system MgO − Cr_2O_3 and obtained concentration profiles of Cr^{3+} in magnesium oxide using EPMA techniques. A zone was found to have formed owing to diffusion of Cr^{3+} cations into magnesium oxide with the accompanying formation of $MgCr_2O_4$. The problem has been analyzed by considering diffusivity to be proportional to the concentration and then solving Fick's second law for nonstationary, one-dimensional diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial l} \left(D_o \frac{C}{C_o} \frac{\partial C}{\partial l} \right) \tag{23}$$

With reference to Figure 3, the initial and boundary conditions used are

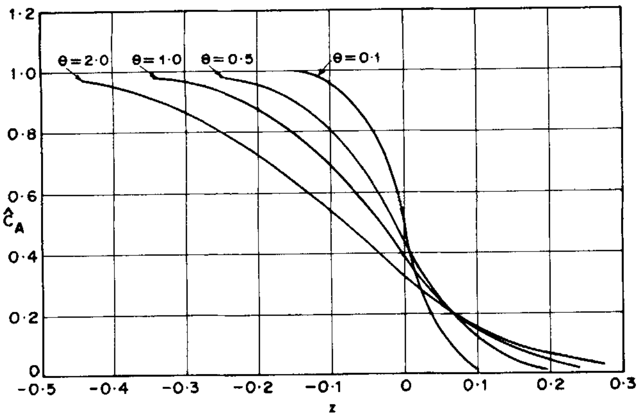
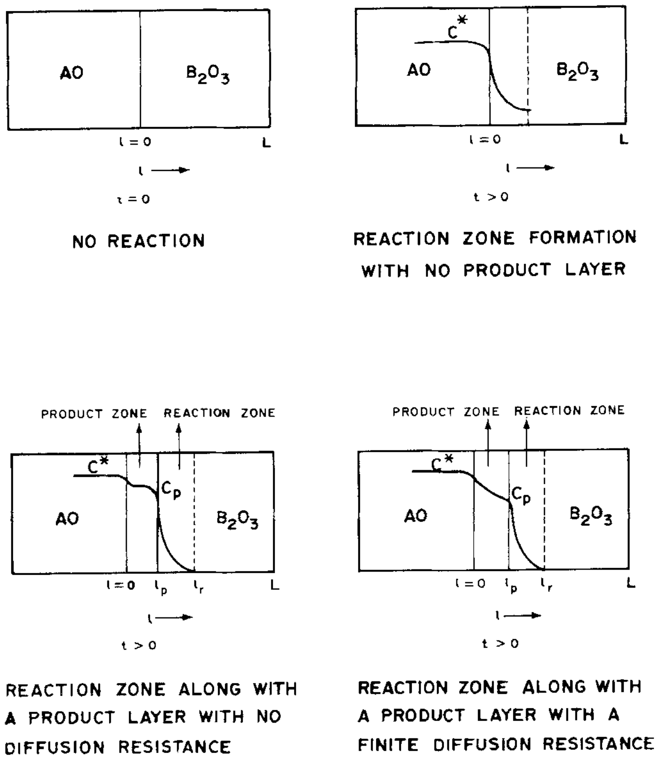


Fig. 4. Variation of C_A with z and θ′ for $C_{Ao} = C_{Bo}$ (Arrowsmith and Smith, 1966). Reproduced from *Ind., Eng., Chem., Fundamentals* 5, 327 (1966).



NO REACTION

REACTION ZONE FORMATION WITH NO PRODUCT LAYER

REACTION ZONE ALONG WITH A PRODUCT LAYER WITH NO DIFFUSION RESISTANCE

REACTION ZONE ALONG WITH A PRODUCT LAYER WITH A FINITE DIFFUSION RESISTANCE

Fig. 5. Stages in the reaction between the solids AO and B_2O_3 in the reaction zone model (Tamhankar and Doraiswamy, 1978).

$$\left.\begin{array}{lll} C = o & x > o, & t = o \\ C = C' & l = l', & t > o \\ C = o & l = l^+, & t > o \end{array}\right\} \quad (24)$$

and

The final expression obtained is

$$C/C' = [1.23]^2 l^+ [l^+ - l']/4\tilde{D}t \quad (25)$$

and hence

$$\tilde{D} = [1.23]^2 l^+ [l^+ - l']/4t \quad (26)$$

From observed values of l' and l^+, $\tilde{D}$ values were calculated and compared with those obtained by using Equation (12) discussed earlier. The chief drawback of this analysis appears to be that there is no term for reaction in Equation (23). However, the authors justify this (indirectly) by assuming diffusion control in the reaction zone.

Arrowsmith-Smith model. Arrowsmith and Smith (1966) attempted an analysis in which they considered simultaneous diffusion and reaction in an organic pellet-pellet system. In their analysis, an irreversible second-order reaction was assumed [$A + B \rightarrow C$]. Mass balances have been written in the form

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial l^2} - kC_AC_B \quad (27)$$

and

$$\frac{\partial C_B}{\partial t} = D\frac{\partial^2 C_B}{\partial l^2} - kC_AC_B \quad (28)$$

with the initial and boundary conditions

$$\left.\begin{array}{lll} C_A = C_{Ao}, & C_B = C_C = 0, & l < 0 \\ C_A = C_C = 0, & C_B = C_{Bo}, & l > 0 \end{array}\right\} \quad (29)$$

$$\left.\begin{array}{lll} C_A = C_{Ao}, & C_B = C_C = 0, & l = -\infty \\ C_A = C_C = 0, & C_B = C_{Bo}, & l = +\infty \end{array}\right\} \quad (30)$$

The density was assumed constant, so that

$$\rho = C_AM_A = C_BM_B = C_CM_C \quad (31)$$

The nonlinear Equations (27) and (28) were then converted into dimensionless form and solved numerically. Thus

$$\hat{C}(= C/C_{Ao}) \text{ vs } \phi'(= l\sqrt{C_{Ao}k/D})$$

plots were prepared for different values of $\theta'(= C_{Ao}kt)$; a typical plot is reproduced in Figure 4 for $\theta' = 0.1$, 0.5, 1.0, and 2.0. From these plots and the diffusivity values determined independently, rate constants were evaluated.

Tamhankar-Doraiswamy model. More recently, Tamhankar and Doraiswamy (1978) have developed a model in which two separate zones, namely, product zone and reaction zone, have been considered. The reaction considered is of the type

$$AO + B_2O_3 \rightarrow AB_2O_4$$

The course of the reaction following the concentration of one of the species, say B^{3+}, can be represented as shown in Figure 5.

Mass balance equations for the two zones have been solved considering effective diffusivity values. In the product zone, only diffusional resistance is encountered, whereas in the reaction zone, diffusion with reaction has to be considered. Thus, in the product zone the differential equation

$$\frac{\partial C}{\partial t} = D_p\frac{\partial^2 C}{\partial l^2} \quad (32)$$

has been solved by the method of Danckwerts (1950) for moving boundary problems. In the reaction zone, steady state has been assumed for simplicity; hence, the differential equation

$$D_r\frac{\partial^2 C}{\partial l^2} - kC = o \quad (33)$$

has been solved considering a finite reaction zone thickness. The expression for the concentration profile in the reaction zone (in the dimensionless form) is given by

$$\acute{C} = \frac{\hat{C}_p \sinh [\phi_r(z_r - z)]}{\sinh (\phi_r\Delta z)} \quad (34)$$

where $\phi_r(= L\sqrt{K/D_r})$ is the Thiele modulus.

An interesting result of the analysis is the expression for the reaction zone thickness Δz in terms of the Thiele modulus ϕ_r; namely

$$\Delta z = \frac{1}{\phi_r} \ln \left(\phi_r + \sqrt{\phi_r^2 + 1}\right) \tag{35}$$

This is similar to the one obtained by Mantri et al. (1976) in the analysis of gas-solid noncatalytic reactions. Equations (34) and (35) can be used to predict concentration profiles in the reaction zone.

The model has been verified using some of the EPMA results reported in the literature. A typical comparison of theoretical and experimental concentration profiles in the reaction zone is presented in Figure 6, from which good agreement between the two may be observed. The model has been further extended to a general n^{th}-order reaction.

Comments

As is evident from the above, several models have been proposed for pellet-pellet systems. The more fundamental models of Wagner and Schmalzried cannot be used in engineering practice, while the parabolic rate law models are too empirical to be used with conviction. It would therefore appear that the models of Arrowsmith and Smith and Tamhankar and Doraiswamy are at present the most suitable ones from the engineering point of view.

