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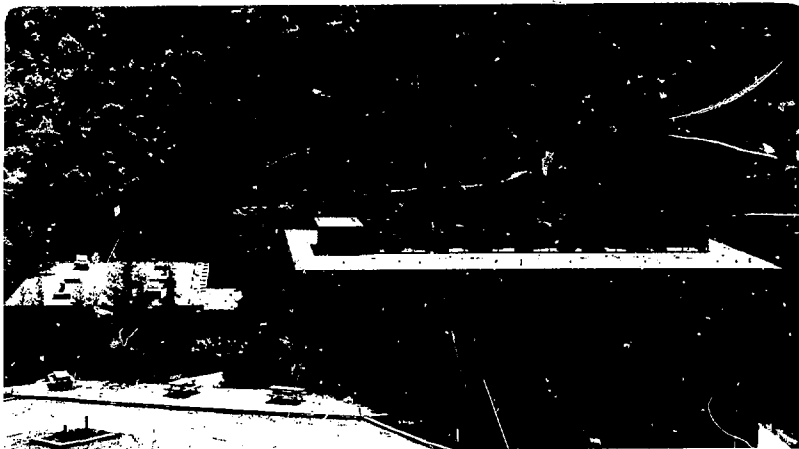
Materials & Molecular Research Division

THEORETICAL ASPECTS OF SOLID STATE REACTIONS IN A MIXED
PARTICULATE ENSEMBLE AND KINETICS OF LEAD ZIRCONATE FORMATION

Sudhir S. Chandratreya
(Ph.D. thesis)

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THEORETICAL ASPECTS OF SOLID STATE REACTIONS IN A
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ABSTRACT

A theoretical analysis was carried out to estimate the quasi-steady-state external mass transport by lattice, surface and gaseous diffusion in terms of the stereologically measurable microstructural parameters of a mixed powder compact. It was shown that the gaseous transport can be described by a single dimensionless quantity termed "sublimation transport modulus." Using these equations, the relative importance of the alternate external transport modes can be evaluated.

Based on the above analysis, "shrinking core" and "grain models" were modified whereby the microstructural parameters appeared explicitly in the kinetic expressions. Conditions under which the mixed powder reactions assume a gas-solid type of kinetic behavior were established.

"Contact-Maintenance theory" based on the volumetric changes on a particulate level was developed to explain the abrupt changes observed in the reaction mechanism. Accordingly, it becomes possible to predict the conditions under which a contact between the reactant particles can break leading to the gaseous external mass transport as a new and possibly, a rate limiting step.

The "Macroscopic Expansion Model" was developed to correlate the particulate volume changes to the pellet dimensional changes for a mixture of powders of arbitrary size distributions and fixed shapes.

The model requires that the volume fractions of various phases in the pellet dimension-determining skeletal structure of the pellet be known. Also, the void content of the pellet must be known as a function of the extent of reaction or pellet dimensions. The model could potentially upgrade dilatometry from a qualitative to a quantitative, continuous, in-situ analytical technique in the reaction studies with many advantages. Difficulties in attaining this objective have been discussed.

Experimental work determined the reaction isotherms for the formation of lead zirconate from yellow PbO and monoclinic zirconia between 710°C to 810°C for two zirconia size distributions. The larger zirconia showed diffusion controlled shrinking core kinetics up to approximately 90 percent reaction while the smaller zirconia indicated a diffusion controlled spherical growth of up to 85 percent reaction after an instantaneous nucleation at a limited number of sites. The difference was attributed to the differences in the mixing time and not to the particulate sizes. It was observed that for the same size range, a longer mixing operation gave a better dispersion of reactants which resulted in a higher nucleation site density required for a 'shrinking core' type of product morphology and faster kinetics. A microprobe profile analysis of partially reacted particles confirmed that for the shorter mixing period, reaction resulted in a nucleation-growth-impingement type of morphology. The activation energy as calculated from the nucleation-growth model fit to the data was 138 Kcal/mole which is close to 131 Kcal/mole reported for Pb^{2+}

diffusion in PbZrO_3 . Approximate calculations show that the gaseous external mass flux of PbO was negligible compared to the lattice or surface diffusive flux.

The above models were not valid above approximately 85 percent and 90 percent reaction for the smaller and the larger zirconia, respectively. Reaction rates decreased suddenly and were relatively independent of temperature indicating a low activation energy typical of gaseous diffusion. For the experimental conditions, this phenomenon could be correctly predicted by the 'contact maintenance theory.'

The 'Macroscopic expansion model' fit the pellet volume expansion data reasonably well when zirconia was assumed to form the entire skeletal structure and the pellet porosity was assumed to be invariant with the reaction. A pre-reaction heat-treatment was found to influence the expansion behavior. Everything considered, results appear encouraging in regard to the use of dilatometry as a quantitative method in powder reaction studies despite the difficulties mentioned.

1. INTRODUCTION AND LITERATURE SURVEY

1.1 Importance of Solid State Reaction Studies

Solid-state reactions are emerging as an extremely important field of technology due to diverse areas of applications and energy intensiveness of the processes involved. Numerous unit operations can be classified in this category in metallurgy, ceramics and chemical engineering. Fundamental understanding of the processes and their representative models are essential for improved process-control and cost-optimization. The field may be broadly divided into two major subfields: fluid-solid and solid-solid reactions. Whereas significant advances have recently been made in fluid-solid, mainly gas-solid, reactions, developments has remained rather limited in the modeling of solid-solid reactions. This situation may partly be attributed to the flexibility available in the experimental design of gas-solid reactions. Solid-solid reactions, such as in a binary powder mixture, are inherently complex due to lack of precise experimental control over the microstructure and the transport conditions. However, for any meaningful advance in the state-of-the-art, incorporation of microstructural parameters into theoretical analysis is essential.

1.2 Classification of the Literature and Some Important Models

According to the classification by Schmalzried,⁽¹⁾ theoretical development of solid state reactions has occurred classically along two lines: a phenomenological approach and a predictive, model oriented approach. In the first, efforts have centered on understanding of "atomistic" reaction processes such as nucleation, phase boundary

reaction and diffusion. Well known monographs by Hauffe⁽²⁾ and Schmalzried⁽³⁾ cover topics predominantly in this category. As the result of a considerable effort by many workers, a reasonable understanding exists today about the mechanisms and kinetics of solid state reactions in simple systems under ideal conditions.⁽¹⁾ For example in some simple quasibinary systems, this phenomena oriented approach can be used to obtain transport properties from macroscopically measured reaction rates, independently measured thermodynamic properties, conductivity and product morphology in a diffusion couple. Conversely, reaction rates can be predicted provided defect equilibrium, and transport properties are known and the number of independent variables are minimized. However, anything more complex than a simple quasibinary system can not be analyzed at the present time. Further, even in simple systems experiments are meaningful only if the reactants are single crystals and in addition to the temperature and pressure, an appropriate number of chemical potentials can be controlled according to the phase rule. Since this control is difficult even under ideal laboratory conditions, the phenomenological approach needs considerable further development before any practical applications can be considered.

The predictive, model oriented, approach has yielded three prominent developments: the 'shrinking core' model, the 'grain model' and the 'nucleation and growth' model, each with a variety of special forms.

1.2.1 Shrinking Core Model for Nonporous Solids

The shrinking core (also called 'unreacted core' or 'topochemical reaction') model has the advantage of physical and mathematical simplicity. Reaction is assumed to proceed by diffusion of one reactant through the nonporous product to a sharp interface of nonporous second reactant. Nucleation occurs instantaneously over the entire reactant surface and therefore does not pose a kinetic barrier. Gas-solid reaction models based on this geometry were developed by St. Clair,⁽⁴⁾ Lu and Bitsianes⁽⁵⁾ and Spitzer et al.⁽⁶⁾ which took into account a variety of factors such as reversibility of reactions, pressure drop across the product layer, etc. Conditions under which both the chemical reaction and the diffusion are of comparable magnitude were modeled by Lu⁽⁷⁾ and multiplicity of reactions was incorporated into analysis by others.⁽⁸⁾ Shrinking core model as modified by Shen and Smith,⁽⁹⁾ further included effects of volume differences between products and reactants as well as the effect of external gas-phase mass transfer. Their model therefore represents the most mature form of shrinking-core model for reactions between gases and nonporous solids.

Shrinking core model indirectly forms the basis of almost all the commonly used solid-solid reaction models in that they usually assume a similar geometry. A surface of a nonporous component with a product layer on it is assumed to be completely and continually covered by the diffusing component. In practice this condition can be realized only for solid-fluid reactions, and therefore such an assumption amounts

to ignoring the effects of external microstructure* on the reaction kinetics. Moreover, almost all models have been devoted to derivation of reaction rates under diffusion control. The well known model by Jander⁽¹⁰⁾ used the parabolic law to predict the time-temperature dependence of fractional reaction. Ginstling and Brounshtein's⁽¹¹⁾ model was similar but made correction for the convergence of flux lines in a spherical particle. Valency⁽¹²⁾ and Carter⁽¹³⁾ modified the kinetic expressions to accomodate effects of volume difference between a product and a reactant. Komatsu and Uemura⁽¹⁴⁾ considered the case in which a product was formed by outward diffusion from a reactant particle, the so-called 'anti-Jander' model. They also modified Ginstling-Brounshtein's and Jander's models as describe reactions proceeding by counterdiffusion at cations, observable by product formation on both sides of a diffusion couple. Since all these models assume that diffusion through the product is rate determining and that diffusivity is solely dependent on the temperature, they are in essence some special cases of the more general shrinking-core model. Therefore, their kinetic expressions can be obtained from the model of Shen and Smith⁽⁹⁾ by appropriate

* By 'external' or 'pellet' microstructure we imply the features associated with arrangement of reactant particulates in the pellet e.g., volume fractions and radii of particles, porosity of pellet, etc. 'Internal' microstructure, on the other hand, refers to the features within a typical reactant particle, e.g., grain size, internal porosity, pore size distribution, etc.

simplifications. In a departure from this trend, Kroger and Ziegler^(15,16) assumed that in addition to Jander's geometry the diffusion coefficient was inversely proportional to the reaction time. This assumption is similar to that by Tamman⁽¹⁷⁾ who treated the rate of change of product thickness as being inversely proportional to the reaction time. Using a similar dependence in Carter-Valency geometry, Hulbert et. al.⁽¹⁸⁾ derived an expression which explained the experimental rates of formation of many spinels. Unfortunately, the resulting expressions of the above three models^(15,16,17,18) have a serious flaw in that they lead to a mathematical singularity at time zero, i.e., under the initial condition. Zuravlev et al.⁽¹⁹⁾ on the other hand, modified Jander's equation by assuming that the activity of reacting species is proportional to the fraction of unreacted material. This is analogous to the kinetics of first order homogeneous reactions and in heterogeneous kinetics would be justified only for a few cases such as selective oxidation of a solute from a dilute or an ideal solid solution. Dunwallt and Wagner⁽²⁰⁾ and Serin and Ellickson⁽²¹⁾ have discussed the kinetics of transient diffusion into a sphere in the absence of a product layer. This analysis too is of limited use since a large number of solid state reactions involve formation of a product layer.

1.2.2 Grain Model for Porous Solids

Whereas the shrinking core topography can be satisfactory for describing the reactions occurring on the surface of an impervious reactant, it is far from accurate when the reactant is porous or when

a significant amount of grain boundary diffusion occurs within a polycrystalline reactant. Under such conditions, the reacted and the unreacted zones of solids are not necessarily separated by a sharp and geometrically well-defined interface. The reaction zone may be diffuse and may extend over a significant part of the reacting solid. In such cases use of the shrinking core model to obtain kinetic parameters can lead to erroneous yet superficially acceptable results. To avoid such pitfalls, it is essential to take into account the internal microstructural parameters such as porosity, grain structures, surface area, etc. From this viewpoint, theoretical analysis of reactions between gases and porous solids has made a remarkable progress with the advent of the 'grain model'. A porous solid* is visualized as a particle of well-defined and unchanging shape consisting of numerous grains, also of well-defined unchanging shape. Reactant gas diffuses across the boundary layer on the external surface, through the pores and finally through the product layer on an individual grain. After the reaction at the interface, product gases, if any, diffuse back into the bulk gas stream. The reaction within an individual grain is assumed to be topochemical, implying instantaneous nucleation over the entire grain surface and hence is described by the shrinking core model.

* "Porous" solid is a solid in which non-uniform diffusion can occur along high diffusivity paths. Thus, a dense polycrystalline solid with no pores can still be considered "porous" if significant mass transport can occur along the grain boundaries.

Szekely and Evans^(22,23) considered a special case of spherical pellet with spherical grains and a uniform constant gaseous diffusivity. They applied their model to the reduction of nickel oxide by hydrogen assuming first order reaction.^(24,25) Sohn and Szekely⁽²⁶⁾ considered a general combination of spherical, cylindrical and platelike grains and pellets. The mathematical formulation was made in terms of dimensionless parameters assuming a first order isothermal reaction. Accordingly, the conditions under which a single or multiple mechanism(s) controls the overall reaction rate may be explicitly written in terms of the magnitudes of three dimensionless parameters: the generalized reaction modulus for the pellet (σ), the generalized reaction modulus for grains (σ_g), and the modified Sherwood number (N_{sh}^*). Each of the above parameters is written in terms of experimentally measurable quantities such as the diffusivity, the specific surface area and the concentration of diffusing species in the bulk fluid. Therefore, the model serves a predictive purpose provided the experimental conditions are well-defined and the governing kinetic parameters are known.

The model was later extended by Song⁽²⁷⁾ to a situation where the gaseous reactant concentration changes during the course of the gas-porous solid reaction. Application of the model to kinetics of reduction of nickel oxide by hydrogen in a fluidized-bed reactor was demonstrated by the same author. It can be shown that analytical asymptotic solutions to the grain-model equations are easy to obtain but yield kinetic expressions which apply only when a single mechanism

controls the overall rate. However, a more interesting use of the grain model pertains to prediction of kinetics under the conditions of mixed control. In general, this can be performed exactly only by numerical methods, a computer program for which has been developed by Evans.⁽²⁸⁾ Fortunately, algebraic sums of asymptotic solutions give reasonably good approximations to the exact numerical solutions. Ranade⁽²⁹⁾ has developed a refined version of the approximate analytical solution for the special case of mixed control by diffusion and phase boundary reaction. His empirical refinement makes the approximate solution almost identical to the exact numerical solution. Extension of the grain model to include effects of Langmuir-Hinshelwood kinetics and its modification to include non-isothermal systems has also been reported.^(30,31)

An important point which has not been brought forth in the existing literature pertains to applicability of the grain model to the kinetics of solid-solid reactions. In such reactions, mass transport of diffusing species through the porous solid may occur by combinations of grain boundary, surface and gaseous diffusion. Since in the derivation of the grain model, no assumptions are made regarding the mode of internal mass transport, the resulting equations are equally valid for all modes of internal mass transport provided the appropriate temperature dependence of diffusivity and the effective cross-sectional area available for transport by each mechanism is taken into account. Therefore, the grain model is potentially as useful for solid-solid reactions as it is for gas-solid reactions provided the underlying assumptions are appropriate for a given system.

1.2.3 Nucleation-Growth Models

Whereas in the shrinking-core and the grain model it is implicitly assumed that the nucleation of the product phase does not represent a kinetic barrier, in nucleation-growth models reaction is assumed to proceed by nucleation of products at randomly distributed active sites followed by growth. The overall transformation rate is governed by relative rates of nucleation and growth which itself may be limited either by the phase boundary reaction or diffusion. A nucleation-growth type of mechanism is especially likely whenever the product phase is partially miscible in one of the reactants.⁽³²⁾ Various forms of nucleation-growth models which describe rates of phase transformation and decomposition have been developed.^(36,37) Avrami's⁽³³⁻³⁵⁾ concept of 'extended' volume is especially important since it has made exact mathematical analysis possible by incorporating the phenomenon of mutual impingement of growing adjacent nuclei. The exact form of kinetic expression is determined principally by the nucleation rate and its time dependence, the rates of phase boundary reaction and diffusion, and the density of nucleation sites. Many of the current efforts in the development of nucleation-growth type of models have been directed to incorporating additional factors such as the lattice mismatch between the parent and the product and the strains associated therewith.

Success of nucleation-growth models in metallurgical phase transformations has been remarkable. Technologically important phase changes, such as the martensitic transformation in steels, are well

described by the model. The model is extensively discussed in monograph dealing with phase transformations.⁽³⁷⁾ Use of these models in mixed powder solid state reactions has not been common except in the case of dissociative reactions where at least one of the products is a gas.⁽³⁸⁾

Hulbert⁽³⁹⁾ has given a brief but succinct description of the general nucleation-growth kinetics which is reviewed in a later part of this thesis.

1.3 Limitations of the Existing Models

In addition to the limitations of individual models, the following general criticism can be made regarding the state-of-the-art.

(a) Inability to incorporate the influence of prior processing: Most of the models commonly used in solid-solid reactions assume that the surface of one of the reactants is continuously and completely covered by the diffusing component. This geometry can be truly realized only in a solid-fluid reaction. In a particulate assembly, unless the gas phase transport is significant, mass transfer to the external surface of the reactant particles must occur by bulk and/or surface diffusion via particulate contact points. Therefore, the arrangement of particulates, i.e., 'external' or 'pellet' microstructure, can be expected to influence the reaction kinetics. Operations such as mixing and pelletizing profoundly affect the microstructure and are known to affect reactions kinetics.^(40,41) Their effect can be predicted only if microstructural parameters are incorporated into the modelling. In this direction, Komatsu⁽⁴²⁾ has modified Jander's model so as to include the number of particulate

contact points as a variable. An empirical relationship between the number of contact points, non-ideality of mixing and time was postulated. The model is supposed to permit calculation of 'true' activation energy. Unfortunately, however, the model involves parameters which cannot be obtained from microstructural examinations and therefore require experimental determinations for each set of processing conditions. This drawback has severely restricted scientific utility of this model. Clearly, the need for a better model remains unfulfilled.

(b) Lack of analysis of structural changes in pellet microstructure: As mentioned above, mass transfer in true solid-solid reactions must occur by surface or bulk diffusion through the particulate contact points. Volume changes accompanying the reaction on a localized (microscopic) level can be expected to increase or decrease contact point area and population. Resulting possible changes in the rate limiting mechanism(s) cannot be predicted using the models available today.

(c) Need for better models pertaining to changes in internal (i.e., particulate) microstructure: Volume changes associated with product formation or a secondary phenomenon such as sintering can alter the microstructure of a porous solid. If the product volume is larger than the volume of reactant consumed, pores may become blocked at some stage and further reaction will proceed as if the solid were nonporous.

If the product volume is smaller, existing pores may become enlarged and new pores may be created. A simplified approach assigns two

different but constant effective diffusivities to the reactant and the product.^(43,44) However, in actuality, structural changes are likely to be more complex in their time-temperature dependence than envisaged in a two-diffusivity approach. Similarly, no theory at present can take into account the stresses generated due to volume changes accompanying the product formation in a nonporous solid. Tangential stresses in the product layer will be compressive or tensile depending on whether the product volume is larger or smaller (respectively) than the volume of the reactant consumed. Resulting changes in the product morphology may effect a change in the rate controlling mechanism, for example, from diffusion control to phase boundary reaction control due to cracking of the product. A model which can predict such changes will be of scientific value.

(d) Lack of data on the exact experimental conditions in the literature: Very few experimental reports on solid-solid reaction studies contain full details about the reactant characteristics such as porosity, pore and grain structure, etc. Therefore, the merits of the models used to analyze the data cannot be effectively judged. Moreover, a large body of previously reported data becomes worthless for testing any new models. Differing values of kinetic parameters are frequently reported by different investigators for an identical reaction system. This situation can be at least partially attributed to indiscriminate use of a model to 'fit' the data without regard to the validity of underlying assumptions in particular reactant and product morphologies.

1.4 Scope of the Present Work

In view of the limitations of the available models, the following theoretical work was considered desirable:

(a) To analyze and obtain quantitative relationships governing various modes of external mass transport. The relationships should include microstructural parameters characterizing the particulate assembly in order to correlate processing with kinetics.

(b) To modify the existing models to make them more suitable for mixed powder reactions as compared to the present forms which are more appropriate for the gas-solid reactions.

(c) To quantitatively analyze effects of localized microscopic dimensional changes accompanying the reaction on the kinetics and the mechanism.

(d) To obtain general theoretical relations between the microscopic particulate dimensional changes due to the reaction and the macroscopic pellet dimensional changes frequently observed in solid state reactions. Based on these relations, to assess the potential of dilatometry as a quantitative tool in the study of mixed powder reaction kinetics.

(e) To provide experimental verification of the theoretical relationships obtained in (a), (b), (c), and (d), if possible.

1.5 The System $\text{PbO} - \text{ZrO}_2$

The system $\text{PbO}-\text{ZrO}_2$ was chosen for the experimental work because it forms an important subsystem in the lead zirconate titanate (PZT) based family of ceramics which have important ferroelectric-piezoelectric properties and applications. Previous work⁽⁴⁶⁾ had

shown that in the synthesis of PZT from the component oxides, the overall kinetics are governed by the processes leading to the formation of perovskite phase at the ZrO_2 interface. Consequently, kinetics of lead zirconate synthesis can provide a valuable insight into the formation of PZT without the additional complications inherent in a ternary system.

Thermodynamic data and the phase diagrams for PZ system have been reported by Holman.⁽⁴⁷⁾ The kinetics of lead zirconate formation has also been a subject of numerous investigations. Kutzendorfer et al.⁽⁴⁸⁾ studied the kinetics of mixed oxides powder reaction and found that the activation energy was 98 Kcal/mole. Gesemann⁽⁴⁹⁾ on the other hand, concluded that lead zirconate forms according to the Jander's model with an activation energy of 40.1 ± 2.8 Kcal/mole. Harris⁽⁵⁰⁾ obtained isotherms for zirconia consumption in PZT synthesis but did not deduce the rate limiting mechanism or calculate the activation energy from the data. Sasaki⁽⁵¹⁾ used PZ system to demonstrate a method of incorporating a particle size distribution into the interpretation of the kinetic data. Accordingly, he calculated the activation energy for the diffusion controlled formation of PZ to be 102.8 Kcal/mole, with the kinetics assumed to follow the Valency-Carter⁽¹³⁾ model. Kapur⁽⁵²⁾ used Sasaki's data but instead of assuming the Valency-Carter model a priori, proved that it was indeed valid. According to the author, the diffusion activation energy was 97.1 Kcal/mole when calculated from a selected part of Sasaki's data. Mangel and Dorskocil⁽⁵³⁾ also

investigated the isothermal mixed powder kinetics of PZ formation and explained the data according to Jander's model with an activation energy of 44 Kcal/mole corresponding to diffusion across the product layer. Their conclusions, however, are based on a very limited part of their data. Most of the data were not suitable for an accurate analysis due to either extremely rapid or very slow reaction rates and hence the reported activation energy is of doubtful significance. Tecilazic-Stevanovic et al.⁽⁵⁴⁾ made use of Sasaki's method of analysis and based on a priori assumption that Valency-Carter model was appropriate for their data, reported an activation energy value of 66.91 Kcal/mole. Their calculated values of reaction constant do not obey Arrhenius equation unequivocally, which raises questions about the validity of the assumed mechanism. Whereas all the above investigations were carried out on the mixed powder systems, Prisedskii et al.⁽⁵⁵⁾ conducted kinetic studies using a diffusion couple experiment. Pressed tablets of lead monoxide and sintered tablets of zirconia were held together and reacted between 710°C and 795°C. Thickness of the product layer was found to obey the parabolic law indicating diffusion control with an activation energy of 131 ± 5.7 Kcal/mole. Based on the effect of modifiers on the kinetics and the product morphology around the natural markers, the authors concluded that an unidirectional diffusion of Pb^{2+} and O^{2-} through the perovskite occurs with Pb^{2+} transport as the rate limiting factor below 900°C.

It is obvious that in the literature the range of values for kinetic parameters is large despite the fact that most studies conclude (or assume) diffusion to be rate controlling. The reasons for this wide range of values are not clear but probably lie in the processing variations and use of models without adequate regard to the underlying assumptions. Part of the present experimental work was therefore carefully designed to study the influence of processing variables, such as mixing, on the kinetics.

The PZ system was also interesting because it displays an anomalous drop in the reaction rates after a certain extent of reaction resulting in an undesirable presence of unreacted oxides in the calcined product. Unreacted zirconia in PZT is especially detrimental to the electrical properties.⁽⁵⁶⁾ Though incomplete reaction is widely evident in literature reports, none of the authors have offered an explanation of this phenomenon nor does there exist any theoretical model of solid state reactions which can either predict or explain the abrupt changes in kinetics. It will be shown in the later part of the thesis that the phenomenon can be explained on the basis of microscopic-dimensional changes and their effect on the reaction kinetics.

2. THEORETICAL CONSIDERATIONS

We shall confine our discussion to a general reaction of the type



where the reactants A and B are in the form of a compacted powder mixture and each reactant consists of monosized particles. If the particles are assumed to be spherical, the microstructure can be schematically shown as in Fig. (1a). If it is further assumed that the reaction product A_aB_b forms as a layer on the surface of B particles by migration of species A, the reaction proceeds by the following sequence of steps:

(a) Transport of A from particulate matrix to the external surface of the product layer, i.e., external mass transport.

(b) Nucleation at the product phase A_aB_b .

