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Reactions in Solid Particles—A Reappraisal of Models

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Models such as the Ishida–Wen, or even more commonly the shrinking core models (Ginstling–Brounshtein being an important example), have long been used in the analyses of reactions in particles, particularly in solid–solid systems. There have been a few analyses of the validity of the assumptions made in these models, but to date, no comparison has been undertaken of these models against a general model to delineate their regions of applicability in the parameter space. In this article, we present a general unsteady-state model that subsumes the earlier models as special cases. Nondimensionalization leads to the identification of two governing parameters in the model, a diffusion-reaction parameter, and a relative abundance parameter. By solving the general model and comparing the solutions with those of the approximate models in the parameter space, conditions under which the approximate models apply, and the errors that result from their application in other situations, have been identified. © 2012 American Institute of Chemical Engineers

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Introduction

Reactions in solid particles occur in several process applications in the chemical, materials and metallurgical industries. Cases, in which a solid reactant is converted to a solid or fluid product by reaction with a second reactant in the fluid phase surrounding the particle, are well described in the literature.[1–6] When the fluid phase is a gas, in the simpler of these models which apply when the pore structure of the solid does not change appreciably due to reaction, the difference in molar densities of the two reactants allows the diffusion into the reacting particle to be treated in a quasi-steady-state manner and analytical results obtain. There have been some analyses of the situations in which the fundamental unsteady state nature of diffusion has to be rigorously accounted for.[7,8] These analyses treat of the diffusion-limited case, in which the reaction is confined to a front that moves progressively into the particle with time. In the domain of solid–solid reactions (reactions between oxides of metals are a prominent class of examples, in the manufacture of ceramics, mixed oxides as catalysts, and Portland cement[6]), similar quasi-steady-state models mentioned above are usually applied,[2,9] in spite of the fact that contact between the two reactants is not continuous. Although recent years have seen more sophisticated approaches to these situations based on considerations of geometries that evolve in particles surrounded by a finite number of particles of the second reactant,[10,11] a rigorous analysis of this situation has not been published to date. It is clear from the approximate analyses[11] however, that in the limiting case of the number of points of contact between the particles becoming large, a continuous-contact approximation with spherically symmetric reaction fronts can apply, except that the assumptions of front reaction and quasi-steady-state diffusion have to be carefully examined. Application of models such as Ginstling–Brounshtein (GB)[2] to solid–solid reactions without taking into cognizance the above issues has resulted in a situation in which the rate parameter estimated depends on experimental conditions of particle size, reactant ratio, and so forth.[12] It thus appears that there is a case for revisiting the reaction-in-a-particle and deriving exact models, so that the conditions under which approximate models apply can be delineated.

In this article, a rigorous formulation is given for a first-order reaction in a spherical solid particle of constant density containing one reactant, surrounded by the second reactant. The theory is general enough to encompass all regimes from uniform reaction to front reaction. While solid–solid reactions (in the limit of a the number of points of contact being large) form the primary area of focus, the theory applies to all cases of reactions in a particle, in which changes in the pore structure of the solid do not have to be taken into account. The model is solved numerically, and its behavior explored in the appropriate parameter space, to identify the regions of the parameter space in which simpler models in the literature apply.

Literature Review

For a reaction between A and B, in which A is the nondiffusing solid phase reactant, and B is the diffusing reactant (either fluid or solid phase), the reaction in the particle containing A has been modeled in the literature under various simplifying assumptions. The case of constant particle size is relevant to the present discussion, and models originating in the gas–solid literature treat the two limiting cases of uniform reaction and reaction-at-a-front, the latter case admitting two further limiting cases of reaction control and

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diffusion control. Ishida and Wen[1] treat the case of uniform reaction and show that the front reaction models arise as a limiting case as the diffusion-reaction parameter becomes large. This model was developed in two stages, with the period of reaction prior to the formation of a product layer as the first stage, and the period following, as the second stage. The expression for conversion and time as function of product zone in the first stage is

$$\alpha = \frac{3}{(\phi)^2}(\phi \coth \phi - 1)k' t \tag{1}$$

where k' is a (first-order) reaction rate constant (in their work, a second-order reaction was assumed, but the solid phase reactant concentration was bundled into the pseudo-first-order rate constant used above), t, the time and α, the conversion of the nondiffusing reactant. The expressions in the second stage are