Sintering

Sintering is a phenomenon in which a neck is formed between particles at the contact, and the neck grows owing to material transfer by various mechanisms. The phenomenon is an extensively studied one, and mathematical expressions have been developed (for example, Kuczynski, 1971). However, we restrict our discussion here to some of the results as they apply to solid-solid reactions.

As mentioned above, in pellet-pellet systems an idealized geometry is achieved, and many complicating factors are eliminated. Since real mixed powder systems are congregates of particles of different sizes and shapes, one step ahead would be to take known but different shapes and study interactions amongst them. Kuczynski (1965) carried out model experiments on the systems nickel oxide-ferric oxide and magnesium oxide-ferric oxide by keeping spheres of one component in contact with plates of the other. The shapes of the necks and their large radii of curvature suggested that the growth was not controlled by vacancy gradient due to surface tension, as is normally the case with unicomponent systems. Also, the neck radius was found to increase roughly proportionally to $(\text{time})^{1/2}$ rather than to $(\text{time})^{1/5}$ as is observed for a pure sintering process. The square root relationship is in accord with the well-known parabolic rate law observed for spinel growth (discussed previously). Thus, physical sintering and sintering with reaction were distinguished. The detailed mechanism has been described by Kuczynski (1971) and Kooy (1965).

Multiphase Product Growth

Our treatment so far has been restricted to a single product phase. In certain industrial systems such as silicates, and some aluminates, which are important components of cement, more than one product phase appears. Titanates which are important in semiconductor materials also exhibit multiphase product formation.

In spite of its importance, this aspect of solid-solid reactions has received scant attention. There have, however, been a few sporadic attempts to study these reactions experimentally. One possible reason for the lack of any theoretical analysis is the complexity of the mathematics involved. In the few studies reported, the simple parabolic law has mostly been used.

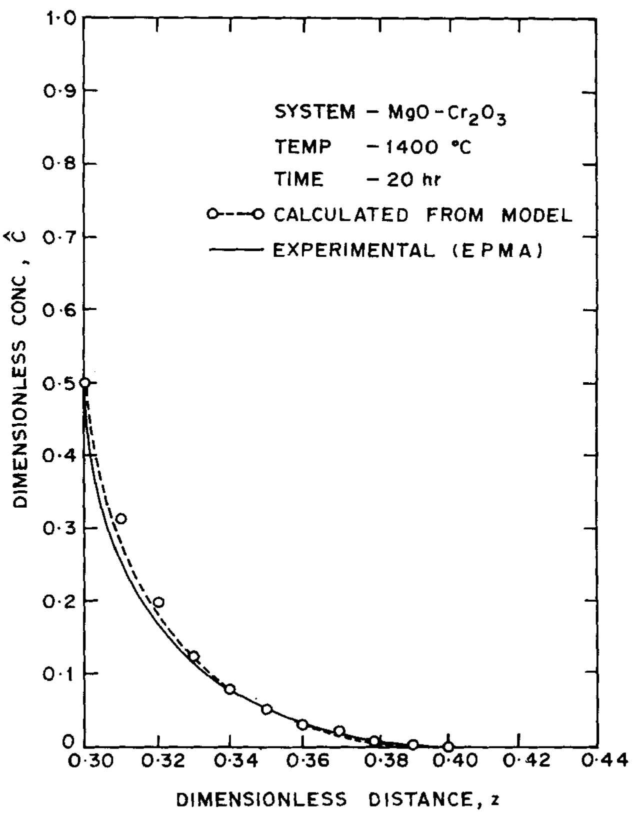


Fig. 6. Comparison of the theoretical profile calculated from the zone model with the experimental profile reported (Tamhankar and Doraiswamy, 1978).

Kohatsu and Brindley (1968) and Brindley and Hayami (1965) have reported pellet-pellet experiments with the systems calcium oxide-α-aluminum oxide and magnesium oxide-silica, respectively. The following sequence of phases was observed in the product layer (for the former)

$$C/C_3A/C_{12}A_7 \quad \text{or} \quad C_{12}A_7H/CA/CA_2/CA_6/A$$

where

$$C = \text{CaO} \quad \text{and} \quad A = \text{Al}_2\text{O}_3$$

The thicknesses of different phases were measured, and corresponding rate constants were calculated applying the parabolic rate law to the growth of each phase. Phases were identified using X-ray and EPMA techniques. Thus

$$\frac{d(\Delta l)}{dt} = \frac{k}{\Delta l} \tag{36}$$

or

$$(\Delta l)^2 = kt \tag{37}$$

where

$$k = \frac{A}{V} \frac{a'b'}{a' + b'} \frac{\Delta\mu}{RT} \tag{38}$$

$$\underset{\text{(for cation)}}{a' = z'_k C_k D_k} \quad \text{and} \quad \underset{\text{(for anion)}}{b' = z'_X C_X D_X}$$

$\Delta\mu$ = the difference in chemical potentials across the product layer. When diffusion of only one kind of ion dominates, $(a'b'/a' + b')$ can be approximated to $z'CD$ for the slow moving ion.

Different rates were observed for different phases (in a given system). These rates were correlated to the melting point and oxygen packing density of the corresponding

TABLE 3. MODELS FOR MIXED POWDER REACTIONS

No.	Reaction model	Mathematical expression	Reference (s)
1	2	3	4
1	Product layer diffusion control:		
	(i) Jander	$kt = [1 - (1 - x)^{1/3}]^2$	Jander (1927)
	(ii) Serin-Ellickson	$(1 - x) = \frac{6}{\pi^2} \sum_{n\,\mathrm{odd}} \left(\frac{1}{n^2}\right) \exp\,(-n^2\pi^2 Dt/r^2)$	Serin and Ellickson (1941)
	(iii) Kroger-Ziegler	$k \ln t = [1 - (1 - x)^{1/3}]^2$	Kroger and Ziegler (1954)
	(iv) Zhuravlev-Lesokhin-Temple'man	$kt = \left[\frac{1}{(1 - x)^{1/3}} - 1\right]^2$	Zuravlev et al. (1948)
	(v) Ginstling-Brounstein	$kt = 1 - 2/3x - (1 - x)^{2/3}$	Ginstling and Brounstein (1950)
	(vi) Dunwald-Wagner	$kt = \frac{6}{\ln \pi^2 (1 - x)}$	Dunwald and Wagner (1934)
	(vii) Valensi-Carter	$kt = \frac{Z - [1 + (Z - 1)x]^{2/3} - (Z - 1)(1 - x)^{2/3}}{(Z - 1)}$	Valensi (1936) Carter (1961*b*)
2	Nuclei growth control	$(kt)^m = -\ln (1 - x)$	Avrami (1939, 1940, 1941)
3	Phase boundary reaction control:		
	(i) Sphere reacting from the surface inwards	$kt = 1 - (1 - x)^{1/3}$	Jach (1963)
	(ii) Circular disk reacting from edge inwards or a cylinder	$kt = 1 - (1 - x)^{1/2}$	Jach (1963)
	(iii) Contracting cube	$x = 8k^3t^3 - 12k^2t^2 + 6kt$	Sharp et al. (1966)
4	Based on the concept of an order of reaction	$kt = \frac{1}{n - 1}\left[\frac{1}{(1 - x)^{n-1}} - 1\right]$	
5	Based on the concept of an index of reaction (Taplin)	$\frac{dx}{d(t^\alpha)} = (1 - \beta x)^{m_\iota}$	Taplin (1974)
6	Empirical:		
	(i) Blum and Li	$\frac{dx}{dt} = \frac{a - x}{t}$	Blum and Li (1961)
	(ii) Patai *et al*	$\frac{dx}{dt} = \frac{k(a - x)^m}{x^n}$	Patai et al. (1961)
		$\frac{dx}{dt} = k(a_1 - x)(a_2 - 0.5x)$	Patai et al. (1962)

phases. Thus, low melting point and low density will facilitate diffusion and thereby growth. In certain cases, exceptions to the rule were observed, for example, growth of CA_6, in which case the behavior was explained to be due to the possible contribution of surface diffusion.

Sockel (1972) studied the system litharge-silica and observed the sequence to be

$$PbO/4\,PbO \cdot SiO_2/2\,PbO \cdot SiO_2/PbO \cdot SiO_2/SiO_2$$

Again, the parabolic rate law was applied for individual phase growths. Also, an expression has been derived relating the parabolic rate constant for a given phase in multiphase growth to that in a single phase growth.

It is usually difficult to assign precise mechanisms of mass transport in such systems. Yamaguchi and Tokuda (1967) have reported EPMA profiles for a few silicate and titanate systems. The nature of these profiles reflects the complexity involved in the analysis. At present, no rigorous analysis is available.