(c) Mass transport to the interface of product A_aB_b and reactant B.

(d) Phase boundary reaction at the reaction interface.

Any of these basic mechanisms can control singly or in combination the overall reaction rate. The form of any rate expression in general will reflect the rate governing phenomenon as well as the reactant and product morphology. The product morphology is itself determined by the reactant morphology, nucleation site distribution and the relative rates of nucleation and growth. In the case of external mass transport, the external microstructure (i.e., pellet microstructure) can be an additional influential factor.

Relationship between these various factors has been schematically shown in Fig. (2).

2.1 External Mass Transport:

Since the parameters influencing the external mass transfer of A are independent of processes internal to the particles of B, for the present discussion particles of B will be treated as though they are sinks of certain shape and size dispersed uniformly within the particulate matrix of A. The size ' r_s ' of the sinks may equal or exceed the size ' r_p ' of particles of B with or without the product layer on it. The interaction between the processes that are internal and external to a particle of B will determine the activity of component A at the sink-matrix boundary. Under isothermal conditions we shall assume that activity of A at the boundary remains constant during the course of the entire reaction and is lower than the activity of A elsewhere in the matrix, thereby providing a driving force for the mass transfer of A towards the sink. In general, the following mechanisms can contribute to the overall process:

- (i) bulk or lattice diffusion of A through particulate matrix to the sink boundary;
- (ii) surface diffusion of A along the particulate surface;
- (iii) evaporation of A followed by vapor phase diffusion through the matrix-pores to the sink boundary.

Since these mechanisms are independent of each other, the one which contributes the maximum flux will determine the overall rate.

2.1.1 Lattice Diffusion of A:

In order to estimate the steady state flux by bulk diffusion, Fick's law can be written for the spherical geometry shown in Fig. (1b).

$$J_b(r) = - D_b A_b \frac{1}{\tau_b} \left(\frac{dC_A}{dr} \right)_b \quad (2)$$

where D_b is the lattice self diffusivity of A;

A_b is the effective cross-sectional area available for bulk diffusion at radius r ;

τ_b is the tortuosity factor for bulk diffusion;

and $\left(\frac{dC_A}{dr} \right)_b$ is the radial concentration gradient in the bulk.

The boundary condition is given by,

$$\left(\frac{dC_A}{dr} \right)_b = 0 \text{ at } (r_s + \lambda) \quad (3)$$

where 2λ is the surface-to-surface mean free path between the nearest-neighbor sinks. The effective cross sectional area for bulk transport at radius ' r ' is

$$A_b = 4\pi r^2 (1 - \epsilon) \quad (4)$$

where ϵ is the volume fraction of other phases including porosity in the matrix. Solution to Fick's law is much simplified if the diffusivity is assumed to be equal everywhere within the matrix. Steady state mass flux from the largest radius of $(r_s + \lambda)$ to (r_s) is then obtained by solving equations (2), (3), (4):

$$J_b = -D_b \frac{4\pi(1-\epsilon)}{\tau_b} \frac{\Delta C_b}{\left(\frac{1}{r_s} - \frac{1}{r_s + \lambda}\right)} \quad (5)$$

where ΔC_b is the concentration difference in A from $(r_s + \lambda)$ to (r_s) in the solid phase.

In the above derivation r_s , λ , τ_b , and ϵ were treated as constants. However, all these parameters will change during the course of reaction and therefore the flux can be considered as quasi-steady-state only if the rate of change of these parameters is much smaller than the rate of change in flux. Equation (5) will then represent the maximum possible contribution to the quasi-steady-state flux by bulk diffusion under isothermal conditions and the stated assumptions.

2.1.2 Surface Diffusion of A:

As in the case of bulk diffusion, Fick's law can again be applied assuming spherical geometry and steady state conditions. Surface diffusive flux across an imaginary spherical surface at radius ' r ' from the center of a sink (Fig. 3a) is given by:

$$J_s(r) = - D_s A_s \frac{1}{\tau_s} \left(\frac{dC_A}{dr} \right)_s \quad (6)$$

where D_s is the surface diffusivity;

τ_s is the surface tortuosity;

A_s is the effective cross-sectional area available for surface diffusion at 'r'; and

$\left(\frac{dC_A}{dr} \right)_s$ is the radial gradient in the surface concentration of A.

Assuming that the surface diffusion occurs in a layer of the same thickness as the lattice parameter ' $\hat{a}$ ',

$$A_s = \hat{a} L_p \quad (7)$$

where L_p is the total length of the perimeter of solid A lying in the imaginary spherical test-plane of radius 'r'. The test plane will intercept $N(r)$ number of spherical particles of A-matrix. As shown in Fig. (3b), the resulting circular cross-section will have a mean perimeter $(2\pi r_A)$ and, if it is considered approximately planar, a mean intercept area $\frac{2\pi}{3} r_A^2$. Therefore,

$$\begin{aligned}
 N(r) &= \frac{\text{Total area of A particles in a test plane at } r}{\text{Mean intercept area of an A particle}} \\
 &= \frac{6(1-\epsilon) r^2}{r_A^2} \quad (8)
 \end{aligned}$$

Consequently,

$$\begin{aligned}
 L_p &= N(r) \times \text{mean perimeter of an A particle} \\
 &= \frac{12\pi(1-\epsilon) r^2}{r_A^2} \quad (9)
 \end{aligned}$$

Substituting equations (7) and (9) in (6),

$$J_s(r) = -D_s \frac{\hat{a}}{r_s} \frac{12\pi(1-\epsilon)r^2}{r_A^2} \left(\frac{dC_A}{dr} \right)_s \quad (10)$$

If the entire diffusing mass is delivered to the sink, flux is independent of r within limits $(r_s + \lambda)$ and (r_s) , whereby

$$J_s = -D_s \frac{12\pi(1-\epsilon)}{r_s} \frac{\hat{a}}{r_A} \left(\frac{1}{r_s} \cdot \frac{\Delta C_s}{r_s + \lambda} \right) \quad (11)$$

ΔC_s being the surface concentration difference in A from $(r_s + \lambda)$ to r_s .

In terms of the surface area of A,

$$J_s = -D_s 4\pi\delta\rho_A S_{WA} \frac{(1-\epsilon)}{\tau_s} \frac{\Delta C_s}{\left(\frac{1}{r_s} - \frac{1}{r_s + \lambda}\right)} \quad (12)$$

where ρ_A is the density; and S_{WA} is the surface area of A per unit mass.

During the course of the reaction particle size, surface area, porosity, λ and r_s are continually changing and the flux can be considered quasi-steady-state provided changes in these variables are small during the relaxation time of the diffusive process.

The main limitation on the use of equations (11) and (12) for calculation of surface diffusive flux is imposed by lack of surface diffusivity data or alternate reliable methods of estimation. Whereas Askill⁽⁵⁸⁾ recommends that the surface diffusion activation energy Q_s be taken as 25 percent of the bulk activation energy Q_b for estimation purposes, reported data⁽⁵⁹⁾ on Q_s of alumina as determined by surface diffusion controlled grain-boundary grooving is close to 66 percent of Q_b reported by Paladino and Kingery.⁽⁶⁰⁾ Shewmon⁽⁶¹⁾ on the other hand has suggested that Q_s is more closely related to the heat of vaporization than to Q_b , since an atom jumping along a surface is well on its way to being an evaporated atom. This approach has been successful in explaining experimental data for FCC metals. Clearly, methods of estimation of surface diffusivity are far from reliable and therefore use of equations (11) and (12) will be largely limited to those few systems for which accurate experimental data are available.

2.1.3 Vapor Phase Diffusion of A:

In gaseous mass transport, two independent kinetic steps are involved; sublimation followed by diffusion by molecular or Knudsen flow. Either of these steps may control the overall rate and among other factors, both are influenced by the total ambient pressure.

First, consider the limiting case of a maximum rate of sublimation. If diffusion is rapid, a uniform partial pressure of A equal to $P(r_p)$ will be maintained everywhere. If in addition the total pressure is low, the maximum rate of sublimation is given by:

$$j_{\max} = \frac{\alpha(P_{\text{Aeq}} - P(r_p))}{\sqrt{2\pi M_A RT}} \quad (13)$$

where $j_{\max}$ is the maximum molar flux per unit solid surface area;

P_{Aeq} is the equilibrium vapor pressure of A;

M_A is the molecular weight of gaseous species of A; and

α is the coefficient of evaporation subject to $(0 \leq \alpha \leq 1)$

The maximum possible flux that can reach a sink is then given by

$$\begin{aligned} J_{V_{\max}} &= (j_{\max}) \times (\text{surface area of solid A per sink}) \\ &= (j_{\max}) \rho_A S_{WA} (1 - \epsilon) \frac{4\pi}{3} [(r_s + \lambda)^3 - r_s^3] \end{aligned} \quad (14)$$

changes in S_{WA} , ϵ , r_s and λ accompanying the reaction can be incorporated into the above equation. Petersen⁽⁶²⁾ has analyzed a similar case where the overall size of the solid remains constant while uniform cylindrical pores with random intersections continually enlarge within the solid due to a reaction. Changes in S_{WA} and ϵ were calculated in terms of initial values and the extent of reaction. The model was reasonably successful in describing structural changes accompanying complete gasification of graphite. In cases where the microstructure of A can be approximated as uniform cylindrical pores with random intersections, Petersen's model may be adopted to estimate the maximum possible sublimation flux under changing structural conditions.

Whereas $J_{v_{\max}}$ represents the maximum possible flux, the actual flux is likely to be much lower due to finite diffusivity and atmospheric pressure. Consider the case where solid A is not a collection of particles but instead a "swiss-cheese" like solid with spherical sinks of radius r_s distributed uniformly (Fig. 4). Mass transport is assumed to occur from the inner surface of the cavities to a concentric surface of radius r_p ($r_p < r_s$) maintained at a partial pressure $P(r_p)$ of species A. Now the general gas phases mass transfer is given by:

$$N_A = -CD_{AG}\nabla X_A + X_A(N_A + N_G) \quad (15)$$

where

N_A , N_G are the molar fluxes per unit area with respect to a stationary coordinate system;

x_A , D_{AG} are the mole fraction and the diffusivity of A in the gas mixture A + G respectively;

C is the total molar concentration equaling $(C_A + C_G)$

Assuming ideal gas law,

$$C = \frac{P_T}{RT} \quad (16)$$

$$\text{and } x_A = \frac{P_A}{P_T} \quad (17)$$

where P_T is the total gas pressure.

Total flux crossing a spherical surface of radius 'r' is then given by:

$$J(r) = 4\pi r^2 N_A = 4\pi r^2 \frac{P_T}{RT} D_{AG} \frac{d}{dr} \ln(P_T - P_A) \quad (18)$$

For a steady-state mass balance,

$$\frac{d}{dr} J(r) = 0 \quad (19)$$

with the boundary conditions,

$$P_A = P_{Aeq} \text{ at } r = r_s \quad (20)$$

$$P_A = P(r_p) \text{ at } r = r_p \quad (21)$$

Solution to equations (18) through (21) gives the desired steady state sublimation flux

$$J_o = \frac{4\pi D_{AG}}{(1/r_p - 1/r_s)} \frac{P_T}{RT} \ln \left[\frac{P_T - P(r_p)}{P_T - P_{Aeq}} \right] \quad (22)$$

When $[P_T \gg P(r_p), P_{Aeq}]$ it follows that

$$J_o = \frac{4\pi D_{AG}}{(1/r_p - 1/r_s)} \left[\frac{P_{Aeq} - P(r_p)}{RT} \right] \quad (23)$$

Equations (22) and (23) represent steady-state sublimation flux from the surface of a spherical sink. Results of similar analysis for cylindrical or planar shaped sinks can be written in a general form:

$$J_o = \frac{D_{AG}}{RT} (P_{Aeq} - P(r_p)) f(r_p, r_s) \quad (24)$$

where for spherical sinks,

$$f(r_p, r_s) = \frac{4\pi}{\left[\frac{1}{r_p} - \frac{1}{r_s} \right]} \quad (25)$$

and for cylindrical sinks of length L ($L \gg r_p$)

$$f(r_p, r_s) = \frac{2\pi L}{\ln(r_p/r_s)} \quad (26)$$

and for flat-plate-like sinks of area A_p ,

$$f(r_p, r_s) = \frac{A_p}{(r_p - r_s)} \quad (27)$$

Once again, the psuedo-steady-state approximation will be valid only if the rates of changes in r_p and r_s are small compared to the rapidity with which flux can adjust to these changes.

In deriving equations (24) through (27) we assumed a 'cheese-like' microstructure that is unsuitable for describing most pellet microstructures encountered in the mixed-powder solid state reactions. However, a useful conclusion that can be drawn from equation (24) is that sublimation is a reaction of first-order when the partial pressure of A is small everywhere when compared to the total pressure. This fact may now be used to obtain the flux under a more realistic microstructure for which external mass transport by lattice diffusion and surface diffusion was discussed earlier, i.e., a porous matrix of particulates of A with spherical sinks distributed within it as shown in Fig. (5a). When the effective diffusivity is finite, the region of the matrix far from a sink will not contribute as much to the mass transport as will the region adjoining the sink. Thus, sublimation will occur mainly from a thin "sublimation zone" adjoining the sink boundary, the radius of which will continually enlarge till the entire solid matrix of A is consumed by the reaction. A mass balance in a unit volume of porous solid can be written as,

$$\text{Input flux} - \text{output flux} + \text{sublimation} = 0 \quad (28)$$

Assuming that

$$(\text{Sublimation rate/unit solid surface area}) = k_s (C_{Aeq} - C_A) \quad (29)$$

the mass balance equation can be written as:

$$D_{Aeff} \nabla^2 C_A - k_s \rho_A S_{WA} (1 - \epsilon) (C_A - C_{Aeq}) = 0 \quad (30)$$

where

C_A is the gas phase molar concentration of A per unit volume of porous matrix;

C_{Aeq} is the gaseous concentration of A in equilibrium with solid; and

k_s is the sublimation rate constant.

The boundary conditions are given by

$$C_A = C_{AS} \text{ at } r = r_s \quad (31)$$

$$\left(\frac{dC_A}{dr} \right) = 0 \text{ at } r = r_s + \lambda \quad (32)$$

Even when the pellet microstructure is initially uniform, due to the "zoned" nature of the mass transport the microstructure of a partially

reacted sample will be non-uniform. That is, due to prior sublimation surface area S_{WA} , porosity ϵ , and effective diffusivity D_{Aeff} will be dependent on the location 'r'. Analytical solution to the mass transport equation then becomes exceedingly complex. Therefore, as an approximation we shall assume that all of the above-mentioned parameters are invariant everywhere within the particulate matrix. We may now define some dimensionless variables as follows:

$$\Gamma \equiv \frac{C_A(r) - C_{Aeq}}{C_{Aeq}} = \frac{P_A(r) - P_{Aeq}}{P_{Aeq}} \quad (33)$$

$$\Gamma_0 \equiv \frac{C_{AS} - C_{Aeq}}{C_{Aeq}} = \frac{P_{AS} - P_{Aeq}}{P_{Aeq}} \quad (34)$$

$$\xi \equiv \frac{r}{r_s} \quad (35)$$

$$\xi_1 \equiv \frac{r_s + \lambda}{r_s} \quad (36)$$

$$h^2 \equiv k_{sA} S_{WA} (1 - \epsilon) r_s^2 / D_{Aeff} \quad (37)$$

The general mass balance equation then becomes

$$\nabla^2 \Gamma - h^2 \Gamma = 0 \quad (38)$$

Under conditions of spherical symmetry,

$$\frac{d^2 \Gamma}{d\xi^2} + \frac{2}{\xi} \frac{d\Gamma}{d\xi} - h^2 \Gamma = 0 \quad (39)$$

with the boundary conditions

$$\Gamma = \Gamma_0 \text{ at } \xi = 1 \quad (40)$$

$$\text{and } \frac{d\Gamma}{d\xi} = 0 \text{ at } \xi = \xi_1 \quad (41)$$

the solution can be obtained in a rather straight-forward manner and is as follows

$$\frac{\Gamma}{\Gamma_0} = \frac{1}{\xi} \frac{(h\xi_1) \cosh[h(\xi_1 - \xi)] - \sinh[h(\xi_1 - \xi)]}{(h\xi_1) \cosh[h(\xi_1 - 1)] - \sinh[h(\xi_1 - 1)]} \quad (42)$$

Flux across a spherical imaginary surface at radius 'r' is given by

$$J(r) = -4\pi r^2 \frac{D_{Aeff}}{RT} \frac{P_{Aeq}}{r_s} \left(\frac{d\Gamma}{d\xi} \right)_{\xi = \frac{r}{r_s}} \quad (43)$$

Total flux J_v reaching a spherical sink is obtained by substituting ($\xi = 1$) in the above equation whereby

$$J_v = 4\pi r_s \frac{D_{Aeff}}{RT} (P_{Aeq} - P_{As}) \frac{(1-h^2 \xi_1) \sinh[h(\xi_1-1)] - h(\xi_1-1) \cosh[h(\xi_1-1)]}{h \xi_1 \cosh[h(\xi_1-1)] - \sinh[h(\xi_1-1)]} \quad (44)$$

Alternately,

$$J_v = 4\pi r_s \frac{D_{Aeff}}{RT} (P_{Aeq} - P_{As}) \frac{(1+h)(1-h\xi_1) \exp[h(\xi_1-1)] - (1-h)(1+h\xi_1) \exp[-h(\xi_1-1)]}{(1-h\xi_1) \exp[h(\xi_1-1)] - (1+h\xi_1) \exp[-h(\xi_1-1)]} \quad (44a)$$

The corresponding result for a thin planar shaped sink of surface area ' A_p ' and thickness ' $2r_s$ ' is:

$$J_v = \frac{A_p}{r_s} \frac{D_{Aeq}}{RT} (P_{Aeq} - P_{As}) h \frac{\exp(-h) - \exp[-h(2\xi_1-1)]}{\exp(-h) + \exp[-h(2\xi_1-1)]} \quad (45)$$

with the concentration profile given by:

$$\frac{r}{r_o} = \frac{\exp(-h\xi) + \exp(-h(2\xi_1 - \xi))}{\exp(-h) + \exp(-h(2\xi_1 - 1))} \quad (46)$$

It is obvious from equations (44) and (45) that the parameter ' h ' is analogous to the "Thiele parameter" of heterogeneous catalysis except that ' h ' will change during the course of the reaction while typically the Thiele parameter does not change. Physically ' h^2 ' represents the ratio of evaporation capacity to diffusion capacity of the system. High effective diffusivity is reflected in a low value of ' h ' while slow diffusion and rapid sublimation is indicated by a large value of ' h '. Therefore, " h " may be defined as the "sublimation-transport modulus".

It is simpler to visualize the case of a single sink in an infinite particulate matrix of A, a condition described by $\lambda \rightarrow \infty$ or $\varepsilon_1 \rightarrow \infty$. Equations (42) and (44) for a spherical sink then assume the following form:

$$(\text{Lim } \varepsilon_1 \rightarrow \infty) = r_0 \frac{\exp[-h(\xi - 1)]}{\xi} \quad (47)$$

$$\text{i.e., } [P_A]_{\lambda \rightarrow \infty} = P_{Aeq} - (P_{Aeq} - P_{As}) \frac{r_s}{r} \exp \left[\left(1 - \frac{r}{r_s}\right) \sqrt{\frac{k_s \rho_A S_{WA}(1 - \varepsilon)}{D_{Aeff}}} \right] \quad (48)$$

$$\text{and } J_V(\text{Lim } \varepsilon_1 \rightarrow \infty) = 4\pi r_s D_{Aeff} r_0 (h + 1) \frac{P_{Aeq}}{RT} \quad (49)$$

$$\text{i.e., } [J_V]_{\lambda \rightarrow \infty} = 4\pi r_s \frac{D_{Aeff}}{RT} (P_{Aeq} - P_{As}) \left[1 + \sqrt{\frac{k_s \rho_A S_{WA}(1 - \varepsilon)}{D_{Aeff}}} \right] \quad (50)$$

Correspondingly, for a planar sink in an infinite particulate matrix

$$r(\text{Lim } \varepsilon_1 \rightarrow \infty) = r_0 \exp[-h(\xi - 1)] \quad (51)$$

$$\text{i.e., } [P_A(r)]_{\lambda \rightarrow \infty} = P_{Aeq} - (P_{Aeq} - P_{As}) \exp \left[\left(1 - \frac{r}{r_s}\right) \sqrt{\frac{k_s \rho_A S_{WA}(1 - \varepsilon)}{D_{Aeff}}} \right] \quad (52)$$

and

$$J_V[\text{Lim } \varepsilon_1 \rightarrow \infty] = \frac{A_D}{r_s} D_{Aeff} \left(\frac{P_{Aeq} - P_{As}}{RT} \right) h \quad (53)$$

$$\text{i.e., } [J_v]_{\lambda \rightarrow \infty} = \frac{A_p}{r_s} \frac{D_{\text{Aeff}}}{RT} (P_{\text{Aeq}} - P_{\text{As}}) \sqrt{\frac{k_s \rho_A S_{\text{WA}} (1 - \epsilon)}{D_{\text{Aeff}}}} \quad (54)$$

Concentration profiles for a spherical sink as given by equation (48) for two cases of $\lambda \rightarrow \infty$ and $\lambda = r_s$ are shown in Figs. (6a,b) for a range of values of 'h'. A strong influence of 'h' on the concentration profiles is evident. Also, for small diffusivities (i.e., large h), most of the mass transfer occurs from a small region adjoining the sink. For example, in the case of $\lambda \rightarrow \infty$ and $h=10$, almost all the sublimation occurs from a region of thickness $(0.4 r_s)$ adjoining the sink. As the sink becomes larger due to sublimation, the relative width of this "sublimation zone" remains unchanged provided 'h' remains the same although physically the zone moves outwards.

Influence of mean distance between adjoining sinks on the flux is shown in Fig. (5b) where dimensionless flux is plotted against dimensionless mean center-to-center distance between the nearest sinks for various values of sublimation-transport modulus. For a given effective diffusivity (i.e., given h), the effect of neighboring sinks on the flux to a sink is negligible beyond a critical range of (λ/r_s) . For mean-free-distances exceeding the critical, the matrix can be treated as essentially infinite and corresponding equations may be used without significant errors. The larger the diffusivity (i.e., smaller h), the larger is the critical mean-free-distance between the adjoining sinks.

In reality, each sink contains a particle of reactant B with a layer of product $A_a B_b$ on it. When radius ' r_p ' of such a

particle exactly equals sink radius ' r_s ', P_{As} may be approximated as the equilibrium partial pressure $P(r_p)$ of component A over the A-saturated product A_aB_b . When the sink radius ' r_s ' is larger than ' r_p ', P_{As} in general will exceed $P(r_p)$ and the flux from r_s to r_p will be given by an equation analogous to (24):

$$J_o = 4\pi \frac{D_{AG}}{RT} \frac{P_{As} - P(r_p)}{(1/r_p - 1/r_s)} \quad (55)$$

Rigorous solution to the diffusion equation requires matching of fluxes and partial pressure at r_s with two different diffusivities D_{Aeff} for the porous matrix and D_{AG} for the mass transfer from r_s to r_p . Flux is then given by:

$$J_v = 4\pi \frac{D_{AG}}{RT} \frac{r_s r_p}{r_s - r_p} \frac{P_{Aeq} - P(r_p)}{1 + \delta} \quad (56)$$

where

$$\delta = \frac{D_{AG}}{D_{Aeff}} \left(\frac{r_p}{r_s - r_p} \right) \frac{\sinh[h(\xi_1 - 1)] - h\xi_1 \cosh[h(\xi_1 - 1)]}{(1 - \xi_1 h^2) \sinh[h(\xi_1 - 1)] - h(\xi_1 - 1) \cosh[h(\xi_1 - 1)]} \quad (57)$$

Equations (56) and (57) represent the most general solution to the external mass transport by sublimation-gas phase diffusion in a spherical geometry under isothermal conditions in a porous matrix. Since we have assumed that S_{WA} , ϵ and D_{Aeff} are identical everywhere within the particulate matrix. This solution will be valid at

least during the initial stage of the reaction. The maximum possible flux, however, is limited to $J_{V_{MAX}}$ as given by equations (13) and (14).

2.1.4 Relative Contributions to the Net External Flux

The total flux of species A to the outer surface of particles of B (with product layer on it) is the summation of individual contributions by bulk, surface and vapor-phase diffusions.

$$J_{ex} = J_b + J_s + J_v \quad (58)$$

where J_b is the bulk diffusion contribution given by Equation (5), J_s is the surface diffusion contribution given by (12) and J_v is gas-phase diffusion contribution given by equation (56) subject to a maximum $J_{V_{MAX}}$ given by Equation (14).

Assuming that the concentration difference ΔC_b equals ΔC_s ; the ratio of bulk and surface diffusion fluxes is given by:

$$\frac{J_b}{J_s} = \frac{D_b}{D_s} \frac{\tau_s}{\tau_b} \frac{1}{\hat{a} \hat{s}_{WA} \rho_A} \quad (59)$$

Tortuosities for the two modes may be assumed to be equal. The above equation can then be written as

$$\frac{J_b}{J_s} = \frac{D_b}{D_s} \frac{r_A}{3\hat{a}} = \frac{D_{b0}}{D_{s0}} \frac{r_A}{3\hat{a}} \exp\left(-\frac{Q_b - Q_s}{RT}\right) \quad (60)$$

It is obvious that at lower temperatures and smaller particle size of A, contribution of surface diffusion in general will be much larger than that of bulk diffusion. Bulk diffusion, on the other hand, will contribute more to the total flux than surface diffusion at larger particle sizes and higher temperatures.