$$\alpha = 1 - \xi_{\mathrm{m}}^3 + \frac{3\xi_{\mathrm{m}}}{\phi^2}[\phi\xi_{\mathrm{m}}\coth(\phi\xi_{\mathrm{m}}) - 1] \tag{2}$$

$$k' t = 1 + \frac{\phi^2}{6}\left(1 - \xi_{\mathrm{m}}^2\right)(1 + 2\xi_{\mathrm{m}}) + (1 - \xi_{\mathrm{m}})[\phi\xi_{\mathrm{m}}\coth(\phi\xi_{\mathrm{m}}) - 1] \tag{3}$$

where ξ_{m} is the nondimensional radius of the reactive core (the shell being purely the product) at time t. ϕ in the above is a Thiele-type diffusion-reaction parameter.

Ishida and Wen,[1] however, treat the diffusion-reaction in a quasi-steady-state manner. The classical front reaction models also treat the diffusion-limited case under the quasi-steady-state assumption.[2,5,6] Simonsson and Lindman[7] quantified the error in the quasi-steady-state treatment in the shrinking core models. These authors were the first to consider the "sucking effect" the moving boundary has on the diffusing reactant and used the convective diffusion equation to model the diffusion of B. More recently, Frade and Cable[8] proposed a model for the diffusion-controlled situation by considering the motion of boundaries and change in volume of particle that generally accompanies reaction. The general situation of uniform reaction in the particle with full unsteady-state treatment applied to the diffusion of B has thus not been considered in the literature and provides the motivation for this work.

The discussion above keeps the case of models used in solid–solid reactions in focus. While these models are applied to other cases of reactions in solid particles as well, mention must be made of a class of models proposed for the fluid–solid case, which take into account the porous structure of the solid, because the reaction in this case essentially proceeds with the diffusion of the fluid-phase reactant "through the pores" of the solid. The most important among these models is the random pore model of Bhatia and Perlmutter[3,4] and its subsequent variants. Such models are not considered in the present analysis, because of the stated focus on the case of solid–solid reactions.

Model Development

Consider a spherical particle containing a reactant A, which is surrounded by a continuum of B. Unidirectional diffusion of reactant B into the solid particle, with simultaneous reaction with the reactant A is assumed, the reaction forming a product according to the stoichiometric reaction $v_a\mathrm{A} + v_b\mathrm{B} \rightarrow v_P\mathrm{P}$. The particle size is assumed to remain constant. The reaction between A and B is assumed to be first order in B.

The differential equation that governs the concentration of B in the particle of A is

$$\frac{\partial c_{\mathrm{B}}}{\partial t} + \left(-\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{\mathrm{B}}}{\partial r}\right)\right) = r_{\mathrm{B}} \tag{4}$$

where r_{B} is rate of reaction of B.

The initial and boundary conditions are

$$t = 0 \qquad c_{\mathrm{B}} = 0 \qquad \text{at all } r$$

$$t > 0 \qquad r = 0 \quad \frac{\partial c_{\mathrm{B}}}{\partial r} = 0 \text{ and } r = R \;\; c_{\mathrm{B}} = c_{\mathrm{B0}}$$

A differential material balance for reactant A gives, at any r $(0 < r < R)$

$$\frac{\partial c_{\mathrm{A}}}{\partial t} = r_{\mathrm{A}} \tag{5}$$

with $C_{\mathrm{A}} = C_{\mathrm{A0}}$ at $t = 0$, where r_{A} is rate of reaction of A.

The reaction rate expressions are

$$r_{\mathrm{A}} = -v_a k c_{\mathrm{B}} u(c_{\mathrm{A}}) \quad \text{and} \quad r_{\mathrm{B}} = -v_b k c_{\mathrm{B}} u(c_{\mathrm{A}}) \tag{6}$$

where u is the Heavyside function

$$\begin{aligned} u(c_{\mathrm{A}}) &= 1 \quad \text{if } c_{\mathrm{A}} > 0 \\ u(c_{\mathrm{A}}) &= 0 \quad \text{if } c_{\mathrm{A}} \leq 0 \end{aligned} \tag{7}$$

In the initial phase of reaction, A is present everywhere in the nondiffusing particle. After a certain time the reactant at the surface is completely exhausted by the reaction, and the particle has an outer zone that is an inert product layer. In the present formulation, the Heavyside function ensures that there is no reaction in this zone, and the movement of the boundary between the zones does not have to be explicitly accounted for.