Detailed mathematical analysis of multiphase product growth considering diffusion as well as chemical reactions at the interfaces has been reported by Zmii and Seryugina (1971*a*, *b*). Solutions have been obtained for short and long times, and the theory has been modified (Zmii and Seryugina, 1976) for the calculation of diffusion and kinetic rate constants. They have also obtained an expression for the time for establishment of quasi stationary equilibrium.

ANALYSIS OF MIXED POWDER REACTIONS

As pointed out previously, analysis of mixed powder reactions is complicated. But, owing to the practical importance of mixed powder systems, they have received greater attention by workers in this field. We attempted to understand the mechanism of transport and the phenomenon of coupled diffusion and reaction in pellet-pellet systems. Now we discuss the various models proposed for mixed powder reactions and see how the results obtained previously can be utilized.

In essence, in any mixed powder reaction, the solid particles of reactants should contact one another, and at least one of them must then diffuse through an increasing product shell, after the initial surface reaction. This situation gives rise to several possibilities:

1. Product growth controlled by diffusion of reactants through a continuous product layer.
2. Product growth controlled by phase boundary reactions.

TABLE 4. EXAMPLES OF SYSTEMS FOR WHICH MIXED POWDER MODELS HAVE BEEN USED

No.	Systems	Model	Experimental technique	Reference
1	2	3	4	5
1	$MgO-Fe_2O_3$	Jander	X-ray diffraction	Fresh and Dooling (1966)
2	$MgO-Al_2O_3$	Serin-Ellickson	Chemical analysis of unreacted MgO	Hlavac (1961)
3	$NiO-Fe_2O_3$	Empirical expression	Saturation magnetisation measurements	Blum and Li (1961)
4	$NiO-Fe_2O_3$	Jander		Economos and Clevenger (1960)
5	$NiO-Al_2O_3$	Serin-Ellickson	Chemical analysis of unreacted NiO by EDTA titration	Stone and Tilley (1965)
6	$ZnO-Fe_2O_3$	Jander (for $T < 1\,000°C$)	(i) X-ray diffraction (ii) Chemical analysis	Duncan and Stewart (1967)
7	$ZnO-Fe_2O_3$	Jander	Chemical analysis of unreacted ZnO	Krishnamurthy et al. (1974)
8	$ZnO-Al_2O_3$	(i) Second-order kinetic (ii) Valensi-Carter ($T > 1\,000°C$)	X-ray diffraction	Branson (1965)
9	$ZnO-BaCO_3$	Nuclei growth	Thermogravimetric analysis	Hulbert and Klawitter (1967)
10	$Fe_2O_3-BaCO_3$	Jander	Chemical and gravimetric analysis	Ward and Struthers (1937)
11	$Fe_2O_3-Li_2CO_3$	Ginstling-Brounstein	Thermogravimetric analysis	Johnson and Gallaghar (1974)
12	Fe_2O_3-NiO Fe_2O_3-ZnO Fe_2O_3-CdO	Reduced time plot of Sharp et al.	Mossbauer spectroscopy	Eiss et al. (1976)
13	$Fe_2O_3-Bi_2O_3$	Second-order kinetic (for simultaneous reactions)	X-ray diffraction	Mukherjee and Wang (1971)
14	$PbO-ZrO_2$	Valensi-Carter	(i) X-ray diffraction (ii) Chemical analysis of unreacted PbO	Sasaki (1964)
15	SiO_2-graphite	(i) Linear rate law (for low temperature and/or short time) (ii) Nuclei growth (for high temperature and/or long time)	Measurement of CO gas formed	Klinger et al. (1966)
16	SiO_2-ZrO_2	Second-order kinetic	X-ray diffraction	Ramani et al. (1969)
17	$CaO-Ag_2SO_4$	Serin-Ellickson	Weight loss measurements	Riemen and Daniels (1957)
18	UO_2-graphite	Carter	Optical microscopy	Lindemer et al. (1969)
19	WO_3-SrCO_3	Serin-Ellickson	Thermogravimetric analysis	Flor et al. (1974)
20	Phthalic anhydride-sulphathiazole	Serin-Ellickson	Chemical analysis	Tomas et al. (1969)
21	Phthalic anhydride-*p*-nitroaniline	Jander	Chemical analysis	Ramachandran et al. (1974)
22	Urea nitrate-tricalcium phosphate	(i) First order (fine particles) (ii) Parabolic (coarse particles)	(i) Electrical conductivity (ii) Chemical analysis	Kutty and Murthy (1974)
23	*p*-divinyl benzene-$KClO_4$	Empirical expression	Volhard method of chloride analysis	Patai et al. (1961)

3. Production growth controlled by kinetic equations based on the concept of an order of reactions
4. Product growth controlled by nuclei growth.

We shall now briefly outline the basic features of the different models proposed for these as controlling mechanisms and also a few others. The effect of particle size distribution and that of additives will then be considered. Finally, a more realistic approach to the analysis will be discussed based on the concept of effective contact.

Reaction Models

Product layer diffusion control. Models based on this mechanism involve: reactant particles are spheres, with a continuous product layer during the initial stages of the reaction, and further reaction takes place by bulk diffusion of mobile reactant species through this product layer, which is the rate controlling step.

Jander (1927) was probably the first to treat a solid-solid reaction mathematically. In addition to the above-mentioned assumptions, he also made the rather drastic assumption of a constant cross-sectional area and an unchanging volume or density during the progress of a reaction. He derived the following expression for the fractional conversion x:

$$[1 - (1 - x)^{1/3}]^2 = kt \qquad (39)$$

where k is given by

$$k = \frac{2k'DA}{r^2} \qquad (40)$$

Thus, if an experiment is designed in such a way that all the assumptions are valid, k values can be calculated for different particle sizes. One assumption that cannot be experimentally realized in a mixed powder system is that of constant reaction cross section, since the surface area of the unreacted particle changes continuously as the reaction progresses.

Serin and Ellickson (1941) attempted to modify the rate expression of Jander by eliminating the assumption of constant reaction cross section. A number of other rate expressions have also been derived based on different approaches. These are summarized in Table 3.

In the Valensi-Carter model, change in volume due to reaction is accounted for by introducing a parameter Z in the expression. This and the first two (Jander and Serin-Ellickson) are the most widely used models in mixed powder reaction rate studies.

The Jander and Valensi-Carter models have been modified by a number of workers to account for particle size, shape, and distribution. These modifications will be discussed later.

Nuclei growth control. The theory of nucleation and growth of the product phase initially formulated for the kinetics of phase change processes (Avrami, 1939, 1940, 1941) has been successfully employed mainly to decomposition reactions (Young, 1966). This theory normally considers two steps: formation of the nuclei of the product phase at active sites, and the growth of these nuclei. The general form of the expression for conversion-time relationship

$$\ln (1 - x) = -(kt)^m \tag{41}$$

The parameter m accounts for the reaction mechanism, number of nuclei present, composition of parent and product phases, and geometry of the nuclei. If a reaction is represented by this model, a plot of $\ln \ln 1/1 - x)$ vs. $\ln t$ should give a straight line with slope m and intercept $m \ln k$.

As would be evident from Table 3, applications of nuclei growth model to solid-solid reactions are rare. Hulbert and Klawitter (1967) have applied it to the reaction between zinc oxide and barium carbonate and obtained the average value of m as 1.52. This, however, could be due to the rate controlling step being the decomposition of barium carbonate.

Phase boundary reactions control. When the diffusion of the reactant species through the product layer is fast compared to reaction, the kinetics is controlled by phase boundary reactions. Models have been developed for different geometries and corresponding boundary conditions. Thus, for a sphere reacting from the surface inwards, the fractional reaction completed x and time t are related by

$$kt = 1 - [1 - x]^{1/3} \tag{42}$$

which is identical with the expression derived for gas-solid reactions (Levenspiel, 1974). For a circular disk reacting from the edge inwards, or for a cylinder, the relation is

$$kt = 1 - [1 - x]^{1/2} \tag{43}$$

and for a contracting cube

$$x = 8k^3t^3 - 12k^2t^2 + 6kt \tag{44}$$

Kinetic Equations Based on the Concept of an Order of Reaction

The general rate equation for an n^{th}-order reaction is represented by

$$\frac{1}{n-1}\left[\frac{1}{[1-x]^{n-1}} - 1\right] = kt \tag{45}$$

Vant Hoff's differential analysis can be used to determine whether a reaction could be classified by a reaction order.