For a comparison of contributions of vapor phase diffusion and bulk diffusion, consider the case of an infinitely long separation between adjoining B particles (i.e., $\lambda \rightarrow \infty$). It follows then

$$\frac{J_b}{J_v} = \frac{D_b}{D_{Aeff}} \frac{1 - \epsilon}{1 + h} \frac{RT}{\tau_b} \frac{\Delta C_b}{P_{Aeq} - P_{As}} \quad (61)$$

where ΔC_b is the concentration difference in the lattice of A corresponding to the difference in the partial pressure ($P_{Aeq} - P_{As}$). The temperature dependence of (J_b/J_v) ratio is complex because of variations in the diffusivities, vapor pressures, concentration gradients and h with the temperature. But at any given temperature, the ratio can be calculated provided the transport and thermodynamic parameters are known.

Comparison of contributions by surface diffusion and vapor-phase mass transfer can be made readily from equations (60) and (61).

2.2 Modification of Shrinking Core Model; Reaction Kinetics for Non-porous Solids

A significant feature of the external mass transport discussion so far has been the incorporation of microstructural parameters λ , r_A and r_B explicitly into the transport equations. Whereas existing

forms of "shrinking core" model cannot account for microstructural influences, the model can now be modified in a straight-forward manner to include these factors (Appendix A). The resulting kinetic expression for mixtures of spherical particles can be written as:

$$\frac{r_{Bo}}{k_r} \phi_r + \frac{r_{Bo}^2}{2k_D} \phi_D + \frac{r_{Bo}^2}{k_{ex}} \phi_{ex} = \hat{t} \quad (62)$$

$$\text{where } \phi_r \equiv 1 - (1 - x)^{1/3} \quad (63)$$

$$\phi_D \equiv \frac{Z - (Z - 1)(1 - x)^{2/3} - [1 + (Z - 1)x]^{2/3}}{(Z - 1)} \quad (64)$$

$$\phi_{ex} \equiv \frac{\beta}{(Z - 1)} \left\{ \left[1 + (Z - 1)x \right]^{1/3} - 1 + \beta \ln \left(\frac{\beta + 1}{\beta + [1 + (Z - 1)x]^{1/3}} \right) \right\} \quad (65)$$

$$\beta \equiv \frac{\lambda}{r_{Bo}} \quad (66)$$

$$\hat{t} \equiv \frac{M_B b}{\rho_B a} C_A (r_p + \lambda) t \quad (67)$$

'x' is the fraction of reaction completed in time 't' assuming monosized nonporous reactant B of initial particle size 'r_{Bo}', 'Z' is the volume of product A_aB_b formed per unit volume of reactant B consumed and M_B, ρ_B are the molecular weight and density of reactant B, respectively. k_r, k_D and k_{ex} are the rate constants

for phase boundary reaction, diffusion across the product layer and external mass transport of A, respectively.

Each of the three terms on the LHS of Equation (62) has the dimension of time. Thus, the total reaction time required for 'x' fractional conversion is a sum of the characteristic times required for the three steps: external transport, diffusion through the product layer and finally the phase boundary reaction. This result is similar to the classical shrinking core model^(4,9) except for the exact form of ϕ_{ex} .

When the rate constant for phase boundary reaction is much smaller than the rate constants for diffusion and external transport (i.e., $k_r \ll k_D, k_{ex}$), the overall reaction rate is governed by phase boundary reaction. General kinetic expression then is the same as that in the classical shrinking core model, given by:

$$\hat{t} = \hat{t}_r \equiv \frac{r_{Bo}}{k_{ro}} [1 - (1 - x)^{1/F_p}] \exp\left(\frac{Q_r}{RT}\right) \quad (68)$$

where the shape factor F_p for reactant particles B is defined as follows:

$$\begin{aligned} F_p &= 3 \text{ for spherical particles} \\ &= 2 \text{ for long cylindrical particles} \\ &= 1 \text{ for flat platelike particles} \end{aligned} \quad (69)$$

and k_{r0} , Q_r are the pre-exponential constant and the activation energy for the phase-boundary reaction, respectively.

When the overall rate is limited by the diffusion across the product layer, the rate constants are such that

$$k_D \ll k_r, k_{ex}$$

The overall kinetic expression then takes the following form:

$$\hat{t} = \hat{t}_D = \frac{r_{Bo}^2}{2k_{D0}} \phi_D \exp\left(\frac{Q_D}{RT}\right) \quad (70)$$

where k_{D0} , Q_D are the pre-exponential constant and the activation energy for diffusive transport across the product layer and function ϕ_D is defined by:

$$\begin{aligned} \phi_D &= Zx^2 \text{ for } F_p = 1 \\ &= \frac{[1 + x(Z-1)] \ln [1 + x(Z-1)]}{(Z-1)} + (1+x) \ln (1-x) \text{ for } F_p = 2 \\ &= \frac{Z - (Z-1)(1-x)^{2/3} - [1 + x(Z-1)]^{2/3}}{(Z-1)} \text{ for } F_p = 3 \end{aligned} \quad (71)$$

This result too, is identical to the classical shrinking core model.^(12,13)

When external mass transport is the limiting factor in the overall kinetics, the rate expression takes the form

$$\hat{t} = \hat{t}_{ex} \equiv \frac{r_{Bo}^2}{k_{ex}} \phi_{ex} \quad (72)$$

where ϕ_{ex} is given by equation (65) for spherical geometry. If the major contribution to the external mass transport is from the bulk or surface diffusion of A, the rate constant k_{ex} is given by:

$$k_{ex} = \frac{D_b(1-\epsilon)}{\tau_b} + \frac{D_s \hat{a}_p S_{WA}(1-\epsilon)}{\tau_s} \quad (73)$$

On the other hand, when the vapor-phase mass transport plays the most significant role in the external mass flux, k_{ex} is given by

$$k_{ex} = \frac{D_{Aeff}}{RT} \frac{P_{Aeq} - P(r_p)}{\Delta C_b} \frac{(1-\xi_1 h^2) \sinh[h(\xi_1-1)] - h(\xi_1-1) \cosh[h(\xi_1-1)]}{\sinh[h(\xi_1-1)] - h\xi_1 \cosh[h(\xi_1-1)]} \quad (74)$$

If the particle size of reactant B is very large in comparison to the mean free path between adjoining B particles (i.e., $r_{Bo} \gg \lambda$), the dimensionless microstructural parameter β approaches zero. Then the logarithmic term in equation (65) becomes negligible. In such a case, the reaction kinetics are described by

$$\frac{r_{Bo} \lambda}{k_{ex}} \frac{[1 + (Z - 1)x]^{1/3} - 1}{(Z - 1)} = \hat{t} \quad (75)$$

This expression is similar to the external mass transfer limited gas-solid reactions with equivalent mass transfer coefficient given by:

$$h_D = \frac{k_{ex}}{\lambda} \quad (76)$$

Little error is involved, therefore, if the classical shrinking-core model for gas-solid reactions is used to analyze solid-solid reaction data provided condition ($r_{Bo} \gg \lambda$) is satisfied. The error involved will be non-trivial when this conditions is not fulfilled as is clear from Fig. (7).

2.3 Modification of Grain Model; Reaction Kinetics for Porous Solids:

In solid reactants in which non-uniform diffusion can occur along high-diffusivity paths, mass transport and chemical reactions can occur simultaneously throughout the solid. The reaction zone in such a case is diffuse rather than well defined. Sohn and Szekeley^(44,45) have given a detailed mathematical formulation of the grain model to analyze such a gas-porous solid reaction under a certain set of assumptions. In order to adapt the model for solid-solid reactions occurring in mixed powder systems it has to be modified to account for surface and/or bulk diffusion in the external mass transport. This has been performed in Appendix B under added assumptions that the initial particle size ' r_{Bo} ' of reactant B is much larger than the mean-free-path between adjoining B particle (i.e., $\delta \gg 0$) and the

product volume formed equals reactant volume consumed (i.e., $Z = 1$).

The approximate solution to the general kinetic problem can then be written as

$$t^* = \phi_{gr} + \sigma_g^2 \phi_{gd} + \sigma^2 \phi_D + \frac{2D}{k_{ex}} \frac{\lambda A_p}{F_p V_p} \sigma^2 x \quad (77)$$

where

$$\phi_{gr} \equiv 1 - (1 - x)^{1/F_g} \quad (78)$$

$$\phi_{gd} \equiv \begin{cases} x^2 & \text{for } F_g = 1 \\ x + (1 - x) \ln(1 - x) & \text{for } F_g = 2 \\ 3 - 2x - 3(1 - x)^{2/3} & \text{for } F_g = 3 \end{cases} \quad (79)$$

$$\phi_D \equiv \begin{cases} x^2 & \text{for } F_p = 1 \\ x + (1 - x) \ln(1 - x) & \text{for } F_p = 2 \\ 3 - 2x - 3(1 - x)^{2/3} & \text{for } F_p = 3 \end{cases} \quad (80)$$

$$\sigma^2 \equiv F_p \left(\frac{V_p}{A_p} \right)^2 \frac{A_g}{F_g V_g} \frac{(1 - \epsilon_B) k_r}{2D_e} \quad (81)$$

$$\sigma_g^2 \equiv \frac{k_r}{2k_D} \frac{V_g}{A_g} \quad (82)$$

$$t^* \equiv \frac{bM_B}{ap_B} k_r \frac{A_g}{V_g F_g} C_{Ao} t \quad (83)$$

X is the fractional conversion of uniform sized particles of volume ' V_p ', surface area ' A_p ', porosity ' ϵ_B ' and shape factor ' F_p ' consisting of uniform sized grains of shape factor ' F_g '. The shape factor is 3 for spheres, 2 for long cylinders and 1 for flat plates. ' D_e ' is the effective diffusivity of A through the pores of reactant B.

As in the case of the shrinking-core model, each of the four terms on the RHS of equation (77) has dimension of time and as such represents the time contribution of the four steps involved viz. external transport, pore diffusion, diffusion across the product layer on a grain and finally the phase boundary reaction. The term which has the largest magnitude will represent the mechanism limiting overall rate while two or more terms of similar magnitude indicate mixed control.

When phase-boundary reaction, pore-diffusion or intragrain diffusion limit the reaction rate, the kinetic expressions are identical to those of the grain model of Sohn and Szekely⁽²⁶⁾ and will not be discussed here further.

When the external mass transfer limits the overall reaction rate, granularity and porosity of the solid B obviously have no relevance to the kinetics. Assumptions ($r_{Bo} \gg \lambda$) and ($Z = 1$) can then be relaxed to obtain a more general kinetic expression which is identical

for porous and nonporous solids. For spherically shaped B particles, the expression is given by:

$$\frac{r_{Bo}^2 (1 - \epsilon_B)}{k_{ex}} \phi_{ex} = \frac{M_B b}{\rho_B a} C_A (r_p + \lambda) t \quad (84)$$

where ϕ_{ex} is given by equation (65). As discussed earlier, the logarithmic term in equation (65) becomes negligible only when ($r_p \gg \lambda$). In such a case the expression can be further simplified to assume a form similar to gas-solid reactions.

2.4 Contact Maintenance Theory: Shift in Rate Controlling Mechanism due to Microscopic Dimensional Changes

External mass transport by lattice or surface diffusion requires physical contact between the particles of two reactants for the reaction to proceed while gas phase external transport can occur without such a contact. In a pellet, adjoining particles of a reactant may be initially in contact but the possibility of loss of contact is real in later stages in view of the dimensional changes on microscopic and macroscopic levels occurring as a result of reactant consumption and product formation. If the contact between the reactant is lost, the main mode of external mass transfer will shift from lattice or surface diffusion to the gas-phase diffusion. Such a change may or may not be accompanied by a change in the overall reaction rate. Presently, no theoretical model exists which can predict the conditions under which such a change is possible. Hence, the effort here will be to develop quantitative conditions which characterize this phenomenon.

For the reaction indicated by equation (1) proceeding by product formation as a shell on the surface of reactant B, we shall make the following additional assumptions:

- (i) Particles of reactant A and B are of uniform size r_{A0} and r_{B0} , respectively.
- (ii) The initial mixture is in the stoichiometric ratio.
- (iii) Each particle undergoes an equal extent of reaction.
- (iv) Reactants maintain their original shape which presently will be assumed to be spherical.
- (v) No sintering, bonding or liquid formation occurs.

If 'Z' is the volume of product formed per unit volume of reactant B consumed, then it follows that

$$Z = \frac{r_p^3 - r_B^3}{r_{B0}^3 - r_B^3} \quad (85)$$

where

r_p is the external radius of partially reacted B particle with product-layer on;

r_B is the radius of the unreacted B core; and

r_{B0} is the initial radius of a B particle.

Since no sintering of either the reactant or the product is assumed to occur during the reaction, Z is a constant given by

$$Z = \frac{M_p \rho_B}{b M_B \rho_p} \frac{1 - \epsilon_B}{1 - \epsilon_p} \quad (86)$$

where

M_p, M_B are the molecular weights, ρ_p, ρ_B are the densities, and ϵ_p, ϵ_B are the porosities of the product $A_a B_b$ and reactant B, respectively.

For monosized particles undergoing a uniform reaction, the extent of reaction 'x' is given by

$$x = 1 - \left(\frac{r_B}{r_{Bo}} \right)^3 \quad (87)$$

Combining equations (85) and (87) gives

$$r_p = [1 + x(Z - 1)]^{1/3} r_{Bo} \quad (88)$$

If the initial mixture is stoichiometric, it can be shown that the extent of reaction is the same for both the reactants at any instant. Hence, for monosized particles of A undergoing uniform consumption,

$$r_A = r_{Ao} (1 - x)^{1/3} \quad (89)$$

From equations (88) and (89) it is obvious that while particles of A continually shrink, particles of B with product layer on it can

continually grow ($Z > 1$) or remain unchanged ($Z = 1$) or shrink ($Z < 1$). Obviously, when $Z < 1$, the contact between the reactants will be lost as soon as the reaction begins unless their centers move towards each other by bond formation or rearrangement under external forces such as gravitation. However, rearrangement is not always possible in a densely packed compact because of the constraints imposed by the surrounding matrix and in such a case a reduction in the effective contact area may occur as a result of initial reaction.

When ($Z > 1$), particles of B with a product layer on them continually expand. Three distinct stages are then involved as shown in Fig. (8).

- (i) Expansion stage: Rate of expansion of (B + product) particles exceeds rate of shrinkage of A particles. That is

$$\frac{dr_p}{dx} > -\frac{dr_A}{dx} \quad (90)$$

In this stage, expanding (B + product) particles exert an outward force on A particles causing an increase in the center-to-center distance or shape deformation leading to increased contact area. Depending upon the ability of the compact to accept rearrangement, microscopic expansion may or may not be accompanied by macroscopic enlargement.

- (ii) Critical stage: Radii of A and (B + product) particles are such that radial shrinkage of A is exactly offset by radial expansion of B, i.e.,

$$\frac{dr_p}{dx} = - \frac{dr_A}{dx} \quad (91)$$

Center-to-center distance remains unchanged.

- (iii) Loss of contact or shrinkage stage: Radius of (B + product) particles is large enough so that any additional reaction increases its radius ' r_p ' only marginally. The radius of A particles is so small that the corresponding increment in reaction decreases its radius ' r_A ' much more significantly. i.e.,

$$\frac{dr_p}{dx} < - \frac{dr_A}{dx} \quad (92)$$

Center-to-center distance will shrink only if bonding occurs or if rearrangement under an external force is possible.

Otherwise the effective contact area between the reactants will diminish.

If we define dimensionless radial separation between the reactants as ' Y ' and dimensionless radius as ' Ω_0 ' where

$$Y \equiv \frac{r_A + r_p}{r_{Ao} + r_{Bo}} \quad (93)$$

$$\text{and } \Omega_0 \equiv \frac{r_{Ao}}{r_{Ao} + r_{Bo}} \quad (94)$$

then from equations (88) and (89) it follows that

$$Y = (1-x)^{1/3} \Omega_0 + [1 + (Z-1)x]^{1/3} (1 - \Omega_0) \quad (95)$$

At critical stage,

$$\frac{dr_A}{dx} = - \frac{dr_B}{dx}$$

$$\text{i.e., } \frac{dY}{dx} = 0 \quad (96)$$

Hence,

$$\frac{d}{dx} \left[(1-x)^{1/3} \Omega_0 + [1 + (Z-1)x]^{1/3} (1 - \Omega_0) \right] = 0 \quad (97)$$

Solving for 'x' gives

$$x_c = \frac{[(Z-1)(1-\Omega_0)]^{3/2} - \Omega_0^{3/2}}{[(Z-1)(1-\Omega_0)]^{3/2} + (Z-1)\Omega_0^{3/2}} \quad (98)$$

Also at the critical stage, center-to-center distance between reactant particles is at maximum given by:

$$Y_{\max} = \left(\frac{Z}{Z-1} \right)^{1/3} \left[\Omega_0^{3/2} + (1-\Omega_0)^{3/2} (Z-1)^{1/2} \right]^{2/3} \quad (99)$$

Thus, the critical stage is completely defined by x_c and $Y_{\max}$ both of which may be calculated under stated assumptions provided parameters Z and Ω_0 (i.e., r_{A0} , r_{B0}) are known. For the case of spherical particles, x_c and $Y_{\max}$ have been plotted as functions of

Ω_0 for various values of Z in Figs. (9a) and (9b), respectively.

Similar analysis can be performed for cylindrical or platelike particles of A and B and the general results in terms of shape factors F_A and F_B are as follows. Extent of reaction ' x_c ' at the critical stage is obtained by solving

$$(1-x_c) \frac{1-F_A}{F_A} [1 + (Z-1)x_c] \frac{F_B-1}{F_B} + \frac{F_A(Z-1)(\Omega_0-1)}{F_B \Omega_0} = 0 \quad (100)$$

The maximum center-to-center distance between the reactant particles ($Y_{\max}$) is obtained from

$$Y_{\max} = (1-x_c)^{1/F_A} \Omega_0 + [1 + (Z-1)x_c]^{1/F_B} (1-\Omega_0) \quad (101)$$

The maximum expansion in the center-to-center distance is given by

$$\% \text{ Expansion} = (Y_{\max} - 1) 100 \quad (102)$$

During the expansion stage, if the force generated is sufficient and particulate packing is appropriate, microscopic expansion may get reflected in a macroscopic enlargement of the pellet. In such a case, dilatometric measurements can provide a useful means of determining ' x_c '.

If contact separation does take place beyond the critical stage, a change to vapor-phase external mass transport may be accompanied by a

sharp change in the overall reaction rate. Whereas external mass transport may not have been the rate controlling step initially, it may become rate limiting after the contact separation. The "Contact maintenance theory" is useful in predicting the conditions under which such a change is likely to occur. It does not, however, assure a change in kinetics. In fact, when the reaction rates do not show any abrupt change at or before the critical stage predicted by the contact maintenance theory, it points to one or more of the following conditions:

- (i) The external mass transport is predominantly due to sublimation-vapor phase diffusion even before contact separation.
- (ii) Sublimation-gaseous diffusion is rapid enough not to form a rate limiting step in the overall kinetics even after the contact breakage.
- (iii) Contact separation does not occur despite microscopic volume changes because of bonding or particulate rearrangement with or without external force.

Utility of the theory, on the other hand, is mainly related to determining conditions to avoid contact breakage in systems susceptible to such a phenomenon, for example, by a proper choice of Ω_0 , etc.

Among the assumptions made in the derivation of the theory, two need to be discussed further. Assuming monosized powders of A and B

is a highly idealized description of mixtures found in practice but is almost mandatory for a mathematically amenable analysis. Assuming that each particle undergoes an equal extent of reaction is once again idealized. This assumption, while statistically appropriate for reactant B particles, may not be true for reactant A particles. Those A particles closest to the reactant B particles may undergo a larger degree of consumption than the particles farther away. Since the critical point of contact breakage is determined not by all A particles but only by those A particles in contact with particles of B, it is obvious that the critical stage in actuality will be reached at an earlier point than predicted by the theory. Therefore, ' x_c ' as calculated from equation (100) will in general be larger than the actual. Furthermore, since temperature dependent diffusivities determine the degree of uniformity in the consumption of the particulate matrix, it is obvious that the critical extent of reaction will be dependent on the temperature though this dependence has not been quantitatively incorporated into the analysis.

2.5 Macroscopic Expansion Model:

As stated in the previous discussion, microscopic (i.e., particulate) dimensional changes accompanying a reaction may also result in macroscopic pellet enlargement or shrinkage under certain conditions. At particulate level, these dimensional changes are directly related to the extent of reaction through nucleation and topological considerations and can be expressed in precise mathematical forms in the case of regularly shaped particles, e.g., as

in equations (88) and (89). Unfortunately, it is frequently impractical to employ direct particulate dimensional measurements as a technique in kinetic studies. Macroscopic pellet dimensions, on the other hand, are quite easy to monitor accurately in a dilatometer and have been employed in kinetic studies in the past, but only on a qualitative level. Also, generally, a great part of effort in reaction studies is spent in determining the extent of reaction through usually non-continuous and cumbersome analytical procedures which limit the amount of data that can be collected in a reasonable period of time. Dilatometry is attractive in this direction, too since it can be used on a continuous, in-situ basis like DTA and TGA. However, use of dilatometry as an analytical tool will require quantitative correlation between the extent of reaction and the pellet dimensional changes, which unfortunately, is not available at the present. Our concern here will be to develop such a correlation so that the potential of quantitative dilatometry in the mixed powder reaction studies can be more accurately assessed.

Consider a pellet formed from a powder mixture of many species. We shall assume that:

- (i) all the particles of a given species have a fixed but arbitrary shape;
- (ii) the number of particles of each species in the pellet is statistically large;
- (iii) the mixing is ideal;

- (iv) the particles are oriented randomly;
- (v) particles do not change shape or relative positions during the course of reaction;
- (vi) all particles of a species undergo an equal extent of reaction.

Let a component 'i' consist of particles of initial volume ' U_{i0} ' and let ' θ_{i0} ' be the fraction of the initial total solid volume in the pellet due to species 'i'. Prior to any reaction, an imaginary test line equalling the length ' L_0 ' of the pellet will intersect ' N_{i0} ' particles of species 'i' with an average intercept length ' l_{i0} '. If ϵ_{v0} is the initial void fraction in the pellet, the total length of the solids along L_0 will equal $L_0(1 - \epsilon_{v0})$ out of which $L_0(1 - \epsilon_{v0})\theta_{i0}$ will be due to particle of species 'i'. It follows then

$$n_{i0} = \frac{L_0(1 - \epsilon_{v0})\theta_{i0}}{l_{i0}} \quad (103)$$

Let the length of the test line be equal to the length of the pellet L_x at an extent of reaction 'x'. Since we assume that no particle rearrangement takes place during the reaction, the test line will pass through the same set of particles as it did before the reaction. Therefore, the number of 'i' particles intercepted by the test line will remain the same, i.e.,

$$n_{ix} = n_{i0} \quad (104)$$

Also the total length of all the solid lying along the test line will be given by

$$L_x(1 - \epsilon_{vx}) = l_{ix} n_{ix} \quad (105)$$

where ' ϵ_{vx} ' is the void fraction in the pellet and ' l_{ix} ' is the average intercept length in 'i' at the extent of reaction 'x'.

Solving equations (103), (104), and (105) gives

$$\frac{L_x}{L_0} = \frac{1 - \epsilon_{v0}}{1 - \epsilon_{vx}} \sum_i \frac{l_{ix}}{l_{i0}} \phi_{i0} \quad (106)$$

From stereology we know that,

$$l_{ix} = \frac{U_{ix}}{\alpha_{ix}} \quad (107)$$

$$\text{and } l_{i0} = \frac{U_{i0}}{\alpha_{i0}} \quad (108)$$

where α_{i0} and α_{ix} are the projected area of an 'i' particle in a plane normal to the test line averaged over all possible orientations. The desired result can then be written as:

$$\frac{L_x - L_0}{L_0} = \frac{1 - \epsilon_{v0}}{1 - \epsilon_{vx}} \left[\sum_i \frac{U_{ix}/\alpha_{ix}}{U_{i0}/\alpha_{i0}} \phi_{i0} \right] - 1 \quad (109)$$

Under the stated assumptions, the above expression represents a most general relation between the extent of reaction and the pellet

dimensions provided the ratio (U_{ix}/a_{ix}) can be expressed in terms of 'x' and the pellet porosity ' ϵ_{vx} ' is known in terms of either 'x' or ' L_x '.

Distribution in the particle sizes of a species does not affect the result as long as the particle shape does not vary since it can be shown that the ratio

$$\frac{U_{ix}/a_{ix}}{U_{io}/a_{io}}$$

is independent of the particle size and depends only on the shape. When the shape changes with the particle size in a distribution, each size must be treated as a separate species in the equation (109).

For particles of regular shape which does not change during the reaction and the nucleation type giving shrinking core morphology, further simplification can readily be made because

$$\frac{U_{ix}/a_{ix}}{U_{io}/a_{io}} = [1 + x(Z_i^* - 1)]^{1/F_i} \quad (110)$$

Where Z_i^* is the apparent product volume formed on the surface of 'i' particles per unit apparent volume of 'i' consumed and the shape factor ' F_i ' equals 1, 2, 3 for thin flat plates, long thin cylinders and spheres, respectively. Other regular shapes, such as cubes, cuboids, etc., can be relatively easily treated. For irregularly shaped particles, however, it is usually not easy to write analytical expressions similar to equation (110) unless the shape can be approximated by a regular shape.