The equations can be rendered dimensionless using the following variables

$$a = \frac{c_{\mathrm{A}}}{c_{\mathrm{A0}}} \quad \rho = \frac{r}{R} \quad b = \frac{c_{\mathrm{B}}}{c_{\mathrm{B0}}} \quad \tau = \frac{t}{R^2/D}$$

where R is the initial radius of the reacting particle.

Using these dimensionless variables in the above equations,

$$\frac{\partial b}{\partial \tau} + \left(-\frac{D}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2\frac{\partial b}{\partial \rho}\right)\right) = -\phi^2 b u(a) \tag{8}$$

and

$$\frac{\partial a}{\partial \tau} = -\frac{\phi^2 b u(a)}{K} \tag{9}$$

for each ρ, where $\phi = R\sqrt{\frac{v_b k}{\mathrm{D}}}$ and $K = \frac{v_b c_{\mathrm{A0}}}{v_a c_{\mathrm{B0}}}$.

The initial and boundary conditions are:

$$\tau = 0 \quad b = 0 \text{ and } a = 1$$

$$\tau > 0 \quad \rho = 0 \quad \frac{\partial b}{\partial \rho} = 0$$

$$\rho = 1 \quad b = 1$$

The model has two dimensionless parameters, ϕ and K. ϕ is a Thiele-type parameter, which compares the reaction rate

Table 1. Models in the Literature as Special Cases of the Present Model

Model	ϕ	K
Ishida–Wen	Any	$\gg 1$
Ginstling–Brounshtein	$\gg 1$	$\gg 1$
Frade–Cable	$\gg 1$	Any

to the diffusion rate in the solid. For small values of ϕ, B is able to diffuse throughout the particle. For large values of ϕ, the reaction is confined to a zone, because B gets reacted before it can penetrate very far into the particle. In the limit, these conditions produce the shrinking core model. Because of the manner in which the model is formulated, it goes over smoothly from a uniform reaction scenario to a front reaction scenario, as the value of ϕ increases, without the need to explicitly account for a convective term as in earlier studies. The parameter κ expresses the relative abundance of the two reactants as compared to their stoichiometric requirements. The value of K determines how important the unsteady-state effect is in a front-reaction situation, because the rate of movement of the boundary in this situation (taken to be at ρ_c) is given, by matching the flux of B at the boundary against the rate of consumption of A by reaction, as

$$\frac{\partial \rho_c}{\partial \tau} = \frac{1}{K}\frac{\partial b}{\partial \rho} \tag{10}$$

As time is nondimensionalized with respect to the diffusion time, the above equation implies that the movement of the reaction zone is slow relative to the diffusion process for large values of K. A pseudo-steady-state assumption for diffusion would therefore be tenable under such conditions. The above arguments allow us to recognize the models available in the literature as special cases of the model presented here, as shown in Table 1.

Solution of Model Equations

The choice of the numerical technique and the computational platform for solving the model equations was made keeping in mind the need to extend the treatment to two- and three-dimensional cases in future extensions of this work, on finite number of contact points, in which complex reaction geometries arise. The model equations were thus solved by the Finite element technique, using the COMSOL multiphysics simulator. Various specific modules are available in COMSOL to simulate particular systems in their respective (1-D or 2-D or 3-D) dimensions. In this work, the chemical engineering module (mass transfer-diffusion) is used to pose the problem on the simulator in 1-D. COMSOL needs the geometry to be specified; here the geometry for the system is a straight line as shown in Figure 1. In Figure 1, point O ($\rho = 0$) represents the center of the particle and point P ($\rho = 1$), the surface of the particle. A Lagrange-quadratic mesh element has been used, the number of elements being 15,360. Preliminary simulations confirmed the adequacy of the above parameters. With these parameters, COMSOL simulator solves model equations and gives concentration profiles of reactants as a function of time. From the concentration profile of A at any time, the conversion at that time is calculated as

$$\alpha = 1 - \frac{\int_0^1 (4\pi\rho^2 a(\rho))d\rho}{\int_0^1 (4\pi\rho^2)d\rho} \tag{11}$$

where $a(\rho)$ is concentration of A as a function of ρ (with an initial value of 1).