Thus, Kutty and Murthy (1974) have applied first-order kinetics to the reaction between urea nitrate and tricalcium phosphate in an ensemble of fine particles. They have attributed this to slow nucleation of one of the products and fast spreading of it further because of negligible diffusion resistance. Branson (1965) observed that for the reaction between zinc oxide and aluminum oxide, the Valensi model is applicable only at high temperatures [>1 000°C], whereas below 1 000°C the rate constant k is time dependent. This was predicted to be due to the possibility of phase boundary controlled kinetics in the early stages of the reaction. Hence, the data were correlated by the second-order kinetic equation

$$k_2t = \frac{1}{a}\left[\frac{x}{a-x}\right] \tag{46}$$

To explain this, two possible mechanisms suggested are:

1. Diffusion through the product layer is so rapid that no reaction is possible at spinel-alumina interface.
2. Nucleation from a supersaturated solid solution of zinc oxide in aluminum oxide.

The first mechanism suggests that reaction does not occur at the phase boundary but in the bulk of the solid, whereas the second suggests the possibility of nuclei growth control. However, nuclei growth models have not been tried.

Generalized approach. The rate equations mentioned above and grouped under different controlling mechanisms can all be represented by

$$F(x) = kt \tag{47}$$

If the time required for 50% conversion is denoted by $t_{0.5}$, then $t/t_{0.5}$ can be determined for a given value of x using the respective form of Equation (47). Sharp et al. (1966) have prepared numerical tables which give values of $F(x)$ and $t/t_{0.5}$ for different values of x between 0 and 1.

Taplin (1974) has suggested a unified treatment for most kinetic expressions used for the reactions of powdered materials by writing the rate equation in the generalized empirical form:

$$\frac{dx}{d(t^\alpha)} = k(1 - \beta x)^{m_i} \tag{48}$$

The exponent of time α depends on the kinetic regime. m_i has been termed as index of reaction, which in many of the previous studies was misinterpreted as the order of reaction. By numerical values and different plots, the expression has been shown to be appropriate, with different values of α, β, and m_i depending on the kinetics. Thus, for linear kinetics where the reaction rate varies as the area of the reaction interface, the equation is shown to be valid for different particles shapes, with α and β values of l and index of reaction (m_i) values of 2/3, 1/2, and 0, respectively, for sphere, elongated cylinder, and thin disk.

Of course, because of particle size distribution, values of m_i other than those mentioned for individual particles are obtained. Thus, values of m_i as high as 1.5 have been reported. However, the shape of a real particle is usually irregular. Generalization can be achieved by considering a right rectangular prism of variable dimensions. Thus, the kinetics of irregular shaped particles can only be approximated by the index-of-reaction equation. In similar fashion, other types of kinetics, such as parabolic kinetics, nucleation based kinetics, limited extent kinetics, etc., are shown to be generalized by Equation (48) with different values assigned to α, β, and m_i.

Remarkably, coupling between linear and parabolic processes leading to joint kinetics has also been approximated by index-of-reaction equation with $\alpha = 2/3$ (Taplin, 1973*a*). Except for this, however, almost in all other studies it has been assumed that only one type of kinetics dominates for the entire reaction, which is obviously not the case; different regimes could be operative in a single reaction during its progress. This has been pointed out by Taplin (1973*b*). In the case of diffusion controlled reactions, in the initial stage, when the product layer is built up by phase boundary or some other process, the kinetics of the reaction are very different. Yet, throughout the course of a reaction, a single equation is applied to describe the progress of a reaction. Such a treatment is justified when the initial induction period is very short (negligible in comparison to the total reaction time).

Empirical equations. Apart from the different models presented above, a number of authors have proposed different empirical equations to describe the kinetics of a mixed powder reaction. Thus, Blum and Li (1961) found that the rate equation

$$\frac{dx}{dt} = \frac{a - x}{t} \tag{49}$$

describes the kinetics of nickel ferrite formation from the observation of a straight line plot obtained for xt vs. t. The equation was found to hold for all ferrite formation reactions.

Patai et al. (1961, 1962), in their studies on the oxidation of *p*-divinyl benzene (*p*-DVB) and carbon black by $KClO_4$, have used the empirical rate expressions

$$\frac{dx}{dt} = \frac{k(a - x)^m}{x^n} \tag{50}$$

and

$$\frac{dx}{dt} = k(a_1 - x)(a_2 - 0.5x) \tag{51}$$

where the values of the empirical constants m and n were found to be 1 and 2/3, respectively, and a_1 and a_2 are the initial concentrations of the reactants. The equations represent different forms of the kinetic rate expression with different values of the order of reaction.

In spite of the drawbacks in some of the models and the empiricism in the others, they have been used to analyze a number of solid-solid mixed powder reactions. In many of these studies, the equations used fitted the data reasonably well. Sometimes, the fit was achieved by adjusting the experimental conditions to match the assumptions made in the theoretical development; sometimes the deviations observed were explained on the basis of experimental errors and other factors. The different systems studied and the models used for their analysis are summarized in Table 4.

Effect of Particle Size Distribution

Particle size distribution, which is invariably encountered in practice, can have important effects on kinetics. The smaller particles in the ensemble will be consumed in a short period of time, while the bigger particles are still reacting. Hence, the reaction rate per unit volume, which is based on the radius of an individual particle, will be affected; in the areas comprising smaller particles, reaction would already be over, and the region would be dead with respect to progress of reaction.

Particle size distribution will also have an effect on voidage and hence on the effective contact area, since smaller particles can go into the interstitial spaces formed by bigger particles. The effect of compaction pressure may also be hampered owing to this. Particle size distribution will also affect the sintering behavior of solids since, owing to different radii, the geometries of the necks formed and consequently their growth kinetics will be different. In fact, Goodison and White (1961) have observed the effect of percentage of fine and coarse particles on sintering behavior.

Sasaki (1964) first attempted to account for the effect of particle size distribution on kinetics. The basic rate expression assumed was the one developed by Carter. Sasaki considered groups of different size particles designated by mean radius (${}_{i}r_o$) for the i^{th} group, fraction of component A in the i^{th} group (f_i), and reacted fraction of the i^{th} group (x_i).

Carter's expression was then applied to obtain for the i^{th} group the expression

$$\frac{Z - [1 + (Z-1)x_i]^{2/3} - (Z-1)(1-x_i)^{2/3}}{2(Z-1)} = \frac{k}{a_o^{2(i-1)}\,{}_{i}r_o^{2}}\,t \tag{52}$$

where ${}_{i}r_o = a_o^{i-1}\,{}_{1}r_o$, and a_o is the ratio of the mean radii of adjacent groups. Hence, summing up for all the groups, an expression for overall conversion was obtained. But in this treatment it was assumed a priori that the Valensi-Carter model fits with $Z = 2$. This was overcome in another modification of the same expression by Kapur (1973) who considered the integrated function of the fraction reaction completed $x(t)$ with r_n and r_u, respectively, as the radii of the smallest and the largest particles in the ensemble. He obtained

$$x(t) = \int_{r'}^{r_u} M(r)x(r, kt)\,dr + \int_{r_n}^{r'} M(r)\,dr \qquad \text{for} \quad t = t_c(r') > t_c(r_n) \tag{53}$$

and

$$x(t) = \int_{r_n}^{r_u} M(r)x(r, kt)\,dr \quad \text{for} \quad t < t_c(r_n) \tag{54}$$

since particles of radius $< r'$ react completely in time $t_c(r')$. Here, $M(r)dr$ is the mass fraction of the reacting particles in the size range r to $r + dr$. Thus, the effect of completion of reaction in smaller particles in a short time interval has been taken care of. Sasaki's data has been tested, and it has been shown that the model fits the data well with $Z = 2$ (without a priori assumption).

Taplin (1974) in his discussion on the generalized rate expression has used log-normal distribution of particle sizes in describing linear kinetics. In general, little consideration has been given to the effect of particle size distribution in solid-solid mixed powder reaction studies.

Effect of Additives

Both catalytic and inhibitory effects are found to be exhibited by the additives in a solid-solid mixed powder system. Thus, they may affect the crystal structure of a solid by increasing or decreasing the number of defects in the lattice, thereby creating or diminishing vacancy concentration. Such effects are well known in solid state chemistry, particularly in connection with the semiconducting properties of a solid. In fact, doping is a well known and very important technique in semiconductor technology. The conductivity of a sample can be increased or decreased, as desired, by addition of the dopants. This has also an important application in catalysis in view of similar dopant effects. These effects depend on the ionic radii of the dopant and the host cation and also on the site preference characteristics of the cations. Thus, in nickel oxide, addition of Li^+ increases the conductivity, whereas in zinc oxide it decreases the conductivity. On the other hand, Ga^{3+} ions have exactly opposite effects on the two. A few studies have been made to investigate such effects in solid state reactions.