It is critical to understand the role of factor ' θ_{i0} ' in the analysis. ' θ_{i0} ' should not be interpreted simply as the volume fraction contributed by 'i' to the total solid volume. Instead it should be treated as the volume fraction of 'i' contributing to that solid volume which determines the 'effective' skeletal structure of the pellet. For example, consider a binary powder mixture where one reactant has a large particle size and a large volume fraction compared to the other. It is very likely that the major constituent will form the skeletal structure of the pellet while the minor reactant will fill in the interstitial volume. The pellet expansion or shrinkage in such a case will be determined almost entirely by the major constituent irrespective of the actual volume fraction of the total solid volume due to it. It is important therefore, to stress that ' θ_{i0} ' should be interpreted as the volume fraction of 'i' contributing to only that solid volume which effectively determines the pellet structure. Study of pellet microstructure may indicate which components form the bulk of the skeletal structure but it is by no means easy to determine the magnitude of parameter ' θ_{i0} ' from microstructural examination.

Similar difficulty also exists with the void fraction ϵ_{vx} of the pellet. Presently, no analytical expression can readily be written for the dependence of ϵ_{vx} on the extent of reaction. Of course, one may determine ϵ_{vx} at various stages of the reaction experimentally but this is not particularly desirable since it cannot be done at present in-situ on a continuous basis.

Successful development of dilatometry therefore is highly dependent on solving two critical difficulties: (a) method of determining and reproducibly controlling 'effective' volume fraction e_{i0} of various constituents and (b) ability to theoretically correlate pellet porosity ϵ_{vx} to the extent of reaction or alternatively ability to monitor ϵ_{vx} in-situ on a continuous basis along with the pellet dimensions. With ingenuity and experimentation, hopefully it will be possible to overcome these problems, which would permit upgrading of dilatometry from a qualitative to a quantitative analytical method for mixed particulate reaction studies complementing other techniques such as DTA And TGA.

2.6 Review of Nucleation-Growth Model:

Both shrinking-core and grain models assume that nucleation of the product phase occurs instantaneously and uniformly over the entire surface of either grains or particles of one of the reactants. Instantaneous nucleation implies that the phenomenon of nucleation does not pose a kinetic barrier, i.e., the nucleation frequency is infinitely large. Uniform-nucleation over the entire surface requires an infinite number of non-random nucleation sites resulting in a shell-type of product morphology over the grains in the case of porous solids and over the particles in the case of non-porous solids. The nucleation-growth model, on the other hand, does not involve such assumptions. It assumes instead, that the product nucleation occurs at sites which are randomly distributed. Then, using Avrami's⁽³³⁻³⁵⁾ concept of "extended volume" to account for impingement of nuclei

after a certain amounts of growth, the following general kinetic expression can be written

$$\ln \frac{1}{1-x} = k_{avr} t^m \quad (111)$$

where k_{avr} and m are parameters determined by the growth limiting mechanism, nucleation rate and shape of the growing nuclei. These parameters are listed in Table I for a few common boundary conditions.

Solid state reactions governed by nucleation-growth kinetics can be identified by plotting $\left[\ln \ln \left(\frac{1}{1-x} \right) \right]$ versus $[\ln(t)]$ to obtain a straight line with slope ' m ' and intercept $[m \ln(k_{avr})]$ from which the mechanism and the activation energy can be calculated.

3. POWDER CHARACTERIZATION AND EXPERIMENTAL PROCEDURES

3.1 Powder Characterization

The starting powders used in the present study were of high purity. Lead monoxide used was Baker reagent grade massicot which is a yellow orthorhombic polymorph stable above 550°C. Zirconium dioxide was reactor grade low hafnium monoclinic polymorph (baddeleyite) manufactured by Wah Chang Albany Corporation. Semi-quantitative spectrographic analysis results are shown in Table II. According to the manufacturer, baddeleyite was manufactured from Australian zircon by a process requiring precipitation of basic sulfate of Zr and contains approximately 0.5 to 1 percent SO_3^{--} trapped in the ZrO_2 lattice.

Scanning electron microscopy indicated that the zirconia consisted of approximately spherical granules up to 40 μ in diameter but the size of the crystallites making up the particles was much smaller (Fig. 10). As received powder was sieved by sonic sifter with precision electroformed nickel sieves to obtain two size fractions ($-30 + 20$) μ and ($-20 + 10$) μ which were used in the isothermal reaction study.

Particle size distributions of sieved zirconia were determined by laser-scattering method employing rotating spatial filters and are shown in Fig. 11. The instrument, Leeds-Northrup microtrack, can detect only those particles which exceed 1.6 μ in size. However, SEM examination indicated negligible amounts of powder below this size. Distributions repeated with 3 different sample sizes (maximum 2.5 gm) were almost identical indicating a high degree of reproducibility.

The crystallite size distribution was determined by X-ray peak broadening technique with Tomandl's⁽⁶³⁾ modification. The method calculates the size distribution of crystallites from the shape of a broadened peak with appropriate corrections for instrumental contribution to the broadening. Crystallite size distributions calculated from (111) peak broadening using CuK α radiation for three particle size ranges of zirconia is shown in Fig. 13. All can be considered to be identical to within the accuracy of the technique and are approximately log-normal, given by

$$W(D) = \frac{1}{2D\sqrt{\pi}(0.58)} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(D/330)}{0.58} \right]^2 \right\} \quad (112)$$

where $W(D)$ is the volume or weight fraction corresponding to the crystallite diameter 'D' angstroms.

Specific surface area measurements were conducted on zirconia of four particle size ranges using two BET methods; volumetric and continuous-flow type with nitrogen as the adsorbant. Agreement between the two methods was excellent and the results are shown in Fig. (12). Interestingly, coarser zirconia exhibited a larger specific surface area which, in view of the equal crystallite size distribution, implies differences in the pore structure. The pore size distribution, as calculated from volumetric adsorption isotherms assuming cylindrical capillaries showed that more than half of the total pore volume was due to pores smaller than 200Å (Fig. 14). Larger zirconia particles had a higher proportion of smaller pores and

therefore a larger specific surface area. The reasons for this type of pore distribution are unknown but are presumed to be an artifact of the manufacturing method. Following the theoretical analysis of De Boer,⁽⁶⁴⁾ the hysteresis loops between adsorption and desorption isotherms (Fig. 14) indicates presence of "ink-bottle" capillaries, open slit-shaped capillaries with parallel walls and tubular capillaries with assorted dimensions. Abrupt desorption at a relative pressure of 0.5 corresponds to emptying of "ink-bottle" capillaries with a neck diameter of approximately $13\text{\AA}$.

Since the pores of sizes above $800\text{\AA}$ are better analyzed by mercury porosimetry, dried zirconia was evacuated to pressures below 10^{-4} Torr and subjected to mercury penetration up to 50,000 psi (345 MPa). Assuming a contact angle of 130° , that the surface tension of mercury is 473 dynes/cm and that the pores are cylindrical, the following relation can be obtained:

$$\text{Pore Diameter } (\mu) = \frac{175}{\text{Pressure in psi}} \quad (113)$$

Unfortunately, in a powdered sample, voids between the particles contribute to the measured penetration volume just like the internal pores do. Since the former contribution is likely to show a large scatter, two samples of different amounts were analyzed (Fig. 15). From the two measurements, it is estimated that the pores smaller than 1 micron in size are mainly internal and the internal porosity of zirconia is nearly 25 percent. Allen's⁽⁶⁵⁾ suggestion that plateaus frequently demarcate the two contributions is also consistent with the

above conclusion. Powder density as measured by a helium pycnometer was close to the theoretical density (5.6 gm/cc), indicating that the bulk of the pore volume was externally accessible.

For transmission electron microscopy, zirconia was pressed into a pellet form, evacuated and impregnated with an epoxy resin (EPO-TEK 301-2). Hardened samples were thinned to about 30 μ by abrading and polishing. Further thinning was accomplished by ion-beam milling. TEM study in bright field and dark field mode showed no significant differences either in the shape or size of zirconia crystallites of various particle size ranges (Fig. 16). However, within a size range, considerable variation was present, some particles being exclusively made up of small crystallites while others had larger crystallites. This too is thought to be an artifact of the zirconia manufacturing method. Crystallites were approximately spherical although certain faceting was frequently evident at the grain boundaries. No intra-crystalline porosity was observed. SAD patterns calibrated by an evaporated gold standard confirmed that the zirconia consisted solely of the monoclinic polymorph which is stable below approximately 1000°C.

SEM examination of PbO indicated that it consisted of nearly micron-size crystallites adnering loosely to each other to form fragile aggregates. Air permeametric measurement showed that the average particle size was 0.7 μ . Multipoint BET measurements showed specific surface area of 1.6 m²/gm with a corresponding equivalent diameter of 0.4 μ . Shapes of PbO particles ranged between approximately spherical to disc-like (Fig. 10c).

3.2 Mixing and Compaction:

ZrO_2 of desired size range and PbO were weighed in the stoichiometric ratio with corrections for small weight losses observed on heating up to $300^\circ C$. For reproducibility in mixing, a standardized procedure was followed. First a uniform layer of ZrO_2 was loaded into a horizontal polyethylene jar (85 mm ID, 170 mm length), which was then covered with a layer of PbO . Isopropyl alcohol and teflon balls were added in amounts proportional to the powders as aids in mixing. The jar was then rotated on a ball mill for a required period followed by drying at $80^\circ C$. The fragile cake formed was then reduced to powder by vibrating on a Sweco vibratory mill for 30 minutes.

A steel die and punch assembly of 1/2" diameter with 2 gm mixture and 4000 psi (27.6 MPa) was used to press pellets. Some of the pellets were enclosed in a polyethylene bag and further isostatically pressed to 20,000 psi (138 MPa). Each pellet was weighed to the accuracy of 10^{-4} gm and its dimensions were measured by a micrometer. An average of three diameter and thickness measurements were used to calculate the green density (GD) as a percent of theoretical (TD) by use of the following relation:

$$GD(\%) = \frac{\text{Pellet Weight}}{\text{Pellet Volume}} \times \frac{100}{TD} \quad (114)$$

where

$$TD = \left[\frac{\text{Weight fraction PbO}}{\text{Density of PbO}} + \frac{\text{Weight fraction ZrO}_2}{\text{Density of ZrO}_2} \right]^{-1} = 7.40 \text{ g/cm}^3$$

Pellets were categorized according to green density and only those within 1 percent of the average green density were used in a given set of experiments. Some pellets were heated to 630°C for 60 minutes before the actual reaction and their green density was measured after the heat treatment.

3.3 Isothermal Heating:

A split-tube furnace (32 mm ID x 460 mm length) with 80 mm hot zone was used for isothermal heating to the reaction temperature. Pelleted specimens placed edgewise in a platinum boat were rapidly inserted in the hot zone of the preheated furnace. The sample temperature was monitored by a (Pt - Pt 10 percent Rh) thermocouple calibrated against an NBS standard. Time measurement was started when a sample reached the required temperature, which was typically within 30 seconds following insertion. Pellets were quickly withdrawn at the end of a desired reaction period and quenched on a cold sheet of platinum. Effective reaction time was estimated to be within a minute or two of the measured reaction time. Accuracy in temperature measurement was judged to be $\pm 2^\circ\text{C}$.

Pellets were weighed and dimensions were measured following the reaction.

3.4 Determination of Extent of Reaction:

The amount of unreacted PbO in the reacted samples was determined by the complexometric titration method. Approximately 500 mg of

crushed sample powder was accurately weighed in a polyethylene bottle. Up to 150 ml of 0.02 M disodium EDTA was added, followed by ultrasonic agitation for 1 minute and vibratory shaking for 30 minutes. In a separate series of experiments, this treatment was determined to be sufficient for dissolution of all unreacted PbO in the sample. The suspension was filtered using 0.1 μ polycarbonate filters. Three grams of triethanolamine, 15 ml of $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer (pH 10.3) and 25 ml of EDTA filtrate were mixed with a few drops of freshly prepared 2 percent Eriochrome Black-T indicator dissolved in ethanol. The solution was back-titrated against 0.2 M MgCl_2 stock solution in a constant rate of addition mode on a potentiograph (Metrohm Herisau model E436). A colorimeter (Brinkmann PC/600) with a fibre-optic probe and 520 nm interference filter served to detect the titration end-point. Spectrophotometry on the solution before and after the end-point was used to determine the filter wavelength with optimum contrast. Potentiograph output was in the form of a first derivative of sample absorption plotted against titrant volume with the end-point denoted by a sharp peak. Calibration was done with solutions containing known amounts of PbO. Atomic absorption spectroscopy on filtrates showed the absence of zirconium in the solution and hence the titration results directly correspond to amounts of unreacted PbO in the samples. The extent of reaction 'x' was assumed to be the same as the fraction of reacted PbO which was calculated as follows:

$$x = 1 - \frac{\text{weight of unreacted PbO}}{\text{weight of initial PbO in sample}} \quad (115)$$

The above procedure is similar to that reported by Robinson and Joyce⁽⁶⁶⁾ except for the instrumental setup. The present procedure is considered to be superior since visual detection of the end-point in this type of titration is highly prone to subjective errors. Titrations repeated on the same filtrates in order to determine the error margin showed values of x within 0.5 percent of each other. Titrations repeated on the same pellet, but different filtrates, gave values of x within 3 percent of each other indicating variation in the extent of reaction across the pellet.

On one of the samples the amount of unreacted ZrO_2 was determined by the acid dissolution technique of Robinson and Joyce. Results were within 3 percent of the results obtained by complexometric titration. Hence, it was considered unnecessary to analyze every sample for unreacted zirconia.

It should be noted that if any PbO is lost due to evaporation, the analytical procedure will erroneously consider it to be "reacted". Therefore, the calculated values of x will be higher than the actual extent of reaction. However, weight measurements on pellets before and after the reaction indicated negligible weight loss.

3.5 Microstructure of the Pellets and Particles:

Some of the unreacted as well as partially reacted pellets were chosen for SEM and microprobe analysis. A small piece of sample pellet was impregnated by epoxy resin followed by polishing with 1/4 μ diamond abrasive.

Quantitative measurements of local composition across the polished cross-sections of many partially reacted zirconia particles were performed by electron beam microprobe. The instrument was operated at 15 KV with pentaerythritol (PET) analyzing crystals and a proportional flow counter using P-10 gas. Lead and zirconium contents were determined from their M_{α} and L_{α} radiations, respectively, with a lead selenide crystal and zirconium metal as standards. Composition was measured at 1μ intervals across the largest cords in 10 particle cross-sections in each sample. Corrections were made for atomic number, adsorption and fluorescence (i.e., ZAF corrections) and the results were used to plot lead to zirconium atomic percent ratio against position along the length of the cord. Ideally, the ratio would equal 1 and 0 when the local composition corresponds to $PbZrO_3$ and ZrO_2 , respectively. Analysis of a dense sintered lead zirconate sample was in excellent agreement with the above criterion. The width and the depth of the region analyzed by the beam are estimated to be nearly 2μ and 1μ , respectively. Thus, the volume analyzed at any point is much larger than the average ZrO_2 crystallite size but much smaller than the particle size. Fortunately, this condition is ideal for deducing the rate controlling mechanism from the composition profile.

Surface-to-surface mean-free-distance between neighboring ZrO_2 particles dispersed in a green pellet was determined by standard stereological method⁽⁶⁷⁾ and was found to be approximately 7μ . Pellet microstructure as it evolved with the extent of reaction is shown in Fig. 17.

4. RESULTS AND DISCUSSION

4.1 Determining Activation Energy

Reactions isotherms for mixtures of two size ranges are shown in Table III and in Figs. 18, 19. It is evident that the reaction rate was highly temperature dependent indicating a large activation barrier. Since the general kinetic expression of most models can be written as

$$\phi(x, Z) = r_{Bo}^{-n} k \exp \left(- \frac{Q_A}{RT} \right) t^m \quad (116)$$

where Q_A is the apparant activation energy it follows that a plot of $\ln t_x$ versus $1/T$ will be a straight line if one of the models is applicable, t_x being the time required for 'x' percent reaction at a given temperature. Slope of the line will then equal $\frac{Q_A}{R}$ and can be used to calculate the apparent activation energy without having to assume any particular mechanism. It can be shown⁽⁵²⁾ that the slope will be independent of the exact nature of particle size distribution provided the rate controlling step is the same for all the particle sizes in the range. Such plots for the two particle size ranges used in the present study are shown in Figs. 20, 22 where time ' t_x ' required for 'x' percent reaction was estimated by interpolation from the isothermal data. The Mean apparent activation energy, as determined by least-square error fit to the isoreaction lines over the entire temperature range, was found to be 114 Kcal/mole. The systematic deviation from the linear behavior at the higher temperatures may be

attributed to the rapid rates of reaction. At higher temperatures, the time required for heating and quenching of pellets may form a significant part of the 'measured' reaction time resulting in a large uncertainty in the effective reaction time. Furthermore, interpolation errors can be significant when reaction rates change rapidly, such as those observed between 70 percent to 90 percent reaction in the Figs. 18, 19.

A small dependence of apparent activation energy on the extent of reaction was found to be approximately linear (Fig. 21), given by:

$$Q_A = 129.9 - (31.1)x \quad \text{for } 0 < x < 0.85. \quad (117)$$

However, it is uncertain whether this represents a significant fact or is simply a result of systematic error in reaction time measurements at higher temperatures as discussed earlier.

The Apparent activation energy for the mixture with larger zirconia ($-30 \pm 20\mu$), as determined from the shape of lines in Fig. 22, showed a large scatter with average Q_A of 111 Kcal/mole. The scatter is probably due to the limited number of data points which can be represented in the isoreaction-Arrhenius form. Apparent activation energies of the two size ranges of zirconia are very close to each other and indicate that the rate controlling phenomenon is the same in both cases.

More significantly, the reaction rates decrease dramatically above nearly 85 percent of the reaction in the mixtures of smaller zirconia

particles and above 40 percent of the reaction in the mixtures of larger zirconia particles. Above this range, the temperature has little influence on the reaction rates signifying a low activation energy. In view of the sample to sample scatter in 'x', it was considered impossible to determine the apparent activation energy with a reasonable accuracy in this range. The abrupt change in the activation energy signals a sudden change in the rate limiting mechanism and this phenomenon will be discussed in light of the contact-maintenance theory in a later part of this study.

4.2 The Rate Controlling Mechanisms

It is evident from the comparison of reaction isotherms that the mixtures with the larger size zirconia underwent a higher extent of reaction than the mixtures with smaller zirconia particles held at the same temperature. This observation suggests that either the rate controlling mechanisms or the nucleation patterns differ in the two cases. The latter appears to be more likely for three reasons: almost identical Q_A values for both size ranges of zirconia suggests the same mechanism, the sigmoidal shape of reaction isotherms for smaller zirconia particles are a typical characteristic of nucleation-growth-impingement behavior while parabolic reaction isotherms as seen for larger zirconia are a characteristic of shrinking core type morphology with kinetics limited by diffusion. To ascertain the exact mechanism and morphology, the extent of reaction was plotted against normalized time for various temperatures. To avoid interpolation and subjective bias, each experimental datum point was used as a reference to

normalize all other data points for the the same temperature. When data with $x > 85$ percent were used as a normalizing reference, scatter from the model was very large indicating a poor fit to the model. Similarly, when data with reaction time less than 10 minutes were used to normalize other points, large scatter was observed, indicating considerable uncertainty. Normalized data for all the temperatures using all the experimental points as references, except those with $x > 85$ percent, have been superposed and shown in Fig. 23.

The nucleation-growth-impingement type of model with instantaneous nucleation at a limited but fixed number of sites and diffusion controlled spherical growth gave the best fit to the data as evident in Fig. 23a and 23b where the theoretical curves were obtained according to the equation:

$$\frac{\ln \left(\frac{1-x}{1-x_0} \right)}{\ln \left(\frac{1-x}{1-x_0} \right)} = \left(\frac{t}{t_{x_0}} \right)^{3/2} \quad (118)$$

where (x_0, t_{x_0}) is the normalizing datum. Comparison of the data was also made to the shrinking core model (i.e., instantaneous nucleation over the entire surface) with external mass transport, phase boundary reaction or diffusion across the product layer as the rate limiting mechanisms. Theoretical plots were obtained by substituting $Z = 2$, $\beta = 7$, and $F_p = 3$, into appropriate kinetic expressions (equations 68 through 72), and correction for the particle size distributions shown in Fig. 11 was performed numerically following Kapur's⁽⁵²⁾ method. Normalized theoretical plots along

with the experimental data are shown in Fig. 24. It is clear that none of the three mechanisms can explain the data when shrinking core type of morphology is assumed. Other modifications of the shrinking core model, such as those by Hulbert et al.,⁽¹⁸⁾ Zuravlev et al.,⁽¹⁹⁾ Kroger-Ziegler,^(15,16) Tamman,⁽¹⁷⁾ and Dunwalt-Wagner⁽²⁰⁾ also failed to fit the data.

To further confirm nucleation-growth type of behavior, data for the smaller ZrO_2 particles is shown in a plot representing equation (111) (Fig. 25). A good linear correlation below 85 percent reaction confirms that the product morphology was indeed of the nucleation-growth type. The average slope of the least-square-error lines was 1.55 ± 0.14 which is very close to the value 1.5 predicted for either a spherical diffusion controlled growth with instantaneous nucleation at a fixed finite number of sites or a long needle-like diffusion controlled growth with constant nucleation at a fixed finite rate (see Table I).

From the intercepts of the above plots one obtains the rate constants (k_{avr}) which, when plotted as a function of temperature in an Arrhenius fashion, give the apparent activation energy of the rate controlling mechanism. From the slope of such a plot shown in Fig. 26, the activation energy for diffusion controlled growth was calculated to be 138 Kcal/mole for spherical nuclei and 414 Kcal/mole for needle-like nuclei. In view of the abnormally large activation energy that would be required, if the growth were indeed needle-like, it appears almost certain that the growth is spherical with nucleation occurring at a fixed finite number of sites. Therefore, the following

kinetic expression describes the data for mixtures with smaller zirconia:

$$\ln \frac{1}{1-x} = (4.4 \times 10^{41}) \left[\exp \left(-\frac{138}{RT} \right) t \right]^{3/2} \quad (119)$$

The activation energy as calculated by the above method differs somewhat from the activation energy calculated earlier from the isoreaction-Arrhenius plots. Since no interpolation errors are involved in the Avrami method, the activation energy of 138 Kcal/mole can be considered more accurate. It is also in a closer agreement with the value of 131 $\pm$ 5.7 Kcal/mole reported by Prisedskii et al.⁽⁵⁵⁾ for PbZrO_3 formation in a binary diffusion couple of PbO and ZrO_2 .

When external mass transport is not a rate determining step, microprobe profile analysis of the reactant particles can be used to obtain information about the rate limiting mechanism in porous or non-porous solids. Compositional variations along a cord in a cross-section of partially reacted particles can be correlated to the nucleation morphology and the rate limiting mechanism as explained in Table IV and Fig. 27. Results of such an analysis on a number of particles in mixtures with smaller ZrO_2 particles are shown in Fig. 28 and 29. For a low extent of reaction, such as $x = 0.17$, the composition profiles are irregular and analogous to that shown in Fig. 27d. This corresponds to nonuniform nucleation occurring at a few sites along the surface of ZrO_2 particles. As the extent of reaction increases, the compositional profiles resemble that shown in

Fig. 27a and correspond to a shrinking core type of product morphology. This stage represents mutual impingement of adjoining nuclei forming a more or less continuous product layer on the surface of the particles.

The reaction mechanism for mixtures with larger zirconia particles was found to be diffusion controlled but with instantaneous nucleation over the entire surface, i.e., of shrinking-core morphology. The theoretical normalized reaction curve along with the experimental data is shown in Fig. 30. The correlation between the data and the model is reasonably good below ≈ 90 percent of the reaction. As in the case of mixtures of smaller ZrO_2 particles, the mechanism appears to change above a critical extent of reaction which in the present case is about 90 percent of the reaction.

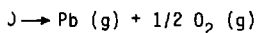
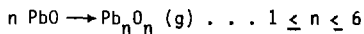
4.3 Influence of Mixing and Compaction:

It was not apparent whether the different nucleation behavior exhibited by the two mixtures was due to differences in particle size and pore structure or due to differences in their processing. Therefore, a series of experiments was conducted on the mixture containing the same size range of zirconia ($-30 + 20\mu$) but mixed for 2 different time periods with PbO . In addition, to study the influence of packing on the nucleation behavior, each mixture was pelletized at two different compaction pressures. The reaction isotherms at 730°C for the four sets of mixing and pressing conditions is shown in Fig. 31. Whereas the compaction pressure seems to have had almost no effect, an increase in mixing time increased the extent of reaction considerably. Theoretical plots assuming 90 percent reaction in 240 minutes for

diffusion limited shrinking core type as well as nucleation-growth type kinetics are also shown. An increase in mixing time results in a change from a nucleation-growth-impingement type of kinetics to a shrinking core type of kinetics. It is thus evident that longer mixing resulted in a larger population of the nucleation sites on the surface of particles either due to comminution or due to better dispersion.