Figure 1. The geometry of the problem as posed in COMSOL multiphysics simulator.

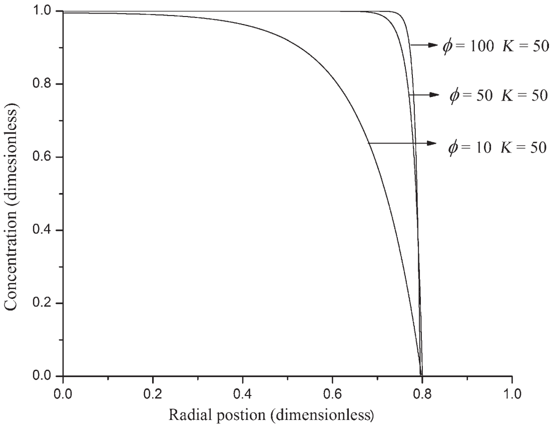

Figure 2. Concentration profiles of A at different ϕ and K, when the dimensionless "core" radius is 0.8.

Results

Typical concentration profiles of A (nondiffusing reactant), at a stage of the reaction when the region containing A has become confined to $0 \leq \rho \leq 0.8$, are shown in Figure 2 for different ϕ values, and a moderate value of K (K values are of $O(1)$ for solid–solid systems and $O(10^3)$ for gas–solid systems). The reaction zone is identified in this figure as the region in which a concentration profile of A exists. While the reaction zone occupies a significant part of the unreacted core for small values of ϕ (see for example the profile for $\phi = 10$), as ϕ increases, the reaction zone thickness decreases. In other words, the model switches to a front reaction model at high values of ϕ. Interestingly, for a given set of parameters (ϕ and K) the reaction zone thickness was found to remain nearly constant with time till the inner bounding surface of this zone reaches the center; this is seen in Figure 3, which compares the concentration profiles for two cases at different stages of conversion. In the final stages of conversion when the zone reaches the particle center, its thickness starts to decrease, finally becoming zero at complete conversion.

For a given value of ϕ, the reaction zone thickness was found to be quite insensitive to the value of K. This is seen from Table 2. The reaction zone thickness, for purposes of comparison, is taken as the (dimensionless) thickness of the region in which the concentration of A falls from 98 to 2% of its original value.

It was remarked earlier that the parameter K determines how important the unsteady-state effect is. Figure 4 shows the effect of K on the conversion-time behavior at not too

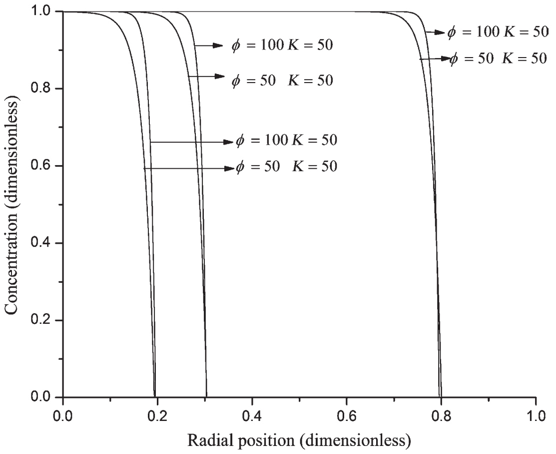

Figure 3. Concentration profiles of A for two combinations of ϕ and K, at different stages of conversion, showing that the reaction zone moves inward while remaining of constant thickness.

large a value of ϕ, at which the reaction zone spreads out to a finite thickness as seen from Figure 2. Also shown for comparison is the curve calculated from the Ishida–Wen model.[1] It is seen that the Ishida–Wen model, in general, overestimates the time required for a given conversion. For values of ϕ such as that considered in Figure 4, the errors are small even for values of K as small as 10. However, as Figures 5 and 6 show, the importance of the unsteady state effect is felt more strongly for larger values of ϕ, as the reaction zone tends to a surface. Larger values of ϕ thus call for larger values of K before the diffusion can be approximated as taking place under quasi-steady-state conditions.