Schwab and Rau (1958) studied the exchange reaction $ZnO + CuSO_4$. Reaction rate was found to be accelerated by the addition of Li^+ to zinc oxide and retarded by the addition of Ga^{3+} to it. On the other hand, in the reaction $NiO + MoO_3 \rightarrow NiMoO_4$, addition of Cr^{3+} to nickel oxide enhanced the rate, while that of Li^+ retarded it. These results can be attributed to the corresponding changes in defect structure, and hence the vacancy concentration, as mentioned above.

Additives may also promote sintering on the surface, facilitating material transport, and they may promote reaction by acting as oxygen transfer agents. They may inhibit the reaction physically by acting as a barrier between reactants or in some cases chemically by trapping the active intermediates. Elucidation of the correct mechanism of promotion or inhibition requires detailed investigation. Patai et al (1961, 1962) have made observations on the effect of certain additives such as $LiCO_3$, PbO, and Zn on the solid phase oxidation of *p*-DVB and carbon by $KCLO_4$. Based on the observations, certain conclusions have been drawn, but further studies are required to support them.

An interesting observation is reported by Szabo et al. (1961). In their experiments with pure nickel oxide and ferric oxide, the activation energy was found to be 95 kcal/mole; addition of 1% chromic oxide to the nickel oxide reduced it to 59 kcal/mole, whereas addition of 1% titanium oxide to the ferric oxide raised it to 132 kcal/mole.

The Concept of Effective Contact

Solid-solid reactions differ from other types of heterogeneous reactions (gas-solid, gas-liquid, etc.) mainly in the nature of contact between the reaction partners. Whereas in other cases at least one of the reactants is in a flow pattern, in solid-solid systems both the reactants are stagnant, unless one of them (or part of it) is transported as a gas. Obviously, therefore, the progress of a solid-solid mixed powder reaction depends to a significant extent on the initial contact between the reactants. The initial contact has to be achieved through proper mixing. Solids mixing has been dealt with in detail by Weidenbaum (1958) and more recently by Cooke et al. (1976) in their review articles.

Apart from mixing, other factors like relative particle sizes of the two, particle size distribution, particle shapes, sintering characteristics, etc., also affect the contact between the reactants. Sintering can sometimes introduce complexity in the analysis since it may change this contact area during the course of a reaction, as a result of contraction or expansion and neck growth (for detailed discussion on sintering, see Coble and Burke, 1961; Kuczynski and Stablein, 1961).

Henrich (1954) for the system cadmium oxide-chromic oxide and Jaky et al. (1965) for the system cadmium oxide-ferric oxide observed that the reaction started earlier in compacted tablets than in the uncompacted powder mixtures, but later the rates were slower in tablets than in the uncompacted samples. According to Jaky et al., this is due to the reformation of the cadmium oxide/ferric oxide contacts, which can be achieved more easily in uncompacted samples than in the tablets. Actually, in either case, movement of solid particles is not possible, so that the reformation of contacts cannot be achieved unless at least one of the reactants diffuses. The observations may be better explained on the assumption of vapor phase diffusion of one of the reactants, since in that case obviously an uncompacted sample will facilitate the diffusion; also, it will provide more surface area for reaction. The initial higher rates in tablets could be due to the initial surface reaction, the rate of which will be lower in uncompacted samples because of less contact area.

Patai et al. (1961, 1962) considered the effect of contact surface area on the rate constants in their studies on the oxidation of *p*-divinylbenzene [*p*-DVB] and carbon by $KClO_4$. The observed rate constants (k) obtained by fitting the data with empirical rate equations were found to depend on the surface areas of the two. New rate constants were obtained using the following expressions:

$$k_1 = k(S_A/S_B) \quad \text{for} \quad S_A > S_B \tag{55}$$

and

$$k_2 = kr^2(S_A/S_B) \quad \text{for} \quad S_A < S_B \tag{56}$$

where S_A and S_B are the surface areas of $KClO_4$ and *p*-DVB or carbon, respectively, and r is the radius of a $KClO_4$ particle. The absolute surface area of the oxidant ($KClO_4$) was found to be more important. The effect of compounding pressure on the k values was also studied. Generally, the contact area between two spheres is proportional to $p^{2/3}$. Here the correlation obtained was

$$k_3 = \frac{k}{p^{1/2}} \tag{57}$$

This is considered to be due to the irregular shape of the particles. Increase in contact area and thereby modification of the kinetics have been considered by Tomas et al. (1969) who studied the sintering of one of the reactants by dilatometry and correlated it to the overall kinetics.

Recently, Johnson and Gallagher (1974) have reported the effect of surface area of the ferric oxide powder on the rate constant in the system ferric oxide-lithium carbonate. They performed experiments with ferric oxide powders of different known surface areas to obtain rate constants. Hence, an empirical relation for the rate constant was established:

$$k = \frac{\alpha'}{r^2} \tag{58}$$

An interesting feature of the above work is that the surface area of the ferric oxide was assumed to be made up of contributions from equidimensioned spheres. Hence, surface area

$$S = \frac{3}{\rho r} \tag{59}$$

Combining (58) and (59), we get

$$S = \frac{3}{\rho\sqrt{\alpha'}}\sqrt{k} \tag{60}$$

Equation (60) was verified by a logarithmic plot, the slope of which was found to be one half, as expected.

Though the importance of the contact area was realized, no attempt was made to treat the problem theoretically. Komatsu (1965) has reported probably the first rigorous attempt based on the number of contact points. The model considered by him for the packing of spherical particles of *A* and *B* is represented in Figure 7. By simple geometrical considerations, he expresssed the number of contact points between one central *B* particle and the surrounding *A* particles in an ideal system by

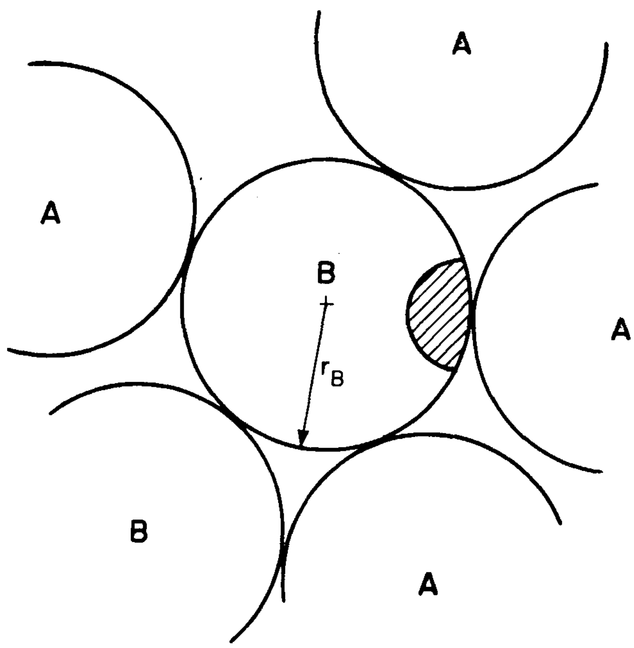


Fig. 7. The model of the packing (Komatsu, 1965). Reproduced from *Proceedings Fifth International Symposium Reactivity of Solids, Munich, 1963*, Elsevier Scientific Publishing Co., p. 182 (1965).

$$N^o(A/B) = N^o{}_B \frac{\gamma \overline{w}}{(1+\gamma\overline{w})} \tag{61}$$

where

$$\gamma = \frac{r_B{}^3 \rho_B}{r_A{}^3 \rho_A} \tag{62}$$

In real systems, irregular shapes are encountered; also, the packing is not perfect. As such, the actual number $N(A/B)$ would be less than $N^o(A/B)$ and is given by

$$N(A/B) = N_B \left[\frac{\gamma\overline{w}}{1+\gamma\overline{w}}\right]^g, \quad g > 1 \tag{63}$$

where the parameter g is introduced to account for the difference in packing state. He applied his theory to modify the Jander equation and obtained the following expression for the rate constant of the Jander equation:

$$k(T, \gamma, \overline{w}) = k^o(T)\left(\frac{\gamma\overline{w}}{1+\gamma\overline{w}}\right)^g \tag{64}$$

The theory was successfully applied to the systems calcium carbonate-molybdenum trioxide, barium carbonate-silica, copper chloride-silicon, and lead chloride-silicon (Komatsu, 1965). Komatsu and Uemura (1970) extended the theory to account for counterdiffusion.