4.4 External Mass Transport in PbO Matrix:

Transport of PbO to the external surface of ZrO_2 particles can occur by bulk, surface or gas phase diffusion. Data on the lattice self diffusivity of Pb^{2+} and O^{2-} in orthorhombic PbO has been reported by Lindner,⁽⁶⁸⁾ Thompson and Strong⁽⁶⁹⁾ and DasGupta et al.⁽⁷⁰⁾ On the other hand, understanding of the role of surface diffusion is limited by lack of data or good methods of estimation. The issue of vapor transport of PbO is further complicated by the complex nature of vapor species existing over solid PbO. Drowart et al.⁽⁷¹⁾ have reported that PbO vaporizes according to the following reactions:



with significant concentrations of higher polymers of PbO. Furthermore, since PbO is a polar molecule, the usual Chapman-Enskog method of gaseous diffusivity estimation cannot be used in the absence of

Krieger potentials data.⁽⁷²⁾ Approximate calculations, however, can be performed assuming nonpolar monomer vapor species as shown in Appendix C. Gaseous diffusion will be predominantly molecular flow type during most part of the reaction when the average PbO particle size exceeds 300Å. In order to estimate relative contributions of lattice and vapor phase diffusion flux using equation 61, the following assumptions can be made:

- (i) PbO at the PbO-PbZrO₃ interface is saturated with ZrO₂;
- (ii) PbO vapor pressure at the PbO-PbZrO₃ interface corresponds to the equilibrium vapor pressure over PbO saturated PZ.
- (iii) Vapor pressure in the bulk of the particulate matrix away from ZrO₂ particles corresponds to the equilibrium vapor pressure over pure PbO.

From the vapor pressure⁽⁷³⁾ and lattice diffusivity data,^(68,69) the estimated gas phase diffusivity, and the PbO-ZrO₂ phase diagram, the following approximate relations can be obtained from equation 61.

$$\text{For } 710^{\circ}\text{C} \quad \frac{J_b}{J_v} \approx \frac{10^5}{(1+h)} \quad (120)$$

$$\text{and for } 810^{\circ}\text{C}, \quad \frac{J_b}{J_v} \approx \frac{10^7}{(1+h)} \quad (121)$$

It follows that for the realistic values of sublimation-transport modulus 'h', the external transport of PbO by bulk diffusion will far exceed the flux due to vapor phase transport.

Similarly from equation 60 and the surface diffusivity estimate shown in the appendix, we have for the temperatures between 710°C and 810°C:

$$\frac{J_b}{J_s} \approx \frac{r_{PbO}}{\hat{a}} \times 10^{-3} \quad (122)$$

Since for lead oxide the lattice parameter a is of the order of 5Å, it follows that the bulk diffusion flux will be comparable to the flux due to surface diffusion in the initial stages of the reaction when the average PbO particle size is close to 0.5μ. However, as the reaction proceeds, the resulting decrease in PbO particle size will reduce the contribution of lattice diffusion as compared to the surface diffusion.

Considering the uncertainty in surface diffusivity estimates, it is likely that the above comparison of J_b and J_s is inaccurate. However, from the viewpoint of the "contact maintenance theory" to be discussed, it is critical to note that bulk diffusion alone will far exceed the gas phase external mass transport of PbO under the experimental conditions in the initial stage ($x < 0.85$) of the reaction.

4.5 Abrupt Changes in the Reaction Mechanism:

The reaction mechanism changed abruptly between 85 percent and 90 percent of the reaction, depending on the temperature, for smaller zirconia particles and was evident from a sharp break in the Avrami plot (Fig. 25) and large scatter in the data when experimental points

above 85 percent ratio were used to normalize the remaining data. The reaction rates decreased almost to the point of stopping and the effect of temperature on the reaction rates was marginal indicating a low activation energy. A similar break in the mechanism was observed above approximated 90 percent of the reaction for the larger zirconia particles as evident from the 810°C reaction isotherm in Fig. 19.

These changes are correctly predicted by the contact-maintenance theory. Corresponding to the average particle sizes of 15 and 1 μ for ZrO₂ and PbO, respectively (i.e., $\Omega_0 = 1/16$) and 25 percent and 0 percent porosities for ZrO₂ and PZ (i.e., $Z = 1.5$), the contact breakage will occur at or before 93 percent reaction for the mixtures with the smaller size range of zirconia. Similarly, corresponding to an average particle size of 25 μ for larger zirconia, the breakage will occur at or before 97 percent of the reaction according to theory. The observed values of contact breakage are reasonably close to the theoretical values. According to the theory, contact breakage prior to the theoretically predicted amount of reaction points to the nonuniformity in the consumption of PbO, those particles closer to the ZrO₂ being consumed faster than PbO farther away. Alternately, deviation from the exact theoretical calculations may be attributed to the uncertainty in exact particulate sizes after the mixing operation, distribution of sizes and the irregular shape of the particles. In view of the uncertainty in Ω_0 , a better support of the contact-maintenance theory is offered by the correlation between the measured pellet dimensional changes and the observed amount of

reaction at the mechanism change. As shown in Fig. (33), the pellet volume increased steadily and significantly up to about 150 percent of the original volume corresponding to about 85 percent reaction. Beyond this point, the pellet volume ceased to increase just as the reaction rate also dropped. Further proof of contact breakage is offered by the lack of sensitivity of reaction rates to changes in temperature beyond the critical stage and reflects the low activation energy associated with gas phase mass transfer.

It must be mentioned that the sudden decrease in the reaction rates are often evident in the kinetic data for PbZrO_3 formation as reported by many authors although the phenomenon has never been explained. Robinson and Joyce⁽⁶⁶⁾ found that up to 3 percent zirconia remained unreacted in the PZT ceramics even after sintering. Reaction isotherms by Mangel and Dorskocil⁽⁵³⁾ show a sharp decrease in reaction rates between 80 to 95 percent of the reaction. Unfortunately, compliance with the contact-maintenance theory can not be checked for references (66) and (53) because they did not provide the appropriate particle size information. Data by Tecilazic-Stevanovic et al.⁽⁵⁴⁾ also shows contact breakage at various extents of reaction depending on the temperature. The maximum extent of reaction at which breakage was observed was below the value predicted by the theory for the appropriate Ω_0 . Decreases in the reaction rates were also observed by Gesemann and Neels⁽⁵⁷⁾ between 64 percent to 92 percent reaction depending on temperature. Volume expansion data has not been provided by any of these authors and therefore cannot be used to confirm the contact breakage theory.

4.6 Macroscopic Pellet Expansion:

Reaction was accompanied by large changes in the pellet volume as evident from Fig. (32). For a binary mixture of spherical particles of PbO and ZrO_2 , equations (109) and (110) can be combined and by substituting $Z^* = 0$ and 2 for PbO and zirconia, respectively, we obtain:

$$\frac{L_x - L_0}{L_0} = \frac{1 - \epsilon_{VO}}{1 - \epsilon_{VX}} \left[(1 - x)^{1/3} \epsilon_{OP} + (1 + x)^{1/3} \epsilon_{OZ} \right]^{-1} \quad (123)$$

Also, the following relation holds

$$\epsilon_{OP} + \epsilon_{OZ} = 1 \quad (124)$$

Where ϵ_{OP} and ϵ_{OZ} are the volume fractions of PbO and ZrO_2 in the solid structure which determines the effective pellet dimensions prior to the reaction. Accordingly, condition $\epsilon_{OP} > \epsilon_{OZ}$ is characterized by a continuous pellet shrinkage while $\epsilon_{OP} < \epsilon_{OZ}$ is indicated by a continuous expansion. Expansion behavior observed as well as SEM examination of the microstructure tend to suggest that zirconia particles effectively determined the skeletal structure of the pellet. This is especially evident in the microstructures of the partially reacted pellets shown in Fig. (17).

Initial shrinkage seen in Fig. (32) is interesting because it can not be explained by the macroscopic expansion model. It was found that the amount of initial shrinkage depends upon the prereaction heat

treatment of the sample. Behavior of the pellets which were heat treated at 630°C for 60 minutes prior to the reaction is shown in Fig. (33) where the volume expansion has been calculated with respect to the measured pellet volume after the prereaction anneal. Reduced initial shrinkage and reduced scatter in the data is evident as a result of the prereaction anneal. It appears that the stresses and shape deformations caused by pelletizing operations are relieved by the prereaction anneal and the actual microstructure approaches the assumed microstructure more closely after the heat treatment than prior to it. This clearly illustrates the critical nature of specimen preparation if dilatometry is to be used on a quantitative basis in solid state reaction studies.

In order to test the macroscopic expansion model, the following approximations were made. If the total void fraction in the pellet does not change significantly due to the reaction, ' ϵ_{vx} ' can be assumed to be only weakly dependent on 'x' and therefore the porosity factor

$$\frac{1 - \epsilon_{v0}}{1 - \epsilon_{vx}}$$

will be almost a constant. Since ϵ_{op} or ϵ_{oz} cannot be determined accurately, we shall assume that the effective skeletal structure of the pellet is determined entirely by zirconia whereby $\epsilon_{op} = 0$ and $\epsilon_{oz} = 1$. Equation (123) can therefore be written as,

$$\frac{L_x - L_o}{L_o} = (\text{constant}) (1 + x)^{1/3} - 1 \quad (125)$$

or in terms of volume expansion,

$$\frac{\Delta V}{V} = 3 (\text{constant}) (1 + x)^{1/3} - 3 \quad (126)$$

Empirical least-square-error fit of a similar expression to the data is shown in Fig. (33) where

$$\frac{\Delta V}{V} = 3 (0.747) (1 + x)^{1/3} - 2.29 \quad (127)$$

The two empirically determined constants in the above expression were dependent on the prereaction heat treatment and the values shown are valid for only those pellets subjected to the prereaction anneal at 630°C for 60 minutes. Comparison of the experimental data to the above expression is very satisfactory considering the assumptions made. Fit to the data will certainly be better if ϵ_{Vx} and ϵ_{OZ} are used as curve fitting parameters in equations (123) and (124).

The results therefore are highly encouraging as far as potential use of dilatometry on a quantitative basis is concerned. At the same time, the results point to the critical nature of sample preparation required for successful application of the technique. As long as the specimen preparation is held invariant in terms of green density, prereaction heat treatment, etc., scatter in the data can be acceptably low as in the present case. However, applicability of the macroscopic expansion model to a given system will depend on fulfilment of the assumptions involved in the model.

5. SUMMARY AND CONCLUSIONS

Existing models for solid state reaction kinetics in a mixed particulate ensemble have limitations because (a) they assume a geometry that can be realized only in gas-solid reactions thereby ignoring the pellet microstructure and the processing steps influencing the microstructure; and (b) such models cannot predict changes in the rate limiting mechanism caused by any localized microscopic volumetric changes associated with the product formation. A theoretical analysis was therefore carried out to estimate the quasi-steady-state external mass transport by lattice, surface and gaseous diffusions in terms of the stereologically measurable microstructural parameters of a mixed powder compact. It was shown that the sublimation-gaseous diffusion behavior can be described by a single dimensionless quantity termed "sublimation transport modulus". Using these equations the relative importance of the alternate external transport modes can be evaluated.

Based on the above analysis, "shrinking core" and "grain models" were modified so that the microstructural parameters appeared explicitly in the kinetic expressions. Conditions under which the mixed powder reactions assume a gas-solid type of reaction behavior were obtained.

A "Contact-maintenance theory" based on volumetric changes on a particulate level was developed to explain the abrupt changes in the rate controlling mechanism. Accordingly, it becomes possible to predict the conditions under which contact between the reactant

particles can break leading to gaseous external mass transport as a new and possibly rate limiting step. The model does not involve any empirical parameters.

A "macroscopic expansion model" was developed to correlate the particulate volume changes to the pellet dimensional changes for a mixture of many component powders of arbitrary size distributions and arbitrary but fixed particle shapes. The model requires that the volume fractions of various phases in the dimension-determining skeletal structure of the pellet be known. Also the void content of the pellet must be known as a function of the extent of reaction or the pellet dimensions. The model could potentially upgrade dilatometry from a qualitative to a quantitative, continuous, in-situ analytical technique for reaction studies, with many advantages. Difficulties in attaining this objective have been discussed.

Experimental work determined the reaction isotherms for the formation of lead zirconate from yellow PbO and monoclinic zirconia between 710°C and 810°C for two zirconia size distributions. The larger zirconia particles showed diffusion controlled shrinking core kinetics up to ~90 percent reaction while the smaller zirconia indicated a diffusion controlled spherical growth up to 85 percent reaction after the instantaneous nucleation at a limited number of sites. The difference was attributed to the differences in the mixing time and not to the particulate sizes of the pore structures. It was observed that for a given size range of zirconia a longer mixing operation gave a better dispersion of the reactants which resulted in

a higher nucleation size density which is required for a "shrinking core" type of product morphology and faster reaction. A microprobe profile analysis of partially reacted particles confirmed that for a short mixing period, reaction followed a nucleation-growth-impingement type of morphology. From nucleation-growth model fit to the data the activation energy was calculated to be 138 Kcal/mole which is close to 131 Kcal/mole reported for Pb^{2+} diffusion in PbZrO_3 . Approximate calculations show that the gaseous external mass flux of PbO was negligible compared to the lattice or the surface diffusive flux.

The above models were not valid above approximately 85 percent and 90 percent reaction for the smaller and the larger zirconia particles, respectively. The reaction rates decreased suddenly and were relatively independent of temperature indicating a low activation energy which is typical of gaseous diffusion. For the experimental conditions, this phenomenon could be correctly predicted by the "contact maintenance theory".

The "macroscopic expansion model" fit the pellet volume expansion data reasonably well when zirconia was assumed to form the entire skeletal structure and the pellet porosity was assumed to be invariant with the reaction. A prereaction heat-treatment was found to influence the expansion behavior systematically, bringing it closer to the theoretical behavior. Everything considered, results appear to be encouraging in regard to the use of dilatometry as a quantitative tool in the powder reaction analysis despite the difficulties mentioned.

APPENDIX A

Reaction Kinetics for Nonporous Solid (Modified Shrinking Core Model):

When reactant B is a nonporous solid and product nucleation occurs instantaneously over the entire surface, reaction at the phase boundary B/A_aB_b is topotactic. The rate of reaction of B is then related to the rate at which the interface between B and A_aB_b moves, given by:

$$R_B = \frac{\rho_B}{M_B} \left(- \frac{dr_B}{dt} \right) \quad (A1)$$

where R_B is the consumption rate of B by the phase boundary reaction in moles/unit area/unit time;

ρ_B and M_B are the theoretical density and molecular weight of reactant B, respectively.

For stoichiometry as shown in equation (1),

$$R_A = \frac{a}{b} R_B \quad (A2)$$

where R_A is the molar consumption rate of A per unit area of phase boundary per unit time.

If the reaction is irreversible and of first order with respect to species A then

$$R_A = k_r C_A (r_B) \quad (A3)$$

where $C_A(r_B)$ is the molar concentration of A at the phase boundary and

k_r is the rate constant for the reaction.

In steady state, all the reactant diffusing to the interface is consumed, hence for spherical case:

$$J_A = 4\pi r_B^2 R_A \quad (A4)$$

steady state diffusion flux of A through the spherical shell of product is given by:

$$J_A = 4\pi k_D \frac{C_A(r_p) - C_A(r_B)}{\left(\frac{1}{r_B} - \frac{1}{r_p}\right)} \quad (A5)$$

where k_D is the rate constant for diffusion of A through product A_2B_3 .

Additionally, the external mass transfer flux must equal the flux by diffusion through the product layer, i.e.,

$$J_A = J_{ex} \quad (A6)$$

When vapor phase transport is negligible compared to surface or bulk transport of A,

$$r_s = r_p \quad (A7)$$

$$C_{AS} = C_A(r_p) \quad (A8)$$

and

$$J_{ex} = 4\pi k_{ex} \frac{C_A(r_s + \lambda) - C_{AS}}{\frac{1}{r_s} - \frac{1}{r_s + \lambda}} \quad (A9)$$

where

$$k_{ex} \equiv \frac{D_b(1 - \epsilon)}{\tau_b} + \frac{D_s \hat{a}_p S_{WA}(1 - \epsilon)}{\tau_s} \quad A(10)$$

Dependence of r_B and r_p on the extent of reaction (x) is given by equations:

$$r_B = (1 - x)^{1/3} r_{B0} \quad (A11)$$

$$r_p = (1 + \lambda(Z - 1))^{1/3} r_{B0} \quad (A12)$$

$$\text{where } Z = \frac{\rho_B}{bM_B} \frac{M_p}{\rho_p} \quad (A13)$$

M_p , ρ_p being the molecular weight and the theoretical density of the product A_aB_b , respectively.

By differentiating equation A(11),

$$-\frac{dr_B}{dt} = \frac{r_{B0}}{3} (1-x)^{-2/3} \frac{dx}{dt} \quad (A14)$$

Equations (A1) through (A14) form a set of equations in twenty two parameters which on simplification gives the following differential equation

$$\begin{aligned} \frac{dx}{dt} & \left\{ \frac{r_{B0}}{k_r(1-x)^{2/3}} + \left[\frac{r_{B0}^2}{(1-x)^{1/3}} - \frac{r_{B0}^2}{(1+x(Z-1))^{1/3}} \right] \frac{1}{k_D} + \right. \\ & \left. \left[\frac{r_{B0}^2}{(1+x(Z-1))^{1/3}} - \frac{r_{B0}^2}{(1+x(Z-1))^{1/3} + \left(\frac{\lambda}{r_{B0}}\right)} \right] \frac{1}{k_{ex}} \right\} \\ & = \frac{3b}{a} \frac{M_B}{\rho_B} C_A(r_p + \lambda) \end{aligned} \quad (A15)$$

The above equation can be integrated in a straightforward manner to obtain 'x' as a function of time and other variables by using the initial condition:

$$x = 0 \text{ at } t = 0 \quad (A16)$$

provided appropriate assumptions are made about dependence of λ and $C_A(r_p + \lambda)$ on x or time. For stoichiometric mixtures or mixtures with excess A; $C_A(r_p + \lambda)$ may be assumed as a constant independent of (x, t) . If the macroscopic expansion of the pellet is proportional to the expansion in r_p as predicted by equation (A12), λ may also be

assumed to be unchanging. Alternately, λ can be empirically correlated to the extent of reaction from stereological examinations. Assuming unchanging λ and $C_A(r_p + \lambda)$, the solution to equations (A15) and (A16) is easy to obtain and is given by equations (62) through (67) of the main text.

APPENDIX B

Reaction Kinetics for Porous Solid; Modified Grain Model:

In porous solids, diffusion and chemical reaction can occur simultaneously throughout the solid; therefore the reaction zone is a diffuse zone and not a sharp boundary. This is true even when the solid is nonporous provided short circuit diffusion paths such as grain-boundaries are available for rapid diffusion to the interior. Therefore, in the grain model a particle of radius ' r_p ' is visualized to be made up of numerous smaller grains of radius ' r_g '. Reactant A diffuses inwards through the pores by gaseous or surface diffusion along pore surface or by grain boundary diffusion. The following assumptions are required for quantitative formulation:

- (a) The pseudosteady state approximation is appropriate for describing the concentration of a gaseous reactant within the pellet.
- (b) The pore structure is macroscopically uniform and remains unaffected by the reaction.
- (c) The system is isothermal.
- (d) Concentration of diffusing species is low everywhere and the viscous flow contribution to mass transport in the pores may be neglected.
- (e) Reaction is irreversible and of first order with respect to the concentration of A.
- (f) Volume changes associated with the product formation are negligible, i.e., $Z = 1$.

- (g) The reaction front within each grain retains its original geometric shape; i.e., the product nucleation occurs instantaneously over the entire grain surface giving a shrinking core topology on a grain level instead of particle level.

Based on the above assumptions, Sohn and Szekely^(44,45) have given a detailed mathematical formulation of the grain model for gas-solid reactions. We shall modify their formulation only to take into account surface and/or bulk diffusion which may take place in a particulate solid-solid reaction. Accordingly, the following variables need to be defined:

Dimensionless concentration within the particle,

$$\psi \equiv \frac{C_A}{C_A(r_p)} \quad (B1)$$

Dimensionless position of the reaction front within the grain,

$$\zeta \equiv \frac{A_g}{F_g V_g} H \quad (B2)$$

Dimensionless time,

$$t^* \equiv \frac{b}{a} \frac{M_b}{\rho_B} k_r \frac{A_g}{V_g F_g} C_{A0} t \quad (B3)$$

Dimensionless position of a grain within a particle,

$$n \equiv \frac{A_p}{F_p V_p} r \quad (B4)$$

Dimensionless reaction modulus for grains,

$$\sigma_g^2 \equiv \frac{k_r}{2k_D} \frac{V_g}{A_g} \quad (B5)$$

Dimensionless generalized reaction modulus,

$$\sigma^2 \equiv F_p \left(\frac{V_p}{A_p} \right)^2 \frac{A_g}{F_g V_g} \frac{(1 - \epsilon_B) k_r}{2D_e} \quad (B6)$$

where $C_A(r_p)$ is the concentration of A at the external surface of the particle;

r is the coordinate of a grain from the center of the particle;

H is the coordinate of shrinking core surface within a grain;

k_D is the diffusivity of A through the product layer on a grain;

D_e is the effective diffusivity of A through the pores or the grain boundaries of B;

C_{A0} is the concentration of A in the particulate matrix and equals $C_A(r_p + \lambda)$ when $\beta \rightarrow 0$;

F_p, A_p, V_p are the shape factor, external surface area and the apparent volume of the particles;

F_g, A_g, V_g are the shape factor, surface area and volume of grains.

A mass balance on species A can then be given by

$$\nabla_{\eta}^2 \psi - 2F_g \sigma^2 \zeta^{F_g-1} \frac{\delta \zeta}{\delta t} = 0 \quad (B7)$$

where ∇_{η}^2 is the Laplacian operator with η as position coordinate, local rate of reaction is given by

$$\frac{\delta \zeta}{\delta t} = -\psi [1 - \sigma^2 q(\zeta)]^{-1} \quad (B8)$$

where	$q(\zeta) = \zeta - 1$	for $F_g = 1$
	$= 2\zeta \ln \zeta^2$	for $F_g = 2$
	$= 6\zeta(\zeta - 1)$	for $F_g = 3$

Boundary conditions for $t^* \geq 0$ are

$$\frac{\delta \psi}{\delta \eta} = 0 \text{ at } \eta = 0 \quad (B9)$$

$$\frac{\delta \psi}{\delta \eta} = \frac{F_g V_p}{A_p \lambda} \frac{k_{ex}}{D_e} (1 - \psi) \text{ at } \eta = 1 \quad (B10)$$

Initial condition is given by

$$\zeta = 1 \text{ for all } \eta \text{ at } t^* = 0 \quad (B11)$$

The results desired are the overall extent of reaction and the reaction rate, which may be obtained by solving

$$x = \frac{\int_0^1 \eta^{F_P-1} (1 - \zeta^F P) d\eta}{\int_0^1 \eta^{F_P-1} d\eta} \quad (B12)$$

and

$$\frac{dx}{dt} = \frac{1}{2\sigma^2} \left[\frac{\partial \psi}{\partial \eta} \right]_{\eta=1} \quad (B13)$$

System of equations (B7) through (B13) can be solved only numerically in general. Fortunately, an approximate general solution can be written which reasonably describes the exact numerical solution under most conditions. This solution is given by equations (77) through (80) of the main text. Also, an empirical analytical refinement of the approximate solution has been reported⁽²⁹⁾ which simulates the exact numerical solution extremely closely over the entire extent of reaction when the external mass transport and intragrain diffusion are not rate limiting steps.

APPENDIX C

Molecular Diffusivity of PbO Vapor in Air:

Assume that the vapor of PbO exists as a monomeric (mol. wt. 223) non-polar species. According to the Chapman-Enskog kinetic theory, the diffusion coefficient of PbO gas in binary mixture with air is given by:

$$D_{12} = 1.8583 \times 10^{-3} \frac{\sqrt{T^3 \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}}{P \sigma_{12}^2 \Omega_{12}} \text{ cm}^2/\text{sec} \quad (\text{C1})$$

where M_1 , M_2 are the molecular weights of the gaseous PbO and air, respectively. P is the pressure in atmospheres and σ_{12} is the Lennard-Jones 12-6 potential function and Ω_{12} is the collision integral which is tabulated as a function of temperature and Lennard Jones parameter ' ϵ_{12} '. Values of σ_{12} and ϵ_{12} can be calculated from:

$$\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}) \quad (\text{C2})$$

$$\epsilon_{12} = \sqrt{(\epsilon_1 \epsilon_2)} \quad (\text{C3})$$

For air, the reported values⁽⁷⁴⁾ are:

$$\sigma_1 = 3.617 \text{ \AA}$$

$$(\epsilon_1/k) = 97^\circ\text{K}$$

For PbO, σ and ϵ can be estimated from its molar volume V_m ($\text{cm}^3/\text{g mole}$) at the melting point T_m ($=888^\circ\text{C}$) as follows:

$$\sigma_2 = 1.222 V_m^{1/3} = 30.3 \text{\AA} \quad (\text{C4})$$

$$(\epsilon_2/k) = 1.92 T_m = 2229^\circ\text{K} \quad (\text{C5})$$

Hence,

$$\sigma_{12} \approx 17 \text{ \AA}$$

$$(\epsilon/k)_{12} = 465^\circ\text{K}$$

From Bird, Stewart and Lightfoot⁽⁷⁴⁾, for the temperature range 710° to 810°C :

$$\Omega_{12} \approx 1.04$$

Substituting these values into equation (C1) gives for 1 atm pressure and above temperature range:

$$D_{12}(\text{PbO in air}) = 4.5 \times 10^{-2} \text{ cm}^2/\text{sec} \quad (\text{C6})$$

Knudsen Diffusivity of PbO in Porous Matrix:

From the 'dusty gas' model of Mason et al. (75,76)

$$D_K = \frac{\sqrt{8\pi}}{8 + \pi} \frac{\epsilon}{1 - \epsilon} \frac{r_g}{\tau} \sqrt{\frac{RT}{M}} \quad (C7)$$

Where D_K is the Knudsen diffusivity of a vapor specie of molecular weight M , ϵ and τ are the porosity and tortuosity, respectively, for the matrix consisting of particles of radius r_g .