The situations under which the present model is well approximated by the quasi-steady, front-reaction model of Ginstling and Brounshtein are investigated next. From the above paragraphs, it is clear that large values of ϕ and K represent such conditions. Figure 7 shows the effect of ϕ and K on the conversion vs. (dimensionless) time behavior. The GB model underestimates the time required for a given conversion for small values of ϕ and overestimates it for small values of K. Clearly, both ϕ and K need to be large, if GB model is to be used to estimate the conversion-time behavior of real systems.

It was confirmed from the calculations that the model of Frade and Cable[8] gives results in agreement with the present model for large values of ϕ, regardless of the value of K, as anticipated from Table 1. As their model also requires numerical solution as does the present one, it does not present any advantage in terms of ease of use, over the present model. Comparisons with the Frade–Cable models are therefore not presented in detail.

Table 2. Reaction Zone Thicknesses at Different Values of ϕ and K

	K			
ϕ	10	50	100	500
10	0.459	0.469	0.471	0.468
50	0.079	0.078	0.079	0.079
100	0.039	0.039	0.039	0.039

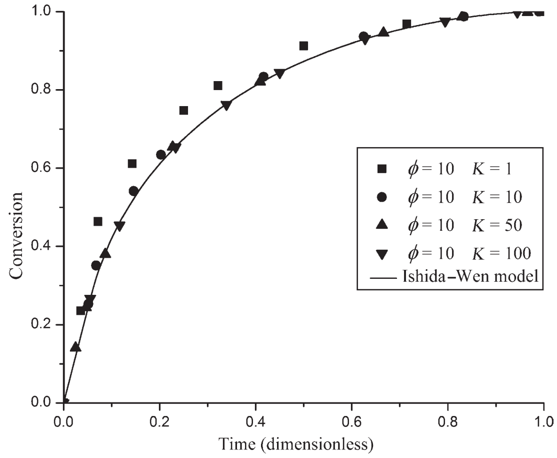

Figure 4. Conversion-time behavior as a function of K for ϕ = 10, and comparison with Ishida–Wen model.

Analysis of Errors in Approximate Models

It will be useful, from the point of view of application, to know beforehand the error inherent in using the simpler models, as the latter are analytical in character and present advantages for parameter estimation from experimental data. With this objective, in this section, we try to analyze how the error from the approximate models depends on the values of the parameters. For this purpose, the relative error of an approximate model (Ishida–Wen[1] or GB[2]) is defined on the basis of the time estimated for a given conversion, as

$$\text{Relative error} = \varepsilon(\alpha) = \left(\frac{\tau_{M,\alpha} - \tau_{\text{approx},\alpha}}{\tau_{M,\alpha}}\right) \qquad (12)$$

where $\tau_{M,\alpha}$ and $\tau_{\text{approx},\alpha}$ stand for the dimensionless times required for a conversion of α, as calculated, respectively, by the present model and an approximate (Ishida–Wen[1] or GB[2]) model.

From the results above, it is clear that, irrespective of the parameter values, the approximate models tend to do well at large and small conversions, and maximum deviations are to

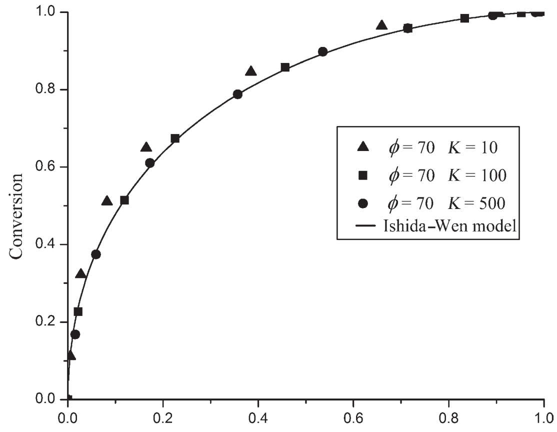

Figure 5. Conversion-time behavior as a function of K for ϕ = 70, and comparison with Ishida–Wen model.