Haber and Ziolkowski (1972) have applied the Komatsu model to the system Co_3O_4-MoO_3. They considered the following relations:

$$k = k_o\left[\frac{\gamma\overline{w}}{1+\gamma\overline{w}}\right]^g, \quad r_A/r_B > 1 \tag{65}$$

and

$$k = k_o\left[\frac{1}{1+\gamma\overline{w}}\right]^g, \quad r_A/r_B < 1 \tag{66}$$

From logarithmic plots, they obtained the values of the parameter g. Thus, g was found to be 13.6 for $r_A/r_B > 1$ and 3.74 for $r_A/r_B < 1$. Notably, the authors calculated the rate constant k for unit surface area of Mn_2O_3 in the system Mn_2O_3-MoO_3 and found that this k was constant with composition.

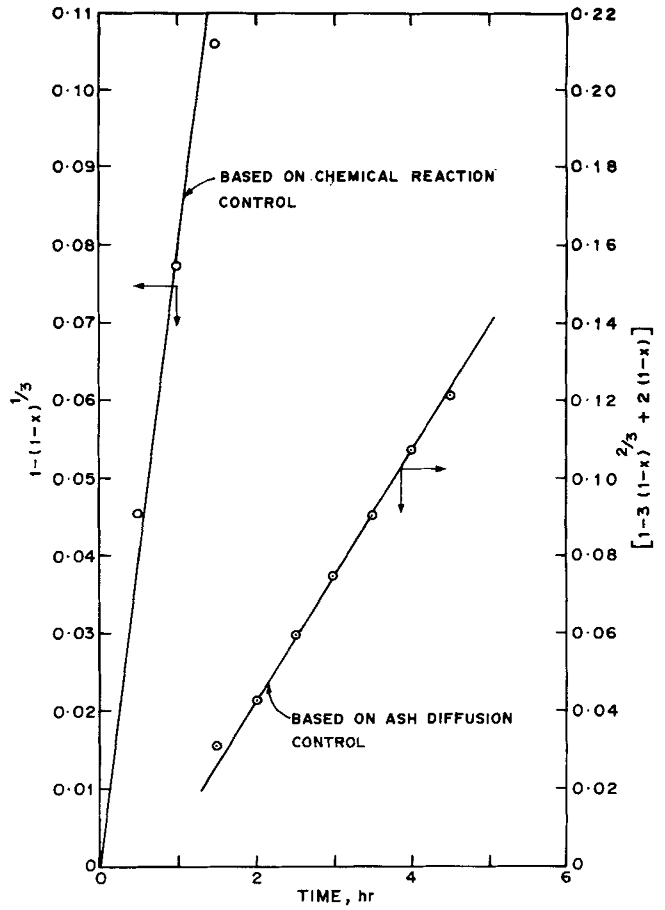


Fig. 8. Conversion data of Ramachandran et al. (1974) plotted according to the expressions for chemical reaction control and ash layer diffusion control for gas-solid reactions (Tamhankar, 1976).

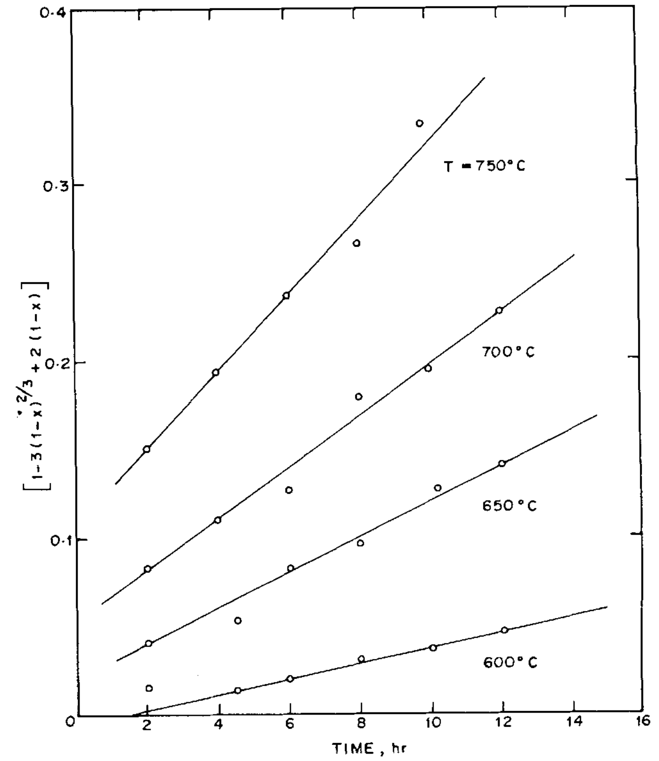


Fig. 9. Data of Krishnamurthy et al. (1974) plotted according to the expression for ash layer diffusion control for gas-solid reactions (Tamhankar, 1978).

Komatsu's theory, though remarkable, has been applied to the Jander model which is known to have its own drawbacks. Also, since different shapes and sizes are encountered in practice, it may be more logical to consider the total contact surface area rather than the number of contact points. In fact, the importance of surface area has been brought out in some of the studies, as already discussed above.

The discussion so far has brought out the complications involved in studies on mixed powder systems. Though some typical mechanistic studies have lead to better understanding of such systems, the models used for the interpretation of rate data are mostly those derived basically for gas-solid systems, in particular the metal oxidation reactions. This suggests the possibility of using the well-known conversion-time relationships derived for different controlling regimes in gas-solid noncatalytic reactions (Levenspiel, 1974) for solid-solid reactions as well. Tamhankar (1976) has successfully applied the equations for gas-solid noncatalytic reactions to the data of Ramchandran et al. (1974) on an organic solid-solid system. Tamhankar (1978) has also used these equations to correlate the data of Branson (1965) on the system zinc oxide-aluminum oxide and of Krishnamurthy et al. (1974) on the system zinc oxide-ferric oxide. The results are reproduced in Figures 8 and 9.

Multicomponent Systems

In some cases, for example, the cement industry, one has to deal with multicomponent solid-solid reactions. Even when one goes from a binary to a ternary system, the phase diagram, if available, reveals the complexity in the system. An additional composition term is involved, and the behavior of the system depends on the region of the phase diagram in which one is operating. If the additional third component is in a minute quantity (<1%), it can be treated as a dopant which affects the system in a particular fashion. This has been discussed separately. When all the three components are present in considerable proportions, a variety of new compounds may be formed. Systems consisting of more than three components will obviously be considerably more complex.

So far, only a few phase equilibrium studies have been reported in the literature. Thus, Reijnen (1965) has studied the system magnesium oxide-iron oxide-ferric oxide; Winkler (1965) has reported structure studies in the systems BaO-MeO-Fe_2O_3 (Me = cobalt, nickel, copper, zinc, manganese, magnesium. Analysis of coupled diffusion and reaction in such systems has not yet been attempted.

ROLE OF THE GAS PHASE

The gas phase has always played an important role in solid-solid reaction studies. Some time back it was a major subject of controversy among the workers in the field. In fact, a group of Russian investigators claimed that all the mixed oxide solid-solid reactions occur via gas phase diffusion, the first step being the dissociation of one of the reactants. This conclusion was based on the argument that contact area between particles presents too small a cross section for rapid diffusion.

The larger chemical reactivity of small particles is often accounted for by Thomson's relation (Parravano, 1962)

$$\ln \frac{p}{p^\circ} = \frac{M}{RT} \frac{2r}{\rho^2} \tag{67}$$

which gives the vapor pressure over the surface of a solid with a radius of curvature r, solid density ρ, and molecular weight M, as a function of the pressure in equilibrium over a flat surface. Thus

$$\text{for} \quad r = 50\text{Å}, \quad \frac{p}{p^\circ} \; (\text{at} \quad T = 0°\text{C}) = 10$$

and

$$\text{for} \quad r = 5\text{Å}, \quad \frac{p}{p^\circ} = 10^{10}$$

Clearly, with decreasing particle size, the vapor pressure increases tremendously. This also corresponds to an increase in free energy of the surface. In fact, the driving force for subsequent sintering in the compacts arises from the excess surface free energy of the pressed compact over that of the final sintered body (Clarke and Williams, 1961).

Many organic substances are known to sublime or have considerable vapor pressure. Certain inorganic oxides such as nickel oxide, zinc oxide, and lead oxide (Pettit et al., 1966; Duckwitz and Schmalzried, 1971; Harris and Cook, 1968) are also known to be transported via the vapor phase, as shown by experiments with nonporous materials or with the reactants kept apart.

Konoyuk and Vashuk (1974) treated the kinetics of solid phase reactions whose rate is limited by the sublimation of one of the reactants. They also applied Thompson's relation in the form

$$\frac{dp}{dr} = \frac{RTj}{4\pi r^2 D}\left(1 - \frac{p}{p^\circ}\right) \tag{68}$$

The final expression obtained was shown to be the same as that of Ginstling and Brounshtein (see Table 3) under certain conditions. Whether it is solid phase diffusion or transport via sublimation of one of the reactants, the barrier of the product layer has to be crossed for the reaction to occur. If sublimation and surface diffusion rates exceed that of the transport across the product layer, the reaction would obviously be controlled by the slower step.