Therefore,

$$D_K (\text{PbO}) = 275 \sqrt{T} \frac{r_g}{\tau} \frac{\epsilon}{1 - \epsilon} \quad (C8)$$

Effective PbO Vapor Diffusivity Through the Porous Matrix:

Effective molecular diffusivity is given by

$$D_{12\text{eff}} = \frac{\epsilon}{\tau} D_{12} \quad (C9)$$

Overall effective diffusivity is

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_{12\text{eff}}} + \frac{1}{D_K} \quad (C10)$$

From (C8) and (C9)

$$\frac{D_{12\text{eff}}}{D_K} = \frac{D_{12}}{275 \sqrt{T}} \frac{1 - \epsilon}{r_g} \quad (C11)$$

For the temperature range 710° to 810°C , assuming porosity $\epsilon = 0.4$, from (C6) and (C11) it follows that

$$\frac{D_{12\text{eff}}}{D_K} \approx \frac{7}{r_g} \times 10^{-6} \quad (\text{C12})$$

Thus, for PbO grain size $r_g \ll 300\text{\AA}$,

$$D_{12\text{eff}} \gg D_K$$

$$\text{and hence, } D_{\text{eff}} = D_K \quad (\text{C13})$$

For PbO grain size much greater than $300\text{\AA}$,

$$D_{12\text{eff}} \ll D_K$$

$$\text{and hence, } D_{\text{eff}} = D_{12\text{eff}} \quad (\text{C14})$$

Estimation of Surface Diffusivity of PbO:

In the absence of any better method, we shall assume that the activation energy of surface diffusion is half that for bulk diffusion and that the preexponential constants are equal. Pb^{2+} transport is known⁽⁶⁹⁾ to be slower than O^{2-} transport in PbO, with the activation energy of 22.4 Kcal/mole. Hence, we may write

$$\frac{D_b}{D_s} = \exp\left(-\frac{22400}{2RT}\right) = \exp\left(-\frac{5636}{T}\right) \quad (\text{C15})$$

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Table I. Nucleation - Growth Kinetics: $\ln(1 - x) = - k_{avr} t^m$

Parameters k_{avr} and m for various boundary conditions for:

Case (i): Nucleation occurs at fixed finite rate 'I'

Case (ii): Instantaneous nucleation but at fixed finite number of sites ' N_0 '

		Phase-Boundary Reaction Controlled		Diffusion Controlled	
		k_{avr}	m	k_{avr}	m
Spherical Nuclei	Case (i)	$\frac{\pi}{3} I k_r^3$	4	$\frac{8\pi}{15} I k_D^{3/2}$	5/2
	Case (ii)	$\frac{4\pi}{3} N_0 k_r^3$	3	$\frac{4\pi}{3} N_0 k_D^{3/2}$	3/2
Thin platelike Nuclei of Thickness 'l'	Case (i)	$\frac{\pi}{3} l I k_r^2$	3	$\frac{\pi}{2} l I k_D$	2
	Case (ii)	$\pi l N_0 k_r^2$	2	$\pi l N_0 k_D$	1
Long Needle-like Nuclei of radius 'r'	Case (i)	$\frac{\pi}{2} r^2 I k_r$	2	$\frac{2\pi}{3} r^2 I k_D^{1/2}$	3/2
	Case (ii)	$\pi r^2 N_0 k_r$	1	$\pi r^2 N_0 k_D^{1/2}$	1/2

Table II. Semi-quantitative Spectrographic Analysis of Raw Materials

	ZrO ₂	PbO
Ti	0.025	<0.003
Zr	P.C.	<0.005
Pb	<0.05	P.C.
Si	0.04	<0.005
Fe	0.02	<0.005
Mg	0.003	-
Al	<0.02	<0.005
Hf	<0.2	-
Ag	—	<0.001

P.C.: Principal Constituent

Table III. Isothermal Data $(-20 \pm 10)_{\mu} \text{ZrO}_2$ Mixed for 24 Hours.
Pressed at 4000 psi.

710°C	t(min) x	150 7.5	240 12.0	480 38.0				
720°C	t(min) x	106 14.5	210 36.5	313 63.0	480 81.5			
730°C	t(min) x	45 9.0	90 27.0	120 46.5	160 65.5	190 72.5	240 76.5	
740°C	t(min) x	30 17.0	60 44.0	100 76.0	153 85.0			
751°C	t(min) x	21 30.0	41 63.0	80 86.5				
760°C	t(min) x	5 7.7	10 18.5	20 45.5	40 85.0	60 86.2	100 88.8	
780°C	t(min) x	3 7.5	5 26.0	7 29.0	10 45.0	20 87.0	40 90.0	60 90.0
810°C	t(min) x	3 70.0	5 80.0	7 85.0	10 88.5	20 91.0	30 92.5	

$(-30 \pm 20)_{\mu} \text{ZrO}_2$

Mixed for 96 Hours, pressed at 4000 psi

710°C	t(min) x	31 11.5	60 14.5	150 30.0	240 49.6			
730°C	t(min) x	10 9.5	25 29.0	45 35.7	90 62.4	180 79.9	240 87.3	
810°C	t(min) x	3 71.0	5 76.0	7 82.4	10 90.1	20 90.6	30 91.6	60 92.0

Table IV: Interpretation of Microprobe Profile Analysis

Requirements: Low Solid Solubility, Crystallite size < effective volume analyzed < particle size, external mass transport not rate limiting.

	Profile	Rate Limiting Mechanism	Features
Non Porous Solid rapid, uniform nucleation on particle surface	Fig. 27(a)	Solid State Diffusion across product layer or Phase Boundary Reaction or Mixed control by above two mechanisms	(1) Relatively sharp transition in composition from fully reacted to unreacted region along certain cords e.g., B and C in Fig. 27(a). (2) Fully reacted composition along some cords without any changes, e.g., cord A in Fig. 27(a). (3) 'Shrinking Core' models applicable.
Porous solid, rapid uniform nucleation on grain surface	Fig. 27(a)	Pore Diffusion (Gaseous and/or Surface) and/or Grain boundary	Same as above
	Fig. 27(b)	First Order Phase Boundary Reaction or Solid state diffusion Across product layer on individual grain or mixed control by above two mechanisms.	(1) Uniform composition along all cords. (2) Composition corresponds to the extent of reaction. (3) Grain size, size distribution and shape important. (4) Kinetics described by 'Grain model'.
	Fig. 27(c)	Mixed control by pore diffusion and either grain diffusion or phase boundary reaction.	(1) Gradual transition in composition along all cords. (2) Kinetics described by 'Grain Model'
Effectively nonporous solid, nucleation at a limited number of sites	Fig. 27(d)	Solid state Diffusion or Phase Boundary Reaction or Nucleation or Mixed Control by above mechanisms.	(1) Relatively sharp transition in composition not necessarily at the cord ends. (2) For the higher extents of reaction, profile gradually appears similar to Fig. 27(a). (3) Kinetics described by 'nucleation-growth model.'

FIGURE CAPTIONS

- Fig. (1) a. (upper) Schematic pellet microstructure for a mixture of two reactants, each of uniform sized spherical particles. b. (lower) Schematic representation of the external mass transport to a spherical sink by the bulk diffusion through a particulate matrix.
- Fig. (2) Relations between the various factors affecting the product morphology and the rate controlling mechanism when a reaction proceeds by the migration of species A to the product covered particles of reactant B.
- Fig. (3) Schematic representation of the external mass transport to a spherical sink by the surface diffusion through a particulate matrix.
- Fig. (4) External mass transport by gaseous diffusion to a spherical reactant particle in an otherwise nonporous matrix, i.e., a "swiss-cheese" like microstructure.
- Fig. (5) a. (upper) Gaseous mass transport to a spherical sink in a porous matrix of particles. b. (lower) Influence of the average intersink spacing on the gaseous flux to a spherical sink through a porous matrix as a function of the sublimation-transport modulus.
- Fig. (6) Concentration profile within a particulate matrix for various values of the sublimation-transport modulus when the intersink spacing is infinite (upper) and when it equals the sink radius (lower).

- Fig. (7) Normalized reaction curves for external mass transport limited kinetics in a mixed particulate ensemble. The dotted line shows the behavior predicted by the classical gas-solid reaction model.
- Fig. (8) Three stages in a solid state reaction leading to a contact separation, drawn to the scale for $\alpha_0 = 0.33$ and $Z = 2$.
- Fig. (9) The extent of reaction (upper) and the microscopic linear expansion (lower) at the critical stage as functions of the dimensionless reactant size α_0 and the volume expansion factor Z for a mixture of spherical particles.
- Fig. (10) Scanning electron micrographs of:
- a. as received zirconia.
 - b. sieved zirconia
 - c. fractured pellet showing a large zirconia particle embedded in a matrix of small PbO particulates.
- Fig. (11) Size distributions of the two zirconia size ranges used in the reaction study.
- Fig. (12) BET specific surface area for zirconia of various size ranges.
- Fig. (13) The crystallite size distributions of three zirconia particle size ranges as determined by the x-ray peak broadening method.
- Fig. (14) Cumulative volume pore size distributions and the adsorption-desorption isotherms for the two zirconia size ranges.

- Fig. (15) Cumulative volume pore size distributions as determined by mercury porosimetry. Curve for the smaller sample is slightly offset from the true position for the sake of clarity.
- Fig. (16) Transmission electron micrographs of zirconia in the bright field mode (a,b,c) and in the dark field mode (d).
- Fig. (17) SEM micrographs of epoxy impregnated, polished pellets showing evolution of the microstructure with the reaction. (a) Green pellet, (b) $x = 0.31$ and (c) $x = 0.63$.
- Fig. (18) Reaction isotherms for the samples with $(-20 \pm 10)\mu$ zirconia, mixed for 24 hours and pressed at 4000 psi.
- Fig. (19) Reaction isotherms for the samples with $(-30 \pm 20)\mu$ zirconia, mixed for 96 hours and pressed at 4000 psi.
- Fig. (20) Isoreaction Arrhenius plots for mixtures with $(-20 \pm 10)\mu$ zirconia mixed for 24 hours and pressed at 4000 psi.
- Fig. (21) Dependence of apparent activation energy as calculated from the isoreaction Arrhenius plot on the extent of reaction.
- Fig. (22) Isoreaction Arrhenius plots for mixtures with $(-30 \pm 20)\mu$ zirconia, mixed for 96 hours and pressed at 4000 psi.
- Fig. (23) Normalized reaction curve and data for samples with $(-20 \pm 10)\mu$ zirconia reacted at various temperatures. Each datum with $(t > 10 \text{ min})$ and $(x < 0.85)$ was used as a reference to normalize other data for the same temperature.

Fig. (24) Normalized reaction data and theoretical curves assuming shrinking core geometry with diffusion (DC), phase boundary reaction (PBRC) or external mass transport (ExTr) as the rate limiting mechanisms. Actual size distribution of $(-20 \pm 10)\mu$ range was taken into account for computing the theoretical curves.

Fig. (25) Isothermal reaction data for $(-20 \pm 10)\mu$ zirconia plotted according to the nucleation-growth model equation.

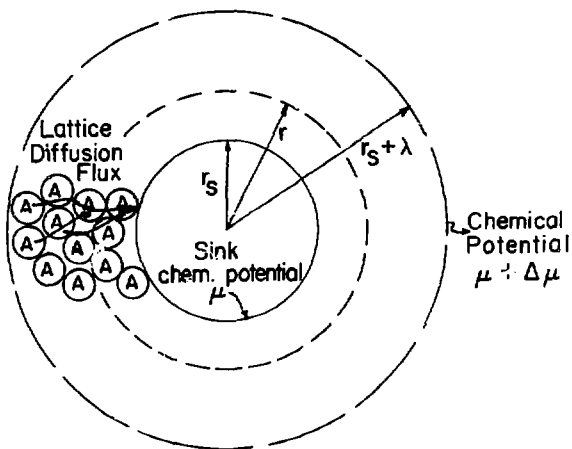
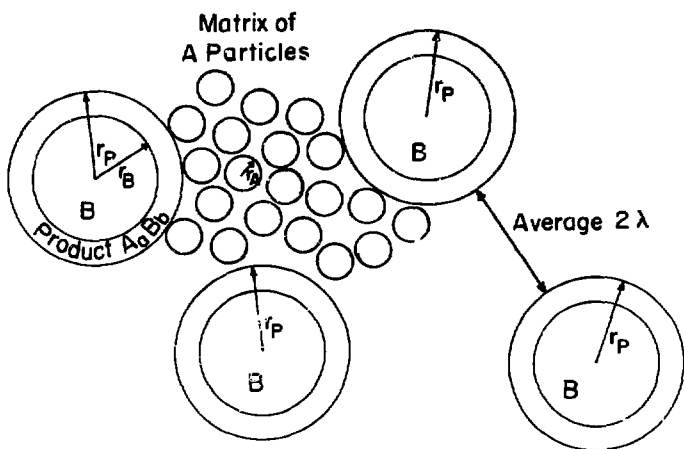
Fig. (26) Arrhenius plot derived from nucleation-growth model fit to the reaction data of mixtures with $(-20 \pm 10)\mu$ zirconia particles.

Fig. (27) Schematic cross-sections and microprobe analysis profiles for porous and nonporous solids under various nucleation morphologies and rate limiting mechanisms. See Table IV for interpretation.

Fig. (28) Results of microprobe profile analysis on the partially reacted samples containing $(-20 \pm 10)\mu$ zirconia particles. All the plots in the a column are from the same sample but different particles. Analysis of a fully reacted and sintered lead zirconate sample is also shown.

Fig. (29) Microprobe profile analysis on a number of particles with $x = 0.44$ and $x = 0.17$ from mixtures with $(-20 \pm 10)\mu$ zirconia.

- Fig. (30) Normalized reaction data for mixtures with $(-30 + 20)_\mu$ zirconia mixed for 96 hours and pressed at 4000 psi. Normalized theoretical curve was obtained from diffusion controlled shrinking core model with $Z = 2$. Each datum with $(t > 10 \text{ min})$ was used as a reference to normalize other data for the same temperature.
- Fig. (31) Reaction data for mixtures containing $(-30 + 20)_\mu$ zirconia particles mixed and pressed under the shown conditions. The theoretical curves were calculated assuming 90 percent reaction in 240 minutes.
- Fig. (32) Pellet volume change as a function of the extent of reaction for mixtures with $(-20 + 10)_\mu$ zirconia particles. The volume expansion was calculated with respect to the as-pressed dimensions.
- Fig. (33) Theoretical plot according to equation (127) along with the experimental data. The volume expansion was calculated with respect to the volume of pellets after a prereaction anneal at 630°C for 60 minutes.



XBL 799-7073

Fig.1

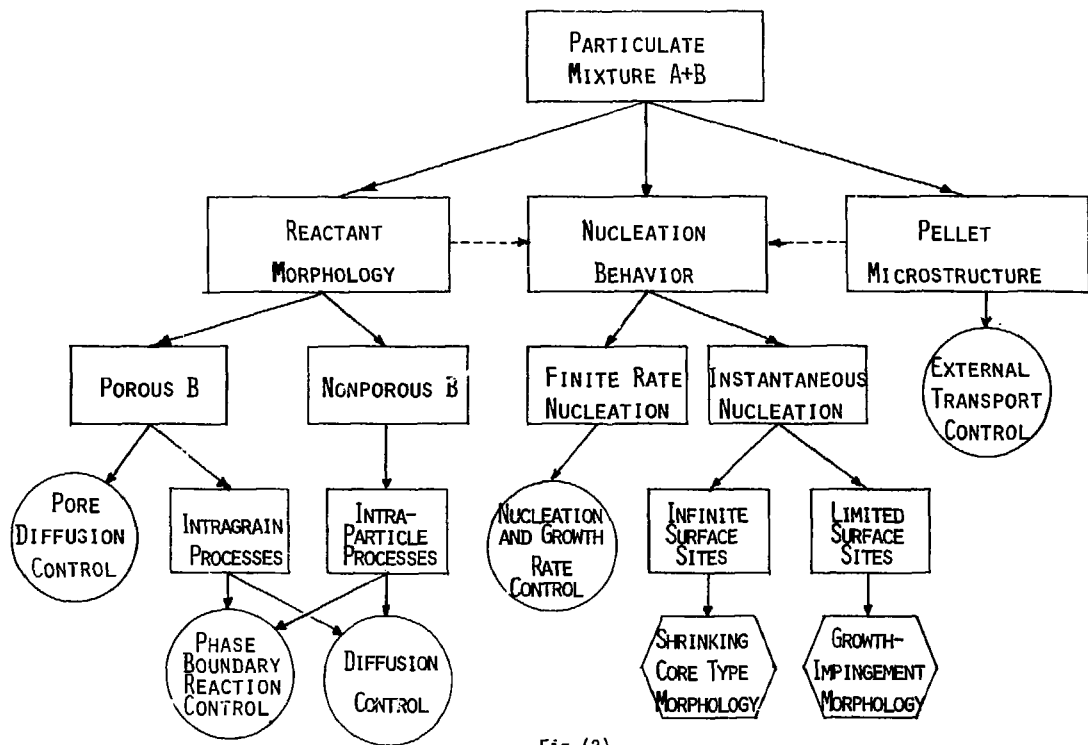
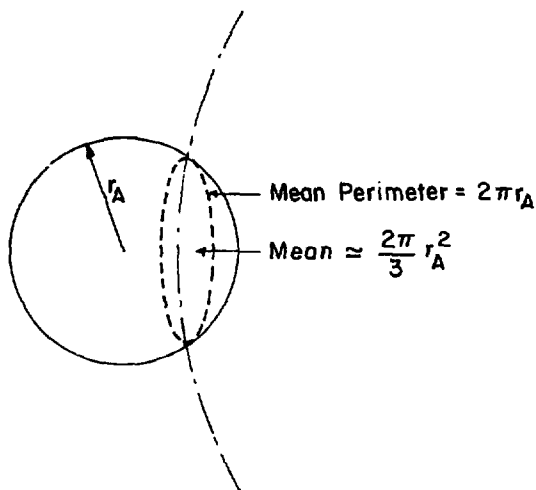
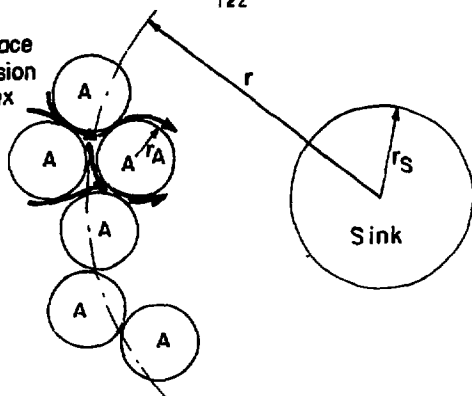


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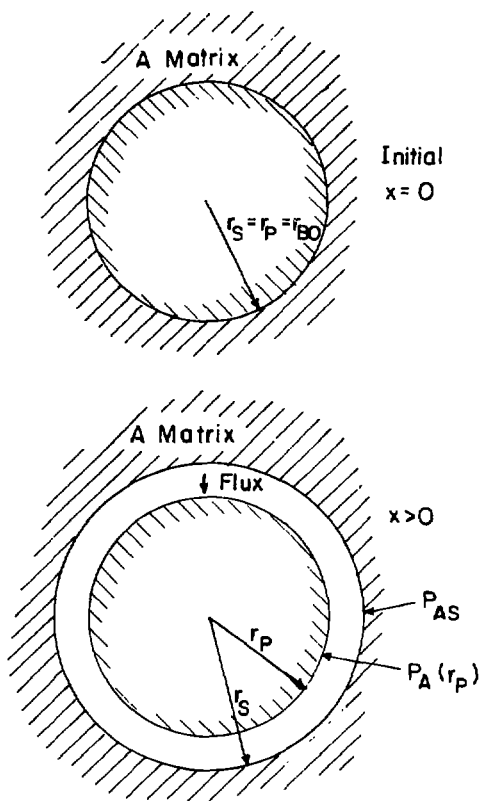
XBL 805-9694

Surface
Diffusion
Flux



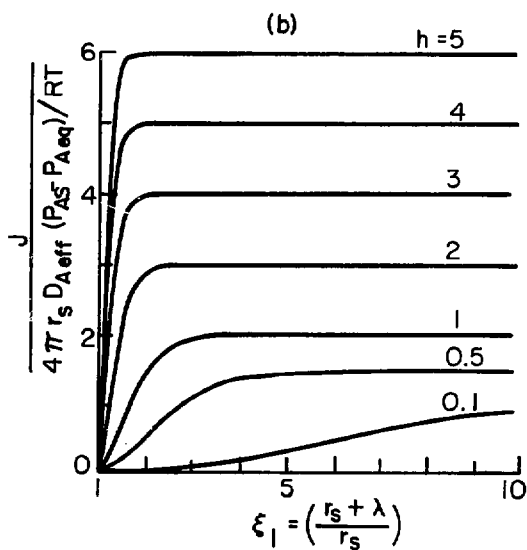
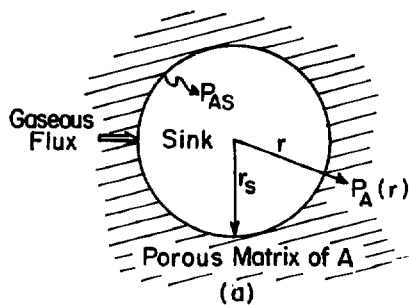
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Fig. (3)



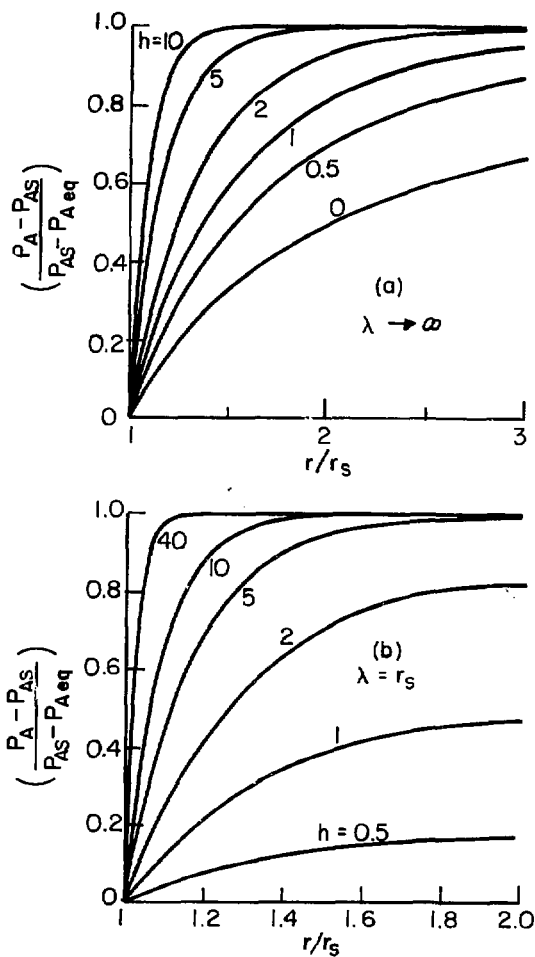
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Fig.(4)