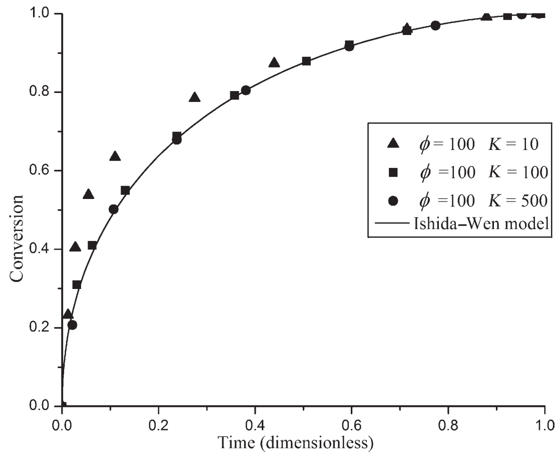

Figure 6. Conversion-time behavior as a function of K for $\phi = 100$, and comparison with Ishida–Wen model.

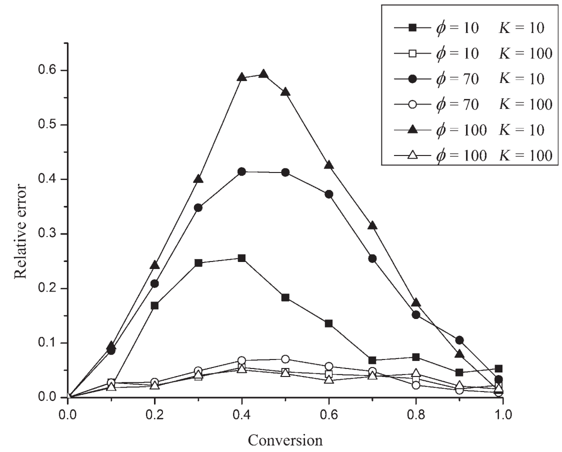

Figure 8. Relative error in the Ishida–Wen model as a function of K and ϕ.

be expected at intermediate conversions. Figure 8 (for the Ishida–Wen model[1]) and Figure 9 (for the GB model[2]) show the relative error defined above as a function of conversion for different values of ϕ and K. It is seen that the maximum error occurs usually at an intermediate conversion for both models (for the GB model, at small values of ϕ, the errors become large at fairly small conversions and decrease as conversion increases; note also that the errors are negative at small conversions for such cases). If one is interested in the time for total conversion, therefore, one can make do with either of the approximate models in most cases. However, care needs to be exercised in the use of the approximate models for parameter estimation from conversion-time data over a range of conversions.

Figures 8 and 9 show that the Ishida–Wen model is generally superior to GB. The performance of the model improves, as K increases. Clearly, the Ishida–Wen model can be used for any value of ϕ, provided the value of K is large enough. However, it is seen that, the larger the value of ϕ, larger does K need to be for the same error.

Figure 10 tries to collapse the error information presented above into a sort of ‘‘phase diagram’’ which helps in deciding which approximate model applies in which part of the parameter space. Indicated are regions in which the approximate models indicated can be used with a relative error of 6–8% or less.

The reactions between calcia and alumina leading to various calcium aluminate species may be considered to illustrate the implications of these results. Solid–solid reaction data are usually interpreted assuming the reaction to be diffusion limited, and hence reaction rate constant data are hard to come by. Ghoroi and Suresh[13] however, made a case for applying the Ishida–Wen model to their data on the conversion kinetics of $C_{12}A_7$ (C stands for CaO and A for Al_2O_3) by reaction with CaO to C_3A_7, and estimated both the rate constant and the diffusivity in the temperature range 1150–1300°C. Calculation from these estimates show that ϕ varies from about 5 to 40 over the above temperature range, while K is less than 1 (ca. 0.3). Figure 10 shows that these conditions require the use of the general model, and hence the estimates of parameters from Ghoroi and Suresh[13] can only be taken as a first guess, to be refined by fitting the general model by a nonlinear regression procedure. While the low value of K here is due to the high molar mass of $C_{12}A_7$, typical values for solid–solid systems will still be of the order of 1 (for the reaction between calcia and alumina, K may be estimated to be ca. 1.15 at reaction temperatures), and the undesirability of using the GB model, popular for data interpretation in such cases, is clear from Figure 10.