Apart from sublimation, the other process that contributes to gas phase diffusion is dissociation. Thus, in many oxide systems, oxygen pressure is shown to affect the kinetics greatly, since transport of oxygen in the gas phase occurs along with the cation diffusion.

Ginstling and co-workers (Ginstling, 1951; Ginstling and Fradkina, 1952; Pozin et al., 1954) carried out several experiments by heating the reactants kept some distance apart and concluded that the reaction proceeds via gas phase diffusion. Yet, this should not rule out the possibility of other mechanisms being operative under mixed powder conditions. In situ elucidation of mechanism was attempted by Borchardt (1959). He derived an expression for the maximum reaction rate for the gas phase diffusion mechanism by considering a dissociation step. The maximum reaction rate is given by

$$R = \frac{265\, M_s p}{\rho s d [M_g T]^{1/2}} \tag{69}$$

Further, using the thermodynamic relationship

$$\ln p = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{70}$$

in conjunction with Equation (69), he derived an expression for the lowest temperature of dissociation at which the initial rate of reaction attains a value of at least 1% conversion/min. Applying this to the reactions between U_2O_8 and iron, chromium, niobium, and nickel, we could positively conclude that for some systems at least (for example, U_3O_8-Fe and U_3O_8-Nb), gas phase diffusion is absent, since reaction occurred even below the lower dissociation temperature calculated.

Gluzman and Mil'ner (1960) studied some organic solid-solid reactions with a view to investigating the role of the gas phase in them. In their experiments, they separated the two reactants with a fine copper wire mesh so that minimum contact is allowed between particles of the two. They analyzed the samples of the two for product formation and concluded that there is little contribution of gas phase diffusion to the reaction, though it was not completely ruled out.

Rastogi and Dube (1967) in their studies on the reactions between iodine and mercurous halides found that diffusion was predominantly via vapor phase. The kinetics could be followed using the expressions

$$(\Delta l)^2 = 2k_1 t \exp(-q\Delta l) \tag{71}$$

or

$$(\Delta l)^2 = k_2 t \tag{72}$$

depending on the fit of the model.

They carried out the experiments by keeping the reactants separated with an air gap of different lengths. The rate constants k_1 and k_2 were correlated with the length of the air gap by

$$k_1 = c_1 e^{q_1/(l_1+c_2)} \tag{73}$$

and

$$k_2 = c_3 e^{-q_2 l_1} \tag{74}$$

where l_1 is the distance of separation (or the length of the air gap), and c_1, c_2, c_3, q_1, and q_2 are constants.

Forestier and Kiehl (1949, 1950) extensively studied the effect of different gases present on the reaction rates at lower temperatures, for example, on nickel ferrite formation reaction. Clear dependence of the rate of formation of spinel on the liquefaction point of the gas was observed (Figure 10). From these studies, Forestier concluded (Forestier, 1956): the rate of reaction increases monotonically with the liquefication point of the gas used and consequently depends on the amount of adsorbed gas, and for the same gas, reaction rate is a linear function of the logarithm of the gas pressure, and the rate tends to zero as the pressure falls to zero. Thus, the effects were mainly attributed to the adsorption of gases.

Weyl (1956) found that gases adsorbed on the surface of a crystal, even chemically inactive gases such as nitrogen or the rare gases, modify the electronic structure of the surface atoms and thus have a considerable effect on the chemical bonds in the solids. Trambouze and Silvent (1961) studied the reaction

$$NiO + MoO_3 \rightarrow NiMoO_4$$

in the presence of various gases. It was observed that inert gases caused higher rates than in vacuum. Reactive gases such as oxygen, hydrogen, and carbon dioxide had greater effect, water vapor having the maximum. They explained the effect as being due to chemisorption of the gases on nickel oxide and considered the controlling process to be surface diffusion. Leonov (1961) observed that in the reaction between magnesium oxide and aluminum oxide the amount of spinel formed in 30 min at 1 150°C in air was 11.8% and in hydrogen 41.0%. Similarly, for the reaction $ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$, he observed that in purified argon the reaction proceeded much more rapidly than in argon containing 0.4% oxygen (Leonov, 1960). Leonov thus concluded that reactions between oxides proceed more rapidly when the partial pressure of oxygen in the gas phase is commensurate with the dissociation pressure of the oxides. The chemical activity (or stability) of oxides is thus determined by their dissociation pressure rather than their melting point as suggested by Tammann (1925).

Certain solid-solid reactions of industrial importance are known to proceed via gaseous intermediates. Thus, in the reaction between silica and graphite, Klinger et al. (1966) have shown that the reaction proceeds through the dissociation of silica:

$$SiO_2 \rightarrow SiO + \frac{1}{2} O_2$$

and

$$SiO + C \rightarrow SiC + \frac{1}{2} O_2$$

Rao (1971) has shown that the reduction of iron ore (for example, hematite) by the solid reductant coke (carbon), the so-called direct reduction process, proceeds via intermediate carbon monoxide formation except for the initial stage. Thus, he has considered a two-step reaction mechanism

$$(1) \quad Fe_gO_h(s) + CO(g) \rightarrow Fe_gO_{h-1}(s) + CO_2(g)$$

$$(2) \quad C(s) + CO_2(g) \rightarrow 2CO(g)$$

where $g = 1, 2$, or 3 when $h = 1, 3$, or 4. The reaction of carbon with carbon dioxide, which was found to be the rate controlling step, was assumed to obey first-order kinetics. The mathematical model based on this was found to represent the results well.

Sohn and Szekeley (1973) have provided mathematical treatment of the general problem of reactions between solids proceeding through gaseous intermediates. A more detailed discussion of the topic can be found in the monograph on gas-solid reactions by Szekeley et al. (1976).

The fact that gas phase diffusion is faster than solid phase diffusion can be used for accelerating the rates of solid-solid reactions by deliberately introducing a gas phase in the system. Schafer (1971) has in fact suggested such synthetic routes for the manufacture of certain materials. Thus, the reaction

$$SnO_2(s) + 2\,CaO(s) \xrightarrow{900°C} Ca_2SnO_4(s)$$

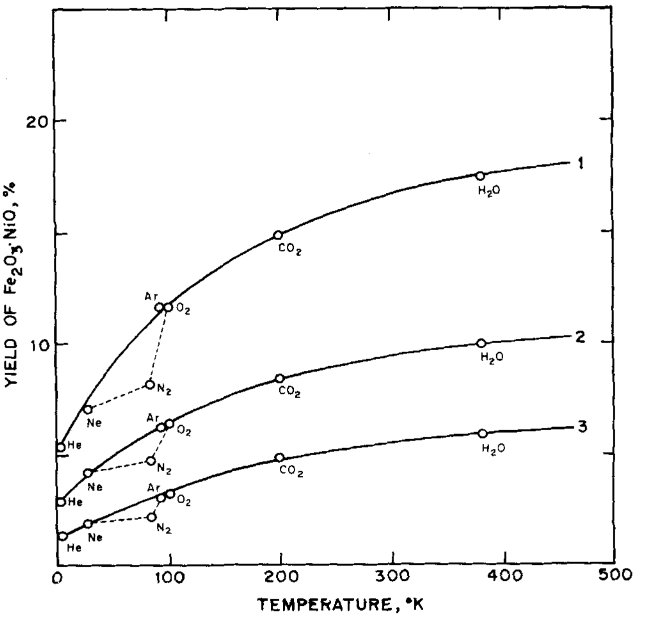


Fig. 10. Relation of the yield of nickel ferrite in atmospheres of various gases (1) 700°; (2) 650°; (3) 600°C. Heating time 15 min (Forestier and Kiehl, 1950).

can be accelerated by adding carbon monoxide or hydrogen to the system, since

$$SnO_2(s) + CO^{(g)} \rightarrow SnO(g) + CO_2(g)$$

and SnO(g) can further react more easily with calcium oxide. Also, in the reaction

$$NiO(s) + Cr_2O_3(s) \xrightarrow{1\,100°C} NiCr_2O_4(s)$$

if oxygen is introduced, we have

$$Cr_2O_3(s) + \frac{3}{2} O_2^{(g)} \rightarrow 2\,CrO_3(g)$$

and $CrO_3(g)$ can further react to give the desired product $NiCr_2O_4$.