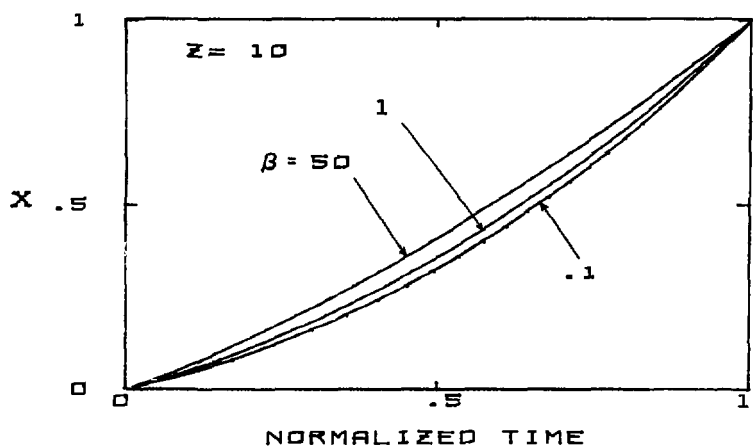
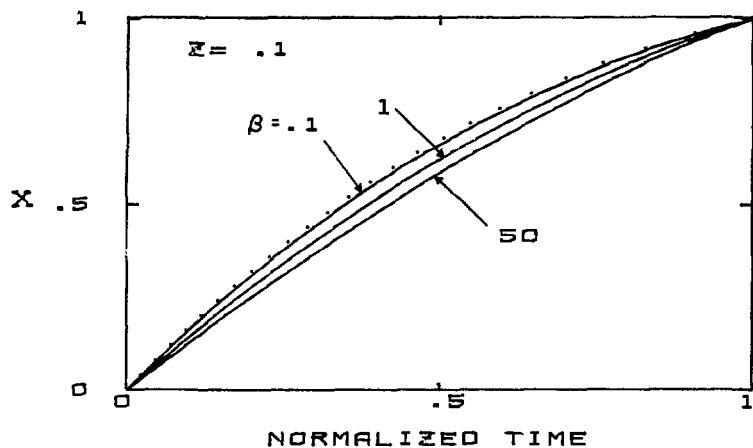
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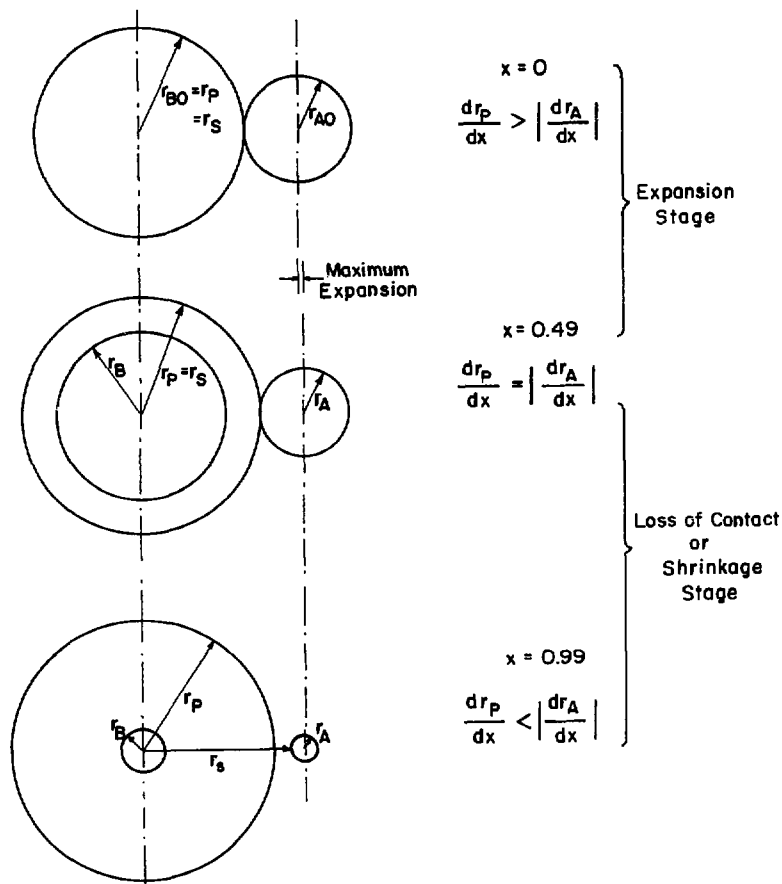
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Fig. (6)



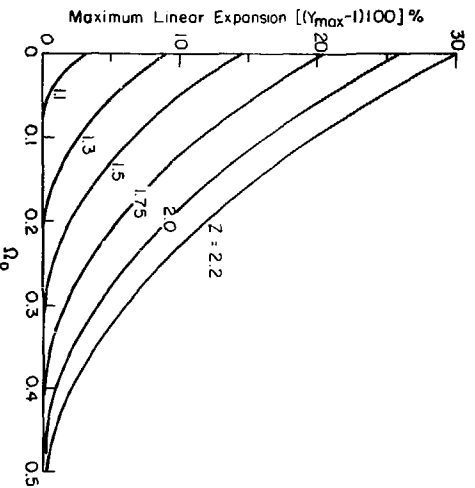
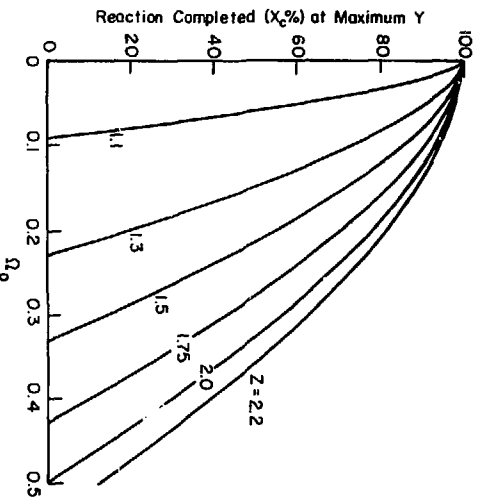
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Fig.(7)



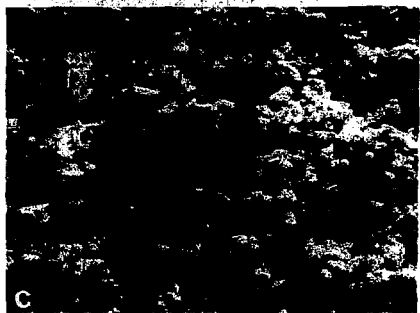
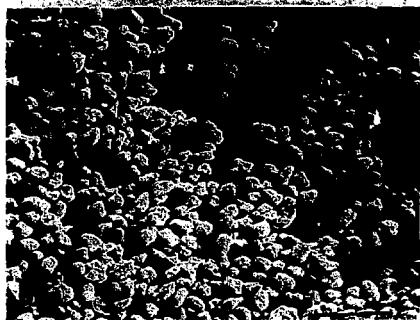
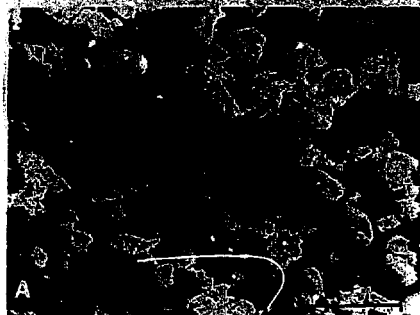
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Fig. (8)



XBL798-6900A

Fig. (9)



XBB 7910-13495

Fig. (10)

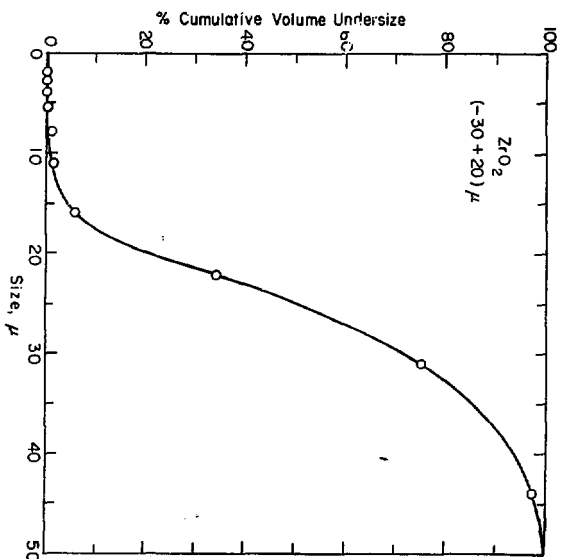
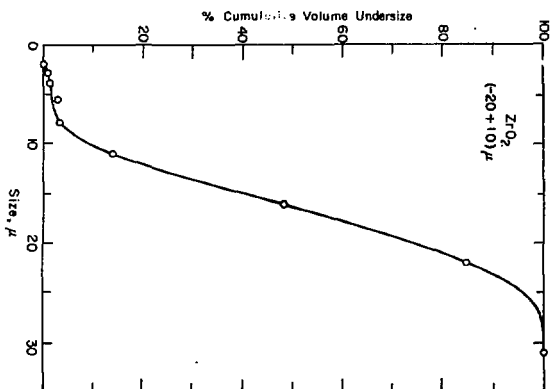
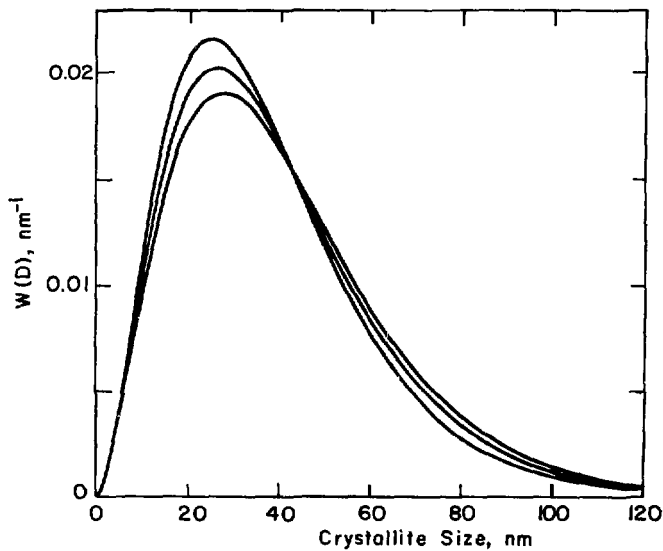
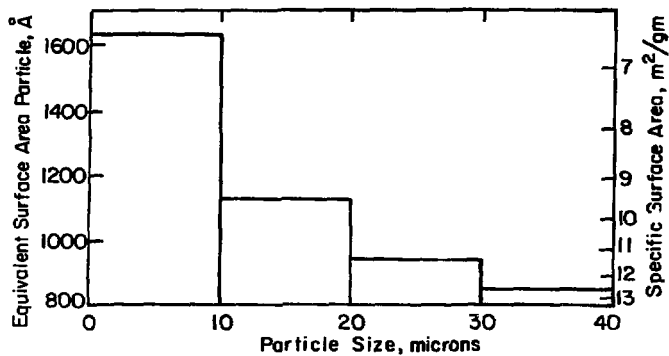


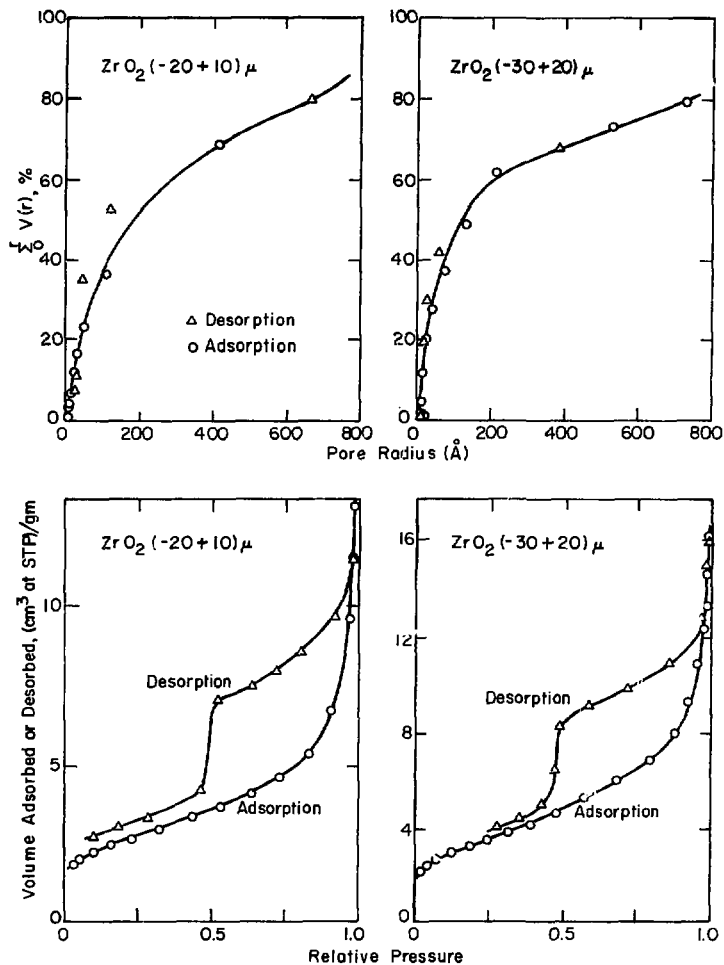
Fig. (11)

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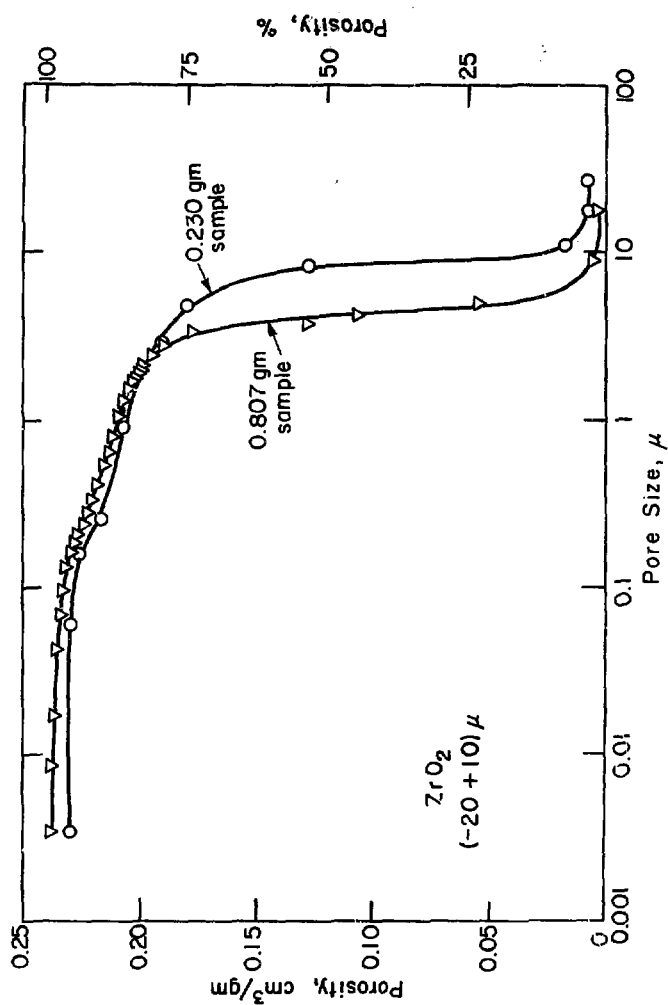
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Fig.(12) Upper Fig.(13)Lower



XBL 798-6902

Fig. (14)



XBL797-6640

Fig. (15)

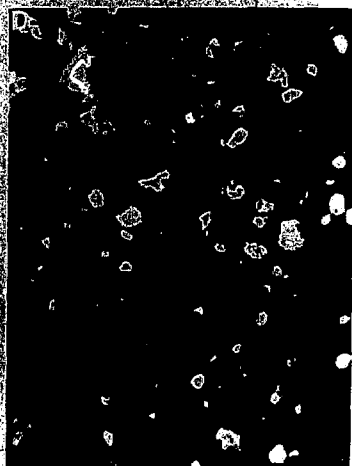
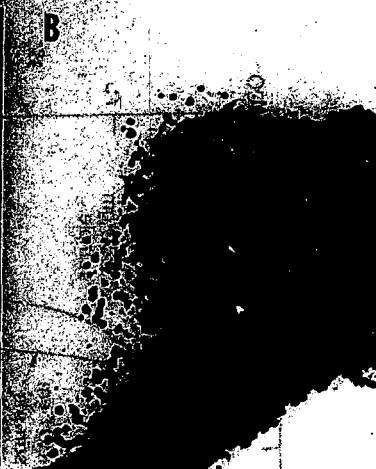
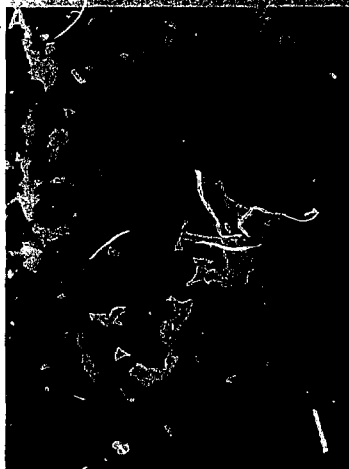
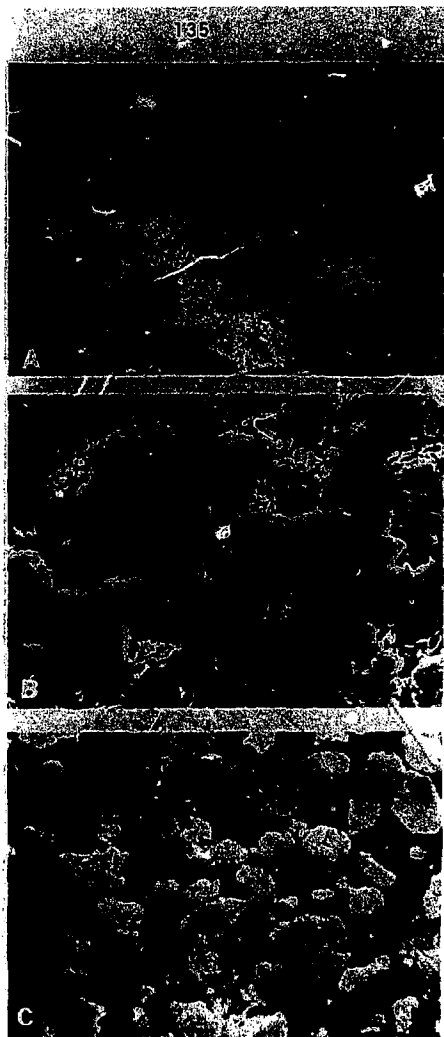


Fig. (16)

XbB 7910-13496



XBB 7910-13494

Fig.(17)

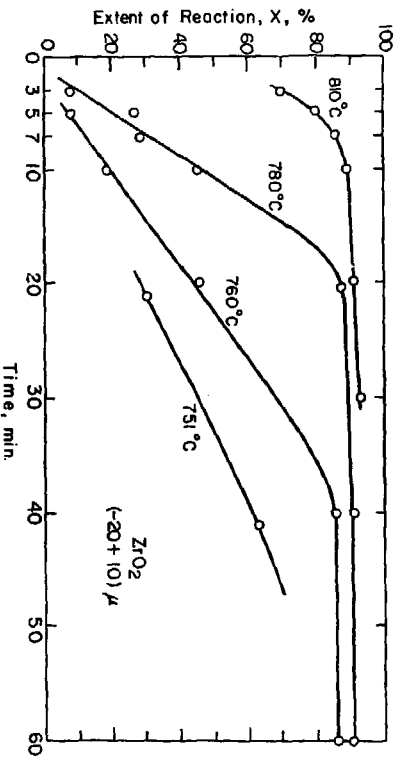
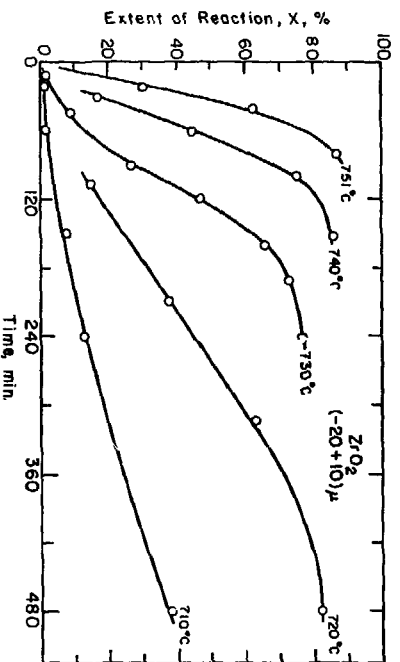


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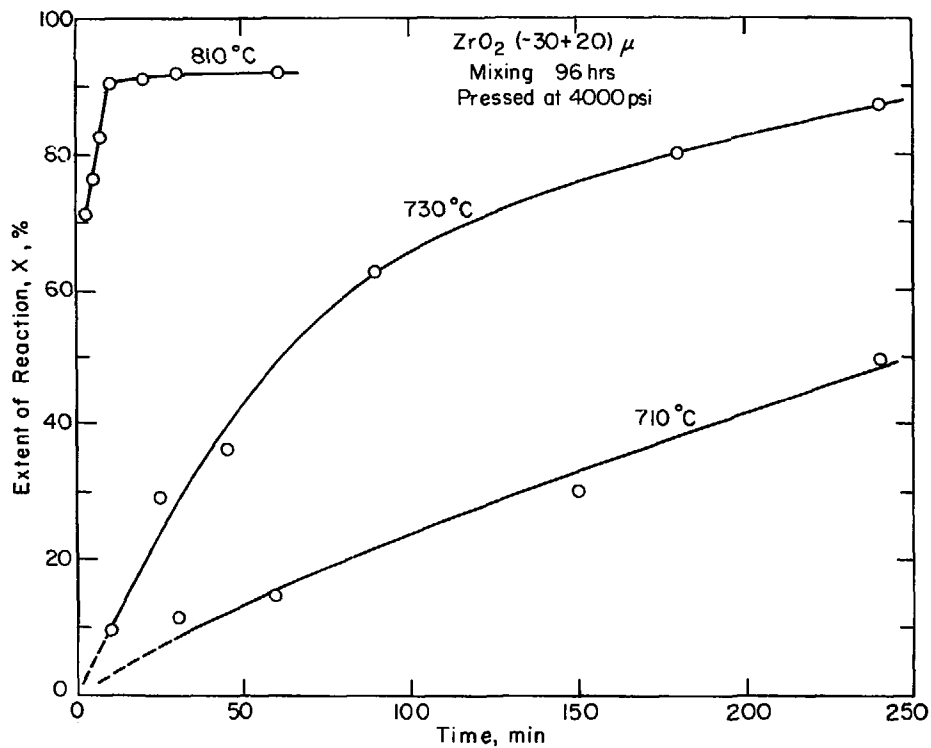
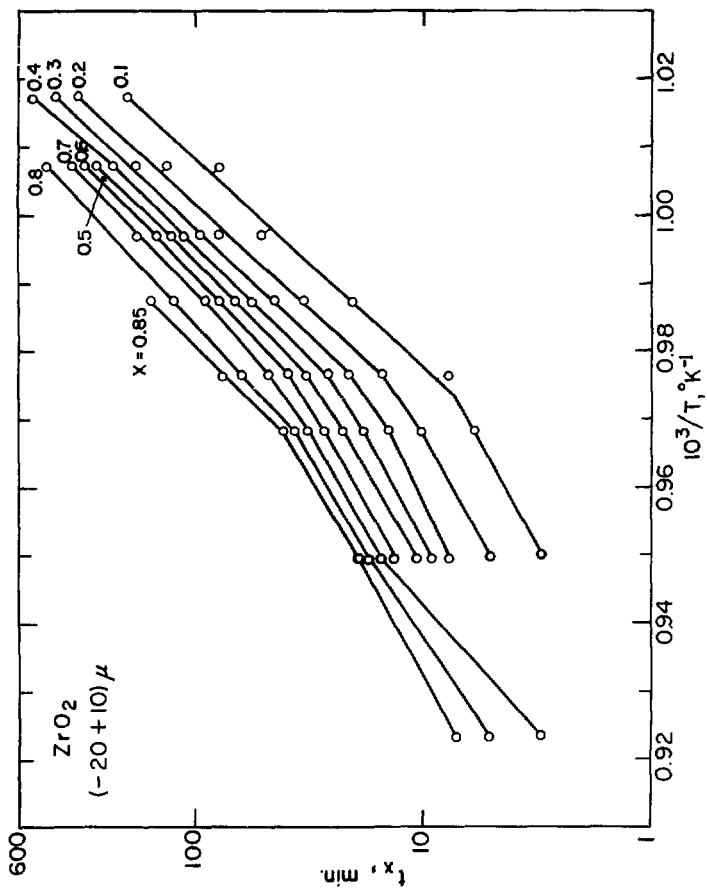


Fig. (19)

XBL 797-6645



XBL 797-6638

Fig. (20)