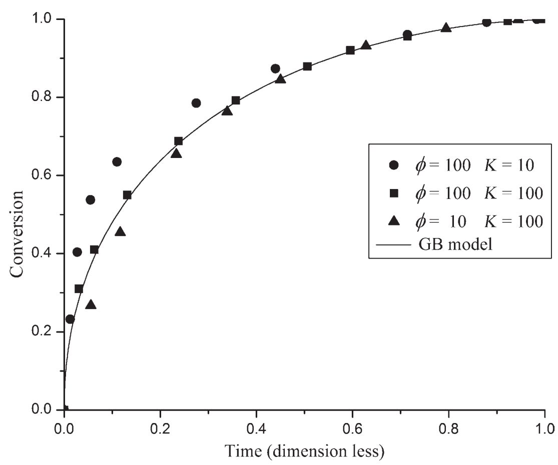

Figure 7. Conversion-time behavior for different values of K and ϕ, and comparison with GB model.

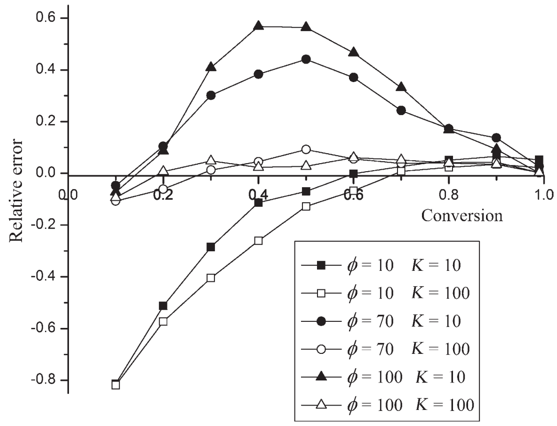

Figure 9. Relative error in the GB model as a function of K and ϕ.

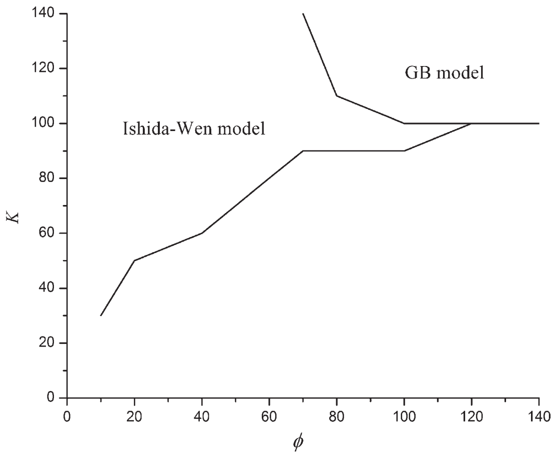

Figure 10. Figure showing the regions of applicability of the approximate models considered in this work, in the parameter space.

Conclusions

The errors inherent in the models generally used for the analysis of solid–solid reactions (and also for fluid–solid reactions in which the reactant solid is either nonporous or the pore structure of the particle is invariant) has been analyzed in this work, by comparing the performance of these models against a general model that does not make either the front-reaction or the pseudo-steady-state assumption. The solid–solid reactions for which this general model applies are those in which the average number of points of contact between particles is large, provided the particle density remains approximately constant. The model equations have been solved numerically on COMSOL multiphysics simulator. Two parameters, one a diffusion-reaction parameter (ϕ) and the other a relative abundance parameter (K), determine the model behavior. It has been shown that at large values of K, the model approaches the Ishida–Wen model, and for large values of both ϕ and K, the model approaches the Ginstling–Brounshtein model. The relative errors of these approximate models (with respect to the present model) have been quantified as a function of the two parameters, and regions of the parameter space in which the approximate models can be used within acceptable error have been quantitatively mapped. The results show that extreme caution needs to be exercised in using the approximate models, particularly GB, in interpreting solid–solid reaction data, because the values of K in these systems is much lower than needs to be for the approximations of that model to be valid. While these results are quantitative for first-order kinetics, qualitatively similar conclusions may be expected for reactions of other orders.

Notation

a = dimensionless concentration of A
b = dimensionless concentration of B
D = diffusion coefficient of B in product layer
K = dimensionless constant, defined following Eq. 9
k = first-order rate constant of the reaction
R = initial radius of the reacting particle
r = radial position within reactant A
t = time for which reaction is in progress
ρ = dimensionless radial position within particle A
ρ_A, ρ_B = molar densities of A and B respectively
α = fractional conversion of A
τ = dimensionless time, Dt/R^2
ϕ = Thiele modulus, defined following Eq. 9
ξ_m = dimensionless radius of unreacted core
v_a, v_b = stoichiometric coefficients of A and B

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