REACTOR DEVELOPMENT

Basic Design Considerations

Standard design procedures have not so far been developed for solid-solid reactors. In most cases, the conventional ceramic technique is used for manufacturing purposes. In this, the finely powdered reactants are first intimately mixed, usually in a ball mill, the powder mixture is pelletized if necessary, and heated at the desired temperature for a predetermined time interval. Often the material thus obtained is reground, pelletized, and heated again. The procedure is repeated two or three times to ensure complete conversion.

The main difficulties in solid-solid reactions are the requirement of complete mixing (and hence initial ideal contact between reactant particles) and continuous removal of the product layer formed in order to promote better contact between yet unreacted phases. Sintering, as mentioned earlier, presents additional complexity. In the conventional ceramic technique, these difficulties are overcome by the repeat cycle procedure.

Unlike in other heterogeneous processes, here none of the reactants can be in a flow pattern; contact between unreacted phases can be achieved only through solid-state diffusion, which is known to be extremely slow. It can be remedied either by having a device in which the processes of mixing, grinding, and heating can be carried out simultaneously (for example, a rotating furnace ball mill) or by deliberately introducing a gas phase in the reaction as suggested by Schafer (1964). The work of Feigl et al. (1944) is worth noting in this connection; they carried out solid-solid reactions even at high temperatures with constant stirring using a platinum stirrer.

Compaction pressure is also known to accelerate the rates of solid-solid reactions (Arrowsmith and Smith, 1966; Ramachandran et al., 1974). In fact, the acceleration of reaction rates by applied pressure is made use of in modifying the ceramic technique; the process is known as pressure sintering or hot pressing. The process normally consists of applying pressure to the ceramic, in powder or cold pressed compact form, in a refractory mold which is heated to an optimum temperature for densification. The pressures employed are of the order of 1 000 to 10 000 lb/in.^{2}; temperatures up to 2 500°C are used.

An obvious advantage of the process is a lower temperature requirement. In addition, it helps in achieving microstructural control, enhanced densification, composite fabrication, and pressure bonding. As such, it is increasingly used as a fabrication process, especially in the ceramic industry. A detailed review has been presented by Vasilos and Spriggs (1966).

Mechanical Design

Information on mechanical design is scanty. There are no standard design procedures; most of the commercial plants are designed from experience and from using some of the empirical expressions. The industries in which this problem is encountered are ceramics, ferrites, semiconductors, metals, and cement. Reactors are either batch type of continuous.

Of these, the ceramic, the ferrites, and the semiconductor industries mostly use batch type of reactors, following the procedure as described above. The problem of reactor design, therefore, reduces to one of designing a furnace and a mixer for the initial mixing stage. This is done mostly from experience.

In the metal industry, one is concerned with the reduction of ores (for example, hematite reduction by coke), wherein solid-solid reactions are encountered. In the cement industry, solid-solid reaction is a major step, since the important constituents are all present as solids and react in the solid state. In both cases, a rotary kiln is used as a reactor. As such, the process is normally a continuous one; the reaction mixture is fed in at one end of the kiln and discharged at the other. A gas is also some times introduced in a concurrent or counter-current flow.

The rotating kilns used in the cement industry are very long (length of the order of 200 to 500 ft and diameter up to 20 to 30 ft); they are positioned slightly inclined to the horizontal (Pollitt, 1964). The entire length is divided into zones for drying, reaction, and cooling. The residence time of the cement raw mix in such kilns is typically 2.5 hr in a 200 ft long kiln and 6 hr in a 450 ft long kiln.

Equations have been developed for calculating the length and diameter; for example, for a dry process the length required is given by (Martin, 1932)

$$L_k = 20(d_k - 1.5) + 0.2(d_k - 1.5)^2 \qquad (75)$$

For design purposes, much depends on the heat requirements in different zones and as such on the heat capacities of the reactants and products. Calculations are thus made on the basic data available, and what is known as a heat treatment schedule is prepared.

Verticle tube reactors are also in use in the cement industry; the heights are of the same order as the length of the rotary kiln. Air is passed from the bottom and the raw mix fed at the top. This somewhat resembles a fluidized bed reactor; the air flow is used to adjust the residence time of the raw mix in the reactor.

Recent Developments

From the above discussion, it may be seen that there is a need to develop newer and better processes for the manufacture of mixed oxides. The conventional ceramic technique has obvious drawbacks; also, the steps involved being slow, it cannot be adopted to continuous production.

Novel processes have recently been developed, particularly for the manufacture of ceramic nuclear fuels; these can be readily adapted in other industries. The processes developed are sol-gel process, gel precipitation, and spray processes (pyrogel process and flame reactor). All of these essentially start with an aqueous phase containing the metal ions in the desired proportions. The main advantages are lower temperature requirement, shorter time of contact needed for conversion, and control over particle size. A brief account of the processes is presented below (Dell, 1972).

Sol-gel process. In essence, this involves forming a concentrated colloidal sol to a semirigid gel by a convenient method. The gelation stage is important since it determines the particle shape and size of the final product. The gel is then dried and calcined to obtain the desired product. The process is best suited to the preparation of coarse products.

Gel precipitation. This process combines the advantages of the sol-gel process with those of the well-known coprecipitation technique used especially in catalyst preparation. In precipitation, often the filtration of hydroxides presents problems since the precipitates are gelatinous. This difficulty is overcome by adding an organic gelling agent, thereby converting the precipitate into a granular form.

Spray processes. The general principle involved here is atomization of the solution to form a fine spray of droplets which are thermally decomposed in a high temperature environment. This is known as flash hydrolysis. During the short residence time (1 to 5 s) of material in the reactor, the solution evaporates, solidifies, decomposes, and undergoes solid state reaction. In this, the particle size can be precisely controlled by adjusting the spray parameters. Two types of reactors are used for the purpose; in one the solution is sprayed into a tube heated externally (pyrogel process), and in the other the solution is sprayed directly into a high temperature flame (flame reactor).

Spray processes can also be adapted to alloy preparation by subsequent reduction of the mixed oxides obtained.

Spray processes are particularly attractive from the chemical engineering view point, since they can be utilized for continuous production. Further effort is needed to explore this novel technique.

NOTATION

A = cross-sectional area
a, a_1, a_2 = initial concentrations of reactants
b = lattice spacing
C = concentration
C' = saturation concentration of C_r^{3+} in magnesium oxide equilibrated with $MgCr_2O_4$ phase
$\hat{C}$ = dimensionless concentration
C^* = bulk solid concentration
d = particle diameter
$D_i, D, \tilde{D}$ = diffusion coefficients
D_i^o = self-diffusion coefficient of rate determining ion when $a_{AO} = 1$
D_o = diffusion coefficient for a reference concentration C_o
j = diffusional flux
K = arbitrary constant
$k_1, k_2, k_3, k', k^o, k$ = reaction rate constants
L = total length of a pellet
l = distance parameter
l' = distance of boundary $MgCr_2O_4/MgO$ at $t > 0$ from original position
Δl = thickness of a zone
l^+ = distance at which concentration of Cr^{3+} tends to zero at $t > 0$
m_i = index of reaction appearing in Equation (48)
m_o = coefficient reflecting defect type of reaction product
m_s, m_g = molecular weights of gas and dissociating solid, respectively
N = number of atoms in a molecule
N_1, N_2, N_2^* = mole fractions of species involved
$N^o(A/B), N^o(B)$, $N(A/B), N(B)$ = number of contact points defined by Equations (61) and (63)
$P_{i \to f}$ = probability
p = pressure
p^o = total pressure
R = reaction rate
r_A, r_B = radii of components A and B
r_o, r, r' = radii of particles
S = surface area of a particle
s = number of moles of gas evolved per mole of solid
T = temperature
t = time
ΔV = increase of product volume due to transport of one equivalent of ions through reaction layer
V = volume
V_m = molar volume
v_1, v_2, v = velocities
$\bar{v}$ = mean molecular velocity
$\bar{w}$ = weight ratio (W_A/W_B)
x = fractional conversion
$\bar{x}$ = numerical factor indicating the fraction transformed into the product in time T
Z = volume of the product formed per unit volume of the reactants consumed
z = dimensionless distance
z' = charge
Δz = dimensionless reaction zone thickness

Greek Letters

α' = constant
γ = defined by Equation (62)
μ = chemical potential
ν = numerical factor of order one
ρ = density
$\bar{\rho}$ = electrical resistivity
ρ_A, ρ_B = densities of components A and B
η = electrochemical potential
τ = relaxation time
ϕ, ϕ' = Thiele modulii as defined in the text
θ, θ' = dimensionless time

Subscripts

A, B, C = reactants
p = product zone
r = reaction zone
k = kiln

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