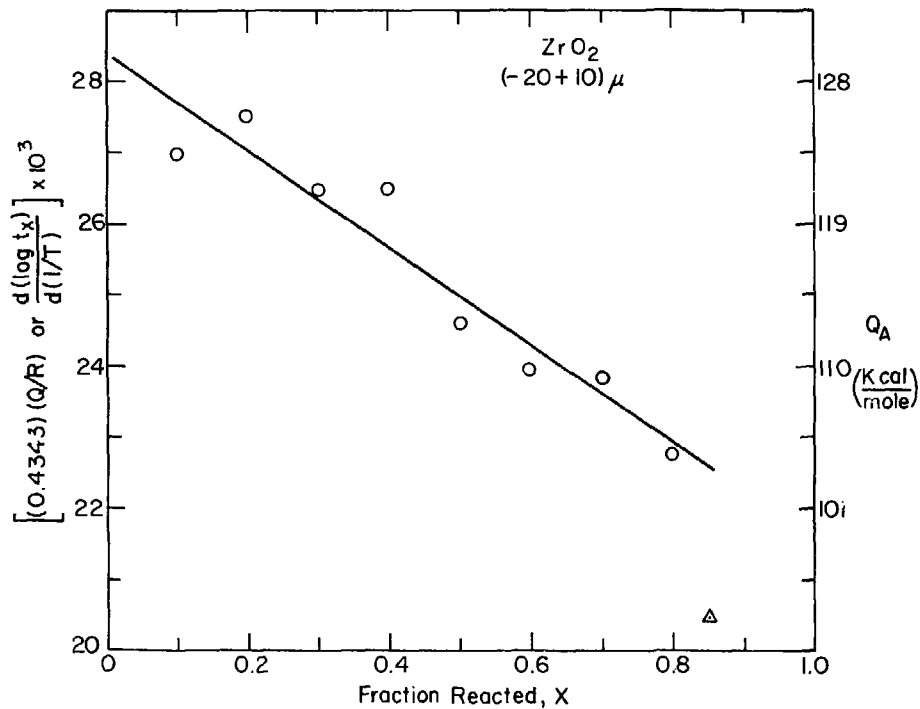
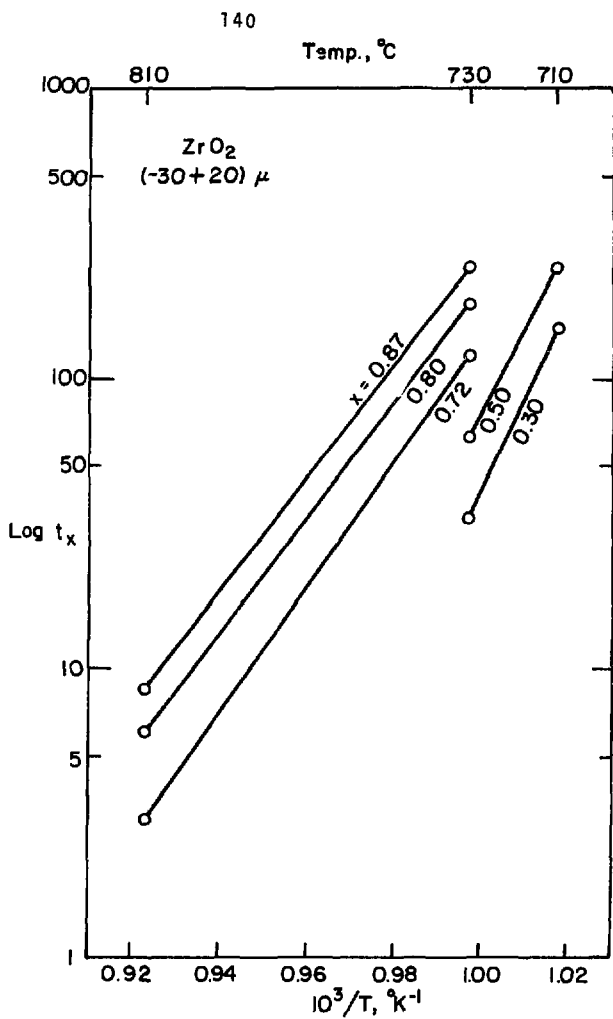


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XBL 797-6649

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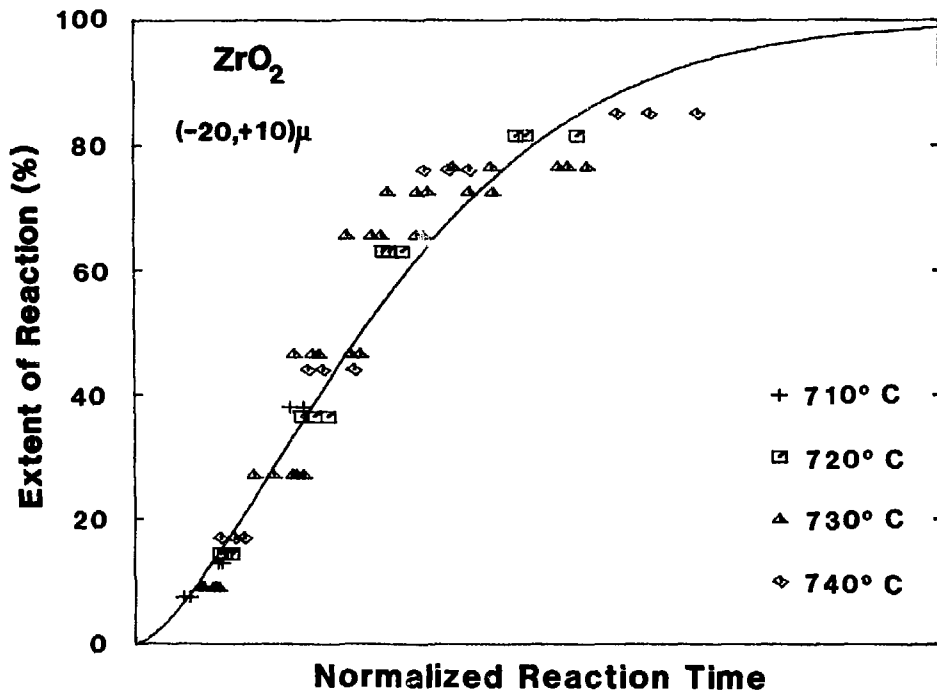


Fig.(23)

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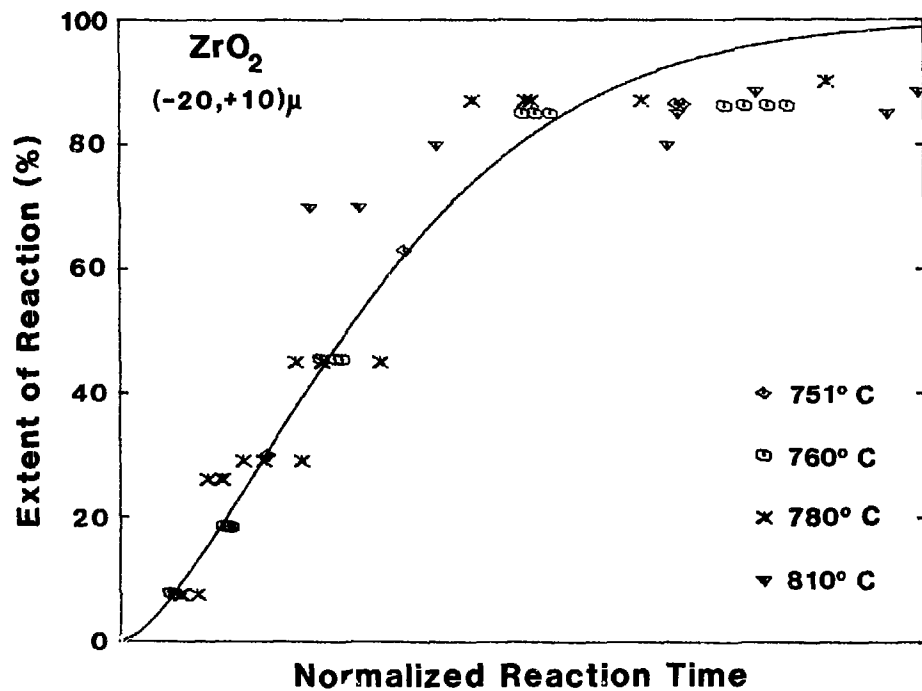
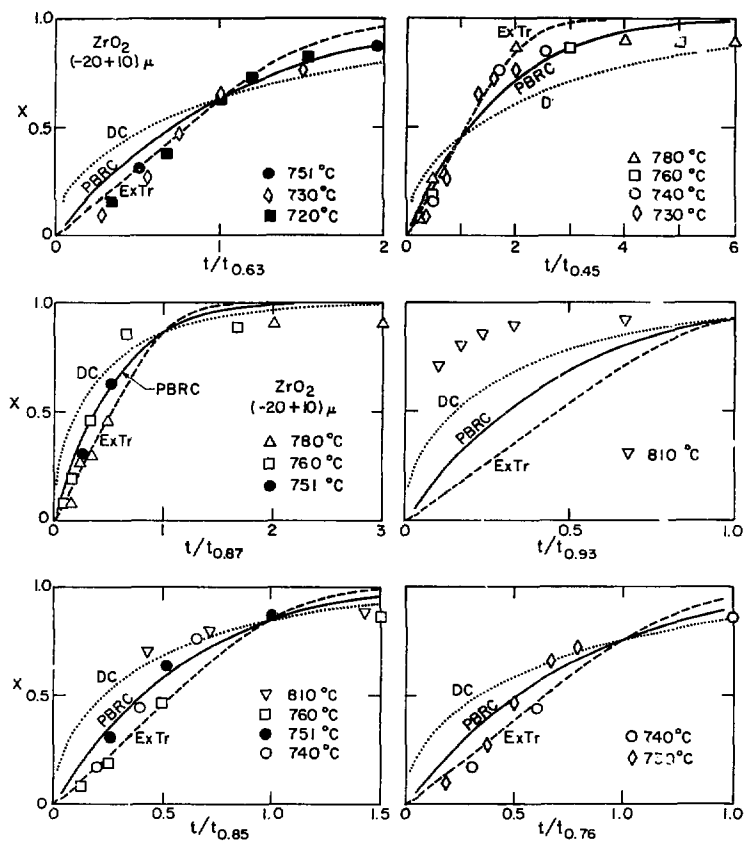


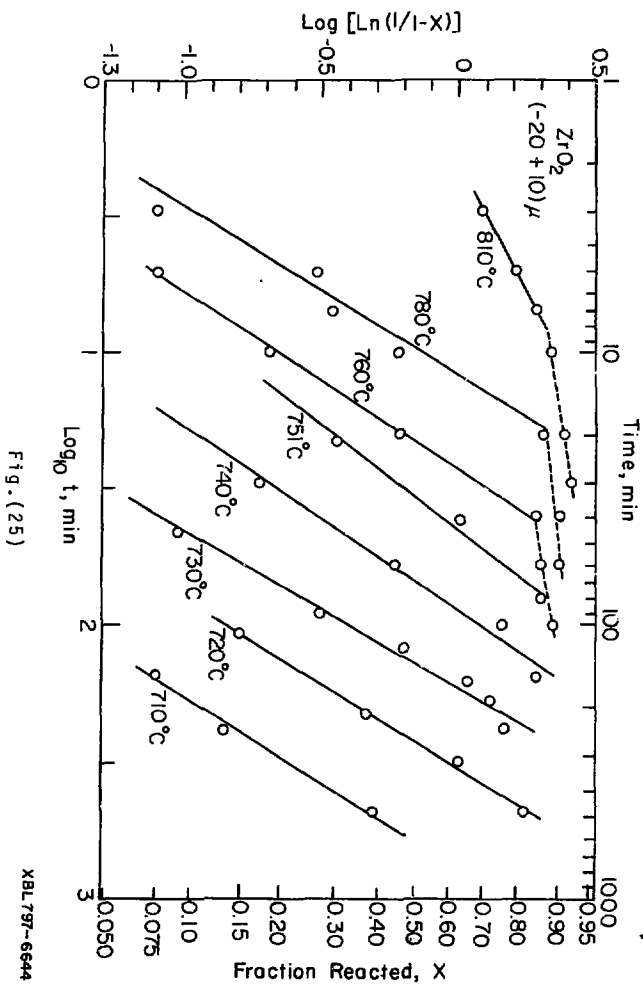
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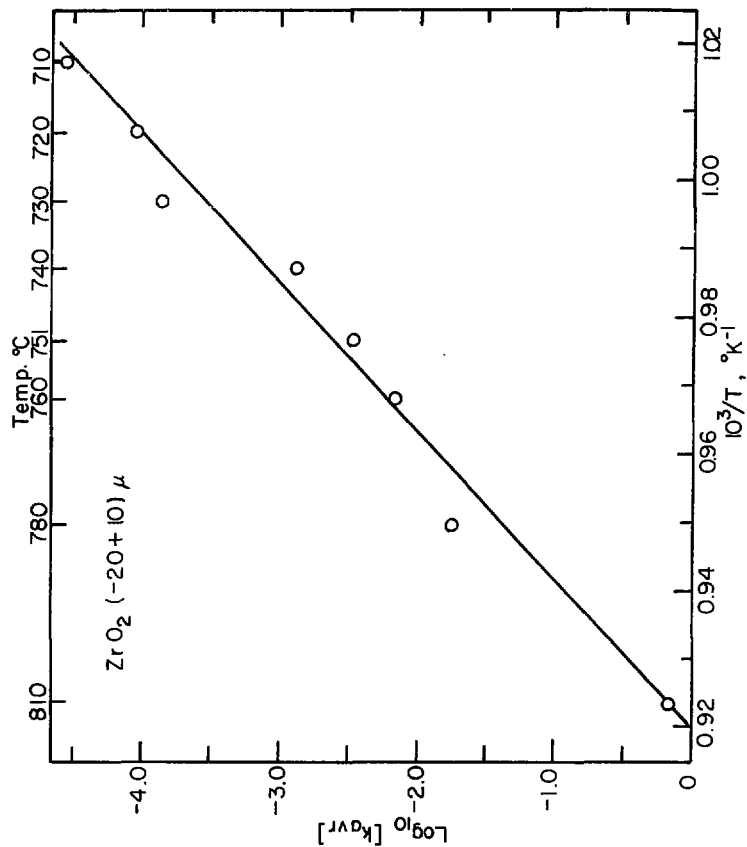
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XBL 797-6656A

Fig. (24)





XBL 797-6643

Fig. (26)

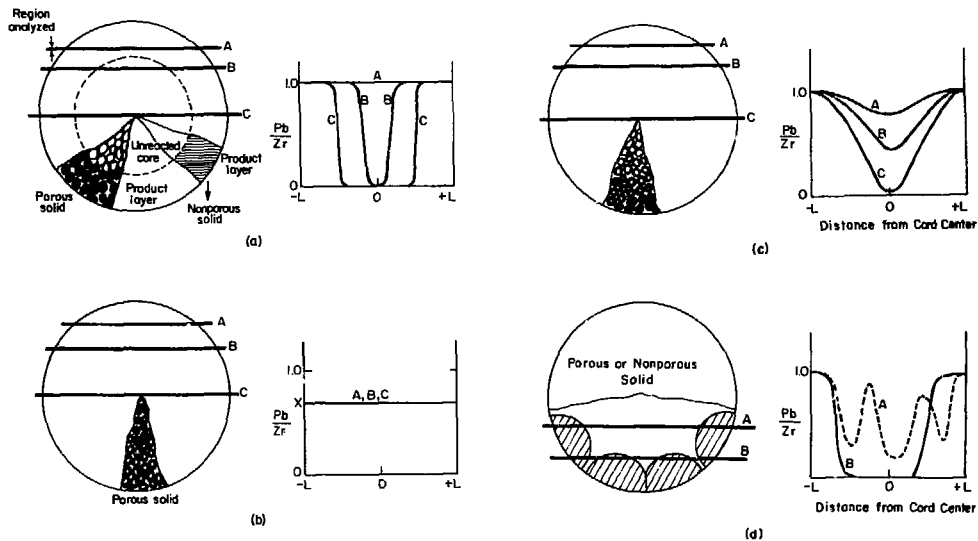
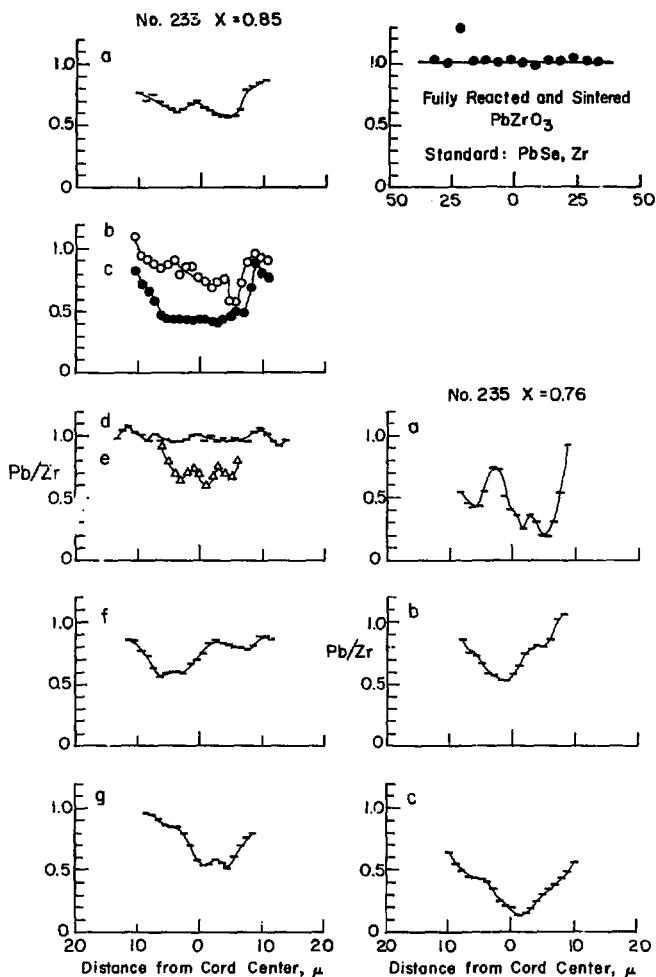


Fig. (27)

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Fig. (28)

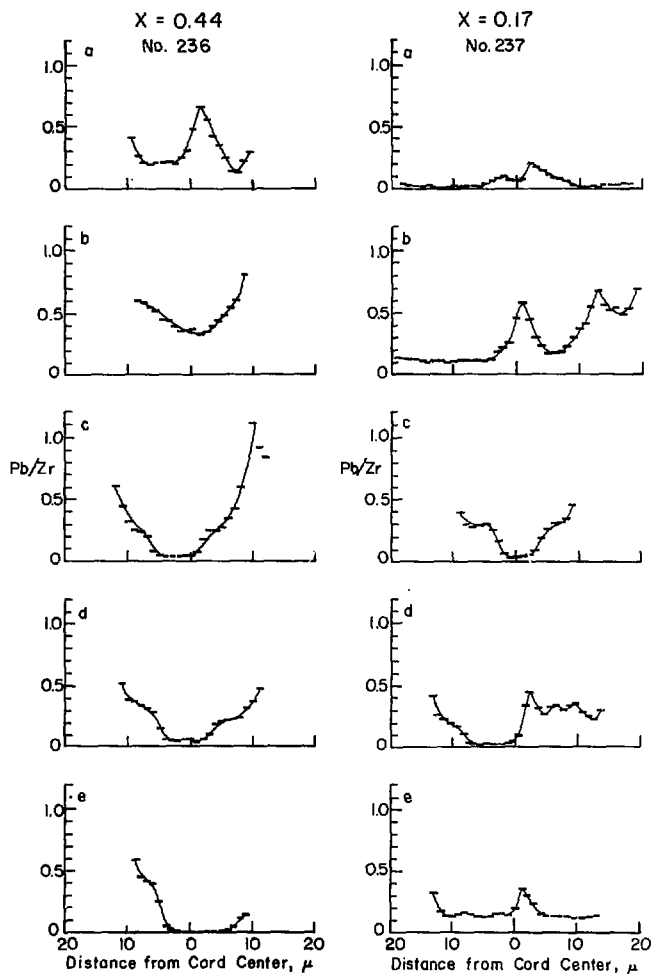


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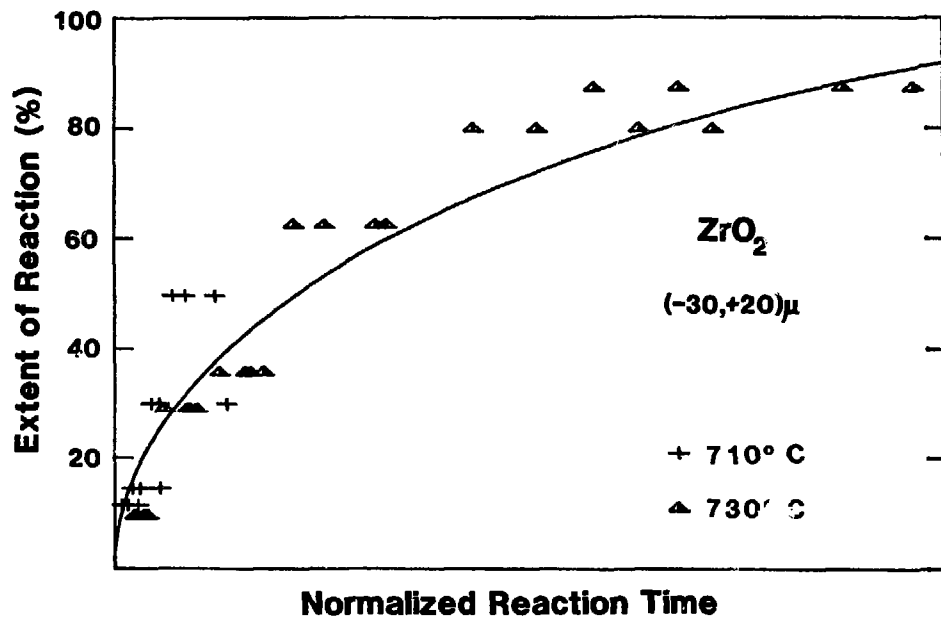


Fig. (30)

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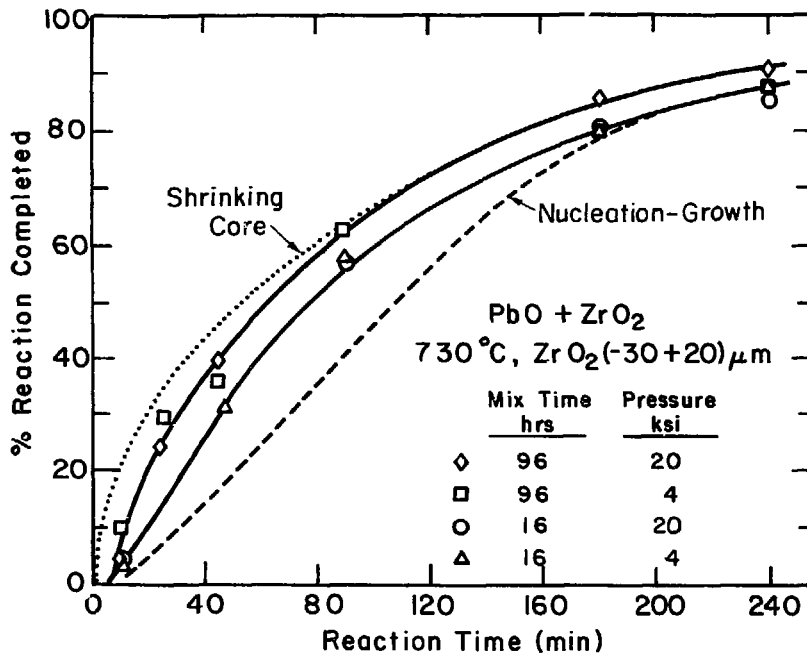


Fig.(31)

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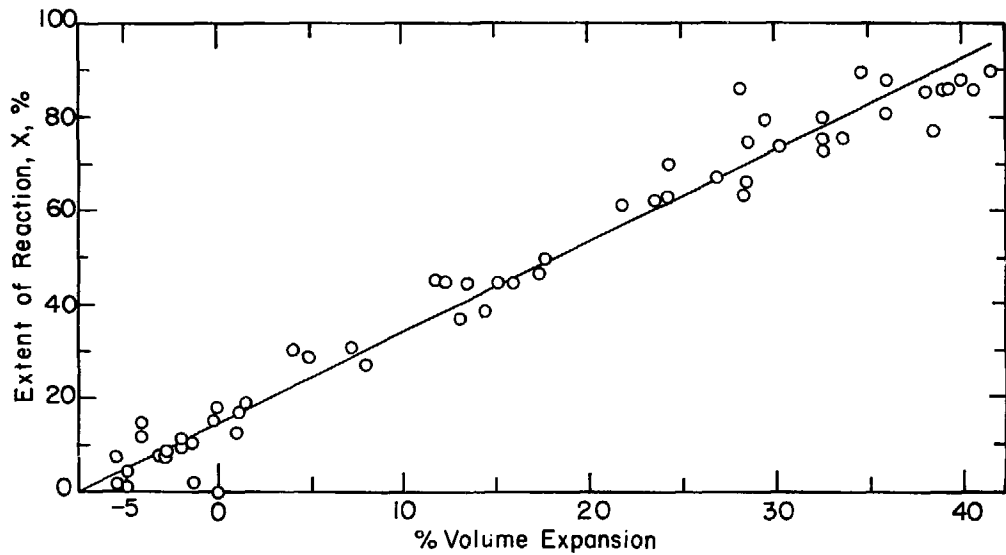


Fig.(32)

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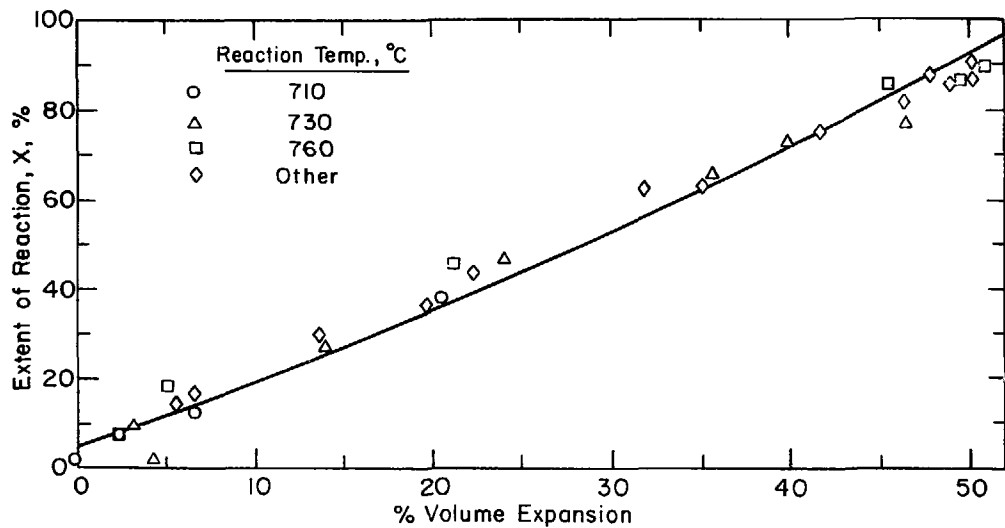


Fig.(33)

XBL 797-6635A